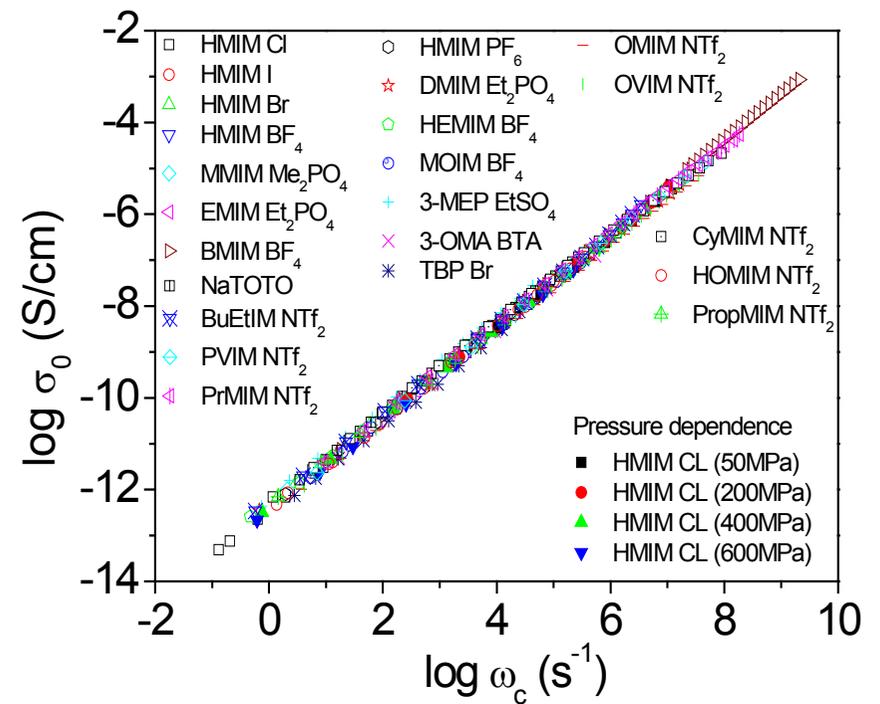


UNIVERSITY OF LEIPZIG

Faculty of Physics and Earth Sciences
Department of Experimental Physics I

GROUP "Molekülphysik"



Annual Report 2009

Cover picture: The dc conductivity, σ_0 , versus the characteristic frequency, ω_c , for different liquids as indicated. The data for all ionic liquids are obtained from dielectric measurements at ambient pressure except for the [HMIM] [Cl] for which the transport quantities are also measured at different pressures as indicated. This plot experimentally demonstrates the universality of charge transport in ionic liquids (project 2.6). J. R. Sangoro, C. Iacob, A. Serghei, C. Friedrich, F. Kremer, *Phys. Chem. Chem. Phys.* 11, 913 (2009). J. R. Sangoro *et al.*, (2010), under preparation.

UNIVERSITÄT LEIPZIG

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5. Graduations

Promotions

Dipl.-Phys. **Gunter Stober**

"Astrophysical Studies on Meteors using a SKiYMET All-Sky Meteor Radar"

Diploma

cand.-phys. **Olaf Ueberschär**

"Quantitative Untersuchungen zu Fluktuation, Dissipation und Irreversibilität anhand einzelner optisch gefangener Kolloide"

cand. phys. **Wilhelm Kossack**

"Struktur-Eigenschaftsbeziehungen in Flüssigkristallinen Elastomeren"

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

The year 2009

Significant progress was made in all the traditional fields of research of our group including Broadband Dielectric Spectroscopy (BDS), time –resolved, polarized FTIR-Spectroscopy and experiments with Optical Tweezers. For “Ionic Liquids”, the inter-relationship between glassy dynamics and charge transport was unravelled and traced back to the laws of Brownian fluctuations as discovered by Einstein and Smoluchowski in 1905. Based on this, Joshua Rume Sangoro found a way to extract diffusion coefficients in a broad temperature and frequency range from dielectric measurements. This opens for BDS a completely new field of applications. Furthermore, the approach using nanostructured electrodes was successfully employed to study the molecular dynamics in nm thin polymer layers. With time-resolved polarized FTIR-Spectroscopy, details of the structural levels of organization of spider silk were explored. Especially, the phenomenon of super-contraction could be understood on a molecular level. Optical tweezers proved to be a versatile tool in Nano-(Bio)-Physics. Pioneering experiments on the interaction between polymer-grafted colloids and Single-Colloid-Electrophoresis could be carried out, to name a few.

Friedrich Kremer

Contents

	page
Preface	1
1. Organization of the group	4
2. Projects	5
2.1 Interfacial interactions and their impact on the glassy dynamics of thin layers of atactic poly(methyl methacrylate) (M. Tress, E. U. Mapesa, A. Serghei and <u>F. Kremer</u>)	5
2.2 Molecular weight dependence of the glassy dynamics of thin polystyrene layers (E. U. Mapesa, M. Tress, A. Serghei and <u>F. Kremer</u>)	6
2.3 Real and apparent changes in the glassy dynamics of thin polymer layers – theoretical considerations (M. Tress, A. Serghei and <u>F. Kremer</u>)	7
2.4 Impact of a novel preparation method on the glassy dynamics of thin polymer layers studied by means of Dielectric Spectroscopy (E. U. Mapesa, M. Tress, A. Serghei and <u>F. Kremer</u>)	8
2.5 Signatures in charge transport and glassy dynamics of molecular liquids (T. Schubert, J. R. Sangoro, C. Iacob, and <u>F. Kremer</u>)	9
2.6 Rotational and translational diffusion in ionic liquids (J. R. Sangoro, C. Iacob and <u>F. Kremer</u>)	10
2.7 Charge transport and dipolar relaxations in hyperbranched polymers (J. R. Sangoro, <u>G. Turky</u> , and F. Kremer)	11
2.8 Characteristic hopping lengths and molecular volumes of Imidazolium-based ionic liquids (<u>J. R. Sangoro</u> , C. Iacob and <u>F. Kremer</u>)	12
2.9 Charge transport and diffusion of ionic liquids in nanoporous silica membranes (C. Iacob, J. R. Sangoro, and <u>F. Kremer</u>)	13
2.10 Charge transport and dipolar relaxations in Imidazolium-based ionic liquids (C. Krause, J. R. Sangoro, C. Iacob and <u>F. Kremer</u>)	14
2.11 Hierarchies in the structural organization of spider silk – A quantitative combined model (R. Ene, <u>P. Papadopoulos</u> and F. Kremer)	15
2.12 Spider silk: A soft solid with a unidirectional phononic band gap (P. Papadopoulos and <u>F. Kremer</u>)	16
2.13 Electromechanical properties of smectic C [*] liquid crystal elastomers under shear (P. Papadopoulos and <u>F. Kremer</u>)	17

4. Financial support

Prof. Dr. F. Kremer

DFG-Teilprojekt im Rahmen des Schwerpunktprogramms "Nano- und Mikrofluidik: Von der molekularen Bewegung zur kontinuierlichen Strömung" SPP 1164
DFG-Schwerpunktprogramm 1164, KR 1138/14-3 (2006-2010)

Prof. Dr. F. Kremer

DFG-Projekt "Physicochemical characterisation of ionic liquids-mediated peptide acylation reactions" SPP 1191
KR 1138/18-2 (2008–2010)

Prof. Dr. F. Kremer

DFG-Projekt "In-situ Untersuchung der Wechselwirkungskräfte an Polyelektrolytbürsten"
KR 1138/20-1 (2007–2009)

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

FOR877, DFG-Projekt: "From local constraints to macroscopic transport: Dynamics of DNA under tension and confinement"
KR 1138/21-1 (2007-2010)

Prof. Dr. F. Kremer

SPP "Polymer-Festkörper-Kontakte: Grenzflächen und Interphasen"
DFG-Teilprojekt "Interfacial dynamic of polymers in interaction with solid substrates"
DFG-Projekt "In-situ Untersuchung der Wechselwirkungskräfte an Polyelektrolytbürsten"
KR 1138/23-1 (2008–2011)

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**". Several Ph.D. projects are supported by that.

13)	Elmahdy, M.M., A. Drechsler, C. Gutsche, A. Synytska, P. Uhlmann, F. Kremer, M. Stamm "Forces between blank surfaces as measured by the colloidal probe technique and by optical tweezers – a comparison" <i>Langmuir</i> (2009) ASAP, DOI: 10.1021/la90180a.		page	
14)	Elmahdy, M.M., A. Synytska, A. Drechsler, C. Gutsche, P. Uhlmann, M. Stamm, F. Kremer "The forces of interaction between poly(2-vinylpyridine) brushes as measured by optical tweezers" <i>Macromolecules</i> (2009) ASAP, DOI: 10.1021/ma901567d.	2.14	Infrared transition moment orientational analysis (IR-TMOA) (W. Kossack, <u>P. Papadopoulos</u> , and F. Kremer)	18
15)	Krause, C., J.R. Sangoro, C. Iacob and F. Kremer "Secondary relaxations in imidazolium- based ionic liquids" <i>J. Phys. Chem. B</i> , 114, 382-386 (2010) - in press -	2.15	A novel position determination technique for polystyrene and silica colloids using video microscopy (C. Gutsche, O. Ueberschär, M. M. Elmahdy, G. Dominguez-Espinosa and <u>F. Kremer</u>)	19
16)	Kremer, F., A. Serghei, J.R. Sangoro, M. Tress and E. U. Mapesa, "Broadband dielectric spectroscopy in nao-(bio)-physics." <i>IEEE Transactions on Dielectrics and Electrical Insulation</i> , in press (2010)	2.16	Forces between blank surfaces as measured by the Colloidal Probe Technique and by Optical Tweezers – A comparison (M. M. Elmahdy, A. Drechsler, C. Gutsche, A. Synytska, P. Uhlmann, M. Stamm and <u>F. Kremer</u>)	20
17)	Serghei, A., J. Lutkenhaus, D. Miranda, K. McEnnis, F. Kremer, T.P. Russel "Density fluctuations and phase transitions of ferroelectric polymer nanowires" <i>Nature Materials</i> submitted 2010	2.17	Forces of interaction between Poly(2-vinylpyridine) brushes as measured by Optical Tweezers (M. M. Elmahdy, A. Synytska, A. Drechsler, C. Gutsche, P. Uhlmann, M. Stamm and <u>F. Kremer</u>)	21
		2.18	Interaction forces between a single pair of blank silica surfaces as measured by Optical Tweezers (T. Stangner, M. M. Elmahdy, C. Gutsche and <u>F. Kremer</u>)	22
		2.19	Electrokinetics and Charge Inversion as studied by Single Colloid Electrophoresis (SCE) (I.Semenov, G.Stober, P.Papadopoulos and <u>F.Kremer</u>)	23
		2.20	Microscopic fluctuations and the emergence of irreversibility: Investigating stochastic thermodynamics (O. Ueberschär and <u>F. Kremer</u>)	24
		3.	Publications	25
		4.	Financial Support	27
		5.	Graduations	28
		6.	Industry collaborations	28
		7.	Patent applications	28
		8.	Awards	28

