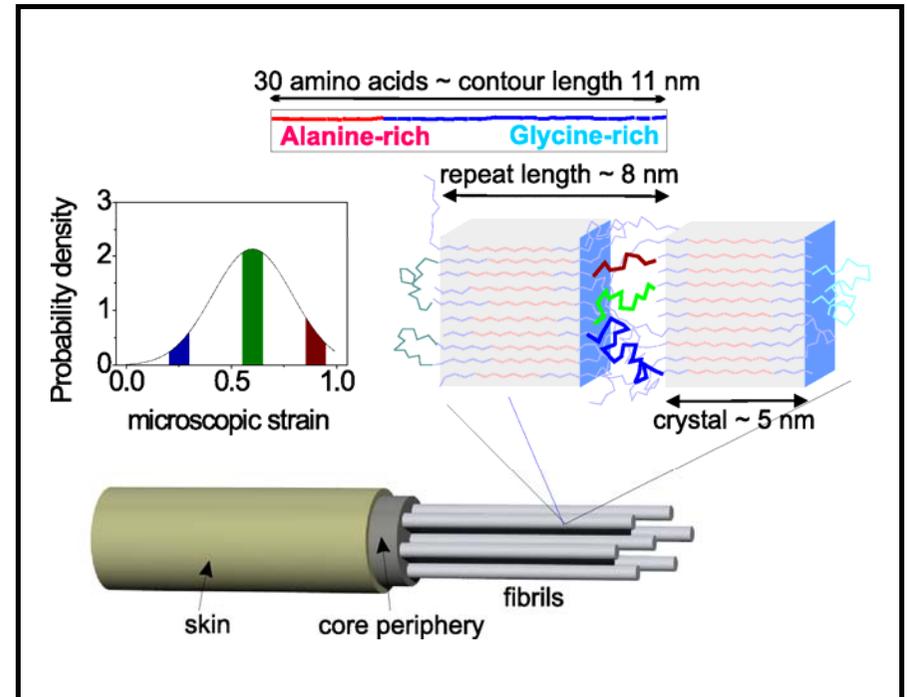


# UNIVERSITY OF LEIPZIG

Faculty of Physics and Earth Sciences  
Department of Experimental Physics I

GROUP “Molekülphysik”



Annual Report 2008

Cover picture:

Proposed structural levels of organization in spider silk. The two constituting proteins of spider silk (MaSp1 and MaSp2) are conceptionally classified in glycine- and alanine rich regions. Alanines and neighbouring glycines are arranged in highly oriented  $\beta$ -sheeted crystals, which are interlinked by glycine-rich chains with amorphous structure. The linkages have a Gaussian pre-strain distribution as indicated by colors and are described by the worm-like chain model. By supercontraction the pre-strain distribution strongly narrows while its mean value approaches zero. The so assembled  $\beta$ -sheeted blocks form a core of fibrils inside the silk fiber. The skin and the periphery of the core balance the internal pre-strain of the fibrils (see Refs. [1],[2] in p. 11).

**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 2008**

In 2008 Ulrich Keyser and his coworkers accomplished their move to Cambridge, UK. Later in the year Anatoli Serghei moved to Amherst, USA and Mahdy Elmahdy joined the group as Postdoctoral coworker. Periklis Papadopoulos was awarded with the "Peter Debye Prize for young investigators for excellence in dielectric research", which was given to him at the IV. Annual Meeting of the International Dielectric Society (IDS) in Lyon from the chairman of the prize committee, Prof. Dr. G. Williams, Swansea, UK and the head of IDS, Prof. Dr. J. Berberian, Chapel Hill, North Carolina, USA. For her excellent diploma thesis and her very good grades Carolin Wagner was awarded with a "Diploma with distinction".

A longstanding open problem in dielectric spectroscopy, the phenomenon of electrode polarization (EP), was unraveled by Anatoli Serghei. He could show – both experimentally and theoretically – that its frequency and temperature dependence is characterized by special features, for which scaling laws exist. By that it is possible – for the first time – to deduce information concerning the bulk conductivity from the dispersion of the complex conductivity and the complex dielectric function on the very low frequency side ( $\leq 10^2$  Hz). The paper is submitted to PRL, but sometimes it is not easy to convince reviewers about new ideas and concepts.

Leipzig, January 2009

Friedrich Kremer

## Contents

	page
Preface	1
1. Organization of the group	4
2. Projects	5
2.1 Apparent changes in the molecular dynamics of thin polymer layers due to the impact of interfacial layers ( <a href="#">A. Serghei</a> , M. Tress and F. Kremer)	5
2.2 Molecular dynamics of isolated polymer chains (M. Tress, <a href="#">A. Serghei</a> and <a href="#">F. Kremer</a> )	6
2.3 Electrode polarization and its scaling laws ( <a href="#">A. Serghei</a> , J. R. Sangoro, M. Tress and F. Kremer)	7
2.4 Universal scaling of charge transport in glass-forming ionic liquids (J. R. Sangoro, C. Iacob, <a href="#">A. Serghei</a> and <a href="#">F. Kremer</a> )	8
2.5 Charge transport and glassy dynamics in imidazole-based liquids (C. Iacob, J. R. Sangoro, <a href="#">A. Serghei</a> and <a href="#">F. Kremer</a> )	9
2.6 Infrared transition moment orientational analysis in liquid crystalline elastomers ( <a href="#">P. Papadopoulos</a> , W. Kossack and F. Kremer)	10
2.7 Combined mechanical and time-resolved polarization-dependent FTIR studies in major and minor ampullate spider silk (R. Ene, <a href="#">P. Papadopoulos</a> and F. Kremer)	11
2.8 In-situ analysis of the forces of interaction in polyelectrolyte brushes (M. M. Elmahdy, G. Dominguez, C. Gutsche, K. Kegler and <a href="#">F. Kremer</a> )	12
2.9 Polyelectrolyte-Compression Forces between Spherical DNA - grafted colloids (K. Kegler and <a href="#">F. Kremer</a> )	13
2.10 Investigating fluctuation and dissipation of optically trapped colloids (Olaf Ueberschär and <a href="#">F. Kremer</a> )	14
2.11 <i>Single</i> colloid electrophoresis (I. Semenov, O. Otto, G. Stober, <a href="#">P. Papadopoulos</a> , U. F. Keyser and <a href="#">F. Kremer</a> )	15
2.12 Drag-induced forces on colloids in polymer solutions at low solvent velocities (C. Gutsche and <a href="#">F. Kremer</a> )	16
2.13 DNA condensation under the action of the protein TmHU as studied on a <i>single</i> molecule level (C. Wagner, M. Salomo, U. F. Keyser, C. Gutsche and <a href="#">F. Kremer</a> )	17

## 5. Graduations

### Promotions:

Dipl.-Biochem. M. Salomo

"Optische Pinzetten zum Studium der Wechselwirkungen zwischen histonähnlichen Proteinen und einzelnen DNA-Molekülen"

### Diploma

cand. phys. Carolin Wagner

"Einzelmolekül-Kraftspektroskopie zur Untersuchung der Protein-DNA-Wechselwirkung am Beispiel von TmHU")

cand. phys. Oliver Otto

"Single Colloid Electrophoresis using Optical Tweezers"

### Master of Science

cand. phys. Hergen Brutzer

"Study of Protein-DNA Interaction with Atomic Force Microscopy"

cand. phys. Jan Henning Peters

"Effects of Laser-induced Heating in a Nanopore- and Microcapillary-Systems"

### Bachelor

Robert Seifert

"Molecular dynamics of polymers confined in ultra-thin films"

## 6. Industry collaborations

### Novocontrol

Hundsangen, Germany

### Clariant Produkte (Deutschland) GmbH

Frankfurt am Main, Germany

### Comtech GmbH

München, Germany

### Freudenberg Dichtungs- und Schwingungstechnik KG

Weinheim, Germany

### Kempchen Dichtungstechnik GmbH

Leuna, Germany

### inotec FEG mbH

Markkleeberg, Germany

## 7. Awards

Peter Debye Prize for Young Investigators for Excellence in Dielectric Research 2008 of the International Dielectric Society (IDS) to Periklis Papadopoulos.

Carolin Wagner was awarded with a Diploma made with distinction for her excellent diploma thesis and her very good grades.

