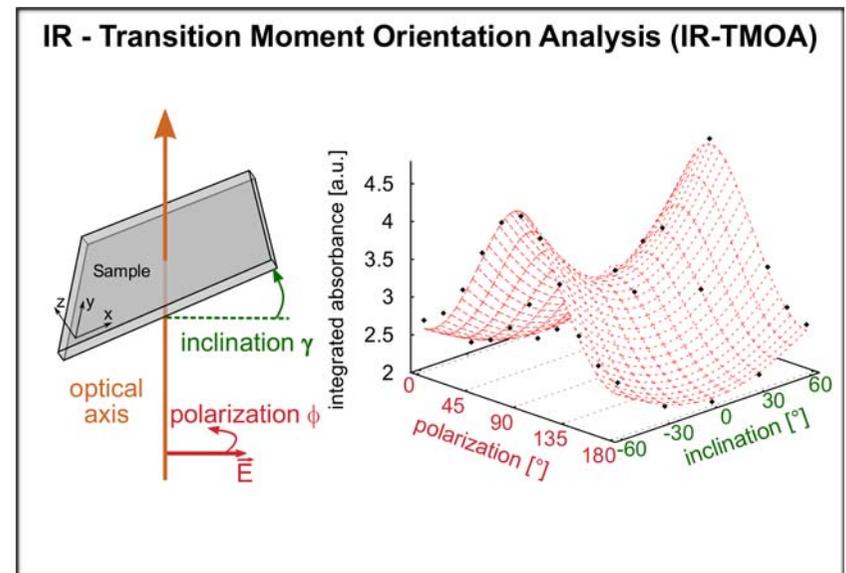


UNIVERSITY OF LEIPZIG

Faculty of Physics and Earth Sciences
Department of Experimental Physics I

GROUP “Molekülphysik”



Annual Report 2011

Cover picture: The approach of Transmission Moment Orientation Analysis (TMOA) recently developed in our group is employed to determine the three dimensional orientation and order of the different IR-active molecular moieties in any IR-translucent material. Based on transmission spectra for varying polarisation *and* inclination the full order parameter tensor and its orientation with respect to the sample coordinate system is obtained.

See references:

Kossack et al., doi: 10.1021/ma101121f and

Kossack et al., doi: 10.1016/j.polymer.2011.10.051

UNIVERSITÄT LEIPZIG

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5. Graduations

Doctoral degree:

Dipl.-Chem. **Roxana Ene** "Structural levels of organization in spider silk as studied by time-resolved polarized FTIR spectroscopy"

Diploma:

Tim Stangner "Wechselwirkungen zwischen Polymer-gepfropften Kolloiden"

Tilmann Schubert "Charakteristische Eigenschaften von molekularen Fluiden und Polymeren am dynamischen Glasübergang"

Bachelor of Science:

Hannes Krauß "FT IR-Messungen zur Temperaturabhängigkeit der Absorption von organischen Glasbildnern"

Benjamin Schott "Untersuchung photophysikalischer Eigenschaften des Photosensibilisators THPTS"

6. Industry collaborations

Novocontrol

Hundsangen, Germany

BOREALIS Polyolefine GmbH

Linz, Austria

Comtech GmbH

München, Germany

inotec FEG mbH

Markkleeberg, Germany

7. Patent applications

Deutsches Patent: 10 2005 045 065. (2011)

Titel: "Detektorvorrichtung zur Funktionsprüfung von Dichtungssystemen"

Erfinder: Prof. Dr. F. Kremer

8. Awards

Prof. Dr. Friedrich Kremer was awarded with the Wolfgang Ostwald Prize of the German Colloid Society.

4. Financial support

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

FOR 877: „ From local constraints to macroscopic transport” TP 7 "Electric field driven motion of single polyelectrolyte grafted colloids" TP3 "Dynamics of DNA under tension and confinement"
KR 1138/21-1 (2007-2011)

Prof. Dr. F. Kremer

FOR 877: „ From local constraints to macroscopic transport” TP 7 "Electric field driven motion of single polyelectrolyte grafted colloids"
KR 1138/21-2 (2011-2014)

Prof. Dr. F. Kremer

SPP 1191 "Ionic Liquids" TP "Charge transport and glassy dynamics in ionic liquids"
KR 1138/18-3 (2010–2012)

Prof. Dr. F. Kremer

SPP 1369 "Polymer-Solid Contacts: Interfaces and Interphases"
TP "Interfacial dynamics of polymers in interaction with solid substrates"
KR 1138/23-1 (2008–2011)
KR 1138/23-2 (2011–2014)

Prof. Dr. F. Kremer

Graduate School "Leipzig School of Natural Sciences –Building with Molecules and Nano-objects" **BuildMoNa**, TP 15 "Dynamics of DNA under tension and in confinement"
GSC 185/1 (2008-2012)

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

Prof. Dr. F. Kremer

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

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

Prof. Dr. F. Kremer

SFB/TRR 102 " Polymers under multiple constraints: restricted and controlled molecular order and mobility"

TP B05 "Structural levels of organisation in spider-silk - a combined mechanical and IR-spectroscopic study" (2011-2015)

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

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

The year 2011

Research requires persistency: After efforts starting in 2008 the universities of Halle and Leipzig successfully applied for a **Collaborative Research Center (Transregio) on "Polymers under multiple constraints: restricted and controlled molecular order and mobility"**. The decisive meeting with the reviewer panel of the DFG took place in April 2011, the letter of approval of the president of the German Science Foundation arrived in June and at the beginning of July the center started to work. Our group is engaged with two projects dealing with "Structural levels of organisation in spider silk – a combined mechanical and IR spectroscopic study" (B5) and "Broadband Dielectric Spectroscopy to study the molecular dynamics in nanometer thin layers of Block copolymers" (B8). The novel SFB is a extraordinary encouragement for the polymer community in the region of the Universities in Halle and in Leipzig. - Fully unexpectedly I was awarded with the Wolfgang-Ostwald-Prize of the German Colloid Society for the year 2011. This reflects nicely that the activities of our group in colloid science, especially the experiments with *single* colloids, are highly acknowledged.

January 2012

Friedrich Kremer

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3. Publications

1. Wagner, C., C. Olbrich, H. Brutzer, M. Salomo, U. Kleinekathöfer, U.F. Keyser, F. Kremer "DNA condensation by TmHU studied by optical tweezers, AFM and molecular dynamics simulations" *Journal of Biological Physics* **37**, 117-131 (2011). DOI: 10.1007/s10867-010-9203-7
2. Gutsche, C., M.M. Elmahdy, K. Kegler, I. Semenov, T. Stangner, O. Otto, O. Ueberschär, U.F. Keyser, M. Krüger, M. Rauscher, R. Weber, J. Harting, Y.W. Kim, V. Lobaskin, R.R. Netz and F. Kremer "Micro-rheology on (polymer-grafted) colloids using Optical Tweezers" *J. of Phys. Condensed Mater* **23**, 184114-184131 (2011) DOI:10.1088/0953-8984/23/18/184114
3. Sangoro, J. R., Iacob, C., Naumov, S., Hunger, J., Rexhausen, H., Valiullin, R., Strehmel, V., Buchner, R., Kärger, J., and Kremer, F. "Diffusion in ionic liquids: the interplay between molecular structure and dynamics". *Soft Matter* **7**, 1678-1681 (2011) DOI:10.1039/C0SM01404D
4. Ueberschär, O.,C. Wagner, T. Stangner, C. Gutsche, F. Kremer "The effective hydrodynamic radius of *single* DNA-grafted colloids as measured by fast Brownian motion analysis" *Polymer* **52**, 1829-1836 (2011) DOI:10.1016/j.polymer.2011.02.001
5. Sangoro, J.R., C. Iacob, R. Valiullin, C. Friedrich, J. Kärger, F. Kremer "Rotational and translational diffusion in glass-forming N,N, -diethyl-3-methylbenzamide (DEET)".*Soft Matter*, **7**, (22) 10565-10568 (2011) DOI: 10.1039/C1SM06377D
6. Serghei,A., J.R. Sangoro, F. Kremer "Broadband Dielectric Spectroscopy on electrode polarization and its scaling" Chapter 15 of the book "Electrical Phenomena at Interfaces and Biointerfaces: Fundamentals in Nano- Bio- and Environmental Sciences" Ed. Hiroyuki Ohshima, accepted by *John Wiley&Sons, Inc. New York*, (2011)
7. Spiess, K., R. Ene, C. Keenan, J. Senker, F. Kremer, T. Scheibel "Impact of initial solvent on thermal stability and mechanical properties of recombinant spider silk films" *J. Mater. Chem.*, **21**, 13594-13604 (2011) DOI: 10.1039/c1jm11700a
8. Wagner, C., D. Singer, O. Ueberschär, T. Stangner, C. Gutsche, R. Hoffmann, F. Kremer "Dynamic force spectroscopy on the binding of monoclonal antibodies and tau peptides" *Soft Matter* **7**, 4370-4378 (2011) DOI: 10.1039/c0sm01414a
9. Ueberschär, O.,C. Wagner, T. Stangner, K. Kühne, C. Gutsche, F. Kremer "Drag reduction by DNA-grafting for single microspheres in a dilute λ -DNA solution" *Polymer* **52**, 4021-4032 (2011) DOI: 10.1016/j.polymer.2011.06.057
10. Hagenau, A., P. Papadopoulos, F. Kremer, T. Scheibel, "Mussel collagen molecules with silk-like domains as load-bearing elements in distal byssal threads" *J. Structural Biology* **175** (3) 339-347 (2011) DOI: 10.1016/j.jsb.2011.05.016
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1. Organization of the group

