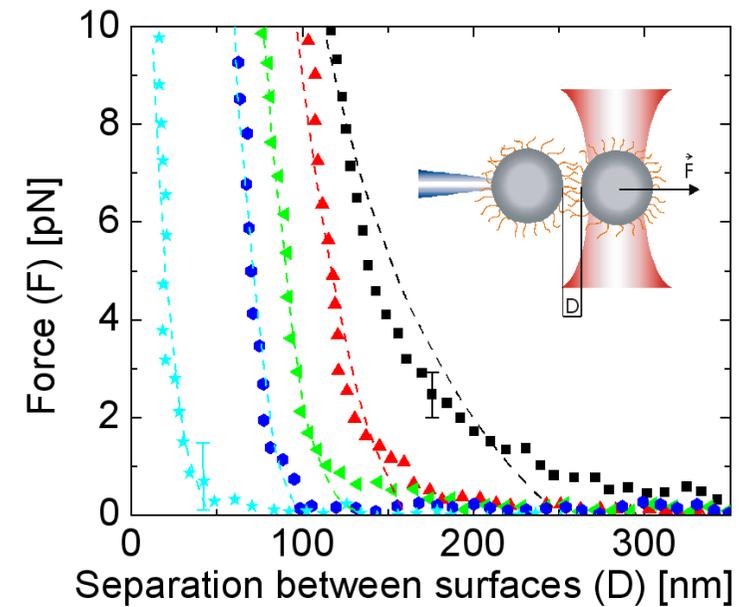


UNIVERSITY OF LEIPZIG

Faculty of Physics and Earth Sciences
Department of Experimental Physics I

GROUP "Molekülphysik"



Annual Report 2007

Cover picture: Forces of interaction between spherical DNA-brushes as measured by Optical Tweezers (project 2.6). The solid lines are fits based on the assumption that chain compression is the dominating mechanism of interaction (Kegler, K.; M. Salomo, F. Kremer, *Phys. Rev. Lett.* **98**, 058304 (2007) and Kegler, K.; M. Konieczny, G. Dominguez-Espinosa, C. Gutsche, M. Salomo, F. Kremer, C. N. Likos, *Phys. Rev. Lett.* (2007) in press).

UNIVERSITÄT LEIPZIG
Fakultät für Physik und Geowissenschaften
Prof. Dr. Friedrich Kremer
Linnéstraße 5
04103 Leipzig
Germany

Tel.: (0341) 97-32550
FAX: (0341) 97-32599
e-mail: kremer@physik.uni-leipzig.de

The year 2007

Πάντα ῥεῖ– everything is in flow. This famous statement of Heraklit holds for the situation of our group in 2007 especially well: In October 2006 Ulrich Keyser joined the group, in Januar 2007 he received an Emmy-Noether award and in October 2007 the offer for a lecturer position at the University of Cambridge, UK. Furthermore Anatoli Serghei was asked if he would be interested in a Post. Doc. position at the University of Massachusetts in Amherst, the center of polymer - research in the USA. So both will leave the group in 2008.- The activities in our „classical“ fields of expertise Broadband Dielectric Spectroscopy, experiments with Optical Tweezers and 2D - Fourier-Transform Infra Red Spectroscopy developed nicely. A variety of important publications appeared in leading journals (see cover picture) and the funding situation – mainly through the Deutsche Forschungsgemeinschaft (German Science Foundation) - substantially improved. This is a solid basis for the future prospects.

Friedrich Kremer

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5. Graduations

Promotions:

Dipl.-Biochem.
M. Salomo
"Optische Pinzetten zum Studium der Wechselwirkungen zwischen histonähnlichen Proteinen und einzelnen DNA-Molekülen"

Diploma

cand. phys. Jan Sölter
"FTIR-Untersuchungen zu Struktur-Eigenschaftsbeziehungen von Spinnenleitfadenseide"

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

Deutsche Patentanmeldung Nr. 10 2005 045 065.2-54
Titel: "Detektorvorrichtung zur Funktionsprüfung von Dichtungssystemen"
Erfinder: Prof. Dr. F. Kremer

8. Awards

Ulrich F. Keyser:
Emmy Noether-Programm der Deutschen Forschungsgemeinschaft
"Nanopores for biological and soft-matter physics"
KE 1452/1-1 (2007-2012)

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2.14 Structural levels of organisation in spider silk as unraveled by combined mechanical and time-resolved polarized FTIR studies (P. Papadopoulos, J. Sölter, I. Weidner and <u>F. Kremer</u>)	18
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1. Organization of the group

Chairman: Prof. Dr. Friedrich Kremer

Academic staff and postdocs

Dr. Ulrich Keyser
Dr. Gustavo Dominguez
Dr. Periklis Papadopoulos
Dr. Mathias Salomo
Dr. Anatoli Serghei

Students

cand. phys. Hergen Brutzer
cand. phys. Benjamin Gollnick
Dipl.-Phys. Christof Gutsche
M. sc. Ciprian Ghiorghita Iacob
M. Sc. Julius Tsuwi Kazungu
Dipl.-Phys. Kati Kegler
cand. phys. Oliver Otto
cand. phys. Jan H. Peters
M. Sc. Joshua Rume Sangoro
cand. phys. Jan Sölter
M. Sc. Ilya Semenov
M. Sc. Lorenz Steinbock
Dipl.-Phys. Gunter Stober
cand. phys. Carolin Wagner
cand. phys. Immanuel Weidner
M. Sc. Michael Tammer

Technical staff

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

Guests

Malgorzata Jasuirkowska
cand. phys. Mario E. del Pozo
Prof. Dr. Gamal Turkey

Alumni

Prof. Dr. Siegbert Grande

4. Financial support

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" SPP 1164
DFG-Schwerpunktprogramm 1164, KR 1138/14-2 (2006-2008)

Prof. Dr. F. Kremer and Dr. A. Serghei

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)

Prof. Dr. F. Kremer and Dr. U. F. Keyser

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

Dr. U. F. Keyser

Emmy Noether-Programm der Deutschen Forschungsgemeinschaft
"Nanopores for biological and soft-matter physics"
KE 1452/1-1 (2007-2012)

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

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

- submitted -

- 13) Papadopoulos, P.; J. Sölter, F. Kremer
"Structural levels of organization in spider silk – a combined mechanical and infrared spectroscopic study"
submitted to *Biophysical J.* (2007)
- 14) Berns, B.; H. Deligöz, B. Tiede and F. Kremer
"Conductive Composites of Polyurethane Resins and Ionic Liquids"
submitted to *Macromol. Mater. Eng.* (2007)
- 15) A. Serghei, H. Huth, C. Schick, F. Kremer,
"Glassy dynamics in thin polymer layers having a free upper interface"
submitted to *Macromolecules* (2007).
- 16) Gutsche, C.; F. Kremer, M. Krüger, M. Rauscher, R. Weeber and J. Harting
"Colloids dragged through a polymer solution: experiment, theory and simulation"
submitted to *J. Phys.: Condensed Matter* (2007)
- 17) Salomo, M.; U. F. Keyser, M. Struhalla, F. Kremer
"Optical tweezers to study single protein A/Immunoglobulin G interaction at varying conditions"
submitted to *European Biophys. J.* (2007)
- 18) Sangoro Rume, J., A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa and F. Kremer
"Charge transport and mass transport in imidazolium based ionic liquids"
submitted to *Phys. Rev. E* (2007)

2. Projects

2.1 Molecular dynamics of isolated polymer chains

A.Serghei* and F.Kremer

A recent experimental development [1] is employed to measure the molecular dynamics of isolated polymer chains (Fig. 1). Three different preparative approaches are followed: (i) spin-coating of strongly diluted polymer solutions, leading to samples which exhibit nearly isolated polymer chains adsorbed on a solid substrate (Fig. 1a); (ii) chemical grafting of polymer chains using a low grafting density to ensure isolated polymer chains; (iii) "physical" grafting by adsorption of strongly asymmetric diblock copolymers (from a diluted solution), with phase separation and large differences in the glass transition temperature between the two blocks, and additionally with the property that one component shows a good wetting of the supporting substrate while the second one exhibits dewetting.