## 4. Financial support

### Prof. Dr. F. Kremer

DFG-Teilprojekt im Rahmen des Schwerpunktprogramms "Nano- und Mikrofluidik: Von der molekularen Bewegung zur kontinuierlichen Strömung" SPP 1164  
DFG-Schwerpunktprogramm 1164, KR 1138/14-2 (2006-2008)

DFG-Teilprojekt im Rahmen des Schwerpunktprogramms "Nano- und Mikrofluidik: Von der molekularen Bewegung zur kontinuierlichen Strömung" SPP 1164  
DFG-Schwerpunktprogramm 1164, AZ: KR 1138/14-3 (2008-2010)

### 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)

DFG-Teilprojekt "Physicochemical characterisation of ionic liquids-mediated peptide acylation reactions",

AZ: KR 1138/18-2 (2008-2010)

### Prof. Dr. F. Kremer

DFG-Projekt "In-situ Untersuchung der Wechselwirkungskräfte an Polyelektrolytbürsten"  
KR 1138/20-1 (2006–2009)

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

FOR877, DFG-Projekt: "From local constraints to macroscopic transport: Dynamics of DNA under tension and confinement"

KR 1138/21-1 (2007-2010)

### Prof. Dr. F. Kremer

SPP "Polymer-Festkörper-Kontakte: Grenzflächen und Interphasen"

DFG-Teilprojekt "Interfacial dynamics of polymers in interaction with solid substrates"

AZ: KR 1138/23-1 (2008-2011)

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

	page
2.14 TmHU-DNA binding studied by atomic force microscopy (H. Brutzer, M. Salomo, U. F. Keyser and <u>F. Kremer</u> )	18
2.15 DNA binding under the action of the protein <i>E.coli</i> HU as studied on a <i>single</i> molecule level (C. Krause, C. Wagner, M. Salomo, J. Reinmuth and <u>F. Kremer</u> )	19
2.16 Optical tweezers to investigate receptor-ligand interactions on a <i>single</i> contact level (M. Salomo, C. Wagner and <u>F. Kremer</u> )	20
2.17 Localized heating effects in micro-capillaries and nanopores (J. H. Peters and <u>U. F. Keyser</u> )	21
2.18 Modelling of colloidal transport in capillaries (G. Stober, L. Steinbock and <u>U. F. Keyser</u> )	22
2.19 Sensing DNA-coatings of microparticles using micropipettes (L. J. Steinbock, G. Stober and <u>U. F. Keyser</u> )	23
3. Publications	24
4. Financial Support	26
5. Graduations	27
6. Industry collaborations	27
7. Awards	27

## 1. Organization of the group

**Chairman:** Prof. Dr. Friedrich Kremer

### Academic staff and postdocs

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

### Students

cand. phys. Hergen Brutzer  
Dipl.-Chem. Roxana Ene  
cand. phys. Benjamin Gollnick  
Dipl.-Phys. Christof Gutsche  
cand. phys. Lukas Hild  
M. Sc. Ciprian Ghiorghita Iacob  
Dipl.-Phys. Kati Kegler  
cand. phys. Wilhelm Kossack  
cand. phys. Christina Krause  
M.Sc. Emmanuel U. Mapesa  
cand. phys. Oliver Otto  
cand. phys. Jan H. Peters  
M. Sc. Joshua Rume Sangoro  
cand. phys. Robert Seifert  
cand. phys. Jan Sölter  
M. Sc. Ilya Semenov  
M. Sc. Lorenz Steinbock  
Dipl.-Phys. Gunter Stober  
cand. phys. Carolin Wagner  
cand. phys. Martin Treß  
cand. phys. Olaf Ueberschär  
cand. phys. Immanuel Weidner

### Technical staff

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

### Guests

Dr. Lidia Okrasa  
Dr. Agnieszka Slazak

### Alumni

Prof. Dr. Siegbert Grande

- [13] Sangoro, J. R., C. Iacob, A. Serghei, C. Friedrich and F. Kremer, "Universality of charge transport in glass-forming ionic liquids " *Phys. Chem. Chem. Phys.* (2008), DOI: 10.1039/b816106b.
- [14] Steinbock, L.J. G. Stober. and U. F. Keyser, "Sensing DANN-coatings of Microparticles Using Micropipettes" *Biosensors and Bioelectronics*, doi:10.1016/j.bios.2008.12.026 (2008)
- [15] Papadopoulos, P., J. Sölter and F. Kremer "Hierarchies in the structural organization of spider silk—a quantitative model" *Colloid and Polymer Science*, **287**, Issue2, 231 (2009)
- [16] Sangoro, J. R., G. Turky, M. Abdel Rehim, S. Naumov, A. Ghoneim, J. Kärger and F. Kremer., "Charge transport and dipolar relaxation in hyper-branched polyamide amines. *Macromolecules* " *Macromolecules*, in press (2009)
- [17] Serghei, A., M. Tress and F. Kremer, "Apparent changes in the molecular dynamics of thin polymer layers due to the impact of interfacial layers" *J. Chem. Phys.*, in press (2009)
- [18] Iacob, C., J. Sangoro, A. Serghei, S. Naumov, Y. Korth, J. Kärger, C. Friedrich, F. Kremer "Charge transport and glassy dynamics in imidazole-based liquids" *J. Chem. Phys.* **129**, 1 (2008)
- [19] Stober, G., L. J. Steinbock, U. F. Keyser "Modelling of colloidal transport in capillaries" accepted, *Journal of Applied Physics* (2009)
- [20] Kipnusu, W. K., G. Katana, C. M. Migwi, I.V.S. Rathore, J. R. Sangoro "Electrical Switching in Nandi Flame Seed Cuticle biopolymer thin films" *International Journal of Polymer Science*, in press (2009).

### - submitted -

- [21] Serghei, A., M. Tress, J. R. Sangoro and F. Kremer, "Electrode polarization and its scaling laws" submitted to *PRL* (2008)
- [22] Papadopoulos, P., R. Ene, I. Weidner, F. Kremer, "Similarities in the structural organization of major and minor ampullate spider silk" submitted to *Macromol. Rapid. Comm.* (2009)

### 3. Publications

- [1] Zorn, R.; M. Mayorova, D. Richter, A. Schönhals, L. Hartmann, F. Kremer, B. Frick  
"Effect of nanoscopic confinement on the microscopic dynamics of glass-forming liquids and polymers studied by inelastic neutron scattering", *AIP Conf. Proc.* **982**, 79–84 (2008)
- [2] Kegler, K.; M. Konieczny, G. Dominguez-Espinosa, C. Gutsche, M. Salomo, F. Kremer and C. N. Likos  
"Polyelectrolyte-Compression Forces between Spherical DNA Brushes"  
*Phys. Rev. Lett.* **100**, 118302 (2008)
- [3] Otto, O.; C. Gutsche, F. Kremer, U. F. Keyser  
"Optical tweezers with 2.5 kHz bandwidth video detection for single-colloid-electrophoresis"  
*Rev. Sci. Instr.* **79**, 023710 (2008)
- [4] Serghei, A. and F. Kremer,  
"Metastable states of arrested glassy dynamics, possibly mimicking confinement effects in thin polymer films"  
*Macromol. Chem. Phys.* **209**, 810 (2008)
- [5] Sangoro Rume, J.; A. Serghei, S. Naumov, P. Galvosas, J. Kärgler, C. Wespe, F. Bordusa and F. Kremer  
"Charge transport and mass transport in imidazolium based ionic liquids"  
*Phys. Rev. E* **77**, 051202 (2008)
- [6] Serghei, A. and F. Kremer,  
"Broadband dielectric studies on the interfacial dynamics enabled by use of nanostructured electrodes"  
*Rev. Sci. Instrum.* **79**, 026101 (2008).
- [7] Serghei, A.; H. Huth, C. Schick, F. Kremer,  
"Glassy dynamics in thin polymer layers having a free upper interface"  
*Macromolecules* **41** (10), 3636 (2008).
- [8] Berns, B.; H. Deligöz, B. Tieke and F. Kremer  
"Conductive Composites of Polyurethane Resins and Ionic Liquids"  
*Macromol. Mater. Eng.* **293**, 409-418 (2008)
- [9] Sangoro Rume, J.; C. Iacob, A. Serghei, S. Naumov, P. Galvosas, J. Kärgler, C. Wespe, F. Bordusa, A. Stoppa, J. Hunger, R. Buchner, F. Kremer  
"Electrical conductivity and translational diffusion in the 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid"  
*J. Chem. Phys.* **128**, 212509 (2008)
- [10] Salomo, M.; U. F. Keyser, M. Struhalla, F. Kremer  
"Optical tweezers to study single protein A/Immunglobulin G interaction at varying conditions"  
*European Biophys. J.* **37**, 927-934 (2007)
- [11] Gutsche, C.; F. Kremer, M. Krüger, M. Rauscher, R. Weeber and J. Harting  
"Colloids dragged through a polymer solution: experiment, theory and simulation"  
*J. Chem. Phys.* **129**, 084902 (2008)
- [12] Dominguez-Espinosa, G.; A. Synytska, A. Drechsler, C. Gutsche, K. Kegler, P. Uhlmann, M. Stamm, F. Kremer  
"Optical Tweezers to measure the interaction between Poly(acrylic acid) Brushes"  
*Polymer* **49**, 4802-4807 (2008)

## 2. Projects

### 2.1 Apparent changes in the molecular dynamics of thin polymer layers due to the impact of interfacial layers

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

The glassy dynamics of ultra-thin polymer films is currently a topic of large scientific and technological interest. Broadband Dielectric Spectroscopy has proven – based on its ability to measure molecular fluctuations over a wide frequency and temperature range – its strength in unravelling the mechanisms of confinement-effects in thin polymer layers. These effects are supposed to rise due to the changes of the polymer glassy dynamics in the nanometric vicinity of confining interfaces (Fig. 1). Thus, the dielectric response of thin polymer films is calculated by taking into account possible modifications of the dielectric function in interfacial polymer sub-layers (Fig. 2). A multitude of mechanisms leading to an apparent faster dynamics in thin capped polymer films is revealed (Fig. 3). None of them corresponds to a faster molecular structural relaxation. It is shown that several reported experimental findings can be traced back to the influence of such interfacial layers: (i) no shifts in the mean-relaxation time for polymeric systems showing a weak alpha relaxation, while (ii) polymers having a large dielectric strength could experience apparent shifts already at thicknesses as large as 200 nm.