1. Organization of the group

Chairman: Prof. Dr. Friedrich Kremer

Academic staff and postdocs

Dr. Mahdy El Mahdy
Dr. Periklis Papadopoulos

Students

Dipl.-Chem. Roxana G. Ene
Dipl.-Phys. Christof Gutsche
M. Sc. Ciprian G. Iacob
Dipl.-Phys. Kati Kegler
cand.-phys. Wilhelm Kossack
cand. phys. Christina Krause
M. Sc. Emmanuel Mapesa
cand.-phys. Christian Rudolf
M. Sc. Joshua Rume Sangoro
cand.-phys. Peter Schlupp
cand.-phys. Tilman Schubert
M. Sc. Ilya Semenov
cand.-phys. Tim Stangner
Dipl.-Phys. Gunter Stober
cand.-phys. Benjamin Suttner
cand.-phys. Martin Treß
cand.-phys. Olaf Ueberschär
cand.-phys. Manos Veroutis
Dipl. -Phys. Carolin Wagner

Technical staff

Hartmut Domröse
Karin Girke
Ines Grünwald
Dipl.-Ing. Jörg Reinmuth
Dipl.-Phys. Wiktor Skokow

Alumni

Prof. Dr. Siegbert Grande

Guests:

Prof. Dr. Gamal Turkey
NRC, Cairo, Egypt
June-Sept. 2009

3. Publications

- 1) Papadopoulos, P., J. Sölter and F. Kremer
"Hierarchies in the structural organization of spider silk - a quantitative model"
Colloid and Polymer Science **287**, Issue2, 231-236 (2009)
- 2) Sangoro, J. R., C. Iacob, A. Serghei, C. Friedrich and F. Kremer,
"Universal scaling of charge transport in glass-forming ionic liquids "
Phys. Chem. Chem. Phys. **11**, 913-916 (2009)
- 3) Sangoro, J. R., G. Turkey, M. Abdel Rehim, S. Naumov, A. Ghoneim, J. Kärger and F. Kremer.,
"Charge transport and dipolar relaxation in hyper-branched polyamide amines. Macromolecules "
Macromolecules **42** (5), 1648-1651 (2009)
- 4) Serghei, A., M. Tress and F. Kremer
The glass transition of thin polymer films in relation to the interfacial dynamics
J. Chem. Phys. **131** 154904 (2009)
- 5) Min, Y., M. Akbulut, J.R. Sangoro, F. Kremer, R.K. Prud'homme, J. Israelachvili
"Measurement of forces between room temperature ionic liquids between mica surfaces"
J. of Physical Chemistry C **113**, (37) pp.16445-16449 (2009)
- 6) Papadopoulos, P., R. Ene, I. Weidner, F. Kremer,
"Similarities in the structural organization of major and minor ampullate spider silk"
Macromol. Rapid. Commun. **30**, 851-857 (2009)
- 7) Semenov, I., O. Otto, G. Stober, P. Papadopoulos, U.F. Keyser, and F. Kremer
"Single colloid electrophoresis"
J. Colloid Interf. Sci. **337**, 260-264 (2009)
- 8) Serghei, A., M. Tress, J. R. Sangoro and F. Kremer,
"Electrode polarization and charge transport at solid interfaces"
Phys. Rev. B **80** 184301 (2009)
- 9) Ene, R. P. Papadopoulos, F. Kremer
"Combined structural model of spider dragline silk"
Soft Matter, **5**, 4568-4574 (2009)
- 10) Serghei, A., M. Tress and F. Kremer,
"The glass transition of thin polymer films in relation to interfacial dynamics"
J. Chem. Phys. **131**, 154904 (2009)
- 11) Kim, Y.W., V. Lobaskin, C. Gutsche, F. Kremer, P. Pincus, R.R. Netz
"Nonlinear response of grafted semiflexible polymers in shear flow"
Macromolecules, **42**, 3650-3655 (2009)
- 12) Kipnusu, W.K., G. Katana, C.M. Migwi, I.V.S. Rathore, J.R. Sangoro, J. Tsuiwi, A. Serghei, F. Kremer
"Molecular dynamics characterization of nandi flame seed cuticle biomaterials"
J. Polym. Mater. **26**, 129 (2009)

2.20 Microscopic fluctuations and the emergence of irreversibility: Investigating stochastic thermodynamics

O. Ueberschär and F. Kremer

Since spring of 2008 we have been working on the experimental verification and application of several universal theorems of stochastic thermodynamics by means of optical tweezers. One of the major objectives of this new branch of modern thermodynamics is to find a consistent linkage between a macroscopic description and approaches at the nano- and micrometre scale. For this purpose, well-known macroscopic quantities such as work, heat and entropy have to be generalized in such a way that their definitions prove reasonable, consistent and eventually useful even for single microparticles, e.g. micrometre-sized colloids. As a result, the corresponding, usually distinct levels of microscopic and macroscopic description of irreversible processes are finally unified.

Starting from the widely accepted formal framework established by U. Seifert and others [7, 8], we follow and extend the experimental approaches of G. M. Wang et al. first published in 2002 [4-6]. In this way, we experimentally demonstrate the validity of several so-called fluctuation theorems for special non-equilibrium states of optically trapped colloids. In general, these fluctuation theorems form rigorous quantitative rules describing the emergence and quantitative evolution of irreversibility from a microscopic point of view. In detail, our measurements confirm the theoretical prediction that the microscopic total system entropy intriguingly may decrease on sufficiently short time scales. Our pertinent results in this context exceed the scope of Wang *et al.* 2002-2005 [4-6]. For instance, we have been able to verify the so-called detailed transient fluctuation theorem (TFT) and the universal integral fluctuation theorem (UIFT) as well as the integral fluctuation theorem (IFT) for a reproducible transient non-equilibrium state of a single colloid system.

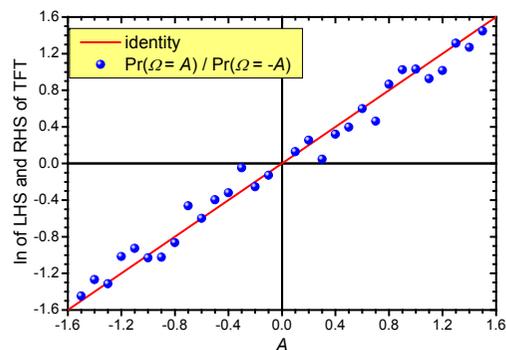


Fig. 1: Experimental verification of the TFT. The graph shows the comparison of the left-hand side (LHS, ●) and the right-hand side (RHS, red line) of the TFT, i.e. $\Pr(\Omega = -A) / \Pr(\Omega = +A) = e^{-A}$, for 6 000 single trajectories were measured in a reproducible transient non-equilibrium state for an identical colloid.

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- [1] O. Ueberschär, C. Gutsche, F. Kremer, J. Phys. D: Appl. Phys, submitted (2009)
- [2] D. J. Evans et al., Phys. Rev. Lett. **71**, 2401 (1993)
- [3] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997)
- [4] G. M. Wang et al., Phys. Rev. Lett. **89**, 050601 (2002)
- [5] D. M. Carberry et al., Phys. Rev. Lett. **92**, 14, 140601 (2004)
- [6] G. M. Wang et al., Phys. Rev. E **71**, 046142 (2005)
- [7] U. Seifert, Phys. Rev. Lett. **95**, 040602 (2005)
- [8] U. Seifert, Eur. Phys. J. B (2008)

Funding:

Financial support by the BuildMoNa Graduate School is gratefully acknowledged.

2. Projects

2.1 Interfacial interactions and their impact on the glassy dynamics of thin layers of atactic poly(methyl methacrylate)

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

Broadband Dielectric Spectroscopy (BDS) and spectroscopic *vis*-Ellipsometry are combined to study the glassy dynamics of thin (≥ 10 nm) layers of atactic poly(methyl methacrylate) (PMMA) prepared under *identical* conditions. In order to unravel a possible effect of the underlying substrate the interfacial interactions are systematically modified ranging from strong attractive interactions for covalently bonded PMMA brushes with high grafting density and for native silicon oxide (Si/SiO_x) to weak and strong repulsive interactions as realized by Au coated and HMDS treated Si/SiO_x surfaces, respectively. Down to the thinnest analyzed PMMA films and independently from the applied substrate both methods deliver - within the experimental accuracy (± 0.5 K for BDS and ± 2 K for Ellipsometry) a coinciding result. The glassy dynamics are *not* altered due to the geometrical confinement in these thin polymer layers.