Leader: Prof. Dr. Friedrich Kremer

Academic Staff and Postdocs

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 Dr. Mahdy M. Elmahdy
 Dr. Joshua Rume Sangoro
 Dr. Malgorzata Jasiurkowska

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 Dipl. -Phys. Carolin Wagner
 M. Sc. Ciprian Ghiorghita Iacob
 Dipl.-Phys. Markus Anton
 Dipl.-Phys. Wilhelm Kossack
 M. Sc. Wycliffe Kiprof Kipnusu
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 M. Sc. Ilya Semenov
 M. Sc. Emmanuel Urandu Mapesa
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 cand. B.Sc. Hannes Krauß
 cand. B.Sc. Benjamin Schott
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 M.Sc. Ignacio Martin-Fabiani Carrato (C.S.I.C., Madrid, Spain)
 Dr. Christina Krywka (Uni Kiel, Germany)

Alumni

Prof. Dr. Siegbert Grande

2.21 Electrophoretic mobility of ds-DNA-grafted single colloids as studied by optical tweezers

I.Semenov, C.Gutsche, M.M. Elmahdy, O.Ueberschär, F.Kremer

The electrophoretic mobility of *single* colloids grafted with double stranded (ds) DNA is studied by Single Colloid Electrophoresis [1, 2]. For that Optical Tweezers (OT) are employed to measure separately the complex electrophoretic mobility of a single colloid and the complex electroosmotic response of the surrounding medium. Parameters to be varied are the concentration ($10^{-5} - 1$ mol/l) and valency (KCl, CaCl₂, LaCl₃) of the ions in the surrounding aqueous medium, as well as the contour length (250, 1000 and 4000 base pairs) of the grafted chains in the latter case.

For the ds-DNA-grafted colloids a pronounced decrease of the electrophoretic mobility is observed in comparison to blank particles and with increasing DNA molecular weight, under identical conditions (Fig. 1(left)). The findings are discussed in terms of the Standard Electrokinetic Model [3]. The electrophoretic mobility of a ds-DNA-grafted single colloid at high ionic strength can be understood quantitatively within the limits of the linearized Poisson-Boltzmann equation, i.e. using the so-called Smoluchowski formula:

$$\mu_e = - \frac{e Z_{eff}^{total}}{4 \pi \eta \alpha_{eff} (1 + \kappa \alpha)} \quad (1)$$

where the *effective hydrodynamic radius* $\alpha_{eff} = R_{bare} + \Delta R$ of a single ds-DNA-grafted particle in varying ionic strength of the surrounding medium is determined by means of Brownian motion analysis and OT accomplished with fast position detection [4]. The *effective charge* Z_{eff}^{bare} is

obtained from the measurements of the interaction forces between two *identical* ds-DNA-grafted colloids in electrolyte solutions of different concentrations assuming that the zeta potential of the *blank* particle is to be defined at the slipping plane of the whole DNA brush, as it show on Fig.1 (right).

$$Z_{eff}^{total} = (Z_{eff}^{bare} - \eta) e^{-x\Delta R} + Z_{eff}^{DNA Layer} \quad (2)$$

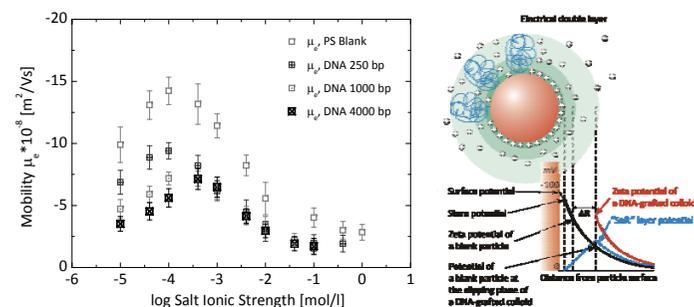


Fig. 1: (left) the electrophoretic mobility vs. salt ionic strength of aqueous KCl solution for the negatively charged blank and ds-DNA-grafted colloids with varying DNA molecular weight (250, 1000 and 4000 base pairs) and grafting density 1250 chains per colloid. (right) Schematic diagram of the EDL (not to scale) at the negatively charged blank particle interface, depicting the probable electrostatic potential distribution above the blank particle's surface and possible shift of the shear plane due to DNA coating, where the Z_{eff}^{bare} is to be considered.

References:

- [1] I. Semenov et al., Journal of Physics: Condensed Matter **22**, 494109 (2010).
- [2] I. Semenov et al., Journal of Colloid and Interface Science **337**, 260 (2009).
- [3] R. W. O'Brien, and L. R. White, J. Chem. Soc., Faraday Transactions 2: Molecular and Chemical Physics **74**, 1607 (1978).
- [4] O. Ueberschär et al., Polymer **52**, 1829 (2011).

Funding: Sächsische Forschergruppe FOR 877, DFG

2.20 A novel video-based microsphere localization algorithm for low contrast silica particles under white light illumination

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

On the basis of a brief review of four common image recognition algorithms for microspheres made of polystyrene or melamine resin, we present a new microsphere localization method for low-contrast silica beads under white light illumination. We compare both the polystyrene and silica procedures with respect to accuracy and precision by means of an optical tweezers setup providing CMOS video microscopy capability. By that we demonstrate that our new silica algorithm achieves a relative position uncertainty of less than ± 1 nm for micron-sized microspheres, significantly exceeding the precision of the other silica approaches studied. Second, we present an advancement of our single microsphere tracking method to scenarios where two polystyrene, melamine resin or silica microspheres are in close-to-contact proximity. While the majority of the analysis algorithms studied generate artefacts due to interference effects under these conditions, we show that our new approach yields accurate and precise results. In summary, we recommend using our new algorithms with preference when tracking silica microspheres in video microscopy, as it is often required in optical tweezers experiments.

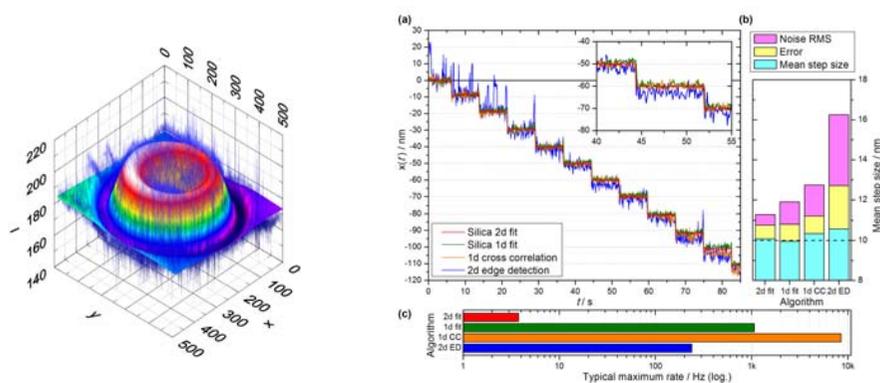


Fig. 1. The new algorithm *Silica 2d fit*. Left: The intensity profile of silica microsphere (diameter of $(4.71 \pm 0.47) \mu\text{m}$) is plotted (blue shaded noisy surface) and fitted to an empirical function (colour spectrum smooth surface). Right: Experimental investigation of the accuracy and precision of our two new and two established single silica algorithms. The experimentally acquired video microscopy images of a piezo stage position ramp are analyzed and plotted. The accuracy, the precision as well as the execution (i.e. computation) speed of these four algorithms are compared on the basis of this image analysis process.

References:

[1] O. Ueberschär, C. Wagner, T. Stangner, C. Gutsche, F. Kremer, *Optics and Lasers in Engineering* **50**, 423–439 (2012)

Funding: Graduate School BuildMoNa

2. Projects

2.1 Glassy dynamics of isolated polymer coils

M. Treß, E. U. Mapesa and F. Kremer*

For the first time, the glassy dynamics of randomly distributed, *isolated* poly(2-vinylpyridine) (P2VP) polymer coils is studied by means of Broadband Dielectric Spectroscopy (BDS). This is achieved by recently developed nano-structured electrode arrangements where isolated polymer coils are deposited onto ultra-flat, highly conductive silicon electrodes. Atomic Force Microscopy scans (see Fig. 1a) to c)) of the identical sample before and after the BDS measurement prove that the volume of the coils matches, within a factor of 10 (reflecting the broad molecular weight distribution), with the expected volume of a single chain (considering bulk density and the respective molecular weight) as depicted in Fig. 1d). The observed dynamics compares well with that of bulk (presented in Fig. 2a) but is slowed down by up to a factor of about 10 (demonstrated in Fig. 2b)). This is attributed to attractive interactions of the P2VP segments with the supporting silica surface - effects which were not observed before in our investigations on polymer layers down to thicknesses of 5 nm [1,2].

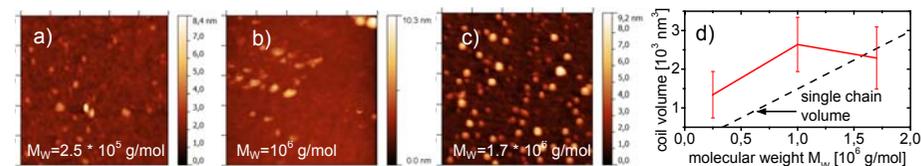


Fig. 1: a) to c) AFM pictures ($1 \times 1 \mu\text{m}^2$) of isolated P2VP polymer coils of different molecular weight as indicated: d) average coil volume (deduced by AFM) plotted vs. molecular weight, the dashed line indicates the volume of a single chain as expected under bulk conditions.

