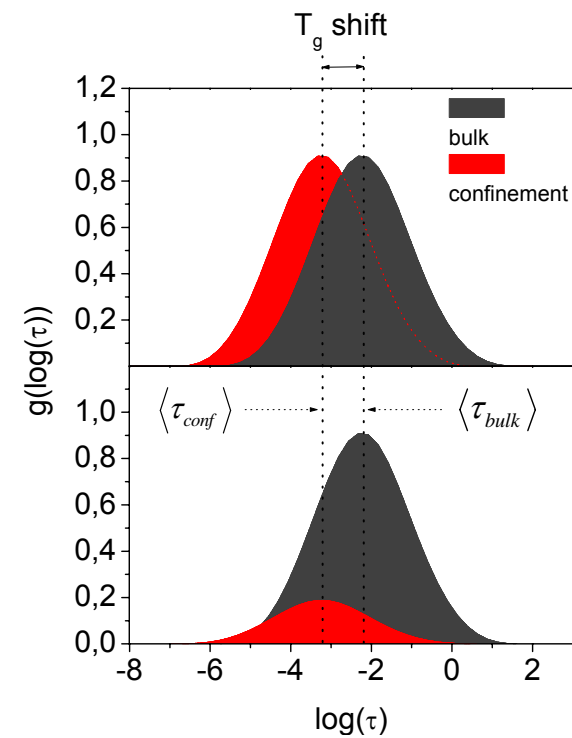


UNIVERSITY OF LEIPZIG

Faculty of Physics and Earth Sciences
Department of Experimental Physics I

GROUP "PHYSIK ANISOTROPER FLUIDE"



Cover picture: Molecular dynamics in thin polymer layers; schematic representation of two alternative mechanisms leading to a shift of the mean relaxation time: (a) shift of the relaxation time distribution as a whole due to the fact that the polymer segments fluctuate faster in confinement than in the bulk, or (b) freezing-out of the slower relaxation modes. For his experiments (s. project 2.1, p. 5) giving answer to these central questions concerning dynamics in confinements, A. Serghei was awarded with the Young Researcher Prize 2006 of the International Dielectric Society.

UNIVERSITÄT LEIPZIG

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The year 2006

In 2006 we strengthened our activities in the traditional fields like Broadband Dielectric Spectroscopy (BDS), time-resolved Fourier-Transform Infrared Spectroscopy (FTIR) and especially experiments with Optical Tweezers (OT). As outlined in the publications list a variety of novel exiting results were obtained. Additionally our group widened its scope and with Ulrich Keyser a leading expert joined, well experienced in experiments with single molecules and nanopores. Furthermore Periklis Papadopoulos (who graduated with Prof. Dr. G. Floudas, Ioannina) started as Post-Doc.

The biannual meeting of the International Dielectric Society (IDS) took place in Poznan, Poland. Anatoli Serghei was awarded by an international price committee with the Young Researcher Prize of IDS for his achievements in exploring the molecular dynamics in thin polymer films. This is a great encouraging acknowledgement.

Friedrich Kremer

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5. Graduations

Promotions:

Dipl.-Phys. Anatoli Serghei

23.01.2006

"Confinement-effects on the molecular dynamics in thin polymer films"

M. Sc. Julius LTsuwi Kazungu

16.10.2006

"Dynamics in emulsions and fluorinated side-chain polymers studied by Broadband Dielectric Spectroscopy"

M. Sc. Michael Tammer

19.12.2006

"Fourier-Transform-Infrarotspektroskopie an verstreckten Elastomernetzwerken"

6. Industry collaborations

Novocontrol

Hundsangen, Germany

Comtech GmbH

München, Germany

Freudenberg Dichtungs- und Schwingungstechnik KG

Weinheim, Germany

Kempchen Dichtungstechnik GmbH

Leuna, Germany

inotec FEG mbH

Markkleeberg, Germany

7. Patent applications

Internationale Patentanmeldung: WO 2004/070333 A3

"Verfahren zur Feststellung wenigstens eines Zustandsparameters eines Dichtungssystems sowie Dichtungssystem"

Erfinder: Prof. Dr. F. Kremer

8. Awards

Young Researcher Prize 2006 of the International Dielectric Society (IDS) to Anatoli Serghei.

4. Financial support

Prof. Dr. F. Kremer

Optische Pinzette als mikroskopische Sensoren und Aktuatoren zum Studium der Wechselwirkung zwischen einzelnen Biomolekülen
SMWK-Projekt 7531.50-02-0361-01/11 (2001-2006)

Prof. Dr. F. Kremer

Einzelmolekülanalyse: Optische Pinzetten zum Studium der Wechselwirkung von einzelnen Rezeptor/Ligand-Komplexen
SMWK-Projekt 4-7531.50-02-0361-06/1 (2006-2007)

Prof. Dr. F. Kremer

DFG-Teilprojekt im Rahmen des Schwerpunktprogramms "Nano- und Mikrofluidik: Von der molekularen Bewegung zur kontinuierlichen Strömung"
DFG-Schwerpunktprogramm 1164, KR 1138/14-1 (2004-2006)

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 1138/14-2 (2006-2008)

Prof. Dr. F. Kremer

Industrie- und Handelskammer Leipzig:
Messplatz zur temperatur- und lösungsmittelabhängigen Bestimmung der dielektrischen Funktion verschiedener Sensormaterialien
Projektpartner: inotec FEG mbH Markkleeberg
AZ: 435011-6131 (2006)

Prof. Dr. F. Kremer

DFG-Projekt "Confinement effects on the molecular dynamics of polymers with special architectures"
KR 1138/17-1 (2006–2008)