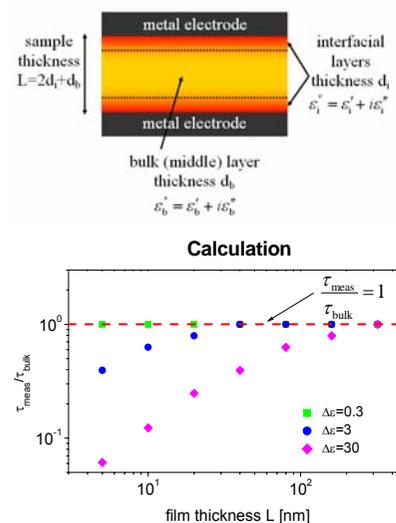


Fig. 1: Sketch of the proposed layer model of a polymer film confined in a so called capped geometry.

Fig. 2: Calculated thickness dependence of the apparent relaxation peak of the net dielectric function of a layer arrangement like shown in Fig. 1 assuming constant measures of the interfacial layers. A pronounced effect is introduced by the variation of the dielectric strength  $\Delta\epsilon$ .

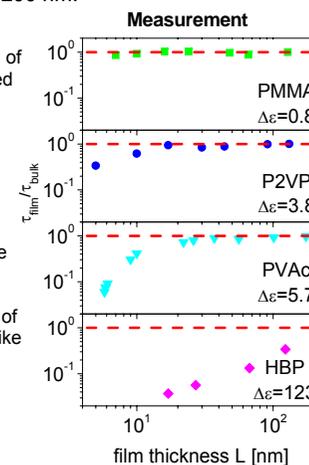


Fig. 3: Thickness dependences of the apparent relaxation peak of several polymers having different dielectric strengths measured in a capped geometry.

#### References:

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

#### Collaborators:

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

#### Funding:

SPP "Polymer-Festkörperkontakte: Grenzflächen und Interphasen"  
DFG-Teilprojekt KR 1138/23-1 (2008-2011)

\* The underlined author has initiated the project.

## 2.2 Molecular dynamics of isolated polymer chains

M. Tress, A. Serghei and F. Kremer

A recent experimental development [1,2] 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 (Fig. 1c) of polymer chains using a low grafting density to ensure isolated polymer chains; (iii) "physical" grafting (Fig. 1d) 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) 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) chemical grafting; (d) physical grafting.

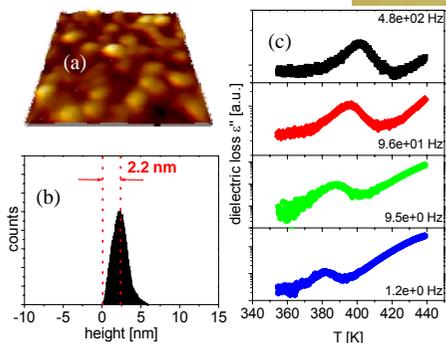
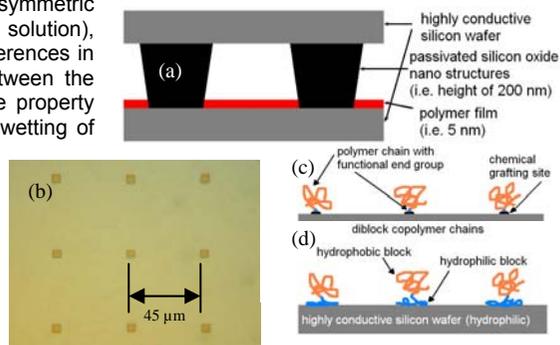


Fig. 2: (a) AFM image ( $300\ \text{nm} \times 300\ \text{nm}$ ) showing individual polymer chains (poly-2-vinylpyridine) adsorbed on the surface of a silicon wafer; (b) the corresponding heights histogram; (c) dielectric loss vs. temperature at different frequencies showing the dynamic glass transition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

### References:

- [1] A. Serghei and F. Kremer, *Rev. Sci. Instrum.* **79**, 026101 (2008)
- [2] A. Serghei, *Macromolecular Chemistry and Physics*, (2008)

### Collaborators:

\* Present address: Polymer Science and Engineering, University of Massachusetts, Amherst  
P. Uhlmann (IPF Dresden)  
MicroFAB Bremen

### Funding:

SPP "Polymer-Festkörperkontakte: Grenzflächen und Interphasen"  
DFG-Teilprojekt KR 1138/23-1 (2008-2011)

## 2.19 Sensing DNA-coatings of microparticles using micropipettes

L. J. Steinbock, G. Stober and U. F. Keyser

The resistive pulse technique is widely used to detect the size of small particles in aqueous solutions. This work demonstrates that a few tens of DNA molecules and thus the charges on a particle can be simply detected by pressure-driven translocation through a microcapillary based Coulter counter [1]. The typical opening of the capillaries ranges from 2 to 6 μm. The custom-built system gives optical access using a high numerical aperture objective allowing to observe colloids passing the sensing volume by optical means. We show the feasibility of our setup by distinguishing colloids with one and two micron diameters. Our measurements prove that a few ten strands of DNA bound to the colloids can be detected. This can be achieved by simple comparison of current amplitudes for blank and coated colloids at low salt concentrations (2-40 mMol [NaCl]). Our results clearly demonstrate that the Coulter counter can be used to detect the surface charges on colloids. Moreover, the results are in good agreement with a dynamical computer model taking into account the full geometry of the capillary [2].

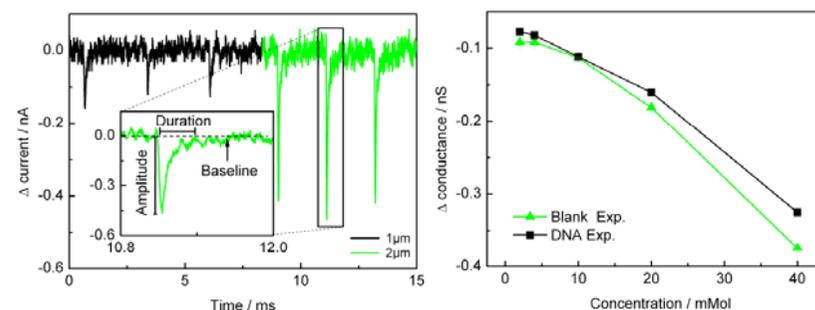


Fig. 1: Left: Characteristic current signal ( $\Delta$  current) as a function of time showing peaks caused by the translocation of  $1\ \mu\text{m}$  (black) and  $2\ \mu\text{m}$  colloids (red). For better presentation the mean current was subtracted. The inset illustrates the characteristics of a single translocation event. The start of an event is defined once a certain current threshold is surpassed. The difference between the baseline and peak current is defined as event amplitude. Once the current reaches the baseline level the translocation event is defined as finished. The start and termination point determines the duration of the translocation event. The  $\Delta$  current divided by the actual potential gives the  $\Delta$  conductance value. Right:  $\Delta$  conductance values as function of the [NaCl] concentration during translocation of blank and DNA-labeled colloids as red and black lines, respectively. The capillary was  $6\ \mu\text{m}$  wide, colloid diameter was  $1\ \mu\text{m}$  and the pressure 10mbar. Due to the charge of the grafted DNA molecules the  $\Delta$  conductance shows higher values for the DNA than for the blank colloids. The standard error of the fits was less than 1% of the actual  $\Delta$  conductance value and lie therefore within the data points.

### References:

- [1] L. J. Steinbock, G. Stober, U. F. Keyser, in press, *Biosensors & Bioelectronics*, 2009
- [2] G. Stober, L. J. Steinbock, U. F. Keyser, accepted, *Journal of Applied Physics*, 2009

### Funding:

Emmy Noether program DFG, BuildMoNa graduate school, Deutsche Telekom Stiftung

## 2.18 Modelling of colloidal transport in capillaries

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

We dynamically model the passage of micron-sized colloids through micro-capillaries in silico. The computer model is able to reproduce the signal shape, the transition time and the amplitude and baseline current with an accuracy of approximately 35%. This is achieved by computing the electrical field in the fluidic cell in dependence from the geometry of the capillary orifice. Further, the model physics includes a numerical implementation of a Hagen-Poiseuille flow profile in dependence of a fee adjustable fluidic cell geometry, the colloid size, the ion mobility, the ionic strength, the colloid charge and coatings and the applied voltage. Additionally, the simulation of the gaussian noise allows to test the custom written detection algorithm to determine the detection threshold for smallest observable colloids.