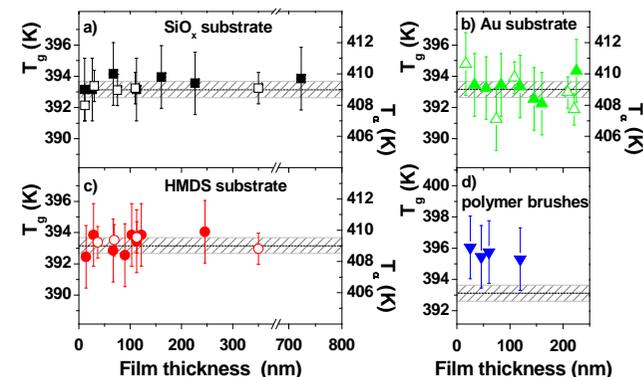


Fig. 1: Glass transition temperature T_g measured by ellipsometry (filled symbols) and characteristic temperature T_a measured by BDS (open symbols) plotted versus film thickness. The measurements were carried out on different substrates having hydrophilic (a, Si/SiO_x) to hydrophobic (b, gold coating; c, silanized with HMDS) surfaces. Additionally, covalently bonded PMMA brushes on Si/SiO_x with strong attractive interfacial interactions were studied. As guidance for the eyes the calorimetrically determined T_g is shown as dashed line (an experimental error of ± 0.5 K was plotted for comparison).

References:

- [1] Erber, M.; Treß, M.; Mapesa, E.; Serghei, A.; Eichhorn, K.-J.; Voit, B. & Kremer, F. *in preparation*

Collaborators:

Ellipsometry: M. Erber, K.-J. Eichhorn, B. Voit, Institut für Polymerforschung Dresden
* Present address: Polymer Science and Engineering, University of Massachusetts, Amherst
MicroFAB Bremen

Funding:

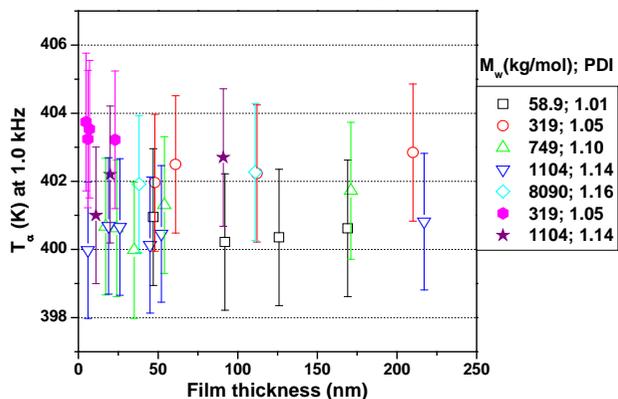
DFG priority program SPP1369 (polymer-solid contacts: interfaces and interphases)

* The underlined author has initiated the project.

2.2 Molecular weight dependence of the glassy dynamics of thin polystyrene layers

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

The glassy dynamics of ultra-thin (≥ 5 nm) layers of polystyrene (PS) is studied 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). This revisits a controversial discussion raised 15 years ago by Keddy and Jones, who found pronounced changes of the glass transition temperature T_g in thin PS layers in their ellipsometric studies. Since that time numerous investigations focussed on this effect which is supposed to be caused by geometrical confinement. Instead of unravelling its origin the results are contradictory as some studies do not observe confinement effects at all while others do definitely and even the used method seemed to affect the particular finding. Knowing about the strong impact of the sample preparation the present investigation emphasizes the identical preparation procedures in



both applied methods and the coincidence of the results. Furthermore no confinement effects, namely no shift of the T_g , no change of the mean relaxation time and no broadening of the relaxation time distribution was found. Additionally the glassy dynamics is hardly affected by the molecular weight. The characteristic temperature of the α -relaxation T_α of all molecular weights under study lies within a range of 4 K while the experimental error is as big as ± 2 K.

Fig. 1: Thickness dependence of T_g at 1 kHz for different molecular weights of polystyrene as indicated. Empty symbols stand for measurements prepared with evaporated electrodes while filled symbols indicate the application of nanostructured electrodes. Within the limits of experimental uncertainty, down to 4.8 nm, dielectric relaxation dynamics are independent of both film thickness and molecular weight.

References:

[1] Mapesa, E. U., M. Erber, M. Tress, A. Serghei, K.-J. Eichhorn, B. Voit and F. Kremer, *in preparation*

Collaborators:

Ellipsometry: M. Erber, K.-J. Eichhorn, B. Voit, Institut für Polymerforschung Dresden

* Present address: Polymer Science and Engineering, University of Massachusetts, Amherst MicroFAB Bremen

Funding:

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

2.19 Electrokinetics and Charge Inversion as studied by Single Colloid Electrophoresis (SCE)

I.Semenov, G.Stober, P.Papadopoulos and F.Kremer

Single Colloid Electrophoresis (SCE) [1] is employed to measure in a specifically designed microfluidic cell the electrophoretic mobility of a single particle and the electro-osmotic mobility of a surrounding liquid using the *identical* colloid. Charge inversion in dependence on concentration and valency is observed and is proved to be fully reversible

In aqueous solution, electrostatic interactions play an important role for various properties of charged systems. The determination and prediction of the surface charge density of the particle's surface are thus of prime importance. This requires an accurate model for the electric double layer at the solid/liquid interface. The standard electrokinetic model [2,3], especially based on its mean field approximation, where the ions are treated as charged hard spheres and the solvent as a dielectric continuum is often used to describe these systems. However, this theory is not accurate in strongly coupled systems. That is, for systems containing multivalent ions, high ionic concentration and/or strong surface charge.. A phenomenon known as *charge inversion* may be seen in electrokinetic measurements such as electrophoresis in presence of multivalent ions, where the sign of the electrokinetic potential appears to be opposite to the expected one. The interpretation of such a result is still controversial. Often it's explained by specific chemical adsorption of multivalent counter-ions [4]. However, the pure electrostatic interactions, i.e. *the ion-ion correlations*, can cause *charge inversion* by the strong accumulation of counter-ions in contact with a charged surface [5]. In the present experimental study the complex electrophoretic response of a *single* colloid in monovalent (KCl), divalent (CaCl₂) and trivalent (LaCl₃) aqueous solutions is measured. Electrophoretic mobility of a *single* particle vs. ionic strength and ion valency are obtained.

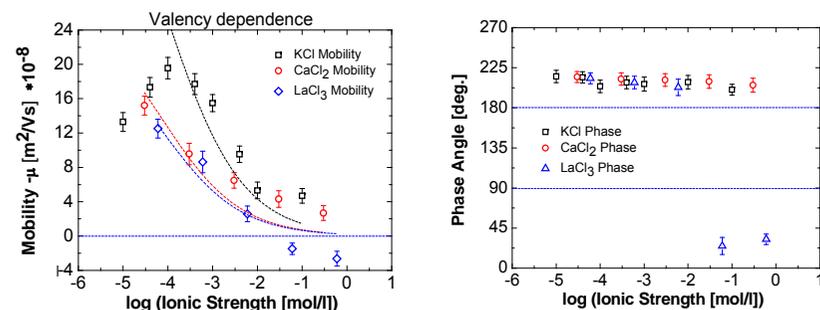


Fig. 1: Electrophoretic mobility and Phase vs. ionic strength as indicated respectively for the *identical* negatively charged PS colloid (diameter: 2.23 μ m), within a channel of length $l = 8$ mm. Laser power 0.2 W. The lines represent the Standard Electrokinetic Model (dashed line represent predictions for monovalent ions, solid line for divalent ions and dotted line for trivalent ions).

References:

[1] I. Semenov, O. Otto, G Stober, P. Papadopoulos, U. F. Keyser and F. Kremer. *J. of Col. and Int. Sci.*, 337 (2009) 260-264

[2] R. J. Hunter. *Zeta Potential in Colloid Science*. Academic Press, London, 1981.

[3] J. Lyklema, *Fundamentals of Interfaces and Colloid Science*, vol. II, Academic Press, New York 1995

[4] Johannes Lyklema. *Col. and Sci. A: Physicochem. Eng. Aspects.*, 291 (2006) 3-12

[5] J. Lyklema. *Adv. in Col. and Int. Sci.*, 147-148 (2009) 205-213

Funding: Sächsische Forschergruppe FOR 877, DFG

2.18 Interaction forces between a single pair of blank Silica surfaces as measured by Optical Tweezers

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

Optical Tweezers are an excellent tool to investigate the interaction force between a single pair of spherical blank SiO₂ colloids (diameter ~ 4.85 ± 0.05 μm) with an extraordinary resolution of ± 0.5 pN. The concentration dependence was recorded under different conditions e.g. varying salt concentration and valancy (see Figure 1). The data are well described by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [3]. The mean results are: i) the potential becomes steep with increasing the salt concentration (fig. (a)), ii) the effective surface charge decreases with increasing valancy (inset) and iii) the interaction length λ decreases with increasing salt concentration and increasing valancy (fig. (b))