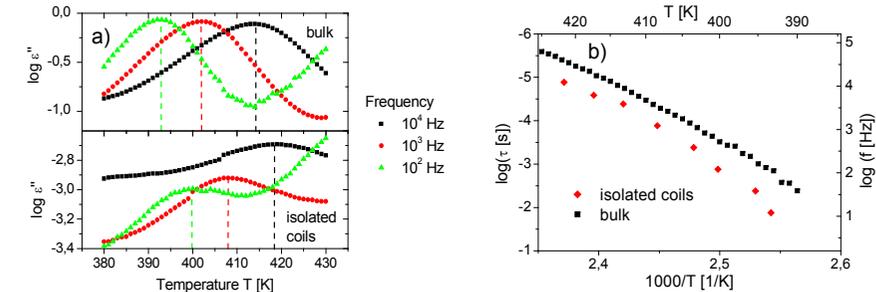


Fig. 2: a) Dielectric loss ϵ'' versus Temperature of bulk and isolated polymer coils of P2VP measured at different frequencies as indicated: b) activation plot of the data shown in a).

References:

[1] M. Tress, M. Erber, E. U. Mapesa, H. Huth, J. Müller, A. Serghei, C. Schick, K.-J. Eichhorn, B. Voit and F. Kremer, *Macromol.* **43**, 9937 (2010)
 [2] E. U. Mapesa, M. Erber, M. Tress, K.-J. Eichhorn, A. Serghei, B. Voit and F. Kremer, *Eur. Phys. J. Spec. Top.* **173**, 189 (2010)

Collaborations:

Dr. M. Reiche, Max-Planck-Institute for Microstructure Physics, Halle

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

*The underlined author initiated the project.

2.2 Nanometric sample capacitors

M. Treß, E. U. Mapesa and F. Kremer

Recently, a sample arrangement for applying Broadband Dielectric Spectroscopy (BDS) to nanometric samples was realized [1] by the application of ultra-flat highly conductive silicon wafers featured with insulating silica nanostructures which act as spacers. Technically speaking, a flat wafer (without nano-structures) is covered with sample material and is then covered by the counter electrode which carries the nanostructures to keep it in defined separation and avoid an electrical short circuit (schemed in Fig. 1a). Initially, this technique was conducted with randomly distributed silica colloidal particles [2], resulting in electrode separations of about a micrometer leading to capacitor volumes of tens of nanoliters. The introduction of nano-structures as spacers [2] (Fig. 1b) displays an array of such structures) and permanent improvement of the insulation quality of the nano-structures as well as the supporting electrode yielded sample capacitors of less than 100 nm in thickness and a probe volume of one nanoliter. Fig. 1c) shows an image of a nano-structure as high as 60 nm obtained by atomic force microscopy (AFM).

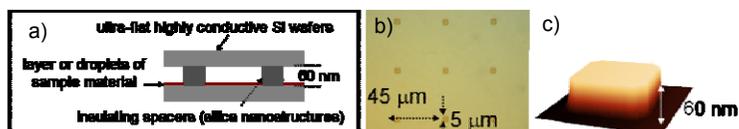


Fig. 1: a) Scheme of the sample capacitor; b) and c) images of the regular nano-structure array and a single nano-structure obtained by optical microscopy and AFM, respectively.

Due to the high electrical insulation of the silica nano-structures, extremely low values of the dielectric loss ϵ'' can be detected in these nanometric probe volumes. Fig. 2 exemplifies this for an empty sample cell built from 60-nm-high nano-structures where in the frequency range from 1 Hz to 10 kHz a dielectric loss of less than 10^{-3} is achieved. This enables us to measure dielectric properties of extremely small amounts of material in these sample capacitors reaching volumes as small as one picoliter [3,4]. Further, the surface of the substrate can be modified [5].

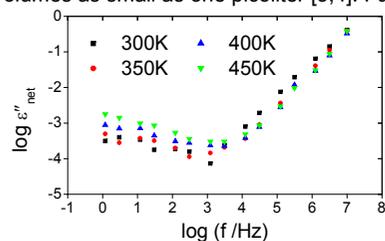


Fig.2: Spectra of the dielectric loss of an empty capacitor built from nano-structured electrodes of 60 nm thickness recorded at different temperatures as indicated.

References:

- [1] A. Serghei and F. Kremer, Rev. Sci. Inst. **79** 026101 (2008)
- [2] A. Serghei and F. Kremer, Rev. Sci. Inst. **77** 116108 (2006)
- [3] M. Tress, M. Erber, E. U. Mapesa, H. Huth, J. Müller, A. Serghei, C. Schick, K.-J. Eichhorn, B. Voit and F. Kremer, F. Macromol. **43**, 9937 (2010)
- [4] E. U. Mapesa, M. Erber, M. Tress, K.-J. Eichhorn, A. Serghei, B. Voit and F. Kremer, Eur. Phys. J. Spec. Top. **173**, 189 (2010)
- [5] M. Erber, M. Tress, E. U. Mapesa, A. Serghei, K.-J. Eichhorn, B. Voit and F. Kremer, F. Macromol. **43**, 7729 (2010)

Collaborations:

Dr. M. Reiche, Max-Planck-Institute for Microstructure Physics, Halle

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

2.19 Drag reduction by DNA-grafting for single microspheres in a dilute λ -DNA solution

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

* Molekulare Onkologie, Universitätsfrauenklinik Leipzig, Arbeitsgruppe Prof. Kurt Engeland, Semmelweisstraße 14, 04103 Leipzig, Germany

The fluid resistance of single micrometre-sized blank and DNA-grafted polystyrene microspheres under shear flow is compared in purified water and dilute λ -DNA solutions by means of optical tweezers experiments with a high spatial (± 4 nm) and temporal (± 0.2 ms) resolution. The measurement results show that the drag experienced by a colloid in a dilute λ -DNA solution (molecular weight of 48502 bp per molecule, radius of gyration of 0.5 μ m) is significantly decreased if the microsphere bears a grafted DNA brush. This newly discovered drag reduction effect is studied for different parameters, comprising the molecular weight of the grafted DNA molecules (250 bp, 1000 bp and 4000 bp), the concentration of the λ -DNA solution (11, 17 and 23 μ g ml⁻¹, all being significantly smaller than the critical entanglement concentration c^*), the microsphere core diameter (2 μ m, 3 μ m and 6 μ m) as well as the flow speed of the medium (10 to 50 μ m s⁻¹). The maximum extent of the drag reduction is found to amount to $(60 \pm 20)\%$ compared to the λ -DNA-induced contribution on the drag acting for blank colloids. We propose a theoretical explanation of this effect based on the combination of the drift diffusion model of Rauscher and co-workers [2] and the stagnation length theory of polymer brushes, as it was established by Kim, Lobaskin *et al.* [3]. In particular, the solution of the Stokes equation (i.e., the Navier-Stokes equation for creeping flow) for the studied system yields a numerical prediction that is found to be in full accord with our experimental results within experimental uncertainty.

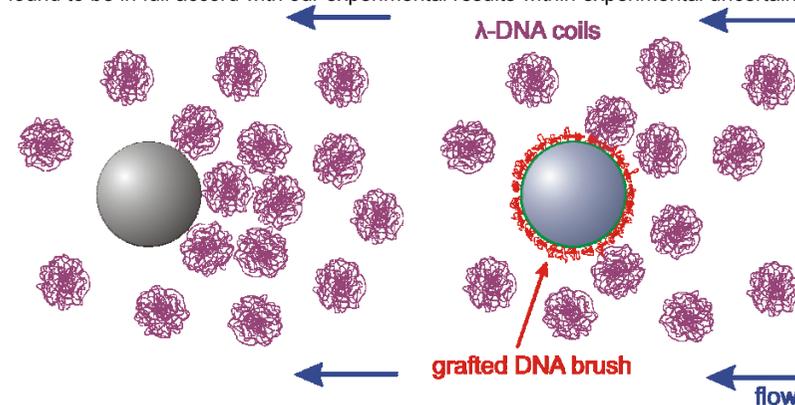


Fig. 1: Schematic of the origin of the drag reduction effect. Left: The flow field around a hard sphere under no-slip condition leads to an accumulation of λ -DNA coils in front of and to the depletion of such behind the colloid. Right: The analogous scenario is shown for a grafted colloid (4000 bp DNA) with an effective hydrodynamic radius increased by 130 nm. While the minimum centre-centre distance for the grafted colloid and λ -DNA coils is the same as in the case of a blank colloid, the flow field vanishes now at an increased distance from the sphere surface. The radial component at the maximum-proximity distance of a λ -DNA coil is thus smaller (by approximately 44% in the depicted case), leading to a decrease of the extent of λ -DNA accumulation and depletion. As a result, the acting drag forces are equally decreased.

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Funding: Graduate School BuildMoNa

2.18 Dynamic force spectroscopy on fluorescence-labeled tau-peptides and monoclonal antibodies measured by Optical Tweezers

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Optical tweezers are experimental tools with extraordinary resolution in positioning (± 1 nm) a micron-sized colloid and in the measurement of forces (± 0.5 pN) acting on it - without any mechanical contact. The combination of optical tweezers and dynamic force spectroscopy is a promising approach to gain deep insight into biological systems on the level of single receptor-ligand-interactions. Here we report about the specific binding of an anti-human tau-monooclonal antibody (mAb), HPT-104, interacting with a synthetic fluorescence-labeled tau-peptide, containing a phosphorylation at Thr231. The fluorescent tagged tau-peptides, anchored on Melanin-resin beads, are presorted with the fluorescence activated cell sorting (FACS) method (Fig. 1. a, b)) in order to achieve homogenous and reproducible surface coverage. By that the results can be more easily compared with other experiments, using different antibodies and/or phosphorylation pattern. Specific binding events between peptide and mAbs, obtained by dynamic force spectroscopy, are described according to the Dudko-Hummer-Szabo-model [1] (Fig. 1 c)). Fitting parameters are bond lifetime (τ_0), binding length (x_{ts}) and depth of the binding potential ΔG . A comparison between labeled and non-labeled tau-peptides [2] and their interactions with mAbs shows that, due to the presence of the fluorescence dye (Fluorescein), the bond lifetime and binding length is reduced.