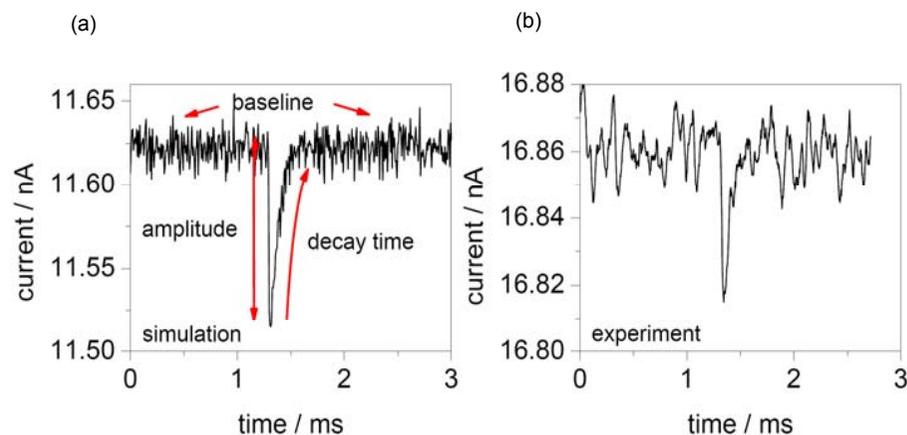


Fig. 1 a: Current as a function of time calculated for a typical capillary geometry showing a sudden rise to the maximum amplitude and a gradual decay. b) The graph shows a detected colloid for the same capillary. The geometry of the capillary required to use two different taper in the simulation, due to a not gradual opening of the orifice.

This simulation was carried out with similar settings as in the experiment, which used a colloid of diameter 1 $\mu$ m and a capillary with diameter of 3.5 $\mu$ m and a taper (1) length of 70 $\mu$ m and a taper (2) with 930 $\mu$ m. The [NaCl] concentration was 20 mMol.

### References:

- [1] K. U. F. eyser, J. van der Does, C. Dekker, and N. H. Dekker, *Rev. Sci. Instr.* **77**, 105105, (2006)
- [2] C. Gutsche, U. F. Keyser, K. Kegler, F. Kremer, P. Linse, *Phys. Rev. E* **76**, 031403 (2007)
- [3] L. J. Steinbock, G. Stober, and U. F. Keyser, *Biosensors and Bioelectronics*, doi:10.1016/j.bios.2008.12.026 (2008)
- [4] G. Stober, L. J. Steinbock and U. F. Keyser, submitted (2008)

### Collaborators:

R. Netz (TU München)

### Funding:

Emmy Noether-Programm der Deutschen Forschungsgemeinschaft

## 2.3 Electrode polarization and its scaling laws

A. Serghei\*, J. R. Sangoro, M. Tress and F. Kremer

Electrode polarization is a ubiquitous phenomenon taking place at the interface between an electrode and an ionic conductor. It shows a characteristic signature in the measured dielectric response of the sample cell in dependence on frequency of the applied electric field, temperature, concentration of the charge carriers and the sample length. Furthermore, it is well known that electrode polarization is strongly affected by the material of the electrodes, a finding which lacks – until now – a microscopic understanding. Despite early theoretical insights into the physics of electrolytes at solid interfaces (resulting in the electrical double layer model), no consistent description of the scaling laws governing electrode polarization effects exists.

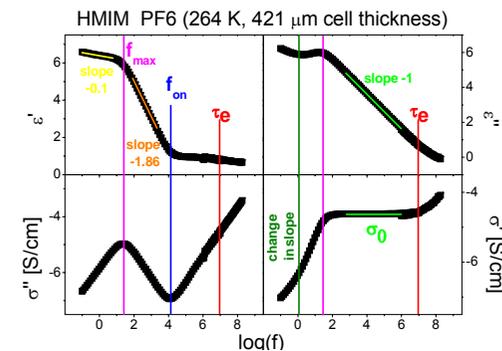
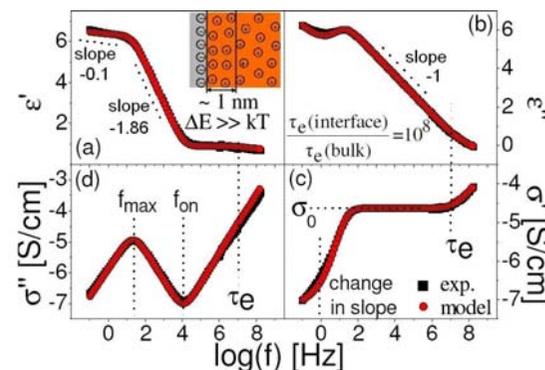


Fig. 1: Dielectric properties of ionic liquids showing electrode polarization exemplified by 1-HMIM-PF6

$\tau_e$ : hopping time  
 $\sigma_0$ : DC conductivity  
 $f_{on}$ : onset of electrode polarization  
 slope of  $-1.86$  in  $\epsilon'$  for  $f < f_{on}$   
 $f_{max}$ : full development of electrode polarization  
 slope of  $-0.1$  in  $\epsilon'$  for  $f < f_{max}$   
 change in slope of  $\sigma'$  for  $f < f_{max}$

Fig. 2: Measured and calculated complex dielectric permittivity and conductivity of HMIM-PF6

Based on the fact that, due to coulombic interactions, the ion mobility is drastically slowed down at the interfaces, a quantitative description of electrode polarization is suggested which describes the observed scaling laws and enables one to deduce – by use of a novel formula – the bulk conductivity of the ionic charge carriers under study.



### References:

- [1] A. Serghei, M. Tress, J. R. Sangoro and F. Kremer, *PRL*, submitted (2008)

### Collaborators:

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

### Funding:

SPP "Polymer-Festkörperkontakte: Grenzflächen und Interphasen"  
 DFG-Teilprojekt KR 1138/23-1 (2008-2011)

AZ: KR 1138/18-2 (2008-2010)

## 2.4 Universal scaling of charge transport in glass-forming ionic liquids

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

Charge transport and glassy dynamics of a variety of glass-forming ionic liquids (ILs) are investigated in a wide frequency and temperature range by means of Broadband Dielectric Spectroscopy, Differential Scanning Calorimetry and Rheology. While the absolute values of dc conductivity and viscosity vary over more than 11 decades with temperature and upon systematic structural variation of the ILs, quantitative agreement is found between the characteristic frequency of charge transport and the structural  $\alpha$ -relaxation. This is traced back to *dynamic glass transition assisted hopping* as the underlying mechanism of charge transport.

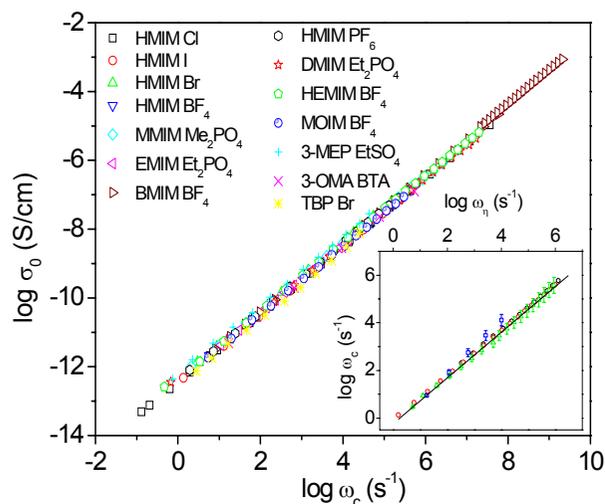


Fig. 1: dc conductivity,  $\sigma_0$ , versus the characteristic frequency,  $\omega_c$ , for different liquids as indicated. This plot experimentally demonstrates the universality of charge transport in ionic liquids. Inset: Correlation of  $\omega_c(T)$  with the characteristic frequency,  $\omega_\eta(T)$ , corresponding to structural relaxation time obtained from viscosity by applying the Maxwell relation.