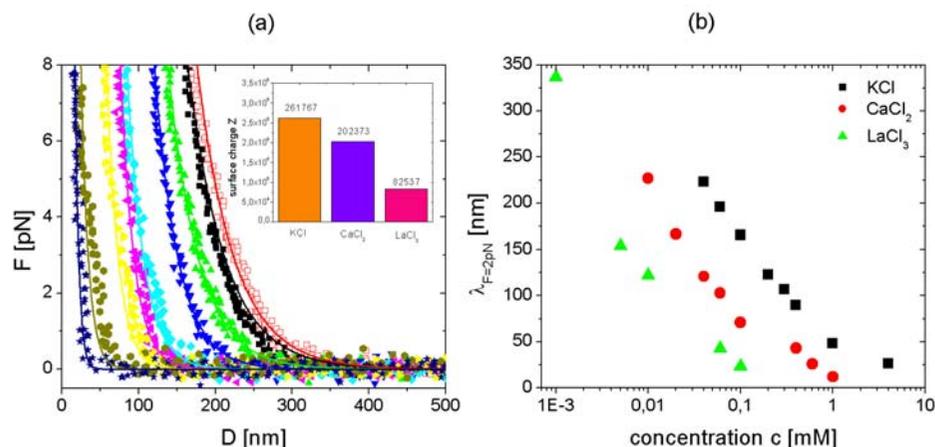


Fig. 1: (a) Force vs. surface – to – surface distance D for a single pair of blank SiO₂ colloids (diameter ~ 4.85 ± 0.05 μm) in aqueous solution of varying KCl concentration: 4x10⁻⁵ M (black squares), 6x10⁻⁵ M (green up-triangles), 10⁻⁴ M (blue down-triangles), 2x10⁻⁴ M (cyan diamonds), 3x10⁻⁴ M (magenta left-triangles), 4x10⁻⁴ M (yellow right-triangles), 10⁻³ M (dark yellow diamonds), 4x10⁻³ M (navy blue stars). At the end of this circle the cell was flushed again with $c = 4 \times 10^{-5}$ M (open red squares) to ensure the full reproducibility of the medium exchange. The dataset was fitted by DLVO theory [3]. Inset: Valancy dependence of the effective surface charge as obtained from the fits. The surface charge decreases with increasing valancy (orange bar: KCl, violet bar: CaCl₂, pink bar: LaCl₃). (b) The interaction length λ at a certain force of 2 pN in dependence of salt concentration and valancy (black squares: KCl, red circles: CaCl₂, green up-triangles: LaCl₃).

References:

- [1] M.M. Elmahdy, A. Drechsler, C. Gutsche, A. Synytska, P. Uhlmann, F. Kremer, M. Stamm, *Langmuir* **25**, 12894 (2009)
- [2] C. Gutsche, U.F. Keyser, K. Kegler, F. Kremer, *Physical Review E* **76**, 031403 (2007)
- [3] B.V. Derjaguin, L. Landau, *Acta Physicochim. URSS* **14**, 633 (1941)

Collaborators:

P. Uhlmann, A. Drechsler, A. Synytska, M. Stamm (IPF, Dresden)

Funding:

DFG Project (Project No. KR 1138/20-1, STA 324/33-1 (2007 - 2009))

2.3 Real and apparent changes in the glassy dynamics of thin polymer layers - theoretical considerations

M. Tress, A. Serghei* and F. Kremer

Manifold methods like Ellipsometry, Calorimetry and BDS were applied to unravel the mechanisms of confinement-effects in thin polymer layers. These effects are supposed to rise due to the changes of the polymer glassy dynamics in the nanometric vicinity of confining interfaces. However, beyond factors that can lead to real changes in the polymer dynamics, in the case of BDS measurements there are passive effects which can mimic confinement effects.

To which extent this passive effect contributes to observed changes of the dynamics depends strongly on parameters describing the heterogeneity of the system. A fairly simple model allows to calculate (equ. 1 and 2 for evaporated and nanostructured electrodes, respectively) some of these dependencies analytically while further investigation requires numerical analysis.

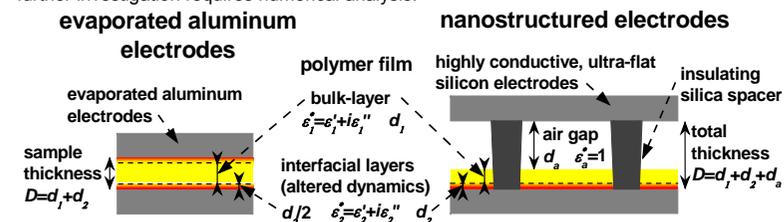


Fig. 1: Sketch of the proposed layer model of a polymer film in two accessible sample arrangements.

In the frame of the simplest approach (a 2-layer-model with one dead layer) it is shown, that the ratio of thicknesses of both layers has strong impact on whether a change in the measured relaxation time is observed or not. This is supported by numerical considerations of more complex model systems. Comparison with experimental results suggests that in thin polymer films an "interfacial" layer of 1-2 nm thickness (which might be immobilised polymer segments as well as oxide layers of the electrodes) can explain the observed effects.

References:

- [1] A. Serghei, A., M. Tress and F. Kremer, *J. Chem. Phys.*, (2009), 131, 154904

Collaborators:

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MicroFAB Bremen

Funding:

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

2.4 Impact of a novel preparation method on the glassy dynamics of thin polymer layers studied by means of Dielectric Spectroscopy

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

The impact of a recently developed preparation method on the measured glassy dynamics of thin polymer layers by means of BDS is investigated for different materials and compared to the results obtained with a common sample preparation. The new sample arrangement employs highly conductive ultra-flat silicon wafers as electrodes whereof one acts as support of the polymer layer while the other one is covered with silica nanostructures as spacers. The latter caps the polymer layer and acts as counter electrode, thus evaporation (like in common sample arrangement) is avoided and an additional air gap is created. The glassy dynamics of thin layers of PS (≥ 5 nm) were studied in both sample geometries. No shift of the mean relaxation time is observed in both geometries. However, using the conventionally evaporated electrodes leads to an increased broadening of the relaxation time distribution with decreasing layer thickness.

Similar measurements were carried out on PVAc layers of constant thickness which were spin-coated onto silica layers of different thicknesses. These systems model the

simplest case of altered dynamics in an interfacial layer, namely a “dead” layer ($\epsilon'' = \text{const.}$). In the samples prepared with evaporated electrodes a broadening is observed which depends on the ratio of the thicknesses of both layers while samples prepared with nanostructured electrodes do not show a broadening in the same range of thickness ratios.

References:

[1] Tress, M., E. U. Mapesa, A. Serghei, and F. Kremer, *in preparation*

Collaborators:

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Funding:

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

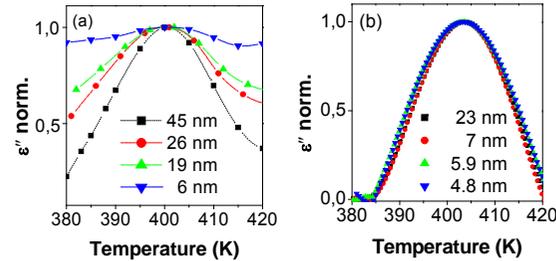


Fig. 1: Normalized dielectric loss of thin PS layers prepared with evaporated (a) and nanostructured (b) electrodes at 0.8 kHz and 1 kHz, respectively.

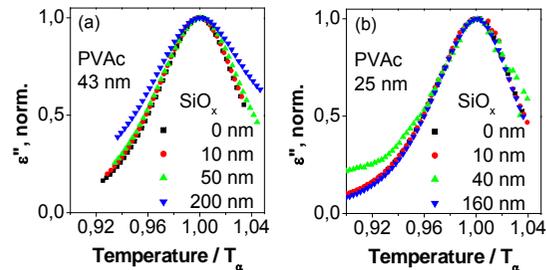


Fig. 2: Normalized dielectric loss of PVAc layers on silica layers (thicknesses varied as indicated) prepared with evaporated (a) and nanostructured (b) electrodes at 123.9 kHz.

2.17 Forces of Interaction between Poly(2-vinylpyridine) Brushes As Measured by Optical Tweezers

M. M. Elmahdy, A. Synytska, A. Drechsler, C. Gutsche, P. Uhlmann, M. Stamm and F. Kremer

Forces of interaction within *single* pairs of poly(2-vinylpyridine) (P2VP) grafted colloids have been measured by optical tweezers (OT) with an extraordinary resolution of ± 0.5 pN [1].

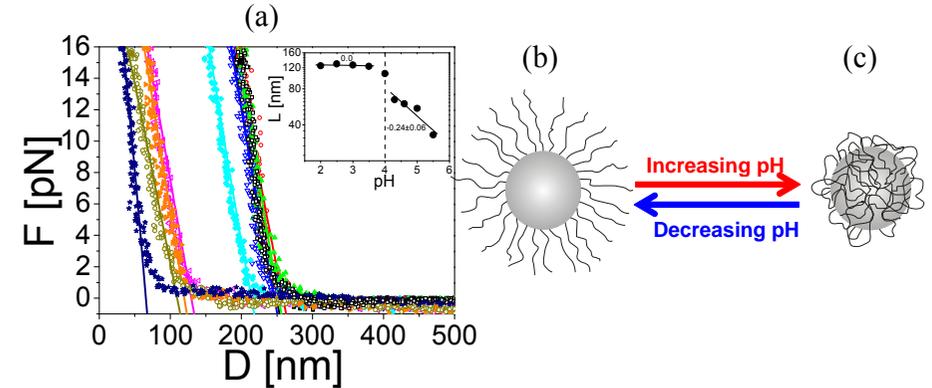


Fig 1: (a) Forces vs. separation D as measured for a *single* pair of P2VP-grafted colloids in media of varying pH: 2 (full squares), 2.5 (full circles), 3 (full up-triangles), 3.5 (full down-triangles), 4 (full diamond), 4.3 (full left-triangles), 4.6 (full right-triangles), 5 (full hexagon) and 5.5 (full stars) at 10^{-3} M KCl. To ensure full reproducibility of the exchange of the medium the sample cell was flushed again with 10^{-3} M at pH 2 (open squares) at the end of a measurement cycle. The solid lines represent the fits to the experimental data with Jusufi model. Inset: brush height L vs. pH at 10^{-3} M KCl obtained from analyzing the data using Jusufi model (full circles). The line of slope 0.24 indicates theoretical scaling law predictions for comparison. Right: Schematic illustration of the P2VP conformations with increasing and decreasing pH values. (b) At pH < 4 the P2VP chains are stretched away from the surface forming a brush-like conformation. (c) At pH > 4 the P2VP segments adsorb strongly to the underlying surface in a “pancake”-like conformation.