Prof. Dr. F. Kremer

DFG-Projekt "Physicochemical characterisation of ionic liquids-mediated peptide acylation reactions"
KR 1138/18-1 (2006–2008)

Prof. Dr. F. Kremer

DFG-Projekt "In-situ Untersuchung der Wechselwirkungskräfte an Polyelektrolytbürsten"
KR 1138/20-1 (2006–2008)

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1. Organization of the group

Chairman: Prof. Dr. Friedrich Kremer

Academic staff and postdocs

Dr. Ulrich Keyser
Dr. Periklis Papadopoulos
Dr. Anatoli Serghei

Students

Dipl.-Phys. Christof Gutsche
M. Sc. Julius Tsuwi Kazungu
Dipl.-Phys. Kati Kegler
Dipl.-Biochem. Mathias Salomo
M. Sc. Joshua Rume Sangoro
cand. phys. Jan Sölter
M. Sc. Michael Tammer

Technical staff

Karin Girke
Ines Grünwald
Dipl.-Ing. Jörg Reinmuth
Dipl.-Phys. Wiktor Skokow
Dipl.-Phys. Uwe Weber

Alumni

Prof. Dr. Siegbert Grande

- in press -

- 13) Kremer, F.
"Broadband Dielectric Spectroscopy to study the molecular dynamics of polymers having different molecular architectures". Chapter in "Physical properties of polymer handbook". J. Mark (Ed.)
in press *Springer-Verlag* (2006).
- 14) Kegler, K., M. Salomo, F. Kremer
"Forces of interaction between DNA – grafted colloids : An optical tweezers measurement"
in press: *Phys.Rev. Lett.* (2006).
- 15) Tsuwi, Julius, D. Pospiech, D. Jehnichen, L. Häußler, F. Kremer
"Molecular dynamics in semifluorinated side-chain polysulfone as studied broadband dielectric spectroscopy"
in press: *JAPS* (M. Kryszewski issue) (2006).
- 16) Jehnichen, D., D. Pospiech, L. Häußler, P. Friedel, S.S. Funari, J. Tsuwi, F. Kremer
"Microphase separation in semifluorinated polyesters"
in press: *Z. Kristallogr. Suppl.* (2006).

submitted -

- 17) Serghei, A., H. Huth, C. Schick, F. Kremer
"Does a free interface shift the dynamic glass transition of ultra-thin polymer films?"
submitted to *Phys. Rev. Lett.* (2006).
- 18) Serghei, A., L. Hartmann, F. Kremer
"Molecular dynamics in thin films of isotactic poly(methyl methacrylate) – revisited"
submitted to *J. Non-Cryst. Solids* (2006)

3. Publications

- 1) Serghei, A. and F. Kremer
"Unexpected preparative effects on the properties of thin polymer films"
Progress Colloid Polym. Sci. **132**, 33 (2006).
- 2) Gutsche, C., M. Salomo, Y.W. Kim, R.R. Netz and F. Kremer
"The flow resistance of single DNA-grafted colloids as measured by Optical Tweezers"
J. Microfluidics and Nanofluidics, ISSN:1613-4982 (Paper) 1613-4990 (Online)
DOI: 10.1007/s10404-006-0080-0 (2006).
- 3) Salomo, M., C. Gutsche, K. Kegler, M. Struhalla, K. Kroy, J. Reinmuth, W. Skokow, C. Immisch and F. Kremer
"The binding of TmHU to single ds-DNA as observed by Optical Tweezers"
J. Mol. Biol. **359**, 769-776 (2006).
- 4) Slotta, U., M. Tammer, F. Kremer, P. Kölsch, T. Scheibel
"Structural analysis of spider silk films"
Supramolecular Chemistry **18** (59), 65-471 (2006).
- 5) Salomo, M., K. Kegler, M. Struhalla, J. Reinmuth, W. Skokow, U. Hahn, F. Kremer
"The elastic properties of single double-stranded DNA chains of different length"
J. of Colloid & Polymer Science **284**, No. 11, 1325-1331 (2006).
- 6) Holtze, Christian; R. Sivaramakrishnan, M. Antonietti, J. Tsui, F. Kremer, K. D. Kramer
"The microwave absorption of emulsions containing aqueous micro- and nanodroplets: A means to optimize microwave heating"
J. of Colloid and Interface Science **302**, 651 – 657 (2006).
- 7) Höfl, S., F. Kremer, H.W. Spiess, M. Wilhelm, S. Kahle
"Effect of large amplitude oscillatory shear (LAOS) on the dielectric response of 1,4-cis-polyisoprene"
Polymer **47**, Issue 20, 7282-7288 (2006).
- 8) Tsui, J. Kazungu; L. Hartmann, F. Kremer, D. Pospiech, D. Jehnichen, L. Häußler
"Molecular dynamics in semifluorinated side-chain polyesters as studied by broadband dielectric spectroscopy",
Polymer (for the special issue for Tadeusz Pakula) **47**, 7189-7197 (2006).
- 9) Serghei, A., Y. Mikhailova, K.-J. Eichhorn, B. Voit, and F. Kremer,
"Discrepancies in the characterization of the glass transition in thin films of hyperbranched polyesters"
J. Polym. Sci. B: Polym Physics **44**, 3006-3010 (2006).
- 10) Serghei, A., M. Tress, F. Kremer
"Confinement effects on the relaxation time distribution of the dynamic glass transition in ultra-thin polymer films"
Macromolecules **39** (26), 9385-9387 (2006).
- 11) Serghei, A., F. Kremer
"Molecular dynamics in thin polymer films", chapter 1 in *Fractals, diffusion and relaxation in disordered complex systems*, Advances in Chemical Physics ACP, edited by Stuart A. Rice (guest editors: W.T. Coffey, Y.P. Kalmykov), John Wiley & Sons, Inc., Vol. 11(2006).
- 12) Serghei, A., F. Kremer
"Broadband Dielectric Spectroscopy on ultra-thin organic layers having one free (upper) interface"
Review of Scientific Instruments **77**, 116108 (2006).