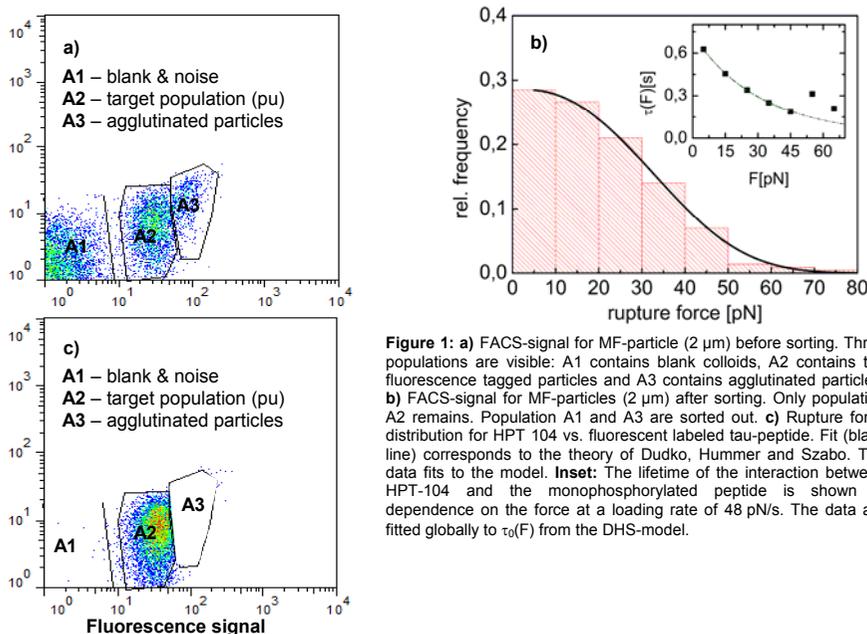


Figure 1: a) FACS-signal for MF-particle (2 μ m) before sorting. Three populations are visible: A1 contains blank colloids, A2 contains the fluorescence tagged particles and A3 contains agglutinated particles. b) FACS-signal for MF-particles (2 μ m) after sorting. Only population A2 remains. Population A1 and A3 are sorted out. c) Rupture force distribution for HPT 104 vs. fluorescent labeled tau-peptide. Fit (black line) corresponds to the theory of Dudko, Hummer and Szabo. The data fits to the model. **Inset:** The lifetime of the interaction between HPT-104 and the monophosphorylated peptide is shown in dependence on the force at a loading rate of 48 pN/s. The data are fitted globally to $\tau_0(F)$ from the DHS-model.

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Funding: ESF, BuildMoNa

2.3 Glassy dynamics of polybutadiene in uniaxial nano-porous membranes

M. Treß, E. U. Mapesa and F. Kremer

The molecular dynamics of polybutadiene (PB) is measured in the confinement of nano-porous membranes of anodized aluminium oxide (AAO) by means of Broadband Dielectric Spectroscopy (BDS). This investigation is part of a project in the framework of DFG priority program 1369 which combines the expertise of several groups. In the collaborating chemistry institute of the University of Osnabrück an anodization setup, particularly developed for this purpose, is used to create uni-axial channels of nanometric diameter in an aluminium template which is thermally oxidized thereafter (see Fig. 1).

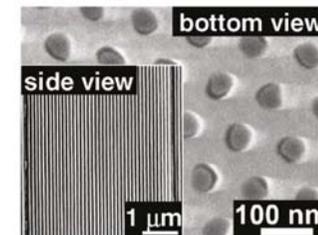


Fig. 1: Scanning electron micrographs of AAO. Bottom of a 100 μ m thick self-ordered AAO membrane (60 nm pore diameter) after infiltration with PB. Inset: cross section of a self-ordered AAO membrane prior to infiltration. Image and caption (modified) taken from [1]

The segmental motion (glassy dynamics) of PB is studied in the confinement of these pores in diameters down to 20 nm. Our measurements reveal that under these conditions the glassy dynamics is not shifted compared to the bulk (Fig. 2). This result coincides with the findings of other project participants who investigate the same samples by means of nuclear magnetic resonance [2] or perform computer simulations on these systems [3].

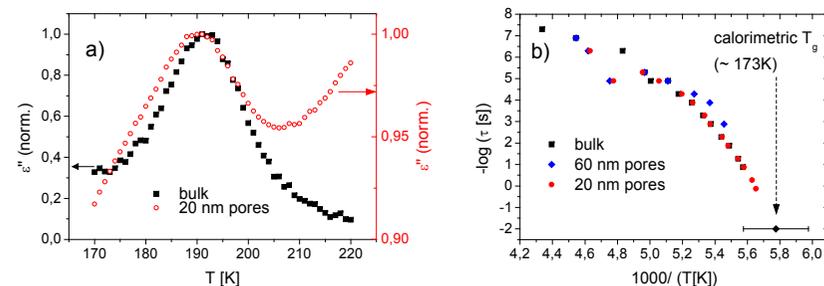


Fig. 2: a) Dielectric loss ϵ'' versus Temperature of PB in nano-porous AAO membranes (pore diameter as indicated) and bulk recorded at a frequency of 1.2 kHz. b) Activation plot of the α -relaxation of PB in nano-porous AAO membranes (pore diameter as indicated) and bulk.

Collaborations:

Fabrication/filling of AAO membranes: F. Thöle, B. Hartmann, M. Steinhart, Universität Osnabrück

References:

- [1] S. Ok, M. Steinhart, A. Şerbescu, C. Franz, F. Vaca Chávez and K. Saalwächter, Macromol. **43**, 4429 (2010)
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Funding: DFG priority program SPP1369 (polymer-solid contacts: interfaces and interphases).

2.4 Segmental and chain dynamics in thin layers of cis-polyisoprene

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

Using a novel capacitor assembly – where silica nanostructures serve as spacers between highly-doped silicon electrodes [1] – thin layers of *cis*-polyisoprene (44.5, 53 and 75 kg/mol) were studied by means of Broadband Dielectric Spectroscopy (BDS). *cis*-polyisoprene has a non-zero component of its dipole moment aligned along the main chain thus enabling the investigation, by BDS, of the fluctuation of its end-to-end vector. Effectively then, two distinct relaxation modes taking place at two different length scales can be studied: 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 [2].

Thin layers were prepared by spincoating polyisoprene/chloroform solutions at 3000 rpm for 20 s, and their thicknesses systematically varied by changing the concentration of the solutions. The topography of the spin-cast samples was checked by AFM before and after dielectric measurement to exclude possible dewetting effects on the measured dynamics. Down to ~7 nm, it is observed (Fig. 1) that: (i) the segmental mode as a local relaxation process is independent of layer thickness; and (ii) the normal mode becomes faster with decreasing layer thickness, in dependence on molecular weight. The former result – consistent with our previous findings [3] – underscores the fact that the dynamic glass transition is invariant, at least in the studied thickness range, while the latter points to a possible alteration of the chain conformation when the polymer is confined in thin films.

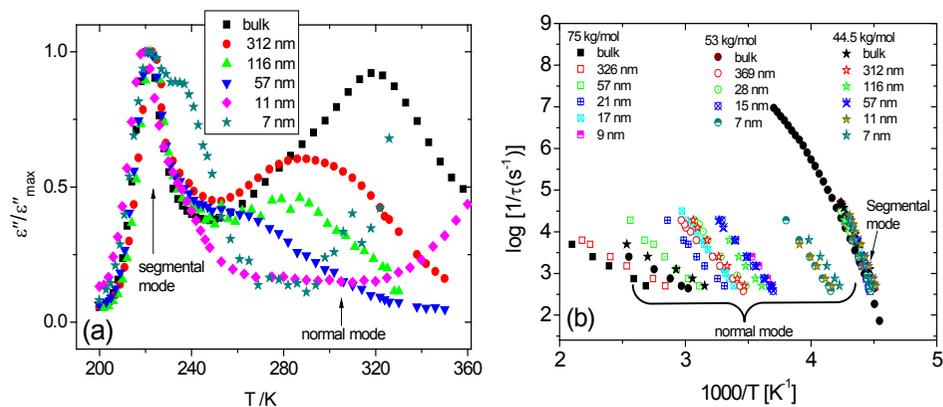


Fig.1: (a) Dielectric loss (normalized w.r.t the maximum value of the segmental mode) plotted versus temperature for polyisoprene (44.5 kg/mol) layers, (b) relaxation rate $1/\tau_{\max}$ as a function of inverse temperature for polyisoprene (Mw: 44.5, 53 and 75 kg/mol) in thin layers (as indicated).

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Collaborations: (1) Max-Planck-Institute for Microstructures, Halle, and (2) MicroFAB Bremen

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

2.17 Friction within Single Pairs of DNA-Grafted Colloids as studied by Optical Tweezers

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

Optical Tweezers are employed to study the transition from sliding to stick-slip friction between two DNA grafted (grafting density ~ 1250 molecules per particle, number of base pairs per grafted chain ~ 4000) colloids [1, 2], which are moved (in y-direction, Fig.1a) in respect to each other with a relative velocity ranging between 50 nm/s up to 3 $\mu\text{m/s}$. For that one colloid is fixed to a micropipet while the other is held in an optical trap hence enabling one to determine and to separate the forces of interaction in the direction parallel (y-direction) and perpendicular (x-direction) to the motion. A transition from sliding (Fig.1b/c) to stick-slip friction (Fig.1d/e) is found. It depends on the salt (NaCl) concentration in the surrounding medium (Fig.1f) and is shown to be controlled by two factors, (i) interaction volume and (ii) interaction time.