Parameters to be varied are the concentration and type of salt (KCl, CaCl_2 , and LaCl_3) of the surrounding medium as well as its pH. The observed force-distance relation is *quantitatively* described by the Jusufi model [2] for spherical polyelectrolyte brushes which takes into account the entropic effect of the counterions and enables one to estimate the ionic concentration inside the brush. The transition from an osmotic to the salted brush regime is analysed in detail. For the scaling of the brush height a power law is found having an exponent of 0.24 ± 0.01 which ranges between the values expected for spherical and planar brushes. At pH 4 a strong transition from a brush to a pancake conformation takes place.

References:

[1] M.M. Elmahdy, A. Synytska, A. Drechsler, C. Gutsche, P. Uhlmann, M. Stamm, F. Kremer *Macromolecules* **42**, 9096 (2009).
[2] A. Jusufi, C.N. Likos, M. Ballauff *Colloid Polym Sci.* **282**, 910 (2004).

Collaborators:

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Funding:

DFG-Project (Project No. KR 1138/20-1, STA 324/33-1 (2007–2009).

2.16 Forces between Blank Surfaces As Measured by the Colloidal Probe Technique and by Optical Tweezers – A Comparison

M. M. Elmahdy, A. Drechsler, C. Gutsche, A. Synytska, P. Uhlmann, M. Stamm and F. Kremer

The well established AFM-based Colloidal Probe Technique (CPT) and Optical Tweezers (OT) are combined to measure the interaction forces between blank SiO₂ surfaces in aqueous ionic solutions (CaCl₂) of varying concentration at pH 7 [1].

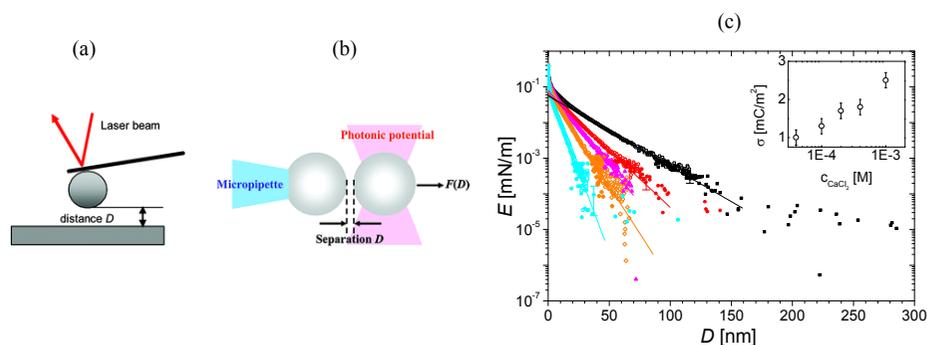


Fig. 1: (a) Scheme of the experimental set-up of the CPT. (b) Scheme of the experimental setup of the OT technique. (c) Combined CPT and OT measurements: Interaction energy E vs. separation D between a blank SiO₂ colloid and a blank SiO₂ surface (CPT: open symbols) and two SiO₂ colloids (OT: full symbols) in media of varying CaCl₂ concentration at pH 7: 4×10^{-5} M (squares), 10^{-4} M (circles), 2×10^{-4} M (up-triangles), 4×10^{-4} M (rhombus), 10^{-3} M (hexagon). All colloids (diameter $\sim 4.63 \pm 0.05 \mu\text{m}$) were taken from the same batch. The lines are fits based on the DLVO equation. Inset: CaCl₂ concentration dependence of the effective surface charge density σ as obtained from the fits.

Spherical colloids (SiO₂, diameter $\sim 4.63 \pm 0.05 \mu\text{m}$) taken out of the *same* batch are used by both methods. In case of CPT – a *single* colloid is glued to a cantilever and the interaction forces with a plain SiO₂ surface are determined in dependence on the concentration of the surrounding medium. For the OT studies *two* colloids (one fixed to a micropipette by capillary action, the other held with the optical trap) are approached to each other in nm-steps and the resulting forces are measured for the same media as in the CPT experiment. Both techniques fit well to each other and enable one to cover interaction energies ranging from 10^{-5} to 1 mN/m. The experimental data are well described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [2] revealing that the effective surface charge density changes slightly with concentration.

References:

- [1] M.M. Elmahdy, A. Drechsler, C. Gutsche, A. Synytska, P. Uhlmann, F. Kremer, M. Stamm, *Langmuir* **25**, 12894 (2009).
 [2] B.V. Derjaguin, L. Landau, *Acta Physicochim. URSS* **14**, 633 (1941).

Collaborators:

P. Uhlmann, A. Drechsler, A. Synytska, M. Stamm (IPF, Dresden)

Funding:

DFG-Project (Project No. KR 1138/20-1, STA 324/33-1 (2007–2009).

2.5 Signatures in charge transport and glassy dynamics of molecular liquids

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

Charge transport and glassy dynamics in a variety of amorphous materials are investigated by Broadband Dielectric Spectroscopy (BDS)¹. Despite the apparently similar Vogel – Fulcher – Tamman – type thermal activation of the characteristic quantities (structural α -relaxation rate, diffusion rate and dc conductivity [Fig.1a]) significant differences are revealed by applying a model free derivative technique^{1,2} [Fig.1b]. A detailed analysis of the dielectric strength and its temperature dependence shows distinct characteristics caused by the differences in the type of molecular interactions involved in the materials studied.

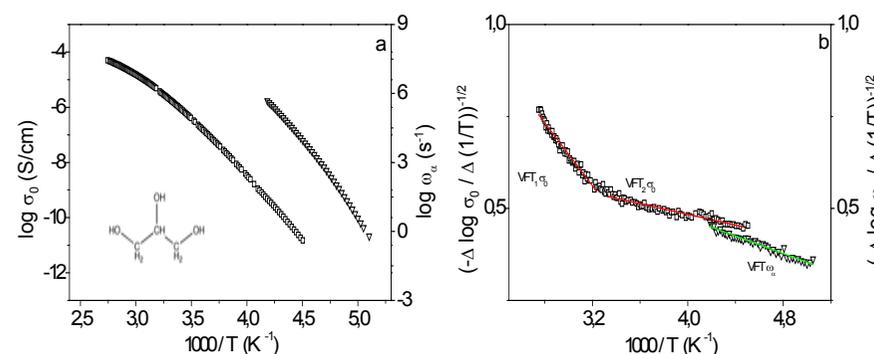


Fig. 1: (a) Temperature dependence of the dc conductivity as well as the activation plot of the structural α relaxation for Glycerol. Inset: structural formula for Glycerol. (b) Experimentally determined difference quotients of the dc conductivity $((-\Delta(\log(\sigma_{dc}))/\Delta(1/T))^{-1/2}$ vs $1000 / T$; two VFT-fits are applied) and the structural α relaxation $((-\Delta(\log(\omega_{\alpha}))/\Delta(1/T))^{-1/2}$ vs $1000 / T$ with one VFT-fit).

References:

- [1] *Broadband Dielectric Spectroscopy*, edited by F. Kremer and A. Schönhal, Springer (2003);
 [2] Stickel et al. Dynamics of glass-forming liquids. I. Temperature-derivative analysis of dielectric data *J. Chem. Phys.* **102**, 6251-6257 (1995)

Funding:

DFG, priority program SPP 1191 on "Ionic Liquids"

2.6 Rotational and translational diffusion in ionic liquids

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

Charge transport and glassy dynamics of a variety of glass-forming ionic liquids (ILs) are investigated in a wide frequency and temperature range by means of Broadband Dielectric Spectroscopy (BDS), Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR), AC Calorimetry, Differential Scanning Calorimetry and Rheology. 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. While the absolute values of dc conductivity and the characteristic charge transport rate vary over more than 11 decades with temperature, pressure and upon systematic structural variation of the ILs, a universal plot of the transport parameters is obtained (Fig. 1 (a)). This is discussed within the framework of the concept of *dynamic glass transition driven hopping* traced back to Einstein, Einstein-Smoluchowski, and Maxwell relations. A novel approach is applied to extract diffusion coefficients from BDS spectra in quantitative agreement with PFG NMR values but in a much broader range. It becomes possible to extract from the dielectric spectra separately the number density and the mobilities of the charge carriers and the type of their thermal activation (Fig. 1 (b)). It is shown that the observed Vogel-Fulcher-Tammann (VFT) dependence of the dc conductivity can be traced back to a similar temperature dependence of the mobility while for the number density an Arrhenius-type thermal activation is found.