2. Projects

2.1 Molecular dynamics in thin films of polymers with different macromolecular architectures

A. Serghei, F. Kremer

The changes in the relaxation time distribution of the dynamic glass transition in thin films of polymers having different (linear, hyperbranched, star-branched and dendritic) macromolecular architectures is investigated. Based on measurements of the molecular dynamics by means of Broadband Dielectric Spectroscopy, the following issues are addressed:

- (a) What role plays the macromolecular architecture in the dynamics of confined polymers?
- (b) Do different experimental techniques deliver similar results when applied to investigate the glassy dynamics of confined polymers?
- (c) What is the molecular mechanism of the confinement effects, i.e. shifts and broadening of the dynamic glass transition in thin polymer films (Fig. 1)?
- (d) Does the presence of free interfaces influence the glassy dynamics of confined polymers?

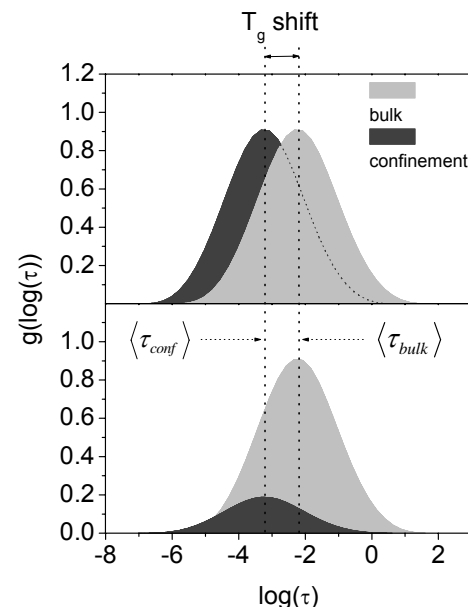


Fig. 1: Schematic representation of two possible mechanisms leading to a shift of the *mean* relaxation time: (a) shifts of the relaxation time distribution as a whole due to the fact the polymer segments fluctuate faster in confinement than in the bulk, or (b) freezing-out of the slower relaxation modes.

References:

- [1] A. Serghei et al., *J. Polym. Sci. (B)* **44**, 3006 (2006).
- [2] A. Serghei et al., *Eur. Phys. J. E* **17**, 199 (2005).
- [3] A. Serghei et al., *Macromolecules* **39**, 9385 (2006).

Collaborators: C. Schick (Rostock University), B. Voit, D. Appelhans (IPF Dresden, Germany)

Funding: DFG project KR 1138/17-1

2.2 Novel developments in the preparation of thin polymer films

A. Serghei, F. Kremer

In this work novel methods for the preparation of thin polymer films are developed. One approach is schematically described in fig. 1. Silica nano-colloids are used as spacers between two ultra-flat highly conductive silicon wafers. On one of the two wafers a thin polymer film was previously deposited by spin-coating from solution. This preparation procedure enables one – in contrast to conventional dielectric studies – the investigation of the dynamic glass transition in thin films having a free upper interface.

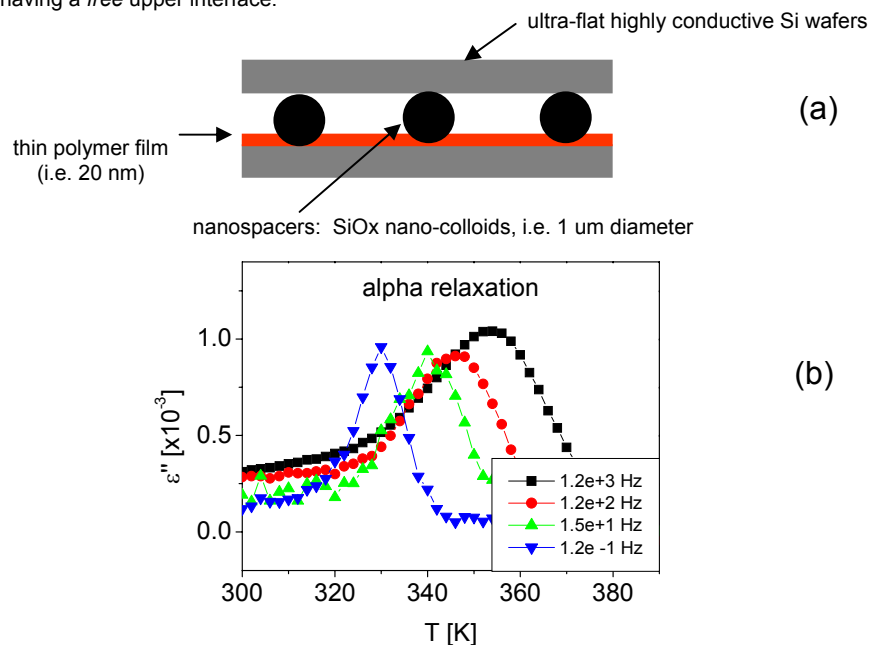


Fig. 1: (a) Schematic representation of the sample preparation; (b) dielectric loss vs. temperature at different frequencies, as indicated, for a thin film of PMMA having a thickness of 7 nm and the upper interface free.