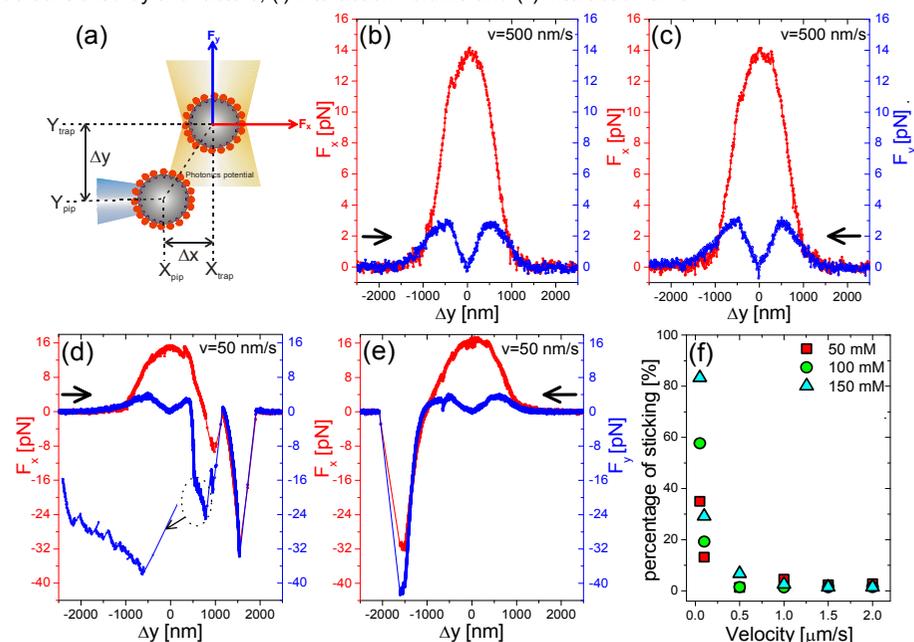


Fig. 1: (a) scheme of the geometric arrangement of the two colloids; one is fixed by a micropipet and moved in y-direction while the other is held in the optical trap. The forces of interaction in x- and y-direction (F_x , \rightarrow) and (F_y , \uparrow) are determined separately from the displacement of the latter out of the equilibrium position. All measurements are carried out within single pairs of DNA-grafted colloids immersed in 10 mM Tris buffered solution with different NaCl concentrations (50, 100 and 150 mM) at pH 8.5. (b, c) At high relative velocity (500 nm/s), the forces of interaction in x (F_x , filled red symbols) and y (F_y , open blue symbols)-directions, show sliding friction while at low velocity (50 nm/s), stick-slip friction takes place. The forces of interaction between the two colloids are 15 ± 5 pN. Arrows (\rightarrow) and (\leftarrow) illustrate the forward and backward motion, respectively. (f) Percentage of sticking events versus relative velocity at different salt concentrations as indicated.

Reference:

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Funding: DFG.

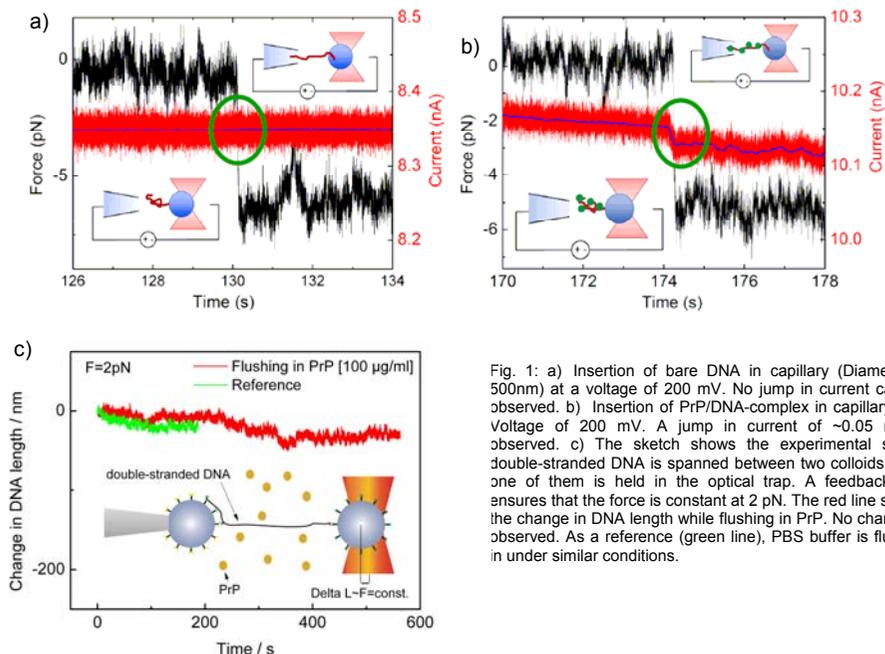
2.16 Optical Tweezers to study DNA/PrP-Interaction on a Single Molecule Level

C. Wagner, O. Otto*, R. Bujdoso⁺, U.F. Keyser*, F. Kremer

* Cavendish Laboratory, University of Cambridge, Cambridge, UK

⁺ Department of Veterinary Medicine, University of Cambridge Cambridge, UK

PrP (Prion Protein) plays a crucial role in neurodegenerative diseases called transmissible spongiform encephalopathies (TSE). The prion diseases affect the structure of the brain or other neural tissue by causing a “spongy” architecture. Up to now these diseases are untreatable and fatal. The infective PrP^{Sc} is the misfolded form of PrP^C, which is ubiquitous in cell membranes. For a long time, the generally accepted hypothesis for the initiation of the transformation was the “protein only-hypothesis” saying that contact with PrP^{Sc} reforms PrP^C. However, new results suggest that also a contact with DNA or RNA is necessary for the misfolding [1,2]. The interaction of recombinant ovine PrP^C with a single DNA strand is investigated by nanocapillaries and optical tweezers. A change in current is observed suggesting an interaction of DNA and PrP (Fig.1a,b). In order to characterize this interaction, an optical tweezers setup with force clamp is employed. At a force of 2 pN no reduction of the DNA length is observed implying that PrP does not condensate the DNA (Fig.1c).



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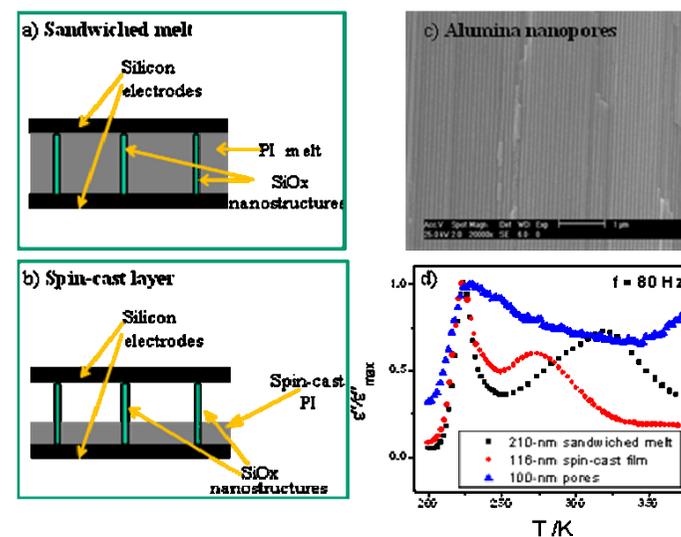
Funding: BuildMoNa, European Social Fund (ESF)

2.5 Dynamics of cis-polyisoprene in 1D and 2D geometrical confinement

E.U. Mapesa, W. Kipnusu, M. Tress and F.Kremer

A fundamental question must be addressed: how does the dimensionality of geometric confinement affect the dynamics of the constrained material? For the same material, 1-D and 2-D confinements can be attained by preparing thin films and by filling in nanopores, respectively. Cis-polyisoprene, being a *Type A* [1] polymer, is the apt candidate for this study because both the local and global dynamics of the chain can be accessed by Broadband Dielectric Spectroscopy.

In a current study, thin films of polyisoprene (53 kDa) are measured in a nano-structured electrode arrangement that employs highly insulating silica structures as spacers (Fig. 1a & b). The same polymer is also filled - under conditions of high vacuum - into porous media of anodized aluminium oxide (AAO) (Fig. 1c) for dielectric studies. Preliminary results (Fig.1d) show that, compared to bulk (the 210-nm sandwiched melt), (i) the temperature position of the segmental mode is independent of the dimensionality of confinement, (ii) a spin-cast thin film exhibits a faster normal mode, while (iii) the normal mode of the molecules confined in porous media is drastically suppressed. The optimization of the pore-filling procedure as well as a reduction of the pore diameter are the subjects of an on-going effort.