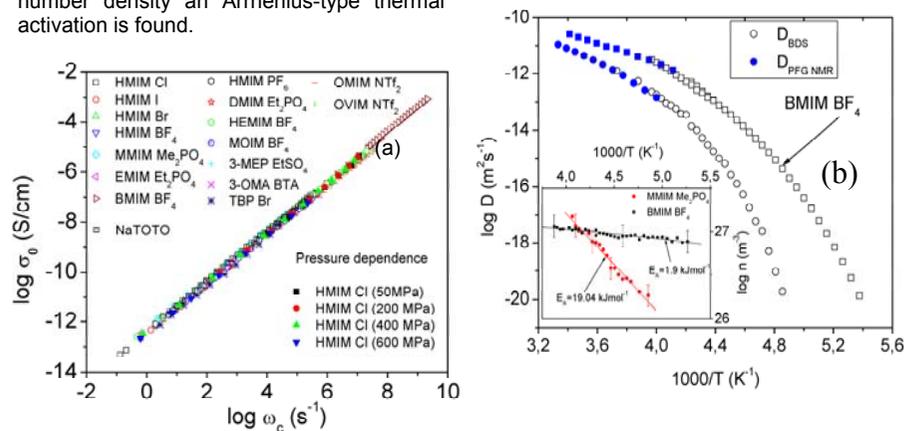


Fig. 1: (a) The dc conductivity, σ_0 , versus the characteristic frequency, ω_c , for different liquids as indicated. The data for all ionic liquids are obtained from dielectric measurements at ambient pressure except for the HMIM Cl for which the transport quantities are also measured at different pressures as indicated. This plot experimentally demonstrates the universality of charge transport in ionic liquids. (b) Diffusion coefficient determined by the novel approach involving application of the Einstein-Smolukowski equation to dielectric spectra compared to diffusion coefficients measured by PFGNMR (blue colour) for two ionic liquids: BMIM BF₄ and MMIM Me₂PO₄ [1]. Inset: effective number density of charge carriers as a function of inverse temperature (the respective activation energies are as indicated). The error bars are comparable to the size of the symbols, if not specified otherwise. Log is used to refer to logarithm to base 10.

References:

[1] *Broadband Dielectric Spectroscopy*, edited by F. Kremer and A. Schönhals, Springer (2003); J. R. Sangoro, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa, and F. Kremer, *Phys. Rev. E* 77, 051202 (2008); J. R. Sangoro et al., *J. Chem. Phys.* 128, 214509 (2008); J. R. Sangoro, C. Iacob, A. Serghei, C. Friedrich, F. Kremer, *Phys. Chem. Chem. Phys.* 11, 913 (2009). J. R. Sangoro et al., (2010), under preparation. Collaborators: Prof. Dr. J. Kärger (University of Leipzig); Prof. Dr. R. Buchner (University of Regensburg); Prof. Dr. M. Paluch (University of Silesia, Poland)

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

2.15. A novel position determination technique for polystyrene and silica colloids using video microscopy

C. Gutsche, O. Ueberschär, M.M. Elmahdy, G. Dominguez-Espinosa and F. Kremer

Common position detection methods in video microscopy typically produce significant artefacts when two or more colloids under observation are in close proximity to each other. In the paper [1] we present a new technique (Fig. 1) which is not subject to such artefacts up to a spatial resolution of ± 2 nm, the latter being the experimental uncertainty and thus lower limit of the used optical tweezers setup.

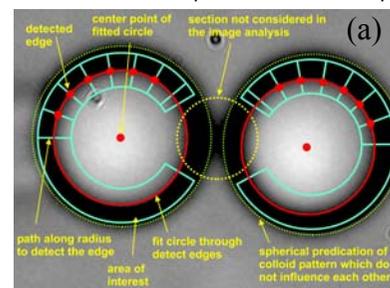


Fig. 1. (a) Example of an obtained video image of polystyrene beads in the described experimental situation. The left-hand colloid is held by the tip of a micropipette whereas the right-hand one is trapped by the photonic potential. The effects of the superposition of the corresponding diffraction patterns as the cause for the deformation of the outer dark diffuse ring are apparent for distance-diameter ratios of $r/d < 1.4$. The yellow dotted circle indicates the area of deformation while the green small dotted circles adumbrate the (hypothetical) spherical diffraction patterns of the single colloids.

The cyan and red lines illustrate the fitting framework for the position detection. (b) (top) Obtained step width of the colloid fixed to the pipette which was moved by the piezo stage in 10 nm steps versus the distance between the two colloids. The step width was measured by means of the discussed edge detection algorithm. The black spheres represent a measurement on polystyrene beads with a diameter of 2.24 μm whereas the green spheres correspond to an experiment with silica beads having a diameter of 2.04 μm . The red error bar indicates the position uncertainty of the piezo stage. (bottom) Distribution of the measured step widths. The upper histogram shows the distribution for polystyrene beads (black bars) while the lower histogram was obtained for silica beads (green bars). The red lines indicate the respective Gauss fits.

References:

[1] C. Gutsche, O. Ueberschär, M.M. Elmahdy, G. Dominguez-Espinosa and F. Kremer submitted to *Rev. Sci. Instrum.*

Funding:

DFG priority programm 1164 (Nano- & Microfluidics)

2.14 Infrared transition moment orientational analysis (IR-TMOA)

W. Kossack, P. Papadopoulos, F. Kremer

A novel spectroscopic method is developed for unravelling the mean orientation and molecular order parameter in any IR-transparent or translucent material. Combining the variation of inclination and polarization of the incoming electromagnetic wave the electric field can be chosen nearly arbitrarily. Taking advantage of the specificity of the IR spectral range, the directional dependence of the absorption coefficient provides detailed information concerning the directional distributions of the molecular moieties of the sample under study [1]. Furthermore a theory was developed, that takes into account the special properties of polymer films in the near infrared region and corrects for scattering and reflection [2]. Based on numerical solutions of Maxwell's equations the (three-dimensional) complex refractive index tensor can be determined for non-scattering samples [3].

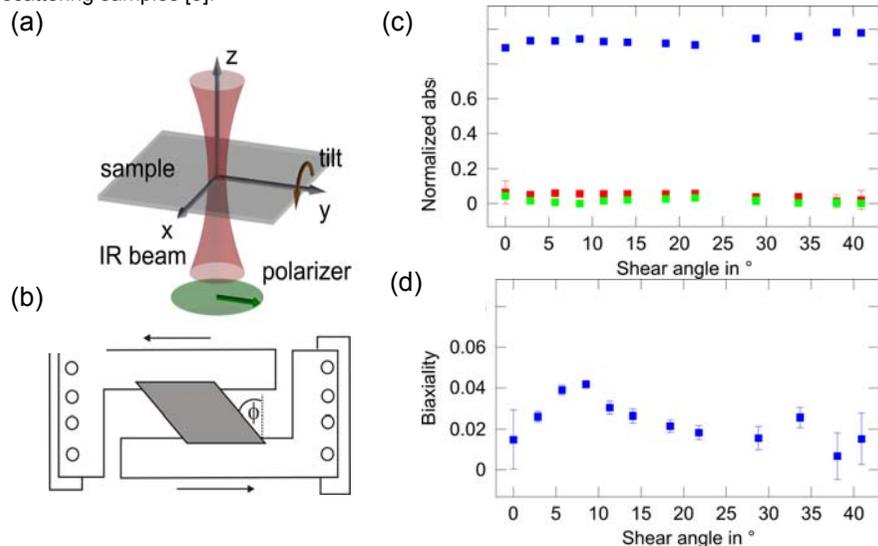


Fig. 1: (a) Measurement principle used for the IR TMOA technique. The electric field vector of the IR beam (green) can be rotated with a polariser, while the sample can be tilted. This way the electric field can have any direction. (b) Geometry of the shear measurement with definition of the shear angle Φ ; The sample is indicated as the grey rhombus. (c) and (d) Application of IR-TMOA to a smectic liquid crystalline elastomer, (c) Normalized absorption coefficients are shown for three perpendicular directions. Since they are proportional to the quadratic averaged probabilities to find a molecule in that direction, it can be seen, that the sample is nearly uniaxial at the beginning but evolves with shear to a biaxial configuration before it returns to uniaxiality. The corresponding biaxiality parameter, which records the difference of the two minor absorption axes, is shown in (d).

References:

- [1] Skupin, Dissertation (2001)
- [2] Kossack, P. Papadopoulos, F. Kremer in preparation (2010)
- [3] Yeh: Optical Waves in Layered Media (1948)

Collaborators:

H. Finkelmann (Universität Freiburg)

Funding:

Leipzig School of Natural Sciences, "Building with Molecules and Nano-Objects" (BuildMoNa)

- 18 -

2.7 Charge transport and dipolar relaxations in hyper-branched polymers

J. R. Sangoro, G. Turky, and F. Kremer

Broadband Dielectric Spectroscopy, Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) and differential scanning calorimetry are combined to study charge transport and dipolar relaxations in novel hyper-branched polyamide amines (1-3). The dielectric spectra is dominated by conductivity contributions at higher temperatures (masking out the structural α -relaxation process)- whereas two secondary dipolar relaxation processes are observed at lower temperatures for the two samples investigated (Fig. 1). Based on Einstein and Einstein-Smoluchowski relations the diffusion coefficient is extracted from the dielectric spectra – in quantitative agreement with independent PFG NMR measurements. It exhibits a Vogel-Fulcher-Tammann-temperature dependence, while the effective number density of the charge carriers varies only weakly with temperature. Charge transport and structural α -relaxation are found to be characterized by a decoupling index of ~ 7 for the hyper-branched polymers studied.

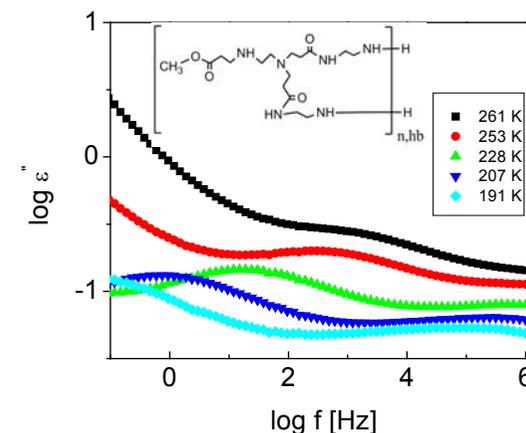


Fig. 1: Imaginary part of the complex dielectric function versus frequency at different temperatures illustrating the secondary relaxation processes in the hyper-branched polyamide amine (see inset).