This method avoids the evaporation of metal electrodes on thin organic layers (and the related drawbacks) and gives rise to a multitude of possible applications in soft matter physics: thin liquid layers, thin films of polyelectrolytes, biomolecules and liquid crystals, organic nano-colloids, dielectric studies on single (isolated) macromolecules.

References:

[1] A. Serghei, and F. Kremer, *Rev. Scient. Instrum.* **77**, 116108 (2006).

Collaborators: M. Alexe (MPI, Halle)

Funding: DFG project KR 1138/17-1

2.11 Study of the receptor / ligand - interactions by the use of optical tweezers

M. Salomo, K. Kegler, M. Struhalla, J. Reinmuth, W. Skokow, and F. Kremer

Receptor / ligand - interactions are crucial for a manifold of biological processes like the transport of substances within cells or the exchange with their environment. They also have central impact on signal transduction by initializing signal cascades (e.g. in the synaptic gap or for endocrine reactions). Most studies have been performed with the reactants in solution. This does not reflect the general conditions that are relevant *in vivo* [1, 2].

By the use of optical tweezers we want to study the interactions between receptors and their ligands that are attached to the surface of microparticles. The measurements will be carried out with high resolution (≤ 0.1 pN, ≤ 1 nm) on a *single molecule* level. As a model system we want to utilize protein A which acts as an antigen for a wide variety of antibodies. At the moment we develop a procedure that will allow us to immobilize protein A on the surface of microparticles. Different types of antibodies will be attached to one end of a DNA linker which is immobilized at another particle (Fig. 1). The DNA acts as a spacer to avoid unspecific interactions between the surfaces of the particles. Using the optical tweezers contacts between antigens and antibodies will be established and then disrupted. This will enable us to unravel the static and dynamic properties of the receptor / ligand - interaction.

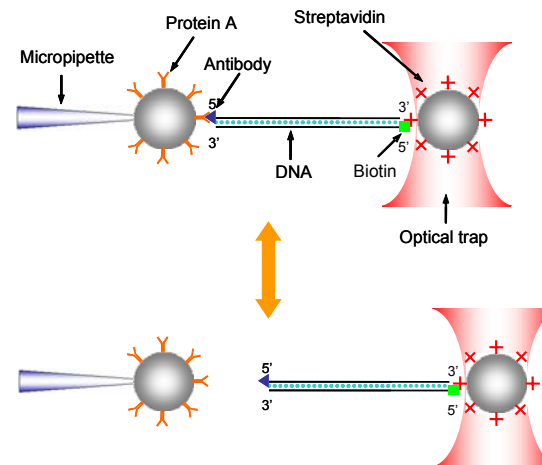


Fig. 1: One particle with protein A on its surface is fixed at a micropipette by suction. The other one is held in the optical trap. Between them a single DNA strand is spanned. One end is immobilized on the particle in the photonic potential. The other end carries an antibody that interacts with the protein A. By pulling the colloids apart the junction breaks and the resulting forces can be measured directly.

References:

[1] Stout L., *Biophysical Journal* **80**, 2976-2986 (2001).

[2] Kienberger F., Kada G., Mueller H., Hinterdorfer P., *J. Molecular Biology* **347**, 597-606 (2005).

Funding

SMWK project 4-7531.50-02-0361-06/1 (2006-2007)

2.10 Kinetics of TmHU binding to DNA as observed by optical tweezers

M. Salomo, K. Kegler, M. Struhalla, J. Reinmuth, V. Skokow, U. Keyser, and F. Kremer

The kinetics of binding for the histone-like protein TmHU (from *Thermotoga maritima*) to DNA was analysed on a *single molecule level* by use of optical tweezers. The histone-like protein TmHU from the hyperthermophilic eubacterium *Thermotoga maritima* belongs to the group of HU proteins that are small basic proteins occurring in all prokaryotes. Its major function consists in binding and compacting DNA into structures similar to eukaryotic chromatin. TmHU binds the DNA tightly ($K_D = 73$ nM) without detectable sequence specificity. It bends the DNA ($\sim 160^\circ$) and simultaneously increases its flexibility.

For our experiments we developed a special flow cell which enables us to immobilize a single DNA molecule between two functionalized polystyrene beads. Further more it is possible to flush the cell with buffers or protein solution. After establishing a single DNA chain between two beads the sample cell was flushed with TmHU-solution with different concentration (0-250 $\mu\text{g/ml}$). If the protein bound to DNA a rapid decrease in the length of DNA-chain was observed. For the reaction rate a pronounced concentration-dependence was found with an "all or nothing"-limit indicating towards a cooperative nature of the binding-reaction. By analyzing the statistics of mechanically induced disruption-events of TmHU from DNA multiple reaction sites are observed to become more likely with increasing TmHU concentration (Fig. 1a/b). This is interpreted as a hint for a secondary organisational level of the TmHU / DNA complex. The reaction rate of TmHU is remarkably higher than that of the HU protein from *E. coli*.

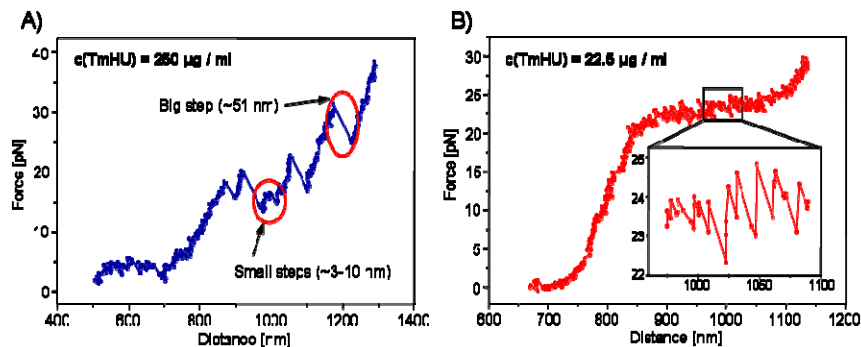


Fig. 1 a) Force-distance plot at a TmHU-concentration of 250 $\mu\text{g/ml}$. b) Force distance plot at a TmHU-concentration of 22.5 $\mu\text{g/ml}$.