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Collaborations: (1) Max-Planck-Institute for Microstructures, Halle, and (2) MicroFAB Bremen

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

2.6 Molecular dynamics of glass forming-liquids confined in two dimensional constraints of uni-directional nanopores

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

Broadband Dielectric Spectroscopy (BDS) and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR) spectroscopy, are combined to study the molecular dynamics of low molecular weight glass forming liquids (e.g. alkylcitrates) in the bulk state and when confined in unidirectional nanopores (diameter: 4, 8, and 10.4 nm, length: 50 μm) prepared by electrochemical etching of highly doped p-type < 100 > silicon and subsequent oxidation. By converting diffusion coefficients obtained from PFG-NMR to relaxation rates via Einstein-Smoluchowski relation and merging with the BDS data, the temperature dependence of structural α -relaxation is traced by more than 12 orders of magnitude (fig.1a). Under confinement, an additional process (slower than the α - process) assigned to relaxation of interfacial layers is observed for the alkylcitrate studied. Exact thickness of these layers can be obtained by analysis of dielectric strength of the bulk and confined molecules. Silanization of the pores removes the interfacial layer process and lowers the structural α - relaxation (inset: fig.1b) which, is however enhanced by more than 2 orders of magnitude (at lower temperatures) for molecules constrained in coated 4 nm pores in comparison to the bulk. This is attributed to changes in molecular packing due to geometrical constraints.

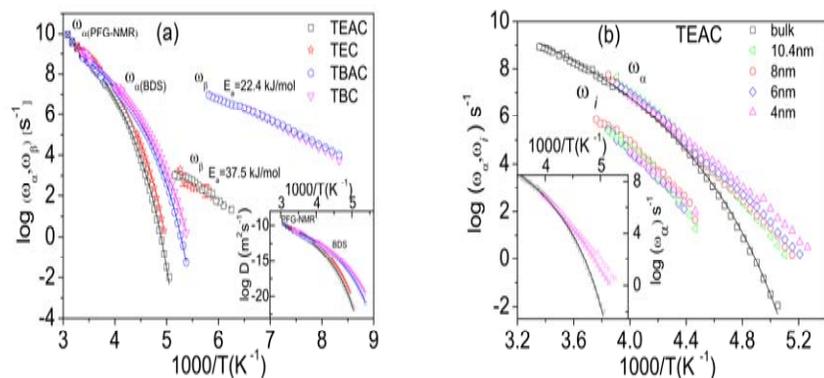


Fig.1 (a) Thermal activation plot of the structural (α) and the secondary (β) relaxation processes for Triethylacetylacrylate(TEAC), Triethylacrylate (TEC), Tributylacetylacrylate(TBAC), and Tributylacrylate(TBC). Structural α -relaxation at higher temperatures (crossed symbols) is obtained from PFG-NMR measurements. Solid lines are fits by the VFT equation while dotted lines are Arrhenius fits. Inset: Diffusion coefficients from both PFG-NMR and BDS measurements. (b) Structural α -relaxation versus inverse temperature for bulk and confined TEAC molecules. Inset: Comparison of α - relaxation in silanized and unsilanized (crossed symbols) 4nm pores.

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2.15 Optical tweezers setup with optical height detection and active height regulation under white light illumination

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

An optical tweezers setup with optical detection in three dimensions and active height regulation has been developed [1]. The presented novel method to determine the relative height of a microparticle from its microscopic image is based on the analysis of the integrated light intensity of the main maximum of the diffraction pattern ($S(z)$). After the determination of a master curve as reference (Fig.1a), the height can be detected with an accuracy of up to 2 nm. The method is applicable under microscopic white light illumination and is simple to implement. As an example of measurements where active height regulation is indispensable, force-distance curves are discussed. Furthermore, the colloid height is calculated geometrically. In the range where the geometrical estimation provides reliable results, the values are found to be in quantitative agreement with the suggested algorithm (Fig.1b).

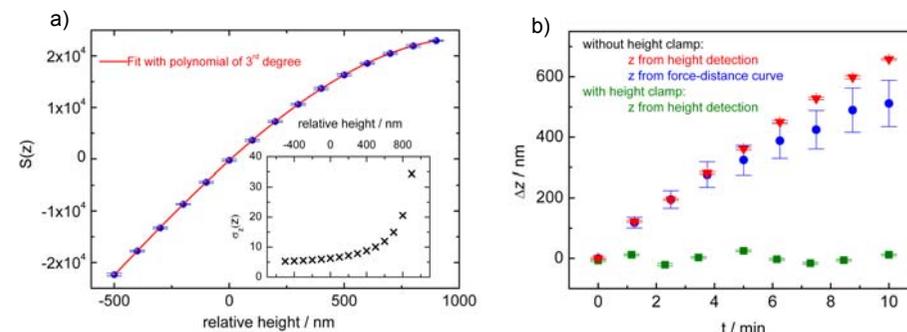


Fig. 1 (a): The values of $S(z)$ are shown in dependence on the shift in z -direction with respect to a reference height ($z=0$). The height of the particle is changed in steps of 100 nm by use of the piezo stage. Each data point represents the average over 20 images at a constant height. The error bars are defined by the standard deviation. For the whole range of 1400 nm a monotonically increasing dependence of $S(z)$ on the height is found. It can be fitted to a polynomial of degree 3, constituting a master curve. The height of a colloid is then determined by calculating $S(z)$ for the actual image and finding the root of the master curve. Inset: The standard deviation of the height obtained from single images is shown. It is calculated for each height from the standard deviation of $S(z)$. An optimum standard deviation in z of 5 nm is obtained. (b) The height values in different time intervals of 1.25 min are shown for the measurements with and without height clamp. The green squares are the mean values of Δz obtained by the height detection in an experiment with active drift compensation. The height difference as determined by the height detection in the experiment without height clamp is depicted by red triangles. The error bars constitute in both cases the standard deviation over 50 images. The blue circles correspond to the height difference of the particles in the experiment without height clamp as calculated from the force-distance curves by geometrical considerations. The error bars are determined by the limitations of the position detection in the xy -plane together with the error of the fit. For a drift of less than 500 nm ($t < 6.5$ min), the results for Δz obtained by the geometrical calculation coincide with those of the height detection within the experimental uncertainty.

References:

- [1] C. Wagner et al., Journal of Optics **13** 115302 (2011)

Funding: BuildMoNa, European Social Fund (ESF)

2.14 Dynamic force spectroscopy on the binding of the monoclonal antibody HPT-101 to tau peptides

C. Wagner, D. Singer*, T. Stangner, O. Ueberschär, C. Gutsche, R. Hoffmann* and F. Kremer
 * BBZ, Fakultät für Chemie und Mineralogie, Universität Leipzig, Deutscher Platz 5, 04103 Leipzig

Optical tweezers-assisted dynamic force spectroscopy (DFS) is employed to investigate specific receptor/ligand bindings on the level of single binding events [1]. Here, the specific binding of the anti-human tau monoclonal antibody (mAb), HPT-101, to synthetic tau-peptides with 2 potential phosphorylation sites is analyzed (Fig.1a). According to Enzyme-linked Immunosorbent Assay (ELISA) measurements, the antibody binds only specifically to the double-phosphorylated tau-peptide. It is shown by DFS that HPT-101 binds also to each sort of the mono-phosphorylated peptides, but with a shorter lifetime (Fig.1b). By analyzing the measured rupture-force distributions characteristic parameters like the lifetime of the bond without force τ_0 , the characteristic length x_{ts} and the free energy of activation ΔG are determined for all interactions. Thereby it can be investigated how the attachments with the mono-phosphorylated peptides add up in the case of the double-phosphorylated peptide in order to form the strong specific binding.

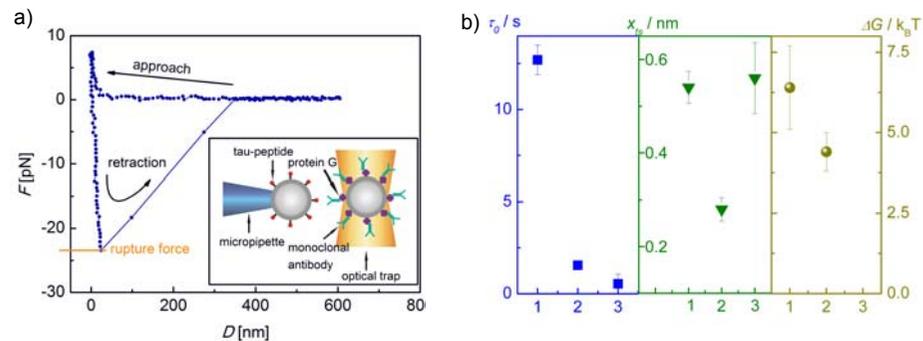


Fig. 1: a) Fig. a: A typical force-distance dependence is shown. The beads are brought in contact and pulled apart with a preset velocity. Due to an individual binding between the tau-peptide and the mAb the particle in the optical trap is shifted out of the equilibrium position. Inset: The experimental configuration. b: The characteristic parameters lifetime of the bond without force τ_0 , characteristic length x_{ts} and free energy of activation ΔG are shown for the interactions of HPT-101 to (1) the double-phosphorylated peptide, (2) the peptide phosphorylated at Thr231 and (3) the peptide phosphorylated at Ser235.

References:

[1] C. Wagner et al., *Soft Matter* **7** (9) 4370 - 4378 (2011)

Funding: BuildMoNa, European Social Fund (ESF)

2.7 Rotational and translational diffusion in glass-forming N,N,-Diethyl-3-methylbenzamide (DEET)

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

Rotational and translational diffusion in N,N-Diethyl-3-Methylbenzamide (DEET) are investigated in wide frequency and temperature ranges by a combination of broadband dielectric spectroscopy (BDS), pulsed field gradient nuclear magnetic resonance (PFG NMR), dynamic mechanical spectroscopy (DMS) and calorimetry (Fig. 1). It is proven that the (dynamic) glass transition (as measured by BDS, DMS and calorimetry) and charge transport (as measured by PFG NMR and BDS) follow *quantitatively* the Einstein and Einstein-Smoluchowski relations. The effective number densities of molecules participating in rotational and translational diffusion are found to coincide within the limits of experimental accuracy [1].