References:

1. Broadband *Dielectric Spectroscopy*, edited by F. Kremer and A. Schönhals, Springer (2003).
2. Sangoro, J. R., Turky, G., Abdel-Rehim, M., Naumov, S., Ghoneim, A., Kärger, J., and Kremer, F. (2009). *Macromolecules*, 42(5) 1648-1651.
3. Turky, G., Sangoro, J. R., Abdel-Rehim, M., and Kremer, F. (2010). *J. Polym. Sci. B: Polym. Phys.*, in press

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

2.8 Characteristic hopping lengths and molecular volumes of imidazolium-based ionic liquids

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

Translational diffusion in bis(trifluoromethylsulfonyl)imide-based glass-forming ionic liquids (ILs) is investigated in a wide frequency and temperature range by means of Broadband Dielectric Spectroscopy (BDS), and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) [1-3] as shown in Fig. 1. It is experimentally shown that in the time-scale characterising the cross-over from sub-diffusive to diffusive ion dynamics, the hopping lengths are of the order of molecular diameters determined from quantum-chemical calculations [3]. This provides a direct means – via Einstein-Smoluchowski relation – to determine diffusion coefficient by BDS over more than 8 decades unambiguously and in quantitative agreement with PFG NMR measurements. Unprecedented possibilities in the study of charge transport and dynamic glass transition are thus opened.

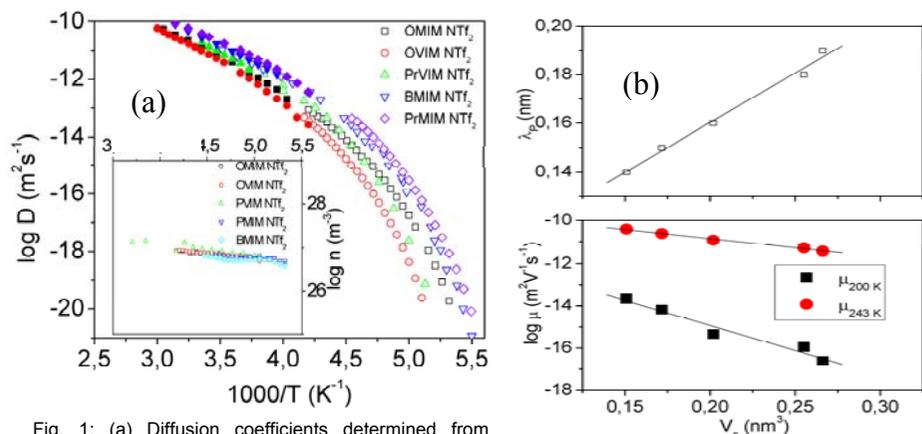


Fig. 1: (a) Diffusion coefficients determined from broadband dielectric spectra (open symbols) upon applying the Einstein-Smoluchowski equation for a series of ionic liquids based on bis(trifluoromethylsulfonyl)imide anion as well as the diffusion coefficient measured by PFG NMR (filled symbols) versus inverse temperature. Inset: the effective number density of charge carriers as a function of inverse temperature. (b) The experimentally obtained hopping lengths (upon combining PFG NMR and BDS) versus the sum of molecular volumes of anions and cations obtained from quantum chemical calculations for the different ionic liquids based on the same bis(trifluoromethylsulfonyl)imide anion. The calculations are carried out in the temperature ranges spanned by both techniques. The mobility at two selected temperatures are also compared to the computed volumes.

References:

- [1] *Broadband Dielectric Spectroscopy*, edited by F. Kremer and A. Schönhal, Springer (2003).
- [2] J. R. Sangoro, A. Serghi, S. Naumov, P. Galvosas, J. Kärgler, C. Wespe, F. Bordusa, and F. Kremer, *Phys. Rev. E* 77, 051202 (2008); J. R. Sangoro et al, *J. Chem. Phys.* 128, 214509 (2008); J. R. Sangoro, C. Iacob, A. Serghi, C. Friedrich, F. Kremer, *Phys. Chem. Chem. Phys.* 11, 913 (2009).
- [3] J. R. Sangoro et al, (2010) Under preparation; J. R. Sangoro (2010), Doctoral dissertation, submitted.

Collaborators: PD Dr. V. Strehmel (University of Potsdam), Prof. Dr. R. Buchner (University of Regensburg), Prof. Dr. C. Friedrich (University of Freiburg), Prof. Dr. B. Kirchner (University of Leipzig)

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

2.13 Electromechanical properties of smectic C* liquid crystal elastomers under shear

P. Papadopoulos and F. Kremer

Liquid crystal elastomers combine the electrical and optical anisotropy of liquid crystals with the mechanical properties of polymer networks. In smectic C systems, doping with chiral mesogen induces the formation of domains with permanent electric dipole moment. During the simultaneous crosslinking and orientation of the mesogen in a uniaxial mechanical field a polydomain morphology is obtained, where the piezoelectric effects are averaged out. Shear breaks the symmetry and induces the formation of monodomain structure (Fig. 1a) [1]. The piezoelectric coefficient reaches its maximum at a certain shear angle that corresponds to the completion of polydomain to monodomain transformation (Fig. 1b). The complex coefficient shows a strong dependence on temperature, especially near the smectic to isotropic transition (Fig. 2), but also on the static mechanical stress and frequency [2].

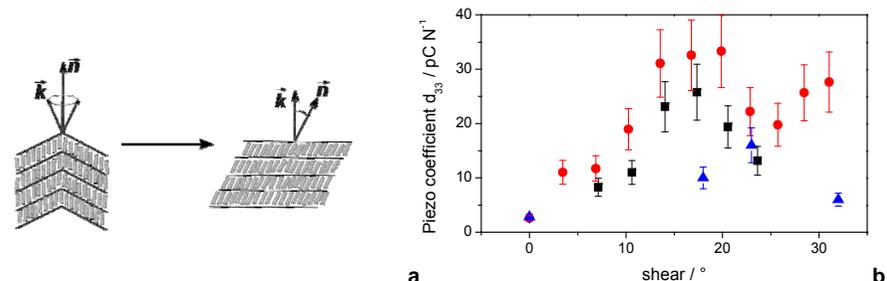


Fig. 1. Shear dependence of the piezoelectric coefficient. (a) The polydomain morphology is converted to monodomain after shearing. (b) In all three independent measurements (three different samples) a clear maximum around 15-20° is observed coinciding with the completion of polydomain to monodomain morphology conversion [1]. The measurements were carried out at 40 °C, 100 Hz, static strain of 0.04 and static stress=0.5 MPa.

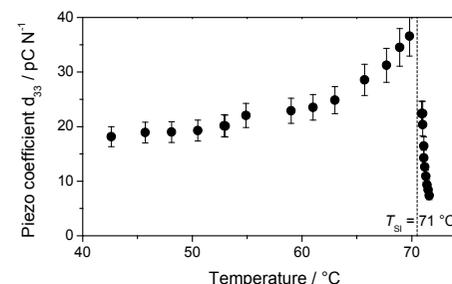


Fig. 2. Dependence of the piezoelectric coefficient on temperature. The strain amplitude is 0.04, shear angle 22°, $f=100$ Hz. The static stress is ~ 0.10 MPa, in the regime where the piezoelectric coefficient is not affected by stress. A sharp drop during the smectic to isotropic transition is observed.

References:

- [1] P. Heinze, H. Finkelmann; *Macromolecules* (2010)
- [2] P. Papadopoulos, P. Heinze, H. Finkelmann, F. Kremer; *in preparation*.

Collaborators:

H. Finkelmann (Universität Freiburg)

2.12 Spider silk: A soft solid with a unidirectional phononic band gap

P. Papadopoulos and F. Kremer

The superior properties of spider dragline silk, compared to synthetic polymers with similar chemical structure, such as polyamides, are due to the hierarchical nanostructure that is created in the spinning duct. Here we employ spontaneous Brillouin light scattering (BLS), a unique non-destructive and non-contact optical technique to probe propagation of thermally excited acoustic waves (phonons) at hypersonic frequencies (and hence wavelengths at the sub-micrometer length scale) in microstructures along different symmetry directions [1]. An unsuspected unidirectional phononic band gap is observed along the fiber axis (Fig. 1). At low wavevector values the dispersion diagram shows an acoustic behavior. The difference between the parallel and perpendicular directions is due to the high orientation of the protein along the fiber axis. At higher wavevector q in the parallel direction a stop band is observed, for the first time in biological structures [2]. Unlike periodic structures, such as colloidal crystals, it is not a Bragg-type band gap, since the nanocrystals do not form a periodic superstructure.

In order to investigate possible relations between the supramolecular structure and the observed unidirectional gap, we study fibers with decreased or increased pre-strain, created by supercontracting or stretching, respectively. The reduced pre-strain increases the contrast ΔZ between nanocrystals and the interconnecting amorphous chains and, therefore, between domains of higher and lower crystallinity. Stretching has the opposite effect, increasing mechanical anisotropy.