Literature:

- [1] Salomo M., Kegler K., Gutsche C., Struhalla M., Reinmuth J., Skokow W., Hahn U., Kremer F., *Colloid and Polymer Science* **284** (11): p. 1325-1331 (2006).
- [2] Salomo M., Kroy K., Kegler K., Gutsche C., Struhalla M., Reinmuth J., Skokow W., Immisch C., Hahn U., Kremer F. *Journal of Molecular Biology* **359** (3): p. 769-776 (2006).
- [3] Salomo M., Keyser U. F., Kegler K., Gutsche C., Struhalla M., Immisch C., Hahn U., Kremer F., Kinetics of TmHU binding to DNA as observed by optical tweezers. Submitted to *European Biophysics Journal*, 2006.

Collaborators: K. Kroy (Universität Leipzig); C. Immisch (ACGT Progenomics AG Halle)

Funding: SMWK project 7531.50-02-0361-01/11

2.3 Dielectric properties of ionic liquids

J. Rume, A. Serghei, and F. Kremer

Salts characterized by low melting points, often below room temperature, have been developed and studied extensively during the last few years. However, the quantitative understanding of the nature and impact of charge transport processes in such room temperature ionic liquids has been elusive. Due to Maxwell's equations the complex dielectric function $\epsilon^*(\omega, T)$ is directly related to the complex conductivity $\sigma^*(\omega, T) = i \omega \epsilon_0 \epsilon^*(\omega, T)$, where ϵ_0 is the permittivity of free space. Broadband Dielectric Spectroscopy (BDS) is the natural experimental tool to measure these quantities. Special emphasis is given to the frequency and temperature dependence of $\epsilon^*(\omega, T)$ but as well to non-linear effects with respect to the applied electric field. This enables one to analyse in detail the mechanisms of charge transport in the materials under study and to determine the underlying molecular relaxation processes.

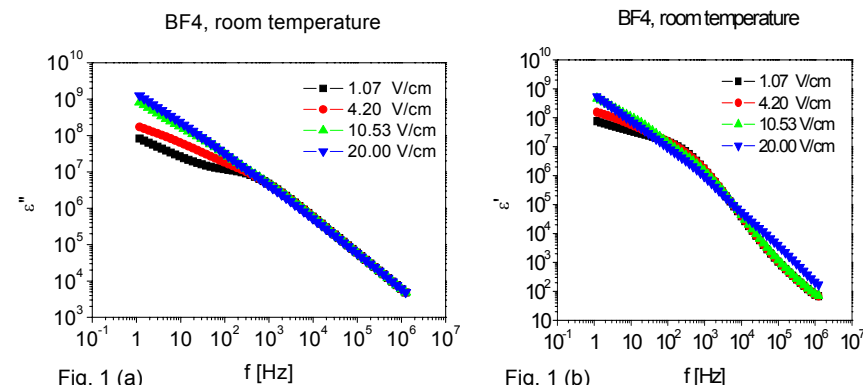


Fig. 1 (a) and (b): The complex dielectric function (real ϵ' and imaginary part ϵ'' of the complex permittivity respectively) vs. frequency at room temperature for tetrafluoroborate (BF4) as measured for electric fields as indicated.

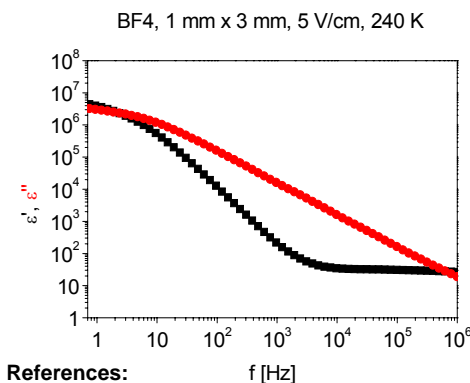


Fig. 2: Scheme of the superposition of charge transport due to electronic and ionic charge carriers

References:

- [1] A. Jarosik et al. *J. Mol. Liquids* **123**, 43-50 (2006)
- [2] F. Bordusa et al, *Angew. Chem.* **6**, 1775-1780 (1997)
- [3] F. Bordusa, *Chem. Rev.* **102**, 4817-4867 (2002)

Collaborators: F. Bordusa, Halle

Funding: DFG Priority Program 1191 (Ionic Liquids)

2.4 Rheo-FTIR on spider silk

J. Sölter, P. Papadopoulos, and F. Kremer

Spider silk has unique mechanical properties which are currently not met by man-made materials [1]. To study the interrelationship between (microscopic) molecular structure and the (macroscopic) mechanical response a polarized time-resolved FTIR-spectrometer is combined with a custom-made setup to measure the complex mechanical modulus. For that a dense wire grid of single parallel arranged spider threads of *Araneus diadematus* is prepared (Fig. 1) and a step-like increase of the strain is applied while measuring the resulting stress. The specificity of the IR spectral range enables one to trace in detail the microscopic response of the different molecular moieties, i.e. the reorientation and the order parameter, the phase relation within the molecular system with respect to the mechanical excitations and possible memory effects. Comparison of silk FTIR spectra to the composition-weighted sum of all polyaminoacid spectra (Fig. 2a) can be very helpful in assigning the absorption bands to certain groups in the macromolecule. The two protein components of dragline silk, referred to as MaSp1 and MaSp2, consist mainly of repetitive sequences with polyaniline and glycine-rich motifs. A characteristic single peak at $\sim 960\text{ cm}^{-1}$ corresponds to vibrations of polyaniline β -sheets. The latter are very well oriented along the fiber axis (Fig. 2b) [2].

