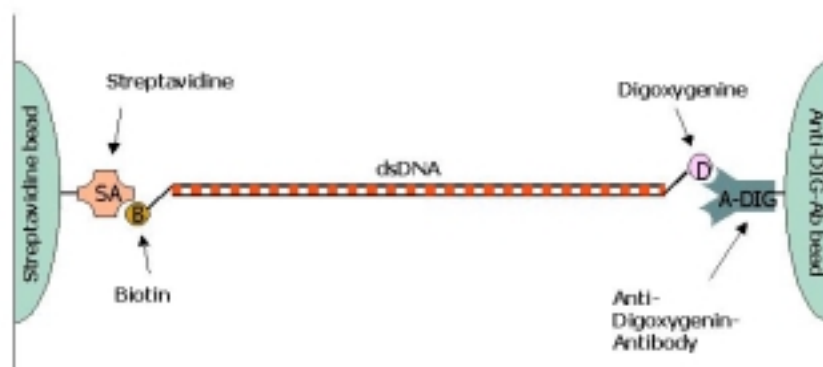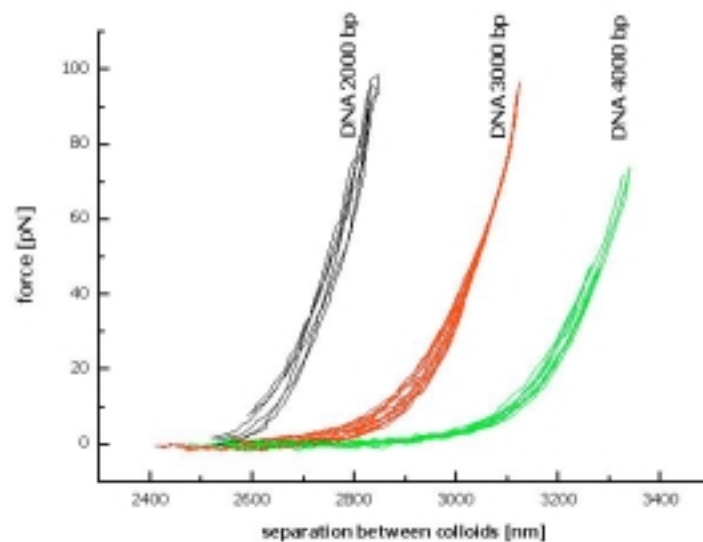# UNIVERSITY OF LEIPZIG

Faculty of Physics and Earth Sciences
Department of Experimental Physics I

GROUP "PHYSIK ANISOTROPER FLUIDE"

Molecular arrangement of the DNA between two separated colloids

Force extension dependence of single DNA chains of various lengths (2000 base pairs (bp), 3000 bp, 4000 bp)

Annual Report 2003

The year 2003

The year 2003 was a year of changes. In April Ralf Stannarius left the group to take over a chair for experimental physics at the University of Magdeburg. In September Christine Papadakis started with her professorship at the TU Munich. The members of the old team in Leipzig wish both all the best in their new positions.

The research in the classical topics (molecular dynamics as studied by broadband dielectric spectroscopy and time-resolved Fourier Transform-Spectroscopy) developed well. Additionally new activities have emerged. The optical tweezer experiments are in good progress and routiveously it is possible now to measure the viscoelastic properties of *single* chains of DNA. This open new perspectives for instance to study DNA protein interaction in great detail on a single molecule level.

Concerning the funding of our research in 2004 we are in a comfortable position: Two major grants were approved one to continue the single molecule experiments with optical tweezers and one within the DFG-Schwerpunkt 1104: Nano- and microfluidics: From the molecular motion to the continuous flow. Two further applications are in preparation. This provides excellent support and strong encouragement for our research.

Friedrich Kremer

Contents

4

1 Organization of the group

Chairman: Prof. Dr. Friedrich Kremer

Academic staff and postdocs	**Students**
PD Dr. Ralf Stannarius	Dipl.-Phys. Tune B. Bonné
Dr. Christine Papadakis	Dipl.-Chem. Peter Busch
	Dipl.-Phys. Lutz Hartmann
	Dipl.-Phys. Thomas John
	M. Sc. Julius Tsuwi Kazungu
	Dipl.-Phys. Kati Kegler
	Dipl.-Biochem. Mathias Salomo
	Dipl.-Phys. Heidrun Schüring
	Dipl.-Phys. Anatoli Serghei
	Dipl.-Biochem. Marc Struhalla
	M. Sc. Michael Tammer

Technical staff

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

Alumni

Prof. Dr. Siegbert Grande

2 Projects
2.1 New developments in the preparation of nanometric thin films

F. Kremer*, A. Serghei

This project aims to develop new methods to prepare nanometric thin layers, which would enable one to investigate the influence of confinement on the molecular dynamics of thin polymeric films. Additionally, the preparation should provide an easy way to adjust the interactions at the interfaces, which will allow us to emphasize their role in the dynamics under confinement.