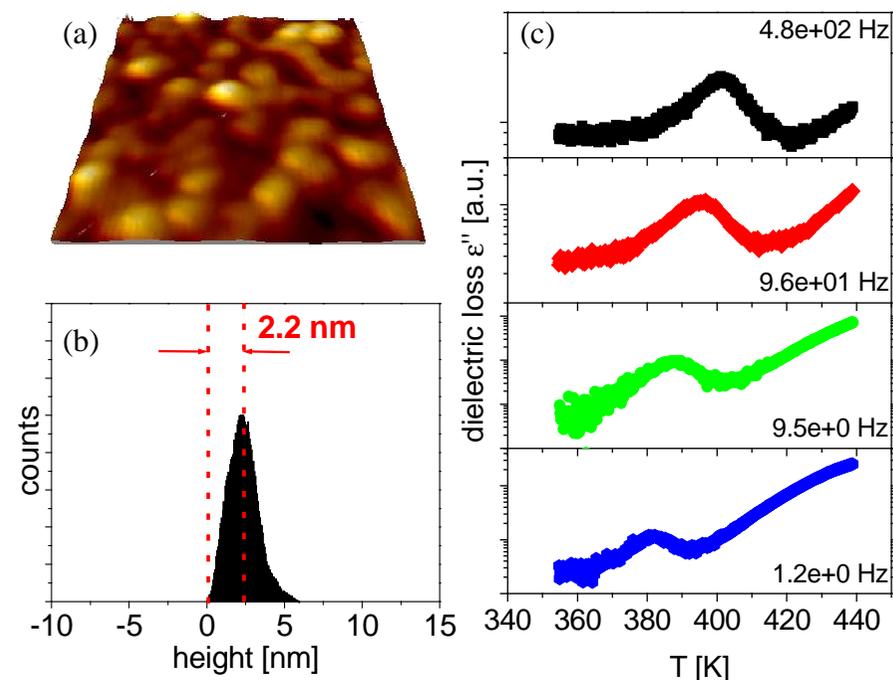


Fig. 1: (a) AFM image (300 nm x 300 nm) showing individual polymer chains (poly-2-vinylpyridine) adsorbed on the surface of a silicon wafer; (b) the corresponding heights histogram; (c) dielectric loss vs. temperature at different frequencies showing the dynamic glass transition of the sample presented in Fig. 1a.

References:

[1] Serghei, A. and F. Kremer, *Rev. Sci. Instrum.*, in press (2007)

Collaborators:

MicroFAB Bremen, P. Uhlmann (IPF Dresden)

* The underlined author has initiated the project.

2.2 Interfacial dynamics of polymers in interaction with solid substrates

A. Serghei and F. Kremer

The aim of the present project is to investigate the dynamics of polymers in the immediate vicinity of solid interfaces. For this purpose, Broadband Dielectric Spectroscopy (BDS) is employed to measure in a wide frequency and temperature range molecular fluctuations of polymer segments taking place in a (nanometric) proximity to a solid substrate. As probes, ultra-thin polymer films are used. A recently developed experimental approach (Fig. 1a,b) has been optimized and employed to render to BDS (traditionally a bulk technique) the character of an interfacial method. A systematic adjustment of the interfacial interactions is furthermore allowed by a controlled deposition on the surface of the electrodes of various (metallic but as well organic) layers prior to the preparation of thin polymer films.

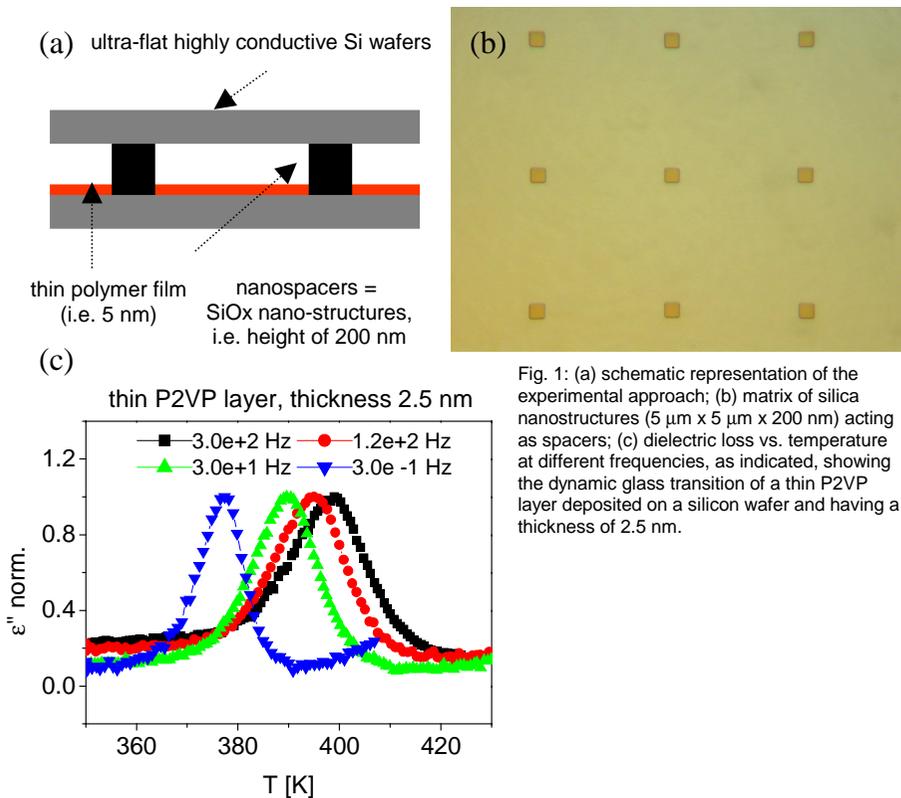


Fig. 1: (a) schematic representation of the experimental approach; (b) matrix of silica nanostructures ($5 \mu\text{m} \times 5 \mu\text{m} \times 200 \text{nm}$) acting as spacers; (c) dielectric loss vs. temperature at different frequencies, as indicated, showing the dynamic glass transition of a thin P2VP layer deposited on a silicon wafer and having a thickness of 2.5 nm.

References:

[1] Serghei, A. and F. Kremer, *Rev. Sci. Instrum.*, in press (2007)

Collaborators:

MicroFAB Bremen

3. Publications

- 1) Kegler, K., M. Salomo, F. Kremer
"Forces of interaction between DNA-grafted colloids: an Optical Tweezer measurement"
Physical Review Letters **98**, 058304 (2007)
 - 2) Tsui, Julius, D. Pospiech, D. Jehnichen, L. Häußler, F. Kremer
"Molecular dynamics in semifluorinated side-chain polysulfone as studied broadband dielectric spectroscopy"
Special issue of *J Appl. Polym. Sci.* (M. Kryszewski issue) **105**, 201-207 (2007)
 - 3) Massalska-Arodz, M.; J. Krawczyk, B. Procyk, F. Kremer
"Dielectric relaxation studies of 4-(2-hexyloxyethoxy)4'-cyanobiphenyl (6O2OCB) enclosed in SiO₂ nanopores"
Phase Transitions **80**, No. 6-7, 687-695 (2007)
 - 4) Gutsche, C., U.F. Keyser, K. Kegler, F. Kremer, P. Linse
"Forces between single pairs of charged colloids in aqueous salt solutions"
Phys. Rev. E **76**, 031403 (2007)
 - 5) Jehnichen, D., D. Pospiech, L. Häußler, P. Friedel, S.S. Funari, J. Tsui, F. Kremer
"Microphase separation in semifluorinated polyesters"
Z. Kristallogr. Suppl. **26**, 605-610 (2007)
 - 6) Serghei, A.; L. Hartmann, F. Kremer
"Molecular dynamics in thin films of isotactic poly(methylmethacrylate)-revisited"
J. of Non-Crystalline Solids **353**, No. 47-51, 4330-4333 (2007)
 - 7) Salomo M., U. Keyser, K. Kegler, M. Struhalla, C. Immich, U. Hahn, F. Kremer
"Kinetics of TmHU binding to DNA as observed by optical tweezers"
Microscopy Research & Technique **70**, No. 11, 938-943 (2007)
 - 8) Papadopoulos, P.; J. Sölter, F. Kremer
"Structure-property relationships in major ampullate spider silk as deduced from polarized FTIR spectroscopy"
Eur. Phys. J. E **24**, 193-199 (2007)
- in press -
- 9) Serghei, A. and F. Kremer,
"Metastable states of arrested glassy dynamics, possibly mimicking confinement effects in thin polymer films"
in press: *Macromol. Chem. Phys.* (2007).
 - 10) Otto, O.; C. Gutsche, F. Kremer, U. F. Keyser
"Optical tweezers with 2.5 kHz bandwidth video detection for single-colloid-electrophoresis"
in press: *Rev. Sci. Instr.* (2007)
 - 11) A. Serghei and F. Kremer,
"Broadband dielectric studies on the interfacial dynamics enabled by use of nano-structured electrodes"
in press: *Rev. Sci. Instrum.* (2007).
 - 12) Kegler, K.; M. Konieczny, G. Dominguez-Espinosa, C. Gutsche, M. Salomo, F. Kremer and C. N. Likos
"Polyelectrolyte-Compression Forces between Spherical DNA Brushes"
in press: *PRL* (2007)

2.18 Localized heating effects in optical tweezers investigated using ionic currents through nanopores

J. H. Peters and U. F. Keyser

Optical tweezers are a powerful and widely used experimental tool in biological physics including single molecule investigations. The strongly focused laser-beam in such a setup can reach power densities in the order of 10^8 W/cm^2 that cause significant heating exceeding 10K per Watt of incident laser power for a 1064nm-Laser [1,2]. As the reaction constants of biomolecules are temperature dependent, heating effects should be considered in biophysical experiments.

The ionic current through a nanopore depends on the local temperature in a well-defined manner and hence can be used for temperature measurements with high spatial resolution [1]. We compare experiments using nanopores with numerical finite element calculations and investigate the dependence of heating effects on parameters like geometry and thermal conductivity of water and nanopore material. We were able to confirm earlier findings as the logarithmic dependence of the maximal temperature on the size of the system [2] and also gain a more detailed insight into the temperature distribution found in optical tweezers.

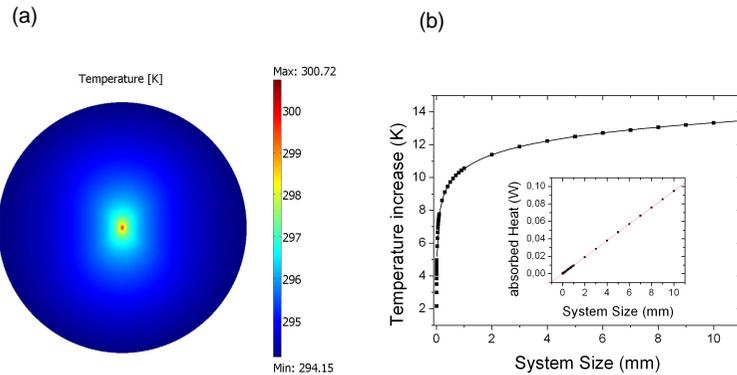


Fig. 1: Left: Temperature-distribution generated by a focussed (gaussian) Laser-beam in a sphere of water ($r = 50 \mu\text{m}$). The distribution has been calculated numerically from the heat equation using the finite-element method (fem). Right: Dependence of the temperature in the focus and of the absorbed heat (Inset) on the system size calculated by fem. The Temperature was fitted (line) with a model based on the analytic solution given in [2].

References:

- [1] U. Keyser, et al., *Nano Letters* **5**, No. 11, 2253-2256 (2005)
- [2] E. Peterman, et al., *Biophys. Journal*, **84**, 1308-1316 (2003)

Collaborators:

D. Stein (Brown University)

Funding:

Emmy Noether program DFG

2.3 A minimal model for the electrode polarization

A. Serghei, J. Rume and F. Kremer

Electrode polarization is a phenomenon manifested when the diffusion of charge carriers is (partially) blocked due to the presence of interfaces. It causes pronounced changes of the dielectric function and hence of the complex conductivity. These changes show a peculiar dependence on the length of the sample cell and on the material of the electrodes. The current project aims to develop a minimal model for electrode polarization, i.e. based on a minimal set of assumptions. It can be shown that, assuming a thin interfacial layer ($\sim 1 \text{ nm}$ thickness) having a much lower dielectric loss than in the bulk ($\epsilon''_{\text{interface}} \ll \epsilon''_{\text{bulk}}$), leads to dielectric spectra which exhibit – on a qualitative as well as quantitative level – all experimental features of the electrode polarization:

- (i) the characteristic spectral dependence of the dielectric response.
- (ii) the experimental observation that the electrode polarization shifts to higher frequencies with increasing temperature.
- (iii) the scaling in respect to the temperature variation.
- (iv) the dependence on the length of the sample cell: the electrode polarization shifts to higher frequencies when decreasing the sample length
- (v) the experimental observation that the dielectric response does not scale in respect to the variation of the sample length.
- (vi) the dependence on the material of the electrodes, by allowing different thicknesses of the interfacial layer.
- (vii) the experimental observation that the dielectric response does not scale in respect to the variation of the electrodes material.

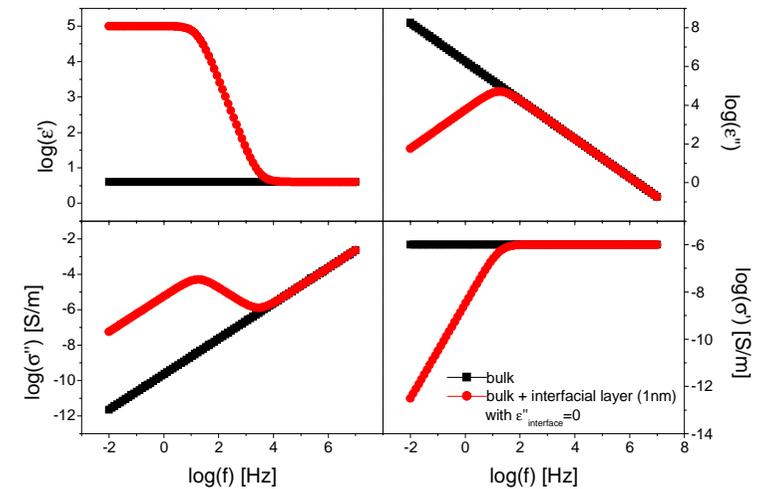


Fig. 1: Complex dielectric function and complex conductivity of a usual ionic conductor in the bulk (black squares) and calculated under the assumption of interfacial layers (1 nm thickness) with negligible dielectric losses (red circles).

2.4 Charge transport and mass transport in ionic conductors

J. Rume, A. Serghei and F. Kremer

The mechanism of charge transport in the imidazolium based ionic liquid 1,3-dimethylimidazolium dimethylphosphate – is analyzed by combining Broadband Dielectric Spectroscopy (BDS) and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR). 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 the Einstein and Einstein-Smoluchowski equation enables one to determine – in excellent agreement with direct measurements by PFG NMR – the diffusion coefficient of the charge carriers. By that, it becomes possible to extract from the dielectric spectra *separately* the number density and the mobilities of the charge carriers and the type of their thermal activation. It is shown that the observed Vogel-Fulcher-Tamman dependence of the DC conductivity can be traced back to a similar temperature dependence of the mobility while for the number density an Arrhenius-type thermal activation is found. Extrapolating the latter to room temperature indicates that nearly all charge carriers are participating to the conduction process.