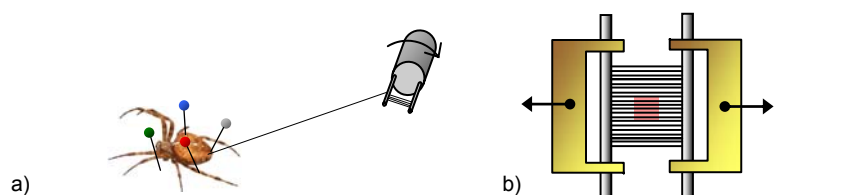


Fig. 1. a) Forced-silking setup. The spider is immobilized using pins between its legs, while the silk is wound around two metal rods whose rotation is controlled by a motor. Finally, the threads are glued to the rods and one of the layers is removed. b) The wire grid of spider silk threads. The IR beam is focused on a $250 \times 250\ \mu\text{m}$ square (indicated in red).

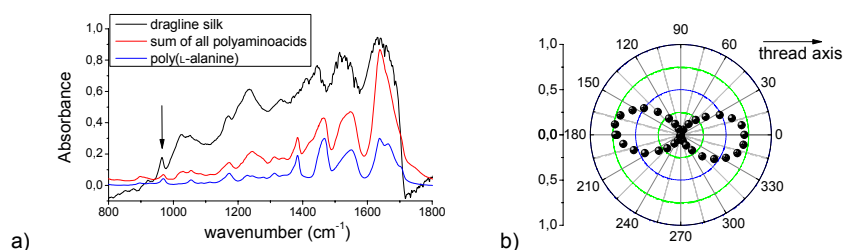


Fig. 2. a) FTIR spectra of dragline silk and poly(L-alanine) and composition-weighted sum of spectra of all polyaminoacids. b) Polar plot of the absorbance at 960 cm^{-1} . Notice the almost perfect orientation of the transient moment along the thread axis.

References:

- [1] F. Vollrath and D. Porter *Soft Matter* **2**, 377 (2006).
 [2] J. Sölter, P. Papadopoulos and F. Kremer *in preparation*.

2.9 Forces of interaction between DNA – grafted colloids : An optical tweezers measurement

K. Kegler, F. Kremer

Optical tweezers are employed to measure the forces of interaction between *single* DNA-grafted colloids. Parameters to be varied are the length of the DNA (1000 base pairs (bp) to 6000 bp), the grafting density (1.84×10^{-4} chains/nm² to 1.97×10^{-5} chains/nm²) and the ionic concentration (10^{-5} M to 10^{-2} M NaCl) of the surrounding medium. From the measured force-separation dependence an interaction-length at a given force (2 pN) is deduced. It shows in the "mushroom"-regime (grafting densities $\leq 6.5 \times 10^{-5}$ chains/nm²) a scaling with the grafting density which levels off for "brushes" (grafting densities $\geq 6.5 \times 10^{-5}$ chains/nm²). For the latter the transition from an "osmotic" to a "salted" brush can be traced in detail by varying the ionic concentration in accordance with meanfield theories. Further experiments are carried out to measure the influence of the valency of the added salt. Special emphasis is given to the interaction between one DNA-grafted and one blank colloid. The results are discussed with respect to the different brush regimes.

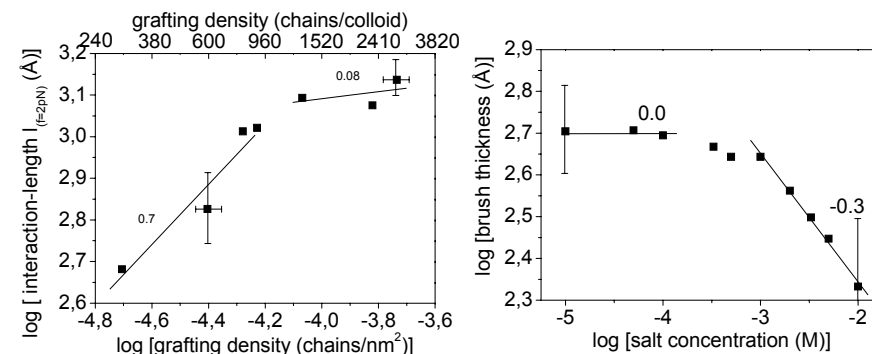


Fig.1 (a) Interaction length $l_{(f=2\text{pN})}$ at a force of 2 pN versus grafting density for DNA (1000bp)-grafted colloids of varying grafting density in buffered (10 mM $\text{C}_4\text{H}_7\text{NO}_3$, pH 8.5) solution. (b) Brush thickness versus salt concentration for DNA(1000bp)-grafted (8.25×10^{-5} chains/nm²) colloids in buffered (10 mM $\text{C}_4\text{H}_7\text{NO}_3$, pH 8.5) solution of varying ionic strength. The scaling relationships are indicated by straight lines.