### References:

- [1] J. R. Sangoro, C. Iacob, A. Serghei, C. Friedrich and F. Kremer, *Phys. Chem. Chem. Phys.* (2008), DOI: 10.1039/b816106b.
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### Collaborators:

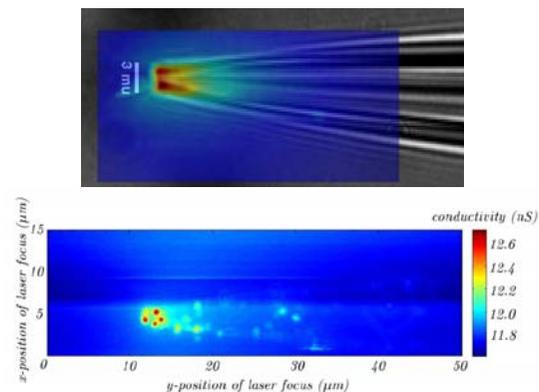
J. Kärger, R. Valiullin, and S. Naumov (U. Leipzig),  
C. Friedrich (U. Freiburg)  
R. Buchner (U. Regensburg)

**Funding:** Deutsche Forschungsgemeinschaft under the DFG SPP 1191 Priority Program on Ionic Liquids, AZ: KR 1138/18-2 (2008-2010)

## 2.17 Localized heating effects in micro-capillaries and 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<sup>2</sup> 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 channel or pore depends on the local temperature in a well-defined manner and hence (i) can be used for temperature measurements with high spatial resolution [1] (ii) map out the ionic current profiles in micron sized capillaries [3]. We compare experiments using nanopores and micro-capillaries 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. There is also a strong correlation with impurities in the glass.



**Fig. 1:** Top: Microscope image (grey) and ionic current map of a micron-scale glass capillary. Red denotes high ionic current and thus high temperature and blue denotes low ionic current. Temperature-distribution generated by a focussed (gaussian) laser beam. Bottom: Ionic conductance map as a function of laser position of a capillary with impurities attached to the glass. The Laser-beam is strongly adsorbed by the impurities and leads to significant and localized heating patterns detected by the ionic current measurements (green, yellow and red spots in the graph). These correlate with optical microscope images (not shown).

### References:

- [1] U. Keyser, et al., *Nano Letters*, **5**, No. 11, 2253-2256
- [2] E. Peterman, et al., *Biophys. Journal*, **84**, 1308-1316
- [3] L. S. Steinbock, G. Stober, and U. F. Keyser, *Biosensors and Bioelectronics*, in press (2008)

**Collaborators:** Prof. D. Stein, Brown University

**Funding:** Emmy Noether program DFG

## 2.16 Optical tweezers to investigate receptor-ligand interactions on a single contact level

M. Salomo, C. Wagner and F. Kremer

The extraordinary features of optical tweezers [1],[2] having a nm- resolution in positioning a micron-sized colloid and an accuracy of ( $\pm 50$  fN) in measuring the forces acting on it, enable one to study the interaction within a *single* receptor/ligand contact. For that ligand and receptor molecules are immobilized on the surface of two different colloids. By holding one of these by a micropipette and the other in the optical trap, it is possible to approach the particles until a certain contact force of typically 5 pN is reached. Directly afterwards the particles are pulled apart. If a receptor/ligand contact was established, the forces of interaction cause the particle in the optical trap to be shifted out of the equilibrium position in the optical trap. This approach benefits additionally from the chance for the identical pair of colloids the measurements can be repeated many times. Furthermore it is possible to modify the surrounding medium (pH, ion concentration, etc) and to study its effect on the binding-characteristics.

It is the goal of the present project to advance this approach to a novel automated screening technique in *single molecule* bio-nano-technology. For that multifold hard- and software developments have to be initiated.

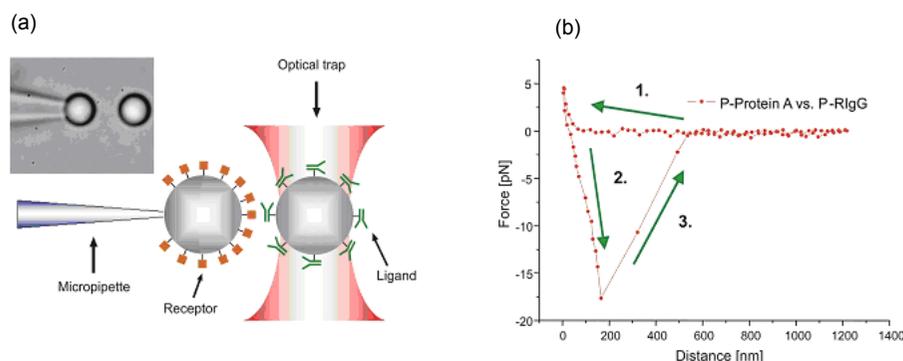


Fig. 1: A) Micro-image of the two colloids and scheme of the experimental setup. For investigating the interaction between a receptor-ligand-pair, the particular interaction partners are immobilized on the surface of microparticles. One of the particles is held by a micropipette, the other one is trapped by the optical tweezers. B) Force-Distance-trace. The particles are approached until a force of 5 pN is reached (1). Afterwards the particles are pulled apart. Due to a single contact between the P-Protein A and the Immunoglobuline P-RlgG the particle in the optical trap is shifted out of the equilibrium position in the optical trap (2). When the force reaches a certain level, the rupture of the binding between the receptor and the ligand can be observed (3) [1].

### References:

- [1] M. Salomo, U. F. Keyser, K. Kegler, C. Gutsche, M. Struhalla, C. Immisch, U. Hahn, F. Kremer, *Microscopy Research and Technique*, **70** (11), 938-943 (2007)
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### Funding:

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ESF (Europäischer Sozialfonds)

## 2.5 Charge transport and glassy dynamics in imidazole-based liquids

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

Broadband Dielectric Spectroscopy (BDS), differential scanning calorimetry, rheology and Pulsed Field Gradient - Nuclear Magnetic Resonance (PFG - NMR) are combined to study glassy dynamics and charge transport in a homologous series of imidazole-based liquids with systematic variation of the alkyl chain length. The dielectric spectra are interpreted in terms of dipolar relaxation and a conductivity contribution. By applying Einstein, Einstein-Smoluchowski and Stokes-Einstein relations, translational diffusion coefficients - in quantitative agreement with PFG NMR measurements are obtained (Fig.1). With increasing alkyl chain length, it is observed that the viscosity increases whereas the structural  $\alpha$ -relaxation rate decreases in accordance with Maxwell's relation. Between the rate  $\omega_e$  of electrical relaxation and the rate  $\omega_\alpha$  of the structural  $\alpha$ -relaxation scaling is observed over more than 6 decades with a decoupling index of about 2.

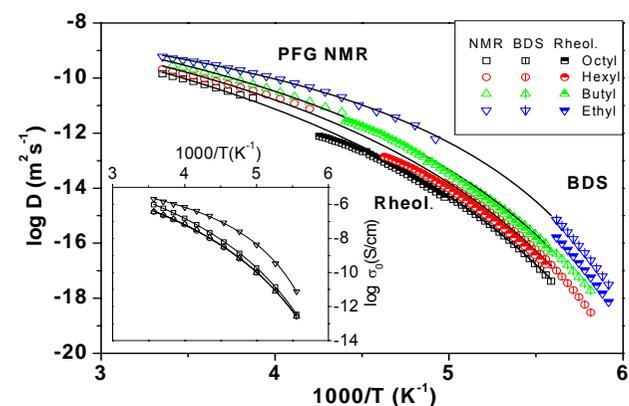


Fig.1: Diffusion coefficient  $D$  vs. inverse temperature as measured by Pulsed-Field Gradient NMR (open symbols), BDS (open symbols with vertical line) and from Stokes-Einstein equation (upper filled symbols). Inset: dc conductivity  $\sigma_0$  vs. inverse temperature (open symbols with vertical line).

### References:

- [1] C. Iacob, J. R. Sangoro, A. Serghei, S. Naumov, Y. Korth, J. Kärger, C. Friedrich and F. Kremer, *J. Chem. Phys.* **129**, 1 (2008)
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- [3] J. R. Sangoro, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa, and F. Kremer, *Phys. Rev. E* **77**, 051202 (2008).

### Collaborators:

J. Kärger, R. Valiullin, S. Naumov (Uni. Leipzig)  
C. Friedrich, Y. Korth (FMF Uni. Freiburg)

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## 2.6 Infrared transition moment orientational analysis in liquid crystalline elastomers

P. Papadopoulos, W. Kossack and F. Kremer

A novel method is suggested for unraveling the mean orientation and the molecular order parameter in any IR-transparent or translucent material under study. It is based on the analysis of IR transmission spectra as a function of polarization *and* an intentional inclination of the sample. Taking advantage of the specificity of the IR spectral range, it is based on the analysis of the absorption coefficient  $\alpha \sim \langle (\vec{\mu} \cdot \vec{E})^2 \rangle$ , where  $\vec{\mu}$  is the transition dipole moment and  $\vec{E}$  the

electric field of the IR beam, in dependence on the polarization and the angle of inclination. Additionally, for non-scattering samples, the complex refractive index tensor can be determined by using the Fresnel equations. The spatial resolution of the technique is only limited by the wavelength. The measurement setup is shown schematically in Fig. 1a. Polarization can be varied from 0°-360° and inclination from -80° ... +80°, allowing the electric field vector to become almost perpendicular to the sample.