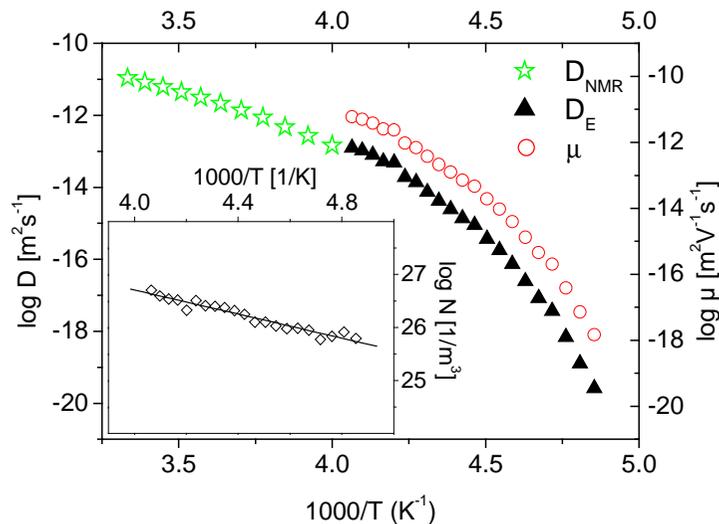


Fig. 1: Diffusion coefficient determined by the Einstein-Smolokowski eq. (using ω_{h} as hopping rate and $\lambda=0.2$ nm as hopping length) compared with the diffusion coefficient measured by PFG NMR. Additionally, the mobility of the charge carriers is determined. Inlet: effective number of charge carriers as a function of inverse temperature.

References:

[1] Rume, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa, F. Kremer, submitted to *Rev. Phys. Rev. E* (2007)

Collaborators:

F. Bordusa (MPI, Halle), J. Kärger (U Leipzig)

2.17 Transport of colloids through glass capillaries

L. Steinbock, G. Stober, B. Gollnick and U. F. Keyser

Nanopores promise a new avenue in DNA sequencing. By restricting the polymer inside the pore, translocating the nucleotides one by one by electrophoresis DNA sequencing could be done at a much faster speed, without the high costs involved in chemicals, proteins necessary in current techniques.

We started to study translocation of colloids through micrometer sized pores, while measuring the ionic current. Once source for these pores are borosilicate capillaries, which are drawn with a pipette puller to pores of several micrometer to sub-micrometer diameters (Fig. 1a). The second source is a focused ion beam (FIB), which allows the fabrication of holes into silicon chips from micrometer to nanometer size (Fig. 1b). While measuring the ion current flowing through the pore the translocating DNA-colloids will disturb the ion signal. This will enable us to estimate the charge of the colloids and the number of attached polymers like e.g. DNA strands.

Further, we will combine the ionic current measurements with an optical trap to manipulate colloids in the capillaries. In the future we aim to decrease the pore size to below 10 nm to detect specific DNA sequences, which are complementary to distinct segments on the DNA. These will be detected, by measuring the ionic current.

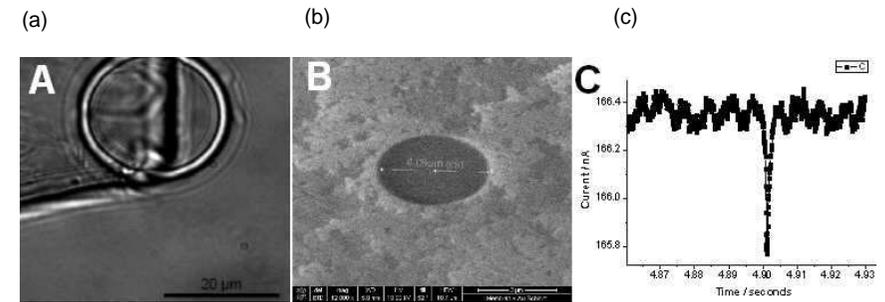


Fig. 1: A, image of a borosilicate glass capillary, which is blocked by colloid. B, image of a 4 micrometer pore within in a gold coated Si3N4 membrane etched by a focused ion beam (FB). C, ionic current measurement through a glass capillary. The peak is caused by the translocation of a colloid, which results in a decreased current

References:

Keyser, U. F., J. van der Does, C. Dekker, and N. H. Dekker, *Rev. Sci. Instr.* **77**, 105105 (2006)

Collaborators:

R. Berg (Kopenhagen)

Funding:

Emmy Noether-Programm der Deutschen Forschungsgemeinschaft "Nanopores for biological and soft-matter physics", BuildMoNa graduate school and the Deutsche Telekom Stiftung.

2.16 Modelling colloidal transport through capillaries

G. Stober, L. Steinbock, B. Gollnick and U. F. Keyser

The charge and diameter of colloidal particles determine their interaction in aqueous solutions. Measuring the surface charge remains a challenge despite the numerous existing approaches. Here we investigate the possibility to determine the diameter and surface charge of colloids passing a small capillary leading to a brief obstruction of an ionic current.

We developed a simple model founded on simple geometrical considerations to understand this process. The ionic conductance in such a system is given by the cross section of the capillary tip. A colloid passing through the tip reduces this cross section and replaces the charges of the ionic solvent in his volume by his own. Using this idea in a computer simulation using Newtons equation of motion for the colloid and a rotational geometry for the capillary, the time dependency of signal could be investigated. Adding some realistic features like an uncertainty in the size of the colloids, a Hagen Poiseuille velocity profile in the capillary and the possibility to manipulate the charges of the colloid, allows simulation of the expected current amplitude.

The model together with the simulation enables one to perform several millions of experiments in a few hours for several sets of parameters (ionic strength of the solvent, colloid sizes and capillary geometries). With the simulations we are able to assess the influence of the surface charge and colloid size on the expected distribution of blockage current.

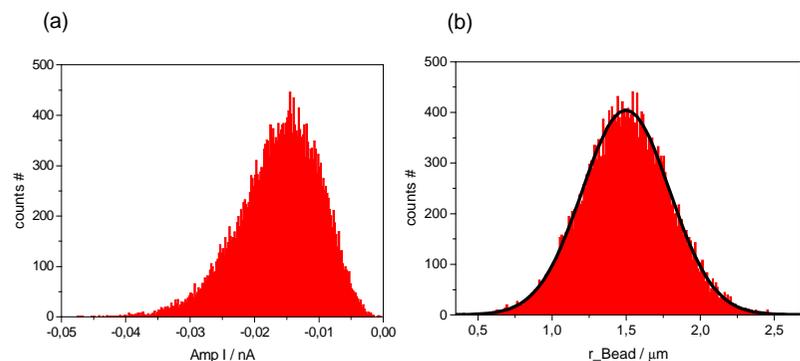


Fig. 1: The histograms were calculated for a 3 μm colloid in a 48 μm capillary. The monovalent salt concentration was $c=10^{-2}$ mol at a voltage of 100 mV. (a) In this simulation a Gaussian size distribution was used with an RMS of 20%. The Gaussian distribution was generated with Marsaglia Pseudo random numbers. (b) The simulated size distribution is clearly Gaussian. Obviously the asymmetry is a real effect due to the dependency of the signal from the cross section and so a further moment enters in the distribution in the amplitudes.