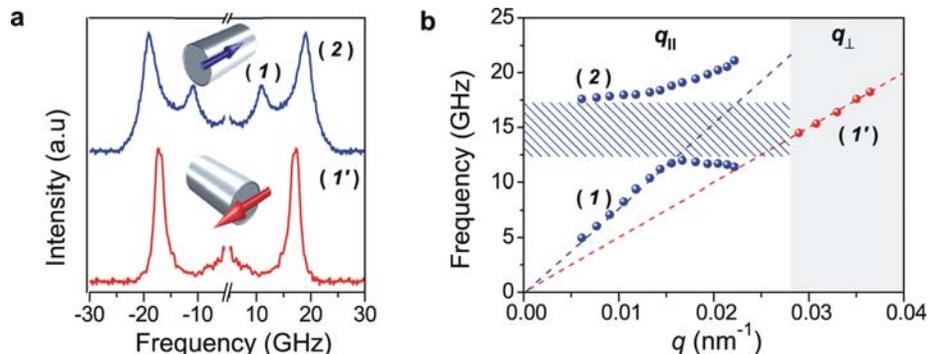


Fig.1. BLS spectra and experimental dispersion diagram of the native spider dragline silk along two symmetry directions. (a) BLS spectra at $q_{||}=0.0167 \text{ nm}^{-1}$ (in blue) with two peaks (1 and 2) along the fiber and at $q_{\perp}=0.0365 \text{ nm}^{-1}$ (in red) with one peak (1') normal to the fiber axis. (b) Dispersion relations for modes (1) and (2) (●) and mode (1') (●) representing elastic wave propagation parallel and normal to the fiber, respectively. The two dashed lines indicate the effective medium sound velocities in the two directions whereas the hatched area denotes the unidirectional stop band.

References:

- [1] N. Gomopoulos, W. Cheng, M. Efremov, P.F. Nealey, G. Fytas (2009) *Macromolecules* 42:7164
 [2] N. Gomopoulos, P.Papadopoulos, F.Kremer, G.Fytas; *submitted to PNAS (2010)*

Collaborators:

G. Fytas (Max Planck Institute for Polymer Research and University of Crete)

2.9 Charge transport and diffusion of ionic liquids in nanoporous silica membranes

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

Charge transport in 1-hexyl-3-methylimidazolium hexafluorophosphate ionic liquid in oxidized nanoporous silicon membranes – 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). By applying the Einstein-Smoluchowski relation to the dielectric spectra, diffusion coefficient is obtained in quantitative agreement with independent PFG NMR measurements (Fig.1). More than 10-fold systematic decrease in the diffusion coefficient from the bulk value is observed in silica nanopores. This is explained within the framework of a model taking into account a decreased mobility at the interface of the pore and the nanoporous membrane due to the ability of the hydrogen-bonded ionic liquid to attach to SiO_2 surfaces. By that, it becomes possible to probe the size of the adsorption layer and its temperature dependence. This has direct technological implications to the use of ionic liquids in fuel cells and nanobatteries.

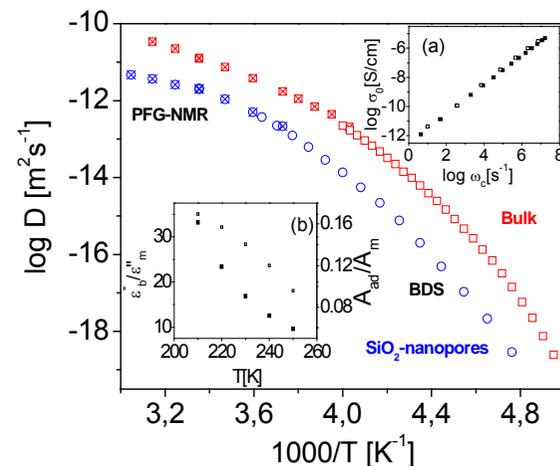


Fig.1: Diffusion coefficient determined by applying the Einstein-Smoluchowski equation to the dielectric spectra of HMIM PF_6 (in bulk and nanopores denoted by empty squares and circles respectively) and measured by PFG NMR (in bulk and nanopores represented by crossed squares and circles respectively) versus inverse temperature. Inset: (a) dc-conductivity σ_0 versus the characteristic rate of charge transport ω_c (in bulk and nanopores represented by square filled symbols and empty square symbols respectively), (b) Temperature dependence of the ratio of the dielectric loss in bulk to the total dielectric loss in nanopores ($\epsilon''_b/\epsilon''_m$) (full squares). The ratio of the surface area of the pores as a function of temperature are also given as shown (A_{ad}/A_m) (empty

squares). This plot illustrates the origin of the deviation of the measured dc conductivity (and consequently diffusion coefficient) in nanopores from the bulk values.

References:

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2.10 Charge transport and dipolar relaxations in Imidazolium-based Ionic Liquids

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Charge transport and dipolar relaxations in a series of imidazolium-based ionic liquids are studied by means of broadband dielectric spectroscopy. Despite the shift of more than 5 decades in the dielectric spectra upon systematic variation of the anion, scaling with respect to the dc conductivities and the characteristic rates yields a collapsing plot. The dielectric spectra are described at higher frequencies in terms of dipolar relaxations whereas hopping conduction in a random spatially varying energy landscape is quantitatively shown to dominate the spectra at lower frequencies. The β -relaxations observed for both the precursor and the ionic liquids are assigned to librational motion of the imidazolium ring. The corresponding dielectric strength exhibits a strong dependence on the anion.

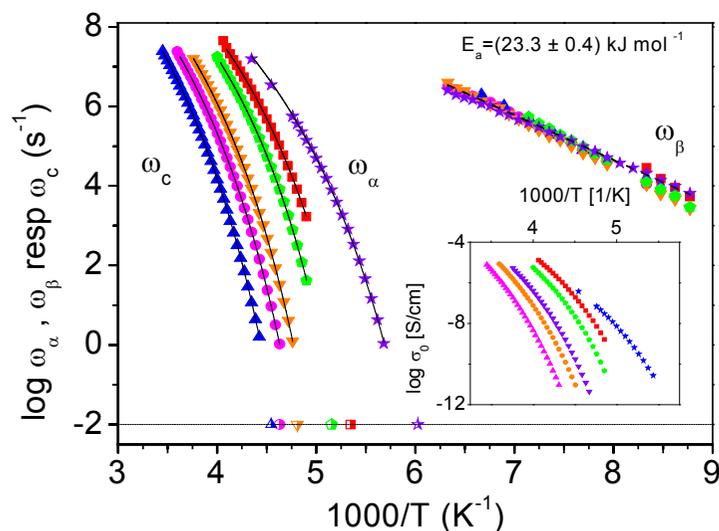


Fig.1: Temperature dependence of the structural α -relaxation rates of 1-hexyl-2-methylimidazole and the characteristic rates of charge transport as well as β -relaxations for the different ionic liquids. Inset: dc conductivity σ_{dc} as a function of inverse temperature ([HMIM][BF₄] (open squares), $T_g = 187$ K; [HMIM][Br] (open circles), $T_g = 216$ K; [HMIM][Cl] (open triangles), $T_g = 220$ K; [HMIM][I] (inverted open triangles), $T_g = 208$ K; [HMIM][PF₆] (open pentagons), $T_g = 194$ K; 1-hexyl-2-methylimidazole (open stars), $T_g = 166$ K). The error bars are smaller than the size of the symbols, if not specified otherwise. The experimentally determined values of calorimetric glass transition temperature T_g indicated by open symbols with vertical line.

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Krause, C., Sangoro, J.R., Iacob, C., Kremer, F. *J.Phys.Chem. B*, **114**, 382–386 (2010)

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2.11 Hierarchies in the structural organization of spider silk-A quantitative combined model

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Combined time-resolved mechanical and polarized Fourier-transform infrared measurements allow us to determine the interconnection of the nanocrystal and amorphous phases in major ampullate spider silk in the native and supercontracted states [1]. Crystal stress can be measured from the frequency shift of main-chain vibrations (Fig. 1a) [2]. In native silk the crystal stress is proportional to the external stress, regardless of strain, suggesting that a serial arrangement between the crystalline and amorphous phase dominates the nanostructure. However, supercontracted silk shows a different behavior. At low strain, before being stretched to a threshold of ~ 0.2 GPa, the ratio of crystal to external stress is higher. At higher strain is irreversibly reduced to a value similar to native. These observations suggest that a hydrogen-bonded network is formed in the amorphous phase, due to release of pre-stress and hydrophobic effects. 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 1a)-inlet [3].

The understanding of the role of water in the formation of the hydrogen-bonded network in the supercontracted state is essential in the effort of relating the mechanical properties to the nanostructure. For this reason, water permeability of dragline silk is studied by measuring changes in amide deuteration (Fig.1b) [4]. The results show that the chemical exchange of amide hydrogen occurs in a large fraction of amino acids, including β -sheeted alanine residues, suggesting that also the crystalline regions are accessible to water. It is noteworthy that hydrogen at highly oriented moieties are most easily exchanged.

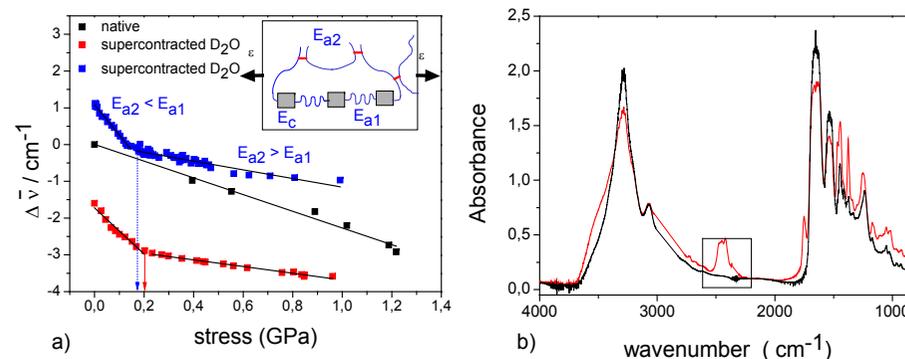


Fig. 1a) Crystal stress as a function of external stress. Inlet-combined structural model of organization in native and supercontracted spider silk. b) IR absorption spectrum of major ampullate silk from *Nephila edulis* in native state (black curve) and supercontracted state (D_2O -red curve). The spectral region between 2750 and 2250 cm^{-1} contains the ND bands resulted from the exchange of hydrogen with deuterium.

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