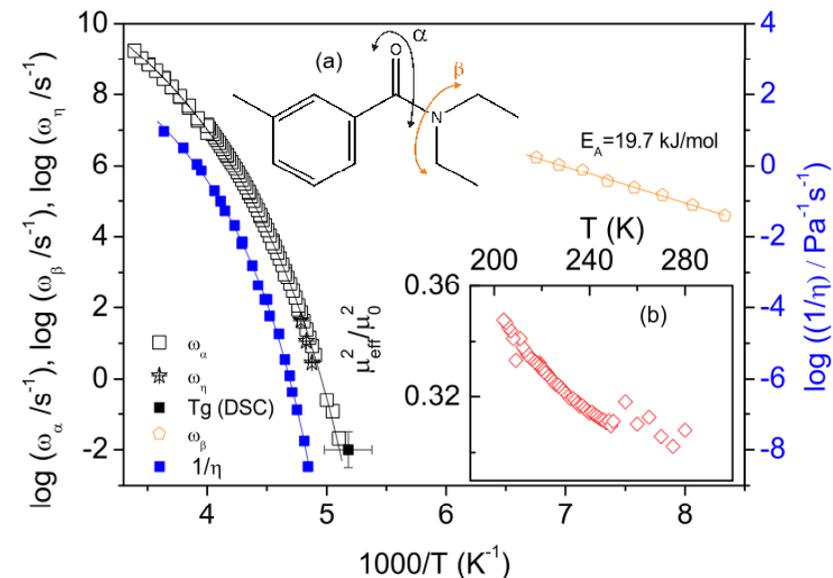


Fig. 1: Activation plot of the structural α -relaxation rates as measured by broadband dielectric spectroscopy (ω_α) and dynamic mechanical spectroscopy (ω_β) as well as the secondary dipolar relaxation rates (ω_β). Fluidity ($1/\eta$) as a function of inverse temperature is shown as well. The solid lines are fits by the empirical Vogel-Fulcher-Tammann equation. The calorimetric glass transition temperature determined by differential scanning calorimetry (DSC) (time-scale of 100 seconds assumed) is also indicated. Inset: (a) Chemical structure of N,N-Diethyl-3-methylbenzamide. The possible molecular motions corresponding to the α - and β - relaxations are indicated. (b) The temperature dependence of the Kirkwood/Fröhlich correlation factor

Reference:

[1] J.R. Sangoro et al., *Soft Matter* **7** 10565-10568 (2011)

Funding by DFG priority program SPP 1191 (Ionic Liquids) is gratefully acknowledged.

2.8 Brownian dynamics determine universality of charge transport in ionic liquids

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

Broadband Dielectric Spectroscopy is employed to investigate charge transport in a variety of glass-forming ionic liquids over wide frequency, temperature and pressure ranges (Fig. 1). 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. Using Einstein, Einstein-Smoluchowski, Maxwell and Langevin equations, the universality of charge transport in ionic liquids is traced back to the dominant role of Brownian dynamics in these systems. It would be interesting to check the extent to which the current description could be applicable to other classes of amorphous ion-conducting materials.

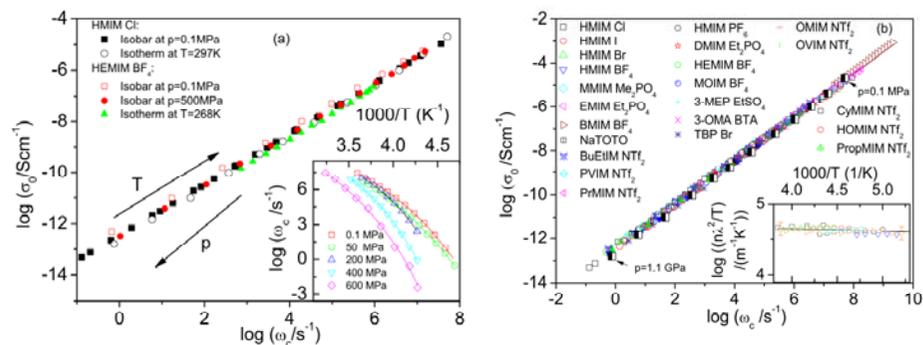


Fig. 1: dc conductivity, σ_{dc} , versus the characteristic rate, ω_c , for: (a) two ionic liquids obtained from isobaric and isothermal dielectric measurements. Inset: The temperature dependence of ω_c at different pressures as indicated. (b) various ionic liquids at 0.1 MPa and [HMIM][Cl] at different pressures (denoted by filled symbols, may not be completely visible due to overlap with other data sets: (black squares): 50 MPa, (red circles): 200 MPa, (green triangles): 400 MPa, (blue inverted triangles): 600 MPa). Additionally, values obtained from dielectric measurements at different pressures between 0.1 MPa and 1.1 GPa at 297 K for [HMIM][Cl] are included. Inset: the term nA^2/T versus inverse temperature for arbitrarily selected ionic liquids (the symbols are consistent with the main figure). For [HMIM][Cl], the isobaric data obtained at 600 MPa for the different temperatures is plotted.

References:

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Collaborations:

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

Funding:

Funding by DFG priority program SPP 1191 (Ionic Liquids) is gratefully acknowledged

2.13 Structural levels of organization in spider silk - a combined mechanical and IR-spectroscopic study

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The unique mechanical properties of spider silk are based on a refined architecture at a molecular and mesoscopic scale. Nanocrystals are interconnected with prestrained amorphous regions causing an internal pressure, which is counterbalanced by the fiber's elastic matrix and outer skin. By that, external stress is directly transferred to a molecular level and can be determined by a shift of an IR absorption band (964 cm^{-1}) being specific for the Alanine-rich nanocrystals [1,2].

The intention of the project is to unravel the interplay between external and internal constraints by analyzing the pressure and temperature dependence of specific IR absorption bands in response to hydrostatic pressure provided by a diamond anvil cell. For calibration a pressure-dependent spectral shift of the R_1 and R_2 -fluorescence lines of chrome doped Al_2O_3 [3] is used (Fig.1) which is inserted in the cell.

Preliminary measurements in collaboration with Prof. Dr. Christine Kuntscher from the university of Augsburg led to promising results. The pressure-dependent frequency shift of the Alanine specific absorption band follows (Fig. 2) a linear dependence and exhibits the same slope as known from uni-axial stress-dependent measurements [1].

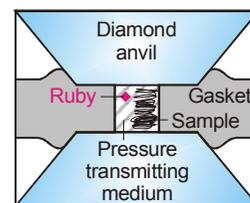


Fig. 1: Basic construction of a diamond anvil cell. Sample and ruby embedded in a pressure transmitting medium and surrounded by a gasket undergo hydrostatic pressure.

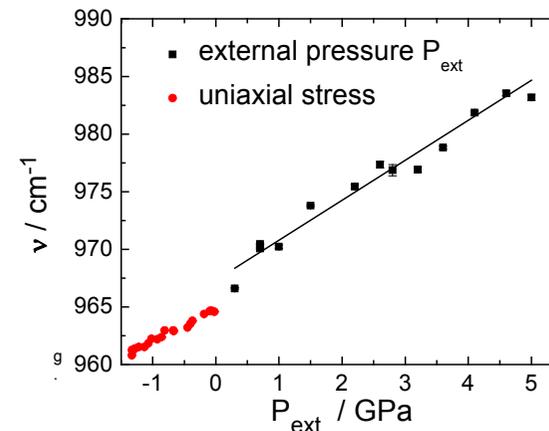


Fig. 2: Spectral position of the Alanine-specific absorption band versus (external hydrostatic or uniaxial stress-induced) pressure.

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 [2] P. Papadopoulos et al., Macromol. Rapid Commun. **30** 851 (2009)
 [3] K. Syassen, High Press. Res. **28** 75 (2008)

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2.12 The Infrared signature of glassy dynamics

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Glassy dynamics reflects a continuous slowing down of molecular fluctuations in a glass forming system. It is characterized by a temperature dependence according to the empirical Vogel-Fulcher-Tammann (VFT) law and scales with the calorimetric glass transition temperature (T_G), typically taking place at a relaxation rate of 0.01 Hz. Combining methods measuring *intermolecular* interactions (Broadband Dielectric Spectroscopy, Calorimetry, Dilatometry) with IR spectroscopy sensing *intramolecular* vibrations of the specific signature of a glass forming system is unraveled by analyzing the temperature dependent spectral features of IR-absorption bands corresponding to the different molecular moieties. First results for polystyrene are shown (Fig. 1).

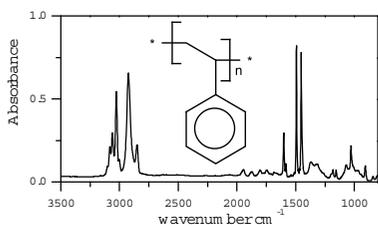
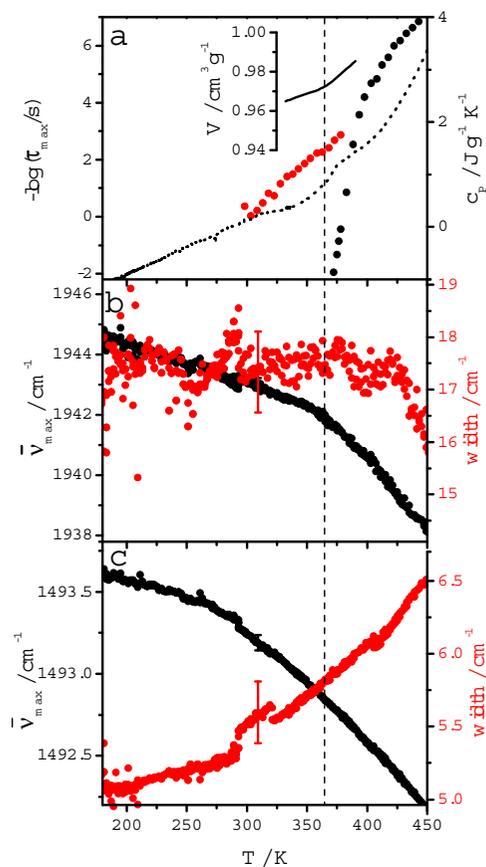


Fig. 1 (above): IR spectrum of Polystyrene at 300K. The inset shows the chemical structure of the monomer.