References:

- [1] Keyser U. F., J. van der Does, C. Dekker, and N. H. Dekker, *Rev. Sci. Instr.* **77**, 105105, (2006)
- [2] Gutsche, C., U.F.Keyser, K. Kegler, F. Kremer, P. Linse, *Phys. Rev. E* **76**, 031403 (2007)
- [3] Otto, O.; C. Gutsche, F. Kremer, U. F. Keyser, in press: *Rev. Sci. Instr.* (2007)

Collaborators:

R. Netz (TU München)

Funding:

Emmy Noether-Programm der Deutschen Forschungsgemeinschaft

2.5 Correlation between rotational and translational diffusion under conditions of geometrical confinement

C. Iacob, A. Serghei and F. Kremer,

The molecular dynamics, as reflected on the microscopic scale by rotational and translation diffusion, exhibits deviations from its bulk behaviour when organic materials are investigated under geometrical confinement (Fig. 1). Although both these components of diffusion are manifestations of the same phenomenon – molecular structural fluctuations – no systematic investigations exist concerning the correlations between the translational and rotational diffusion under conditions of 2D geometrical confinement. (Fig. 2). The goal of the present project is to investigate these correlations (in the bulk but as well in confinement), in dependence on the molecular structure.

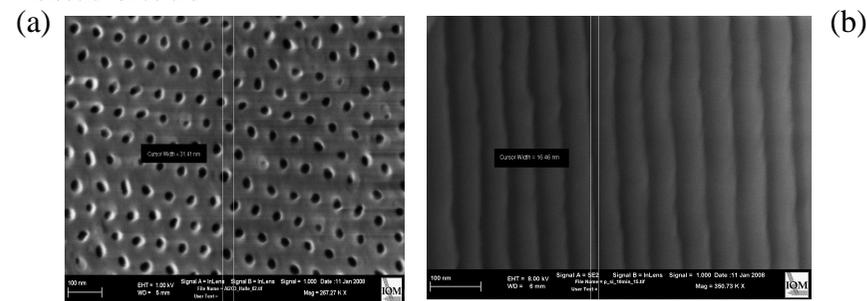


Fig. 1: a) SEM images of the porous alumina Al₂O₃ host membranes (top view, pore size 30 nm); b) the corresponding cross section.

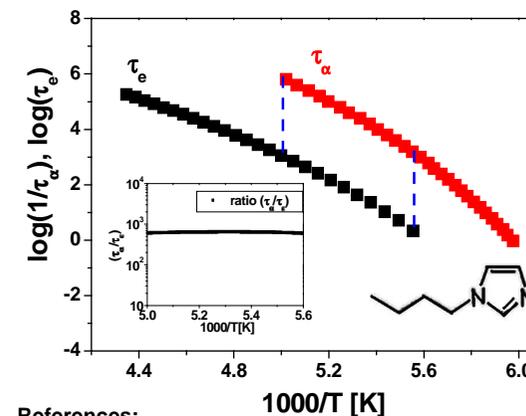


Fig. 2: Correlation between the translational and the rotation diffusion for 1-butylimidazole: τ_e represents the hopping time of the charge carriers, as defined by the Dyre theory, while τ_α is the fluctuation time related to the dynamic glass transition. Inlet: left - the ratio between τ_α and τ_e , right - formula for 1-butylimidazole.

References:

- [1] Lehmann, V., R. Strengl, A. Luigart, *Mat.Sci.and Eng.*, B69-70 (2000)
- [2] Arndt, M., R. Stannarius, W. Gorbatschow, F. Kremer, *Phys. Rev. E* **54**, 5377-5390 (1996)
- [3] Kumar P., P. Huber, *J. of Nanomaterials*, doi.10.1155/2007/89718 (2007)
- [4] Ronkel, F., J. W. Schultze, *J. of Porous Mat.* **7**, 11–16 (2000)

Collaborators:

J. Kärger, R. Valiullin (U Leipzig), M. Alexe (MPI, Halle), D.Hirsch (IOM, Leipzig)

2.6 Polyelectrolyte-compression forces between spherical DNA brushes

K. Kegler and F. Kremer

Optical tweezers are employed to measure the forces of interaction within a *single* pair of DNA-grafted colloids in dependence of the molecular weight of the DNA-chains (250 basepairs (bp), 500 bp, 750 bp, 1000 bp), and the concentration and valence (mono-, di-, trivalent) of the surrounding ionic medium. The resulting forces are short-range and set in as the surface-to-surface distance between the colloidal cores reaches the value of the brush height. The measured force-distance relation is analyzed by means of a theoretical treatment that quantitatively describes the effects of compression of the chains on the surface of the oppositely-lying colloid. Quantitative agreement with the experiment is obtained for all parameter combinations.

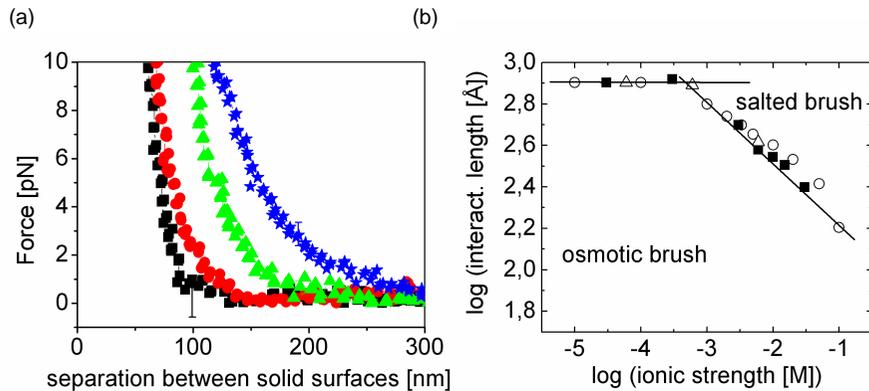


Fig.1 (a) F(D) curves between DNA-grafted colloids in buffered solution (10 mM $C_4H_{11}NO_3$, pH 8.5) for a constant grafting density and various bp-number (250 bp (square), 500 bp (circle), 750 bp (triangle up) and 1000 bp (star)). (b) Double-logarithmic plot of the interaction length for a force $F = 2$ pN versus the ionic strength of the added salt. Here, the molecular weight of the grafted DNA is $N = 1000$. Different types of symbols correspond to different salt valencies (NaCl – circle, $CaCl_2$ – square, $LaCl_3$ – triangle). The line of slope $-1/3$ indicates theoretical scaling law predictions for comparison.

References:

- [1] Kegler, K., M. Salomo, F. Kremer, *Phys. Rev. Lett.* **98**, 058304 (2007).
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Collaborators:

M. Stamm, P. Uhlmann (IPF Dresden)
R. Netz (TU München)
C. N. Likos (U. Düsseldorf)

Funding:

DFG priority programm 1164 (Nano- & Microfluidics)

2.15 Noise in Solid-State Nanopores

U. F. Keyser

We study ionic current fluctuations in solid-state nanopores over a wide frequency range and present a complete description of the noise characteristics. At low frequencies ($f < 100$ Hz) $1/f$ -type of noise is observed. Analysis of this low-frequency noise at different salt concentrations shows that the noise power remarkably scales linearly with the inverse number of charge carriers, in agreement with Hooge's relation. We find a Hooge parameter of $1.1 \pm 0.1 \times 10^{-4}$. In the high-frequency regime ($f > 1$ kHz), the increase in current power spectral density with frequency is modelled through a calculation of the Johnson noise. Finally, we use these results to compute the signal-to-noise ratio for DNA translocation for different salt concentrations and nanopore diameters, yielding the parameters for optimal detection efficiency.