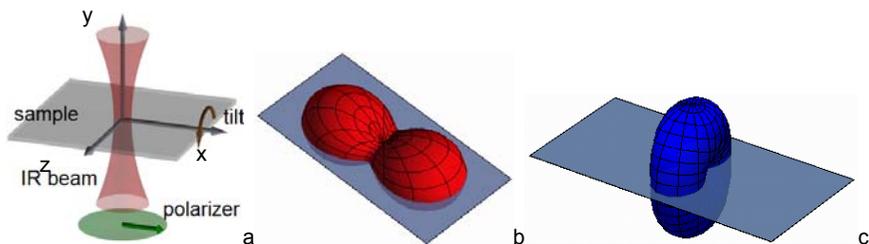


Fig. 1. (a) Measurement principle used for the IR TMOA technique. The electric field vector of the IR beam (green) can be rotated with a polarizer, while the sample can be tilted. This way the electric field can have any of the x,y,z directions. (b) Application of IR-TMOA to a smectic liquid crystalline elastomer (grey plane) at 0% strain. The 3D polar plot (red) shows the dependence of the absorbance on the orientation of the electric field and, therefore, the distribution of transition dipole moments. In this case the corresponding transition moment (C=O stretching) is parallel to the main chains of the elastomer, which consist of the mesogen. The mean orientation is not parallel to the stretching direction (x-axis) and there is no cylindrical symmetry about the mean absorbance axis. (c) Absorbance dependence of an absorption band with a transition dipole moment perpendicular to the main chain (C=O stretching). As one would expect no cylindrical symmetry is observed, but the lowest absorbance is found for the direction parallel to the highest absorbance in (b).

The setup is used in the sample compartment of a FTIR spectrometer to determine the molecular order parameter and the spatial orientation of the director of a smectic Liquid Crystalline Elastomer (sLCE) film as a function of external strain. The molecular moieties exhibit different alignment (Fig. 1b,c). At 0% strain the molecular order parameter of the main chains is 0.8, with the mesogens lying on the film plane. This result could not have been obtained by conventional polarization-dependent studies, where the electric field is only varied in the xz-plane. At a strain value of 190% the order parameter is increased to 0.91 and the mesogens are slightly reoriented (by ~15°) and become parallel to the stretching direction. The findings show that the technique can give detailed structural information for materials with multiple levels of organization.

### Collaborators:

H. Finkelmann (Universität Freiburg)

### Funding:

BuildMoNa

- 10 -

## 2.15 TmHU-DNA binding studied by atomic force microscopy

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

In contrast to the well-characterized processes of formation and destabilization of complexes from eukaryotic histones with DNA, little is known about interactions between histone-like proteins from prokaryotes and DNA. These proteins also kink and bend DNA leading to chromatin-like structures. The histone-like HU protein is nearly ubiquitous in all bacteria. Especially TmHU from *Thermotoga maritima* exhibits some extraordinary properties, such as the protection of DNA inside the bacterium against thermal denaturation. Experiments with optical tweezers suggest the existence of a threshold protein concentration for the formation of TmHU-DNA complexes [1]. Here we use atomic force microscopy to study the concentration dependence by alternative means and minimize influence by external forces. The end-to-end distance and the height of the complexes were measured in dependence of protein concentration (50-5000 nM). With increasing protein concentration the end-to-end distance decreases from 70 to 38 nm while the height increases from 0.7 to 2.2 nm for 250 bp dsDNA, indicative of the formation of a globular structure of the TmHU-DNA complex. Most likely this originates from a secondary organizational level during TmHU-DNA binding observed in optical tweezers experiments.

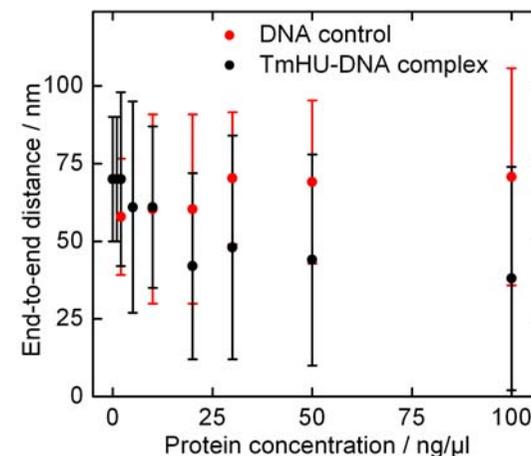


Fig. 1: End-to-end distance dependence of TmHU-DNA complexes on protein concentration. TmHU compacts the DNA above a concentration of 20 ng/μl.

### References:

[1] M. Salomo et al. *Microscopy Research and Technique* **70**, 938 (2007)

### Collaborators:

Prof. M. Mertig, TU Dresden

### Funding:

Emmy Noether program DFG

## 2.14 DNA binding under the action of the protein *E.coli* HU as studied on a single molecule level

C. Krause, C. Wagner, M. Salomo, J. Reinmuth and F. Kremer

In contrast to eucariotic histone proteins, not much is known about the interaction of procaryotic histone-like proteins with DNA. Optical Tweezers enable one to analyse the binding of the histone-like proteins TmHU (from *Thermotoga maritima*) and E.coli HU-protein (from *Escherichia coli*) to DNA on a *single molecule level* [1,2]. The proteins act on the DNA by condensating it. By use of a fast feedback-loop that allows to carry out the experiments under constant force conditions the action of TmHU on DNA has been investigated. TmHU consists of 90 amino acids residues and has a molecular mass of 9994 Da per monomer. In solution it exists as a homodimer containing an  $\alpha$ -helical "core" from which two  $\beta$ -"arms" protrude. Values for  $K_d$  for DNA vary from 5,6 to 73 nM depending on the method and the length of the DNA. The Protein causes within a few seconds a shortening of the DNA-length about 80 %. The dependence on the applied force and the protein concentration allowed to unravel the kinetic and energetic of the reaction. Now similar experiments on E.coli HU are ready to be realized. This HU-protein mainly exists as a heterodimer containing two homologous subunits  $\alpha$  and  $\beta$ , 9,5 kDa each. As can easily be seen from the figures below HU E.Coli binds to DNA very differently in comparison with TmHU. Values for  $K_d$  for dsDNA can vary from 200 to 2500 nM according to the experimental set-up. From the literature it is known that an introduction of Hu E.Coli results in a decrease in the end-to-end length after approximately 800 s [4]. In our Optical Tweezers experiments we now expect to detect a significant difference to the reaction with TmHU.

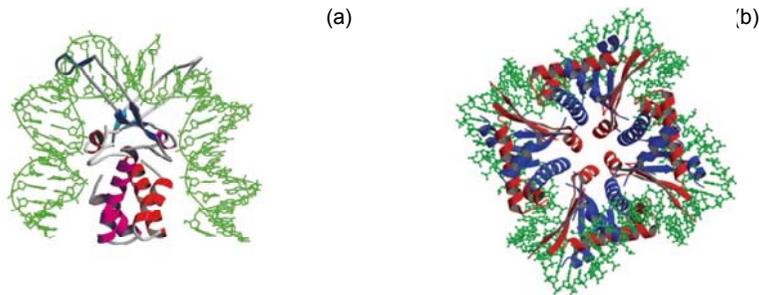


Fig. 1: (a) DNA binds to TmHU by bending it with an angle of  $160^\circ$  around the protein. (b) Stereoviews of modeled  $HU_{\alpha\beta}$  octameric unit of the left-handed multimer with DNA fragment as a repeating unit of a spiral structure. The  $\alpha$ -subunit is in red, and the  $\beta$ -subunit is in blue. [3]

### References:

- [1] M. Salomo, U. Keyser, K. Kegler, M. Struhalla, C. Immisch, U. Hahn, F. Kremer, *Microscopy Research & Technique* **70**, No. 11, 938-943 (2007)
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### Funding:

DFG priority programm SPP 1164 (Nano- & Microfluidics) AZ: KR 1138/14-3

- 18 -

## 2.7 Combined mechanical and time-resolved polarization-dependent FTIR studies in major and minor ampullate spider silk

R. Ene, P. Papadopoulos and F. Kremer

Minor and major ampullate spider silks are studied under varying mechanical stress by static and time-resolved FTIR-spectroscopy. This enables one to trace the external mechanical excitation on a microscopic level and to determine for the different moieties the time-dependence of the molecular order parameters and corresponding band shifts. It is concluded that the hierarchical nanostructure of both types of silk is similar, being composed of highly oriented nano-crystals which are interconnected by amorphous chains obeying the worm-like chain model and having a gaussian distribution of pre-strain. By that it is possible to describe the mechanical properties of both silks by two adjustable parameters only, the center and width of the distribution. For major ampullate silk the observed variability is small in pronounced contrast to the findings for minor ampullate.