Fig. 2: (right): Characteristic features in the dynamic glass transition of Polystyrene: (a) relaxation rates of the α - and β -relaxation (black and red dots) measured by broadband dielectric spectroscopy and heat capacity at constant pressure c_p (from DSC, dotted line) versus temperature. The inset shows the specific volume as measured by dilatometry. All quantities (except the β -relaxation) exhibit a clear change at T_G . Spectral position (black) and width (red) of specific absorption bands for (b) the combined in- and off-plane ring vibration; and (c) the in-plane ring stretching vibration versus temperature. Apparently both modes exhibit strongly different dependencies; while for the former the slope changes the latter is uninfluenced at T_G (dashed line).



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2.9 Glassy dynamics of imidazole-based liquids confined in nanoporous silica

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Broadband Dielectric Spectroscopy (BDS) is employed to study glassy dynamics in homologous series of imidazole-based liquids confined in unidirectional silica nanopores with mean diameters of 4, 7.5 and 9.5 nm. The dielectric spectra are interpreted in terms of dipolar relaxation and a conductivity contribution. In pores of mean diameter 4 nm, the structural α -relaxation rates are faster than the corresponding bulk values by two orders of magnitude (Fig. 1). Experimentally determined difference quotients of α -relaxation rates show *unusual* temperature dependence attributed to a subtle competition between surface and confinement effects [1, 2, 3].

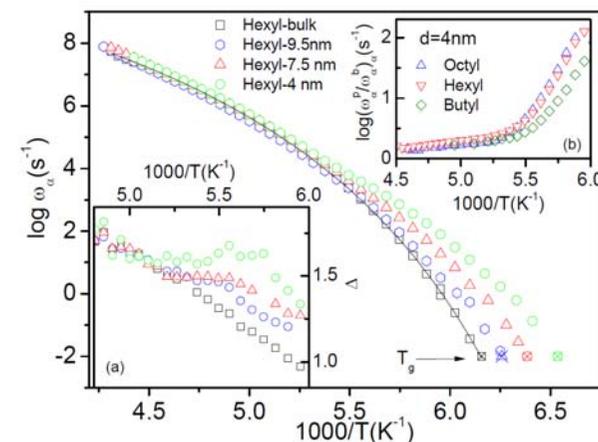


Fig. 1: The mean structural α -relaxation rates, ω_α for bulk and confined 1-Hexylimidazole versus inverse temperature. The solid line is a fit using the Vogel-Fulcher-Tammann (VFT) equation applied to the bulk ω_α . The fit parameters are: $\omega_\alpha = 1.38 \times 10^{12} \text{s}^{-1}$, $D=7.97$, and $T_0=131\text{K}$. Insets: (a) difference quotients versus $1/T$ for the bulk 1-Hexylimidazole (square symbols) and confined in porous silica with mean diameters of 9.5 nm, 7.5 and 4 nm as determined experimentally, (b) the ratio between α -relaxation rates for bulk and under nano-confinement for imidazole in 4 nm pores versus inverse temperature. T_g represents the glass transition temperature for bulk 1-Hexylimidazole obtained from calorimetric measurements (DSC). For the different nanopores, the T_g is taken as the temperature at which ω_α is 10^2s^{-1} .

References:

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- [3] Iacob, C., et al. *J. Chem. Phys.* **129** (23) 234511 (2008).

Funding:

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

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Molecular dynamics and orientational order of 4-heptan-4'-isothiocyanato-biphenyl (7BT) [1] in nanopores of mean diameters from 4 nm to 10.5 nm are studied by a combination of Broadband Dielectric and Fourier-Transform Infrared Spectroscopy. A novel approach: Transition Moment Orientational Analysis [2] is employed to explore the orientational order of molecules in pores. Based on results of both BDS and FTIR methods, we propose a microscopic picture of the morphology of molecules in nanopores of different sizes [3]. It was found that the stiff molecular units are perpendicular to the pore walls in 10.5 nm diameter pores whereas in smaller nanopores (4nm and 6 nm) they show a preferential alignment along the pore axis.

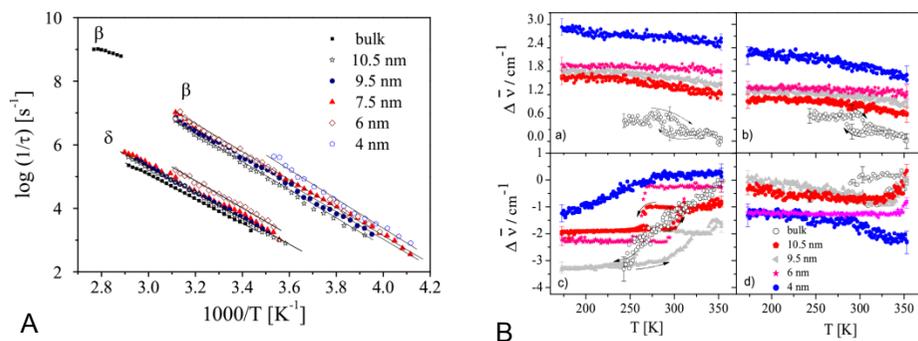


Fig1. (A) Activation plot of 7BT upon cooling in bulk and confined in pores of mean diameters 4 nm, 6nm, 7.5 nm, 9.5 nm and 10.5 nm. (B) Shift of the alky chain absorption band at a) 1400 cm⁻¹, b) 1403 cm⁻¹ and the phenyl absorption band at c) 1602 cm⁻¹ d) 1610 cm⁻¹ compared to the bulk sample in the isotropic phase at 353 K. The error bars denotes the average fitting uncertainty.

References

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- [3] M. Jasiurkowska, W. Kossack, R. Ene, C. Iacob, W. Kipnusu, P. Papadopoulos, J. Rume Sangoro, M. Massalska-Arodz, F. Kremer, submitted to Soft Matter

Collaborations:

Prof. Dr. Maria Massalska Arodz (The Henryk Niewodniczanski Institute of Nuclear Physics Polish Academy of Sciences, Kraków)

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2.11 Infrared Transition Moment Orientation Analysis (IR-TMOA) as applied to semicrystalline polyolefins

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Transition Moment Orientation Analysis, recently developed in our group, is employed to determine the three dimensional orientation and order of the different molecular moieties in semi-crystalline polyolefins [1]. Based on IR transmission spectra for varying polarisation and inclination (Fig. 1), the ensemble averaged square of the transition moments corresponding to specific vibrations is deduced. By that, the full order parameter tensor and its orientation with respect to the sample coordinate system is obtained [1, 2].

Polyethylene and Polypropylene films are widely used materials of high technological importance, because of their remarkable property variability resulting from the films micro structure. Usually produced by blown film processes these materials undergo stress-induced crystallization and molecular orientation depending on process parameters like die gap, blow-up ratio, frost line height, etc. To improve the physical and mechanical properties it is inevitable to understand the relation between these parameters and the micro structure of amorphous and crystalline phases within the sample [1].

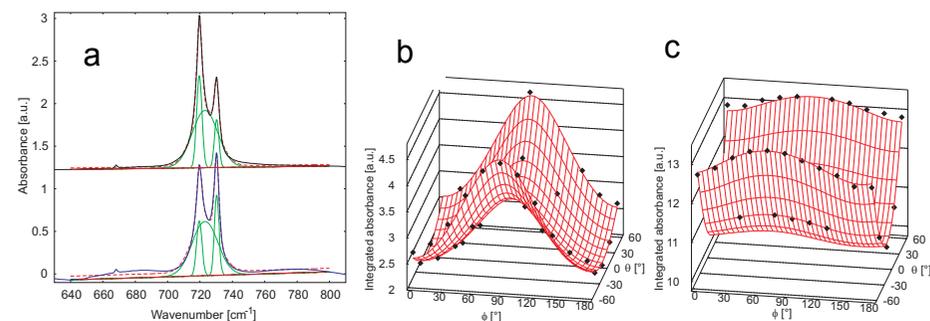


Fig. 1: In (a) the CH₂ rocking band (721 cm⁻¹) is shown for an inclination angle of 60° in "s" (blue) and "p" polarization (black). For semi-crystalline samples this band splits up into three (shown as thin green lines), where the broad unchanged component corresponds to the amorphous state. The baseline used for correction (straight red line) and the fitted bands (dashed red line) are shown as well. Subplot (b) displays the dependence of the integrated absorbance (peak area, black dots) on inclination (θ) and polarization (ϕ) of the incoming light for the crystalline phases CH₂ rocking vibration with its transition moment parallel to the a axis of the lamellar crystallites. (b) shows the dependence for the amorphous phase. The red grid lines in (b) and (c) depict the fit.

References:

- [1] W. Kossack et al., Polymer **52** 6061 (2011).
- [2] W. Kossack et al., Macromolecules **43** 7532 (2010).

Funding: BuildMoNa, Leipzig school of natural sciences; Borealis Polyolefine GmbH