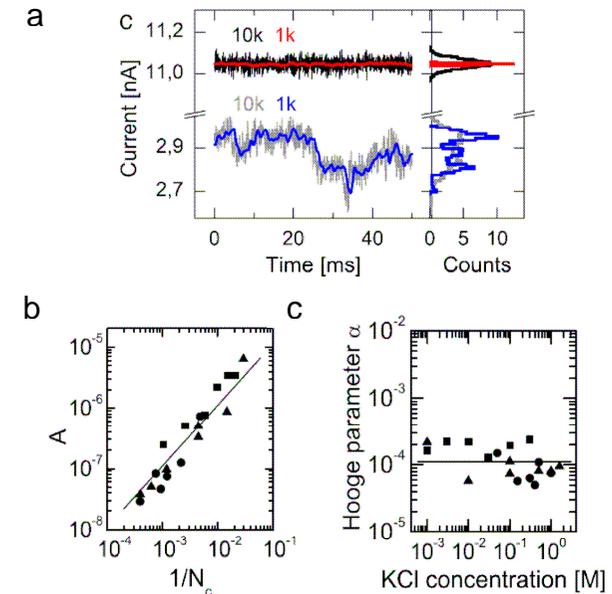


Fig.: (a) Current recordings and histograms of two nanopores (at 100 mV) with substantially different resistance values, illustrating clear differences in current noise. The nanopores diameters are 20.8 nm (bottom traces) and 22.0 nm (top traces). The current was filtered at 10 and 1 kHz, as indicated. (b) Noise power as a function of the calculated inverse number of charge carriers in the nanopore. (c) The value of the Hooge parameter over the salt concentration. The Hooge parameter is constant and results from the product of the noise power and the number of charge carriers.

References:

- Smeets, R. M. M., U. F. Keyser, N. H. Dekker, C. Dekker, *Proceedings of the National Academy of Sciences, USA* **105**, 417 (2008)

Collaborators: C. Dekker (Delft University of Technology)

Funding:

Emmy Noether-Programm der Deutschen Forschungsgemeinschaft

2.14 Structural levels of organisation in spider silk as unraveled by combined mechanical and time-resolved polarized FTIR studies

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

The understanding of the mechanical properties of the various types of spider silk requires a combination of techniques which can trace the effects of external fields on the microscopic level. FTIR is particularly suitable, because it can distinguish between different amino acid groups as well as different secondary structures. The simultaneous stress-strain measurements unravel the microscopic response under equilibrium and non-equilibrium conditions.

In the case of major ampullate silk, crystalline and amorphous regions are affected in different ways by external strain. The alanine-rich crystals remain always almost perfectly aligned parallel to the fiber axis, whereas the glycine-rich amorphous chains exhibit a very low order parameter. An important effect is the frequency shift of vibrations corresponding to crystalline structures, which depends on stress rather than strain and can be used as a microscopic probe of the force [1]. The linear thresholdless response implies that crystals are interconnected by *pre-stained chains*. This pre-stress is counterbalanced by the fiber skin and is released upon hydration. A model assuming a gaussian distribution of pre-strain and a *worm-like behavior* of the amorphous chains can reproduce the mechanical properties of both native and supercontracted silk [2]. This model applies also to minor ampullate silk, which has different properties, even though its chemical structure is not very different. The difference can be explained by a lower degree of pre-strain [3].

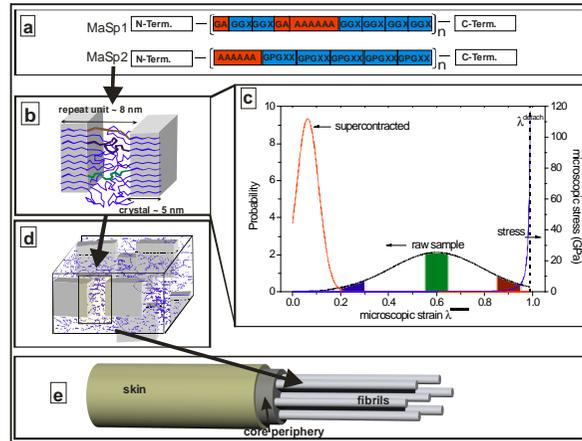


Fig. 1. Proposed structural levels of organization in spider silk. The alanine-rich protein parts (a) form highly oriented crystals (b) which are interconnected by amorphous worm-like chains with a Gaussian pre-strain distribution (c). The so assembled β -sheeted blocks (d) form a core of fibrils inside the silk fiber (e). The skin balances the internal pre-strain.

References:

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Collaborators:

F. Vollrath (University of Oxford), A. Sponner (Institute of Entomology, Ceske Budejovice, Czech Republic)

2.7 Drag-induced forces on colloids in polymer solutions of varying concentration

C. Gutsche and F. Kremer

We present a first direct experimental observation of jamming-induced drag-enhancement on colloids pulled through a solution of λ -DNA (used here as a monodisperse model polymer) with an optical tweezer. The experiments show a drag force which is larger than expected from the Stokes formula and the independently measured viscosity of the DNA solution. We attribute this to the accumulation of DNA in front of the colloid and the reduced DNA density behind the colloid. This hypothesis is corroborated by a simple drift-diffusion model for the DNA molecules, which reproduces the experimental data surprisingly well, as well as by corresponding Brownian dynamics simulations.

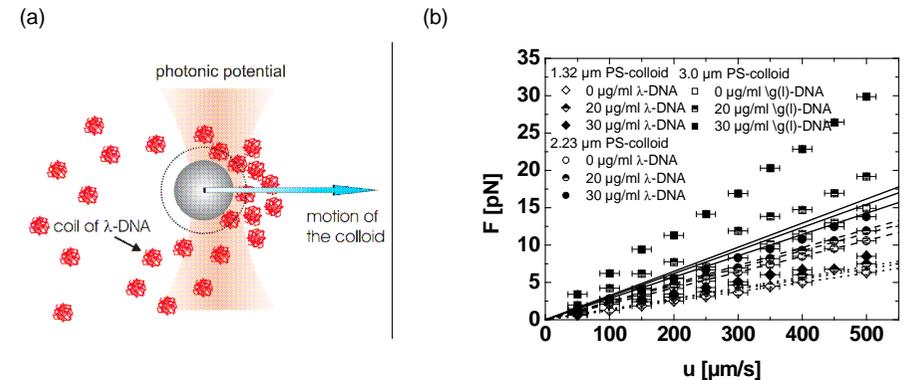


Fig. 1: (a) Illustration of the experimental set up. The colloid (grey) surrounded by coils of DNA (red) is held in an optical trap (magenta); (b) Drag force F on colloids in λ -DNA as a function of the pulling speed u . Also shown is the Stokes force on the colloids in λ -DNA (solid line) as expected for the viscosities measured for the given DNA concentration in a viscosimeter.

References:

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Collaborators:

M. Krüger, M. Rauscher (U Stuttgart)
R. Netz (TU München)
J. Harting (U Stuttgart)

Funding:

DFG priority programm 1164 (Nano- & Microfluidics)

2.8 In-situ analysis of the forces of interaction in polyelectrolyte brushes

G. Dominguez and F. Kremer

The forces of interaction between colloids being grafted with poly acrylicacid (PAA) brushes are measured by means of Optical Tweezers. Parameters to be varied are the ionic strength, the valence of the counterions and the pH of the surrounding medium.

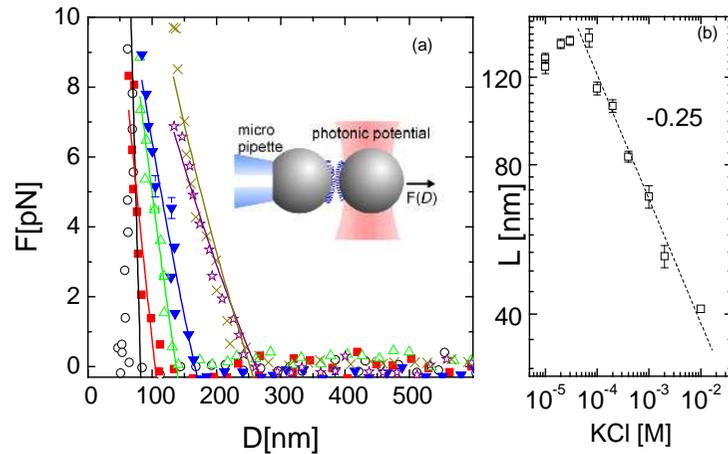


Fig. 1: (a) Force vs. separation (D) between the solid surfaces of two PAA-grafted particles under conditions of varying ionic strength of the surrounding medium at pH 7. Open circles, full squares, open triangles, full triangles, open stars and crosses represent $[KCl]$ in molar units for 10^{-2} , $2 \cdot 10^{-3}$, 10^{-3} , $4 \cdot 10^{-4}$, 10^{-5} , and 10^{-5} (measured at the end of the experimental run to show the reversibility of the process), respectively. Error bars are indicated. The dashed lines represent fits according to a model by Jusufi et al. [1]. Inset: Scheme of the experimental set-up. (b) Brush height (L), vs salt concentration as determined from the Jusufi model; the dashed lines indicates the power law dependence with the exponent $-1/4$.