References:

- [1] K. Kegler, M. Salomo and F. Kremer, *in press Phys. Rev. Lett.* (2006)

Collaborators:

A. Pich (TU Dresden)
 M. Stamm, P. Uhlmann (IPF Dresden)
 R. Netz (TU München)

Funding:

DFG priority program 1164 (Nano- & Microfluidics)

2.8 The flow resistance of *single* DNA-grafted colloids as measured by optical tweezers

C. Gutsche, M. Salomo, Y.W. Kim, R.R. Netz, and F. Kremer

In rheological experiments the flow resistance of *single* blank or DNA-grafted colloids is determined and compared. The length of the double-stranded (ds)-DNA varies between 1000 base pairs (bp), 4000 bp and 6000 bp corresponding to contour lengths between 340 nm and 2040 nm at a grafting density of $0.03 \pm 0.01 \mu\text{m}^2/\text{chain}$. The degree of swelling of the grafted DNA is adjusted by exchanging the ion concentration of the surrounding medium. For all examined flow velocities ranging between $100 \mu\text{m/s}$ to $1200 \mu\text{m/s}$ one observes an interesting deviation from Stokes law which can be traced back to a shear-dependent conformational change of the brush layer. The ratio of the effective hydrodynamic radii of DNA-grafted and blank colloids shows a pronounced dependence on the flow velocity, but as well on the length of the grafted DNA and the ionic strength of the solvent. The experimental findings are in qualitative agreement with hydrodynamic simulations based on an elastically-jointed chain model.

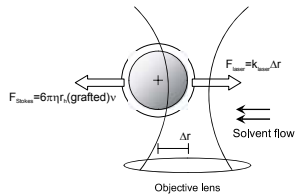


Fig. 1: Forces acting on a grafted colloid in flow

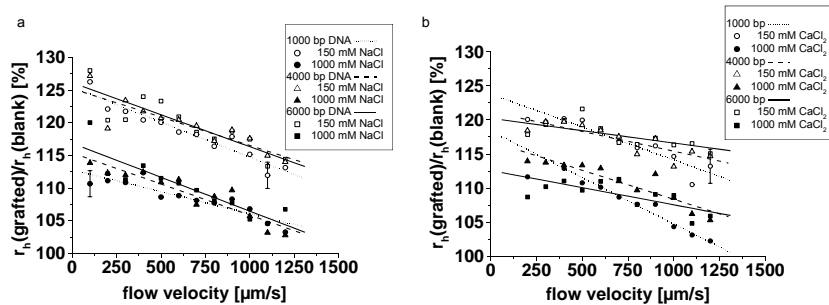


Fig. 2: Ratio of the effective hydrodynamic radii for DNA-grafted and blank colloids versus flow velocity. Three single colloids with different DNA-grafting (1000 bp, 4000 bp and 6000 bp, same grafting density) are measured in two NaCl/CaCl₂-media ((a): 1000 bp DNA-chains \cdots , \circ 150 mM NaCl, \bullet 1000 mM NaCl, 4000 bp DNA-chains \cdots , \triangle 150 mM NaCl, \blacktriangle 1000 mM NaCl, 6000 bp DNA-chains \cdots , \square 150 mM NaCl, \blacksquare 1000 mM NaCl, (b): as (a) but for CaCl₂-solutions).

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Funding:

DFG priority program 1164 (Nano- & Microfluidics)

2.5 Direct force measurements on DNA in solid-state nanopores

U. F. Keyser

Among the variety of roles for nanopores in biology, an important one is enabling polymer transport, for example in gene transfer between bacteria and transport of RNA through the nuclear membrane. Recently, this has inspired the use of protein and solid-state nanopores as single-molecule sensors for the detection and structural analysis of DNA and RNA by voltage-driven translocation. The magnitude of the force involved is of fundamental importance in understanding and exploiting this translocation mechanism, yet so far it has remained unknown. Recently, we demonstrated at the TU Delft the first measurements of the force on a single DNA molecule in a solid-state nanopore by combining optical tweezers with ionic-current detection [1]. The opposing force exerted by the optical tweezers can be used to slow down and even arrest the translocation of the DNA molecules. We obtain a value of 0.24 ± 0.02 pN/mV for the force on a single DNA molecule, independent of salt concentration from 0.02 to 1M KCl. This force corresponds to an effective charge of 0.50 ± 0.05 electrons per base pair equivalent to a 75% reduction of the bare DNA charge.

We will establish a research program combining optical tweezers and nanopores to learn more about the basic physical and chemical processes during voltage driven translocation of DNA. This may shed light on biological relevant processes like the above mentioned transfer of mRNA through the cell nucleus.

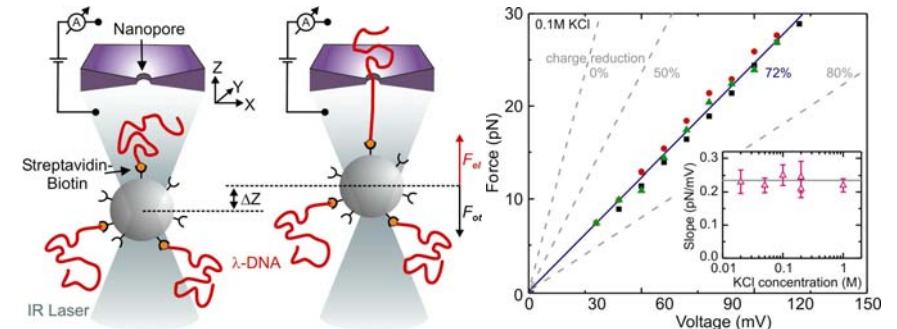


Fig. 1: Left: Combining optical tweezers with a nanopore. A tightly focused laser beam is used to hold a colloid coated with DNA molecules. When DNA is pulled into the nanopore the force exerted by the field is measured and controlled by the optical trap [1]. Right: Force on a single DNA molecule as a function of applied voltage over a single nanopore. The inset shows the dependence on the salt solution [2].