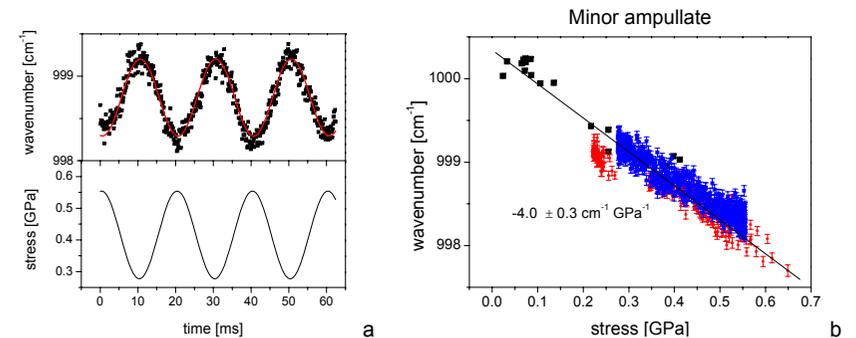


Fig.1. Stress dependence of band shift in different time scales. a) Step scan measurements of the AlaGly vibration frequency in a *Nephila edulis* minor ampullate silk sample. A sinusoidal mechanical field is applied to the sample, while spectra are measured with a time resolution of 125  $\mu$ s. The band shift (sinusoidal fit shown) clearly reflects the field. No phase difference is observed ( $\pm 1^\circ$ ). b) Band shift dependence on stress for static (black), kinetic (red) and step scan measurements (blue) of the same sample. The same linear dependence is observed for all sets, showing that macroscopic and microscopic stress are equal regardless of the time scale. The crystals must be in serial arrangement, otherwise deviations would have to be observed before reaching equilibrium.

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### Collaborators:

F. Vollrath (University of Oxford), A. Sponner (Institute of Entomology, Ceske Budejovice), A. Zankel (TU Graz)

### Funding:

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

M. M. Elmahdy, G. Dominguez, C. Gutsche, K. Kegler and F. Kremer

Optical tweezers are employed to measure the forces of interaction within single pairs of poly(acrylic acid) (PAA) grafted colloids with an extraordinary resolution of  $\pm 0.5$  pN [1]. Parameters varied are the concentration and valency of the counterions (KCl,  $\text{CaCl}_2$ ) of the surrounding medium as well as its pH.

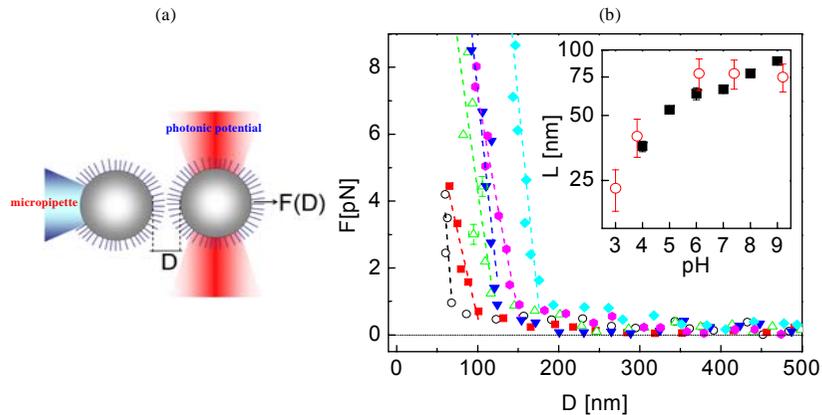


Fig. 1: (a) Scheme of the experimental set-up. One colloid is held with a micropipette due to the capillary action, and the other is kept in an optical trap. (b) Force vs. separation (D) between the solid surfaces of two PAA-grafted particles under conditions of varying pH: 4 (open circle), 5 (full squares), 6 (open up-triangles), 7 (full down-triangles), 8 (full hexagon) and 9 (full rhombus) at  $10^{-3}$  M KCl. The dashed lines represent the fits to the experimental data according to a model by Jusufi et al. [2]. Inset: brush height  $L$  vs. pH at  $10^{-3}$  M KCl obtained from analyzing the Optical Tweezers measurements using Jusufi model (full squares) and as measured by Ellipsometry (open circles).

The force-separation dependence for varying pH (Fig. 1) at a fixed concentration of  $10^{-3}$  M KCl enables one to trace - within a *single* pair of PAA-grafted colloids - the swelling of the polymer brush with increasing pH. The data are well described by Jusufi model of the effective interaction between spherical polyelectrolyte brushes [2]. The brush height  $L$  as obtained from the fits (inset of Fig. 1b) shows a strong pH effect and compares well with independent ellipsometric measurements [1]. The increase in the brush height is caused by the pH-induced augment of the PAA dissociation and results in a stretching of the grafted chains.

### References:

- [1] G. Dominguez, A. Synytska, A. Drechsler, C. Gutsche, K. Kegler, P. Uhlmann, M. Stamm, F. Kremer, *Polymer* **49**, 4802 (2008).  
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### Collaborators:

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

### Funding:

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 DFG-Project AZ: KR 1138/20-1

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

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

The interaction of the histone-like protein TmHU (from *Thermotoga maritima*) to DNA is analyzed on a single molecule level by use of optical tweezers [1], [2]. This technique provides a nm-resolution in positioning a micron-sized colloid and an accuracy of  $\pm 50$  fN in measuring the forces acting on it. As a further refinement, our set-up is now accomplished with a fast feed-back loop (regulation frequency: 30 Hz) which allows to carry out the experiment under conditions of a constant and adjustable force. The proceeding of the condensation and its dependence on the applied force (2-40 pN) is investigated. At a pre-stretching of 2 pN the length of the DNA is reduced by about 80%. At higher forces, the reaction is disrupted at an incomplete level. The process shows two distinct regimes that can be related to different organizational levels. The condensation also shows a pronounced dependence on the concentration. By stretching the TmHU/DNA-complex, it is possible to disrupt the proteins from the DNA. The length of the smallest event conforms with the results of a simulated rupture.

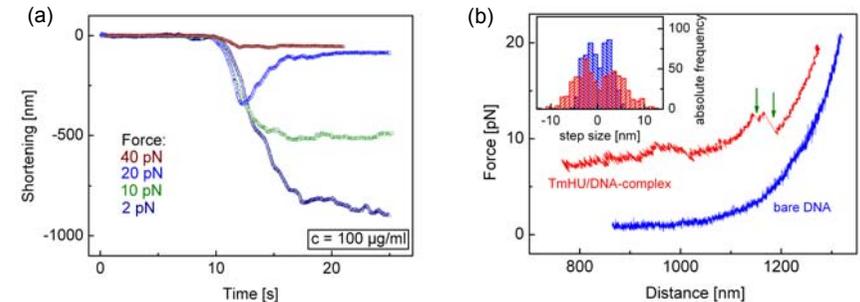


Fig. 1: (a) The TmHU-induced condensation of the DNA at different force levels. The proceeding of the condensation of the DNA as well as the shortening depend on the applied force.

(b) Stretching the TmHU/DNA-complex ( $v = 5$  nm/s) after the condensation at a force level of 10 pN (red line) compared to stretching of bare DNA (blue line). The complex shows a plateau at 5-15 pN as well as an increased noise. Inset: Comparison of the step size of the curves. In case of the TmHU-DNA-Complex there are seen larger steps. These are interpreted as the disruption of single proteins from the DNA strand.

### References:

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 [2] M. Salomo, K. Kroy, K. Kegler, C. Gutsche, M. Struhalla, J. Reinmuth, W. Skokow, C. Immisch, U. Hahn, F. Kremer, *Molecular Biology* **359**, No. 3, 769-776 (2006)

### Funding:

BuildMoNa, DFG-Projekt, AZ: GFC 185/1  
 ESF (Europäischer Sozialfonds)

## 2.12 Drag-induced forces on colloids in polymer solutions at low solvent velocities

C. Gutsche and F. Kremer

We already presented a first direct experimental observation of jamming-induced drag-enhancement on colloids pulled through a solution of  $\lambda$ -DNA (used here as a monodisperse model polymer) with an optical tweezer [1] (fig. 1 (a)). The experiments have shown 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. Now former measurements are expanded to very low solvent velocities, which lead to a nonlinear response based on the soft shape and high flexibility the DNA-coils have on this slow approaches. Therefore the resolution of our optical tweezers setup was increased **up to 5 fN** ( $10^{-15}$  N). Preliminary results are shown in figure 1 (b).

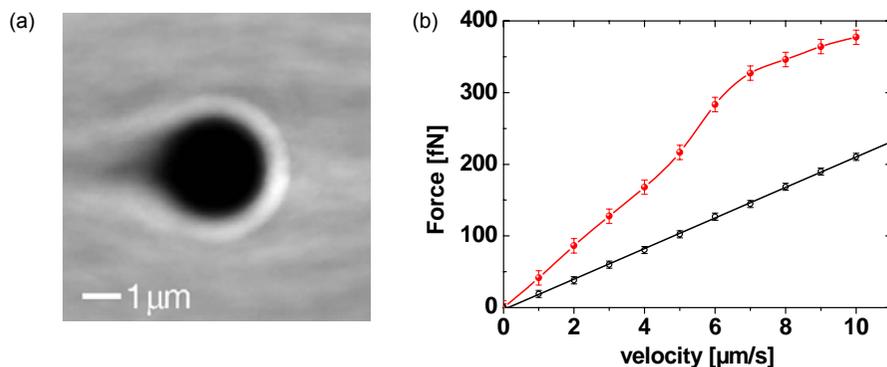


Fig. 1: (a) Polymer density around the colloid averaged over 2000 snapshots of the system by Brownian Dynamics simulations. Brighter areas denote higher DNA concentration. (b) Drag force on colloids in  $\lambda$ -DNA as a function of the pulling velocity (red dots). Also shown is the Stokes force on the colloids (black open circles fitted with solid black line) in pure water.