The observed force distance dependence (Fig. 1) enables one to trace - within a *single* pair of PAA-grafted colloids - the swelling of the polymer brush with decreasing KCl concentration. The data are well described by a recently published theory [Jusufi et al.] of the effective interaction between spherical polyelectrolyte brushes. According to this the dominant term in the interaction arises from the entropic contribution of the counterions inside the brush. This enables one to determine the brush height in dependence of the salt concentration. An exponent of $-1/4$ is found which ranges between the value being predicted for planar ($-1/3$) and spherical brushes ($-1/6$).

References:

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Collaborators:

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

Funding:

DFG-Projekt KR 1138/20-1 (2006–2008)

2.13 Optical tweezers for single-colloid-electrophoresis

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

Properties of colloidal dispersions have been studied intensively for decades. A fundamental understanding is of great importance in many fields of work, e.g. to analyze complex transport mechanisms in living organisms or to examine rheological phenomena of condensed matter. Colloidal dispersions find wide spread industrial applications as coatings, aerosol, ceramics and drugs. Crucial for their properties are the size and charge of the colloids, both can be varied over a broad range and thus the intercolloidal interactions can be adjusted. This makes colloidal dispersions an excellent model system to investigate fundamental issues in condensed matter physics.

We developed an optical tweezers setup to study the electrophoretic motion of colloids in an external electric field. The setup is based on standard components for illumination and video detection. Our video-based optical tracking of the colloid motion has a time resolution of 0.2 ms resulting in a bandwidth of 2.5 kHz. This enables one to calibrate the optical tweezers by Brownian motion without applying a quadrant photo detector. We demonstrate that our system has a spatial resolution of 0.5 nm and a force sensitivity of 20 fN using a Fourier algorithm to detect periodic oscillations of the trapped colloid caused by an external AC-field. The electrophoretic mobility and Zeta-potential of a single colloid can be extracted in aqueous solution avoiding screening effects common for usual bulk measurements.

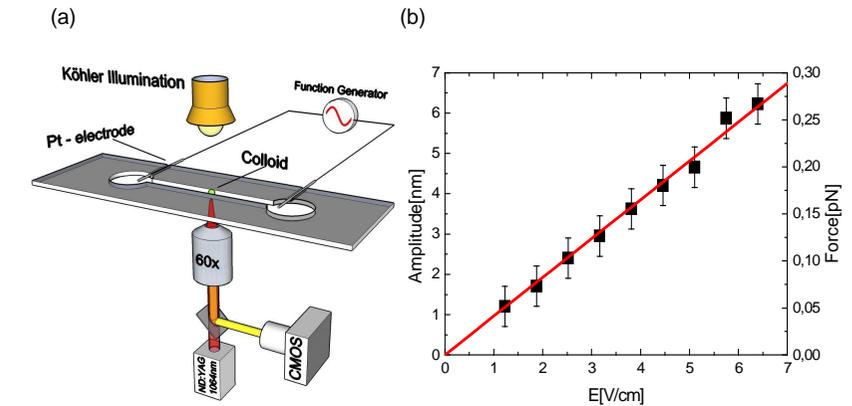


Fig. 1: (a) Schematic of the Optical Tweezers setup with custom made fluidic cell. A single colloid is held in the optical trap and its movement due to an external electrical field recorded by video detection. (b) Amplitude and force as a function of electric field for a single $2.23 \mu\text{m}$ colloid in aqueous solution. Amplitudes as low as 1 nm and forces of 50 fN are detected.

References:

Otto, O., C. Gutsche, F. Kremer, U. F. Keyser, submitted to *Rev. Sci. Instrum.* (2007)

Collaborators:

R. Netz (TU München)

Funding:

Emmy Noether-Programm der Deutschen Forschungsgemeinschaft
Schwerpunktsprogramm „Mikro- und Nanofluidik“, DFG

2.12 Study of Protein-DNA interaction with Atomic Force Microscopy

H. Brutzer, M. Salomo, U. F. Keyser and F. Kremer

Atomic force microscopy (AFM) was used to investigate single macromolecules, in particular DNA, proteins and protein-DNA complexes. DNA contour and persistence length were studied yielding results comparable to literature values. The volume of histone-like HU protein dimers from *Thermotoga maritima* (TmHU) could be determined in good agreement with results calculated from their molecular weight. Furthermore, the concentration dependence of binding for TmHU dimers to DNA was examined. For the end-to-end distance of the DNA strands a concentration-dependence is found with a threshold-limit below which hardly any influence of the concentration is observable. Above that, no DNA molecules can be deposited onto the surface, which suggests the formation of large clusters consisting of TmHU-DNA complexes. By analysing the coverage of TmHU molecules on the DNA strand a simple model of one relatively short binding site per protein becomes highly unlikely. Instead, evidence is found that multiple binding sites for each protein contribute to the creation of globular structures, possibly due to a secondary organizational level of the TmHU-DNA complex.

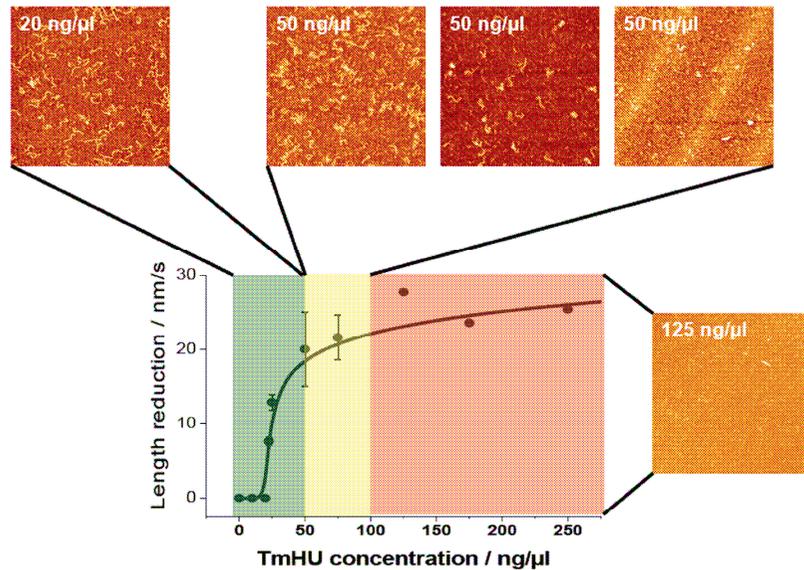


Fig. 1: Results based on AFM measurements compared with data achieved using optical tweezers (taken from [1] and modified). TmHU compacts the DNA above a concentration of 50 ng/µl.

References:

[1] Salomo M., U. Keyser, K. Kegler, M. Struhalla, C. Immich, U. Hahn, F. Kremer, *Microscopy Research and Technique* **70**, 938 (2007)

Collaborators:

M. Mertig (TU Dresden)

2.9 Optical Tweezers to study single receptor / ligand-interactions

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. Most studies have been performed with the reactants in solution. This does not reflect the general conditions that are relevant *in vivo*. Optical tweezers are ideally suited to study the interaction of single receptor-ligand bonds. We developed an assay using optical tweezers to investigate the interactions between Protein A from *Staphylococcus aureus* and Immunoglobulin G from rabbit serum (RlgG) (Fig 1). We demonstrate that the rupture forces depend on the loading rate (Fig. 2) and sodium chloride concentration (Fig. 3). The measured loading rate effect is well known in the literature and the data we obtained were found to be in good agreement with an already published theoretical model. The dependence of the rupture forces on the salt concentration demonstrates the influence of hydrophobic interactions on the bond strength. Our experimental setup can probe the interaction between a single receptor and its specific ligand under changing conditions and hence offers manifold applications in single molecule biotechnology.