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2.6 Nanobubbles in nanopores

U. F. Keyser

Solid-state nanopores are promising as future components for lab-on-a-chip technology because of the possibility to use nanopores as molecular coulter counters for detecting nucleic acids like DNA [1]. Understanding the properties of these nanopores is important to develop better nanopores with lower noise and higher sensitivity. From conductance and noise studies, we infer that nanometer-sized gaseous bubbles (nanobubbles) are the dominant noise source in solid-state nanopores. We study the ionic conductance through solid-state nanopores as they are moved through the focus of an infrared laser beam. In the resulting conductance profiles show strong variations in both the magnitude of the conductance and in the low-frequency noise when a single nanopore is measured multiple times. Differences up to 5 orders of magnitude are found in the current power spectral density. In addition, we measure an unexpected double-peak ionic conductance profile. A simple model of a cylindrical nanopore that contains a nanobubble explains the measured profile and accounts for the observed variations in the magnitude of the conductance [2]. These effects will be studied at the University of Leipzig during the next years.

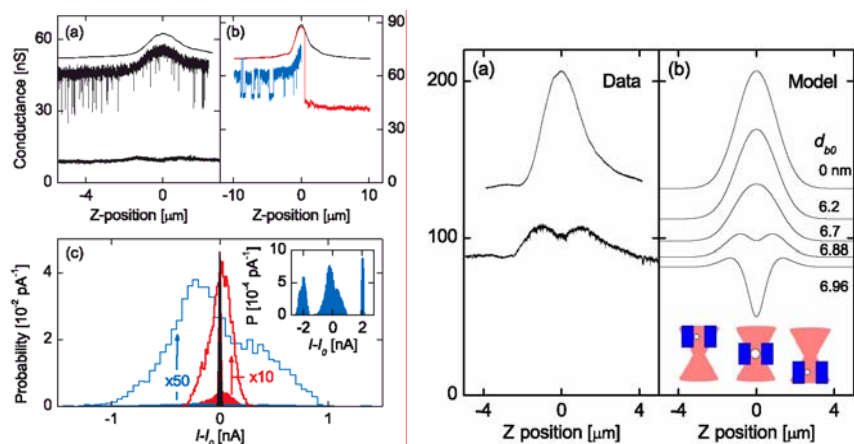


Fig. 1: Left: Typical conductance curves of nanopores with five orders of magnitude different noise levels [2] (a)-(c). Right: (a) Conductance of a nanopore as a function of position of a laser focus with and without nanobubble. Please note the higher noise of the lower curve with nanobubble. (b) A simple model reproduces the measured data very well. We assume a circular bubble in a cylindrical channel and the expansion of the nanobubble follows the ideal gas law [2].

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2.7 Forces of interaction between two colloids in media of varying ionic strength

C. Gutsche, U. F. Keyser, and F. Kremer

Optical Tweezers are employed to measure the forces of interaction within *single* pairs of colloids (Fig. 1) in media of monovalent and divalent ionic aqueous solutions of varying concentrations (Fig. 2). Artefacts are excluded in the measurements by cycling back to the initial salt conditions and find the same force-distance relation within experimental uncertainties. The data are well described for monovalent ions by a novel Poisson-Boltzmann approach based on the Derjaguin approximation and by the classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. For the divalent ions significant deviations between theory and experiment are observed presumably caused by underestimating ion-ion correlations. Assuming for the Debye-length dependence as suggested by the DLVO - theory, the charge per colloid is deduced, which is based on the full data set with different concentrations of the surrounding medium. From the measured force separation dependence an interaction length (at e.g. a force of 2 pN) is obtained, which enables one to analyse quantitatively the limits of the DLVO - theory.

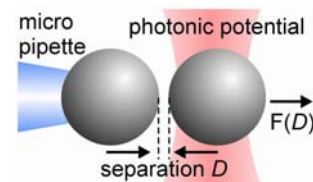


Fig. 1: Scheme of the experimental set up: The force $F(D)$ and separation between two identical, negatively charged colloids is measured using optical tweezers. One colloid is held with a micropipette (blue), the other in an optical trap created by a focused laser beam

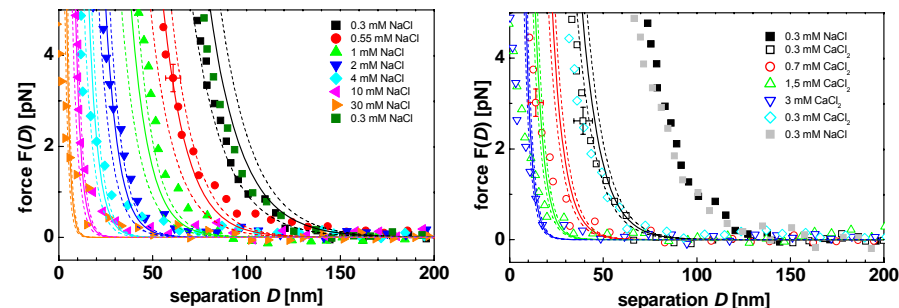


Fig. 2: Force separation dependence for two isolated identical colloids in aqueous solution of monovalent (a) and divalent (b) ions of varying concentrations in sequence as indicated with global fit and its uncertainties, ■ 0.3 mM NaCl, ● 0.55 mM NaCl, ▲ 1 mM NaCl, ▼ 2 mM NaCl, ◆ 4 mM NaCl, ◆ 10 mM NaCl, ► 30 mM NaCl, ■ 0.3 mM NaCl, □ 0.3 mM CaCl₂, ○ 0.7 mM CaCl₂, △ 1.5 mM CaCl₂, ▽ 3 mM CaCl₂, ◇ and back to ■ 0.3 mM NaCl.

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Funding:

DFG priority programm 1164 (Nano- & Microfluidics)