### References:

[1] C. Gutsche, F. Kremer, M. Krüger, M. Rauscher, R. Weeber, J. Harting, submitted to *J. Chem. Phys.* **129**, 084902 (2008)

### Collaborators:

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

### Funding:

DFG priority programm SPP 1164 (Nano- & Microfluidics) AZ: KR 1138/14-3

## 2.9 Polyelectrolyte-Compression Forces between Spherical DNA-grafted colloids

K. Kegler and F. Kremer

The experimental investigation was based on the measurement of the force-distance dependence between two identical, negatively charged DNA-grafted colloids employing optical tweezers. Optical tweezers offer unprecedented accuracy down to the pN domain and 3 nm in measuring forces and position, respectively. By monitoring the force-distance dependencies between two grafted colloids it is possible to learn how the different physicochemical properties (molecular weight, grafting density, ionic strength of the surrounding medium) affect the effective interaction between the grafted colloids. The measured force-distance relation is analyzed by means of a theoretical treatment. Quantitative agreement with the experiment is obtained for all parameter combinations. The physical system provides a convincing verification of the importance of the PE-compression mechanism in sharp contrast to most hitherto studied systems, which were dominated by counterion entropy.

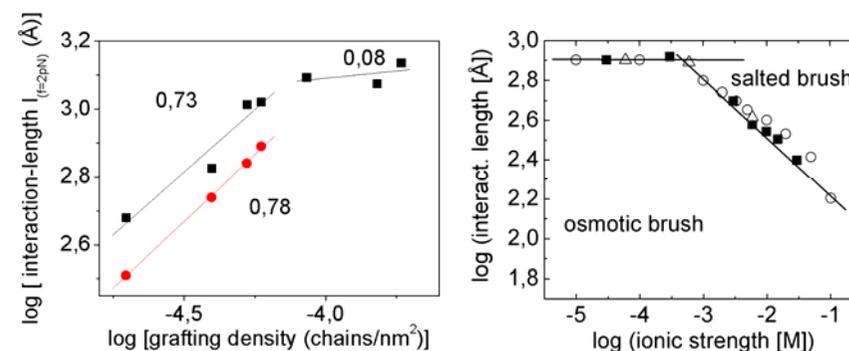


Fig.1 (a) :Interaction length  $l_{(F=2pN)}$  at a force of 2 pN versus grafting density for DNA (1000bp)-grafted colloids of varying grafting density in buffered (10 mM  $C_4H_{11}NO_3$ , pH 8.5) solution (square). The scaling relationships are indicated by straight lines. The circles are predicted by the model [3]. (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.

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### Collaborators:

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

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## 2.10 Investigating fluctuation and dissipation of optically trapped colloids

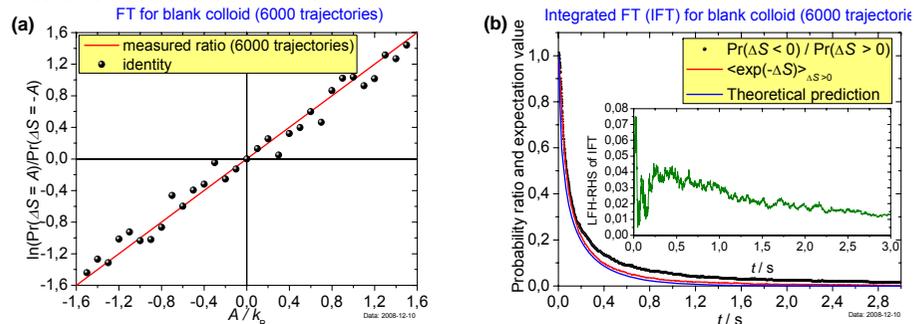
O. Ueberschär and F. Kremer

Fluctuation and dissipation as the dominant mechanisms behind the well-observable Brownian motion of micron-sized particles are investigated and quantified on a single colloid level by means of the optical tweezers technique. Using an outstandingly fast optical diffraction image analysis routine with a sampling frequency of 10 kHz combined with an automated data acquisition loop, we deduce the precise size of the colloid under study. Moreover, we measure the colloid's entropy production and consumption along a large number of different trajectories (e. g. 6000) in a non-equilibrium steady-state. Since our micron-sized single colloid clearly does not fulfil the assumptions of the second law of thermodynamics, i. e. the limit of large numbers of particles ( $N \rightarrow \infty$ ) and a big system size ( $V \rightarrow \infty$ ), entropy is observed to be produced ( $\Delta S \geq 0$ ) or consumed ( $\Delta S < 0$ ) depending on the particular trajectory and time scale. Replacing the second law for arbitrarily system sizes, the fluctuation theorem (FT) by Evans et. al. only discovered in 1993 still holds, however. It quantifies the probability of entropy production compared to entropy consumption,

$$\frac{\Pr(\Delta S = +A)}{\Pr(\Delta S = -A)} = \exp\left(\frac{A}{k_B}\right),$$

where  $A$  is an arbitrary value of entropy change. Obviously, for large positive values of entropy change, i. e.  $A \gg k_B$ , the second law is obtained from the FT. We find quantitative agreement between our measurements and the predictions of the FT.

Running out measurements on both blank and DNA-grafted colloids (DNA properties: molecular weight of 4000 base pairs, contour length of approximately 1360 nm), we compare their average entropy change rates, addressing the issue if there is evidence for an additional dissipative mechanism due to the DNA coat.



**Fig. 1:** (a) (logarithmic plot) Comparison of the left-hand side (LHS, black balls) and the right-hand side (RHS, red line) of the FT for 6000 single trajectories 100 ms after the initiation of a disturbance.

(b) Comparison of the LHS and RHS of an integrated, time-dependent form of FT applied to our system (black line and red line). The theoretical prediction by stochastic dynamics is also shown (blue line). As expected, these three graphs almost collapse. **Inset:** LHS-RHS of IFT.

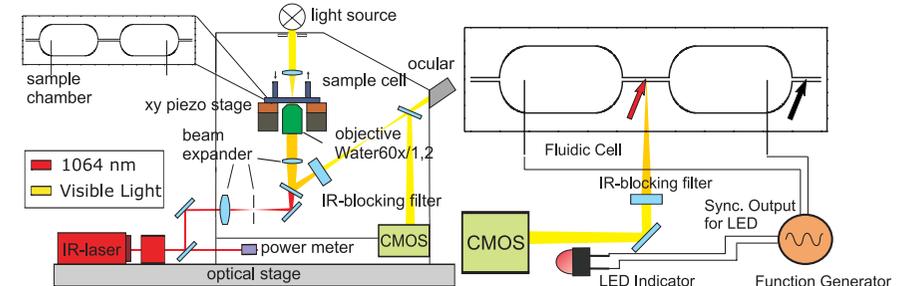
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## 2.11 Single colloid electrophoresis

I. Semenov, O. Otto, G. Stober, P. Papadopoulos, U. F. Keyser and F. Kremer

Optical Tweezers enable one to trap a single particle without any mechanical contact and to measure its position and the forces acting on it with high resolution ( $\pm 1$  nm,  $\pm 100$  fN). Single spherical polystyrene (PS) colloids of a diameter  $d=2.23$   $\mu\text{m}$  are used. The imaging system and experimental setup are based on epifluorescent microscope (Fig. 1(a)). The fluidic cell geometry is defined by the inner shape of the PMMA spacer (Fig. 1(b)): two reservoirs with Pt electrodes are connected by a narrow channel (width: 300  $\mu\text{m}$ , height: 1 mm) that helps to obtain a uniform electric field distribution. The channel is extended to the other sides of both reservoirs and the ends are kept open to avoid back flow. For measuring of phase displacement between applied AC signal and colloidal response, a light-emitting diode (LED), connected to synchronization output of function generator is incorporated right in front of the CMOS sensor (Fig. 1(b)). By applying an outer electrical sinusoidal field the complex (sum of the electrophoretic and electroosmotic contributions) response of the single colloid under study can be directly determined. It is found that the phase is shifted with respect to the applied external field. Hence, this gives rise to observe the complex electrophoretic mobility which is theoretically described by a strongly damped driven harmonic oscillator model. The electroosmotic effect is studied separately with the result that it stays more than one order of magnitude lower than electrophoretic motion of the particle. Exchanging the medium surrounding the colloid allows deducing the (KCl) concentration dependence of a single colloidal complex response. The results are compared with conventional Zetasizer measurements.



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