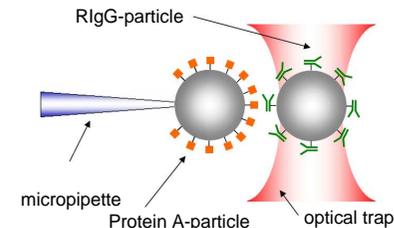


Fig. 1: Experimental setup. One particle with protein A on its surface is fixed at a micropipette by suction. The other one carrying Immunoglobulin G is held in the optical trap. In the course of the measurement the particles are brought together in order to establish a single bond between Protein A and RlgG. By pulling the colloids apart the junction breaks and the resulting rupture forces can be measured directly.

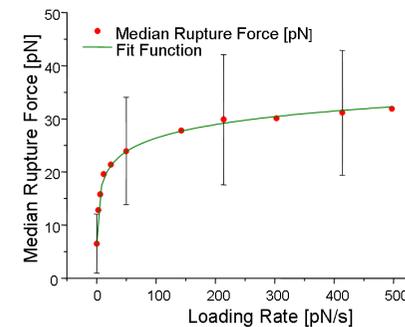


Fig. 2: Loading rate dependence. With increasing loading rates the rupture force rises and levels of above 150 pN/s.

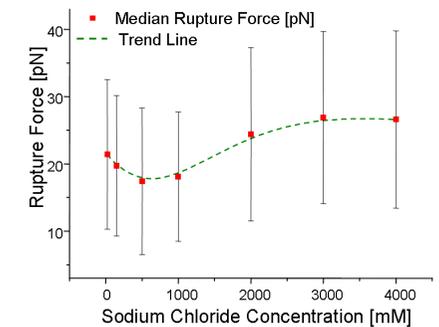


Fig. 3: Salt dependence. Electrostatic forces decrease with higher salt concentrations while hydrophobic interactions increase.

References:

Salomo M., U. F. Keyser, M. Struhalla, F. Kremer, submitted to *European Biophysics Journal* (2007)

Funding:

Einzelmolekülanalyse: SMWK-Projekt 4-7531.50-02-0361-06/1 (2006-2007)

2.10 DNA condensation under the action of the protein TmHU as studied on a *single molecule level*

C. Wagner, M. Salomo, U. F. Keyser, K. Kegler, C. Gutsche and F. Kremer

Optical Tweezers enable one to analyse the binding of the histone-like Protein TmHU (from *Thermotoga maritima*) to DNA on a *single molecule level* [1,2]. Like the eucariotic histone proteins, TmHU acts on the DNA by condensing it. Therefore we give special emphasis to the question if there exist similar levels of organization.

As a further refinement, our set-up is now accomplished with a fast feed-back loop which allows to carry out the experiment under conditions of a constant and adjustable force. By that it should be possible to unravel the energetics and dynamics of the TmHU/DNA-interaction in detail. In the experiment, the DNA molecule is established between two microparticles, the force acting on the DNA is set to the designated value and the TmHU-solution is flushed into the cell. The condensation of the DNA leads to a decrease in the separation of the particles that we can observe with nanometer resolution. By reducing the protein concentration stepwise from 250µg/ml down to 20µg/ml we found that the condensation proceeds with a lower rate and with step-like interruptions (Fig. 1a).

As characteristic for cooperative binding, this rate depends on the concentration in a sigmoidal manner (Fig. 1b) [1,3]. The fact that the condensation is much more efficient than one could explain just by an elementary protein binding as well as the observed retardations (Fig.1a) suggest that higher levels of organization exist.

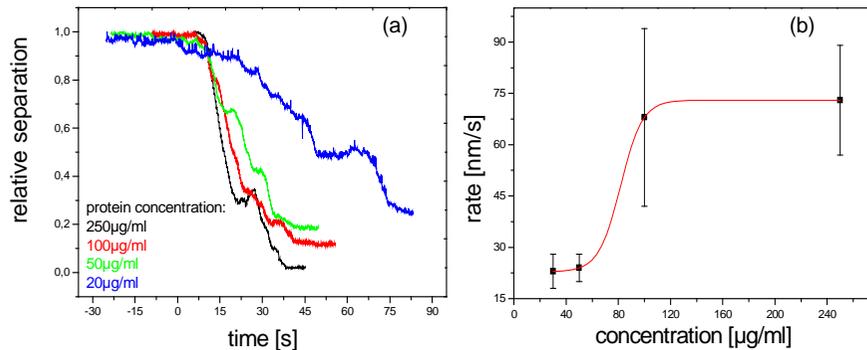


Fig. 1: (a) Temporal evolution of the relative length of a *single* DNA-chain in media of varying TmHU concentration as indicated. The force was kept constant at a level of 2 pN. Especially for low concentrations sequences of progress and arrest are observed reflecting the action of the protein. (b) Sigmoidal dependency of the absolute velocity on the concentration.

References:

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2.11 Dynamics of DNA under tension and in confinement

I. Semenov, U. Keyser, M. Salomo and F. Kremer

While the structural properties of the DNA are well explored, much less is known concerning its dynamics as a single polymer chain and under conditions of geometrical confinement. Extended theoretical studies were carried out to explore the sub-diffusive internal macroscopic dynamics and to study how it is affected by external constraints, constrictions and confinements. [1-3]. Optical Tweezers offer [4,5] the unique possibility to carry out dedicated experiments with respect to this; in detail it is planned to determine the relaxation of single DNA-chain which is held under tension between two colloids with one located in an optical trap (Fig. 1a). The DNA is labeled by a quantum dot and cut by adding restriction enzymes to the surrounding medium. The relaxation of the molecule is observed by monitoring the position of the fluorescently excited quantum dot. Further experiments of highest interest are similar studies in the presence of a polymer gel (Fig. 1b).

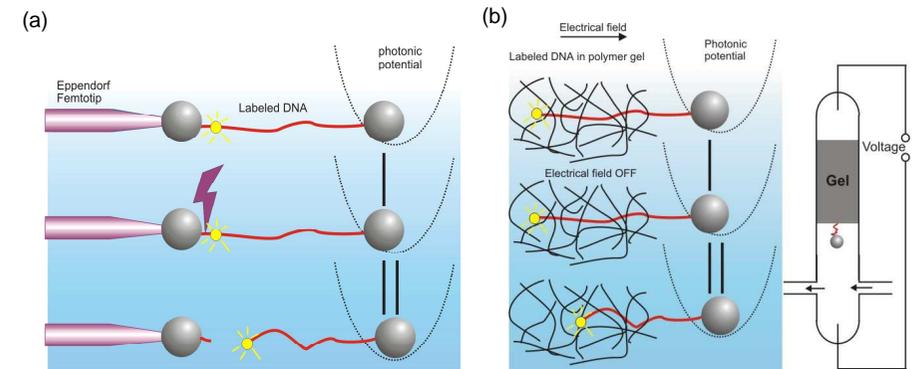


Fig. 1: (a) Relaxation of a *single* DNA-chain kept under a defined tension by use of OT. (b) Relaxation of a *single* DNA-chain kept under a defined tension by use of an external electric field and in the presence of a polymer-gel

It is expected that these studies will deliver detailed novel insights into the dynamics of DNA under conditions of confinement with varying character.

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Collaborators:

K. Kroy (U Leipzig), M. Mertig (TU Dresden)

Funding:

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