One approach to be followed is to use silica nano-colloids as spacers between two flat conductive electrodes (silicon wafers). This procedure starts with the preparation of an empty condenser with a well-defined separation between the electrodes in a nanometric range. After annealing, the measurement of the capacity (of the empty condenser) provides an additional way to control the thickness. The polymer is filled by capillarity, the filling factor being easily estimated from the capacity measurement of the filled condenser. Our first results using this method are presented in Fig. 1, for polyisoprene bulk (using 50 μm glass fibers) and thin films (450 nm and 50 nm colloids as spacers). As expected, two relaxation processes are observed: the segmental and the normal mode, corresponding to the segmental and the chain end-to-end fluctuations. In agreement with our previous study [1] both relaxation processes are not shifted with decreasing the film thickness down to a thickness of 50 nm.

Another approach we want to develop is to use nanostructures as spacers between two silicon wafers. This procedure reduces itself essentially to selective etching of a SiO layer (deposited by evaporation on a silicon wafer), which enables the formation of a nanometric pattern (array of steps) with a well-defined height.
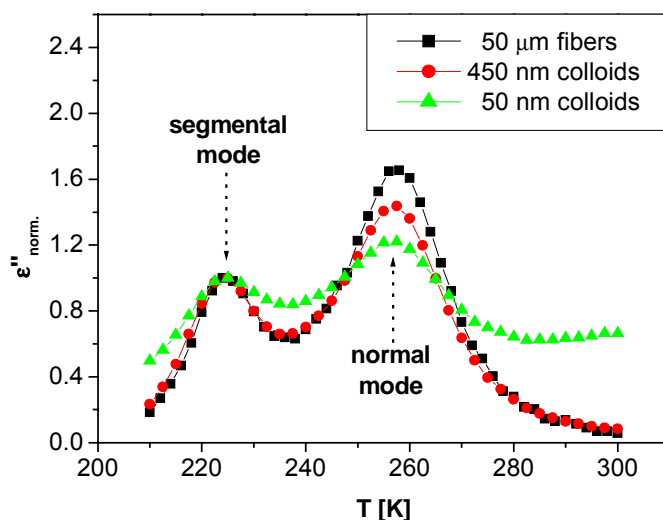

Fig. 1: The temperature dependence of the normalized dielectric loss at 770 Hz for polyisoprene (Mw=5000) bulk and thin films, as indicated

References:
[1] A. Serghei, F. Kremer, *Phys. Rev. Lett.* **91**, 165702 (2003)

The underlined author is the principal investigator of the project.

2.2 Fluctuation of terminal subchains in thin films of polyisoprene

<u>F. Kremer</u>, A. Serghei

A novel relaxation process (confinement-induced mode) was detected in thin cis-1,4-polyisoprene films (Fig. 1) investigated by Broadband Dielectric Spectroscopy. Additionally to the segmental and the normal mode, originating from the segmental and chain end-to-end fluctuations, the confinement-inducted mode shows up when the film thickness becomes comparable with the chain extension, arising from the fluctuations of the terminal subchains formed by the immobilization of the chain segments at the interface (Fig. 2).
This molecular model explains most of the features observed in the experiment, being also in a full-qualitative agreement with the results revealed by the simulations of the chains as ideal random walks: a) the confinement-induced mode becomes faster with decreasing film thickness (experiment) because the terminal subchains become in average shorter (simulation); b) its relaxation strength increases with increasing confinement on the expense of that of the normal mode (exp.) because the relative number of the immobilized chains increases with decreasing film thickness, while the relative number of the free (non-immobilized) chains decreases (sim.); c) the confinement-induced mode shows no molecular weight dependence (exp.) because with increasing the length of the chain increases also its probability to come in contact with the immobilizing interface (sim.); d) the relaxation rate of normal mode is not affected by the confinement down to thicknesses comparable with the chain extension (exp.) because even for such small films a certain fraction of free (non-immobilized) chains still exists (sim.), which exhibits a bulk-like dynamics; e) the segmental mode is not affected by the confinement because it takes place on a length scale much smaller than the film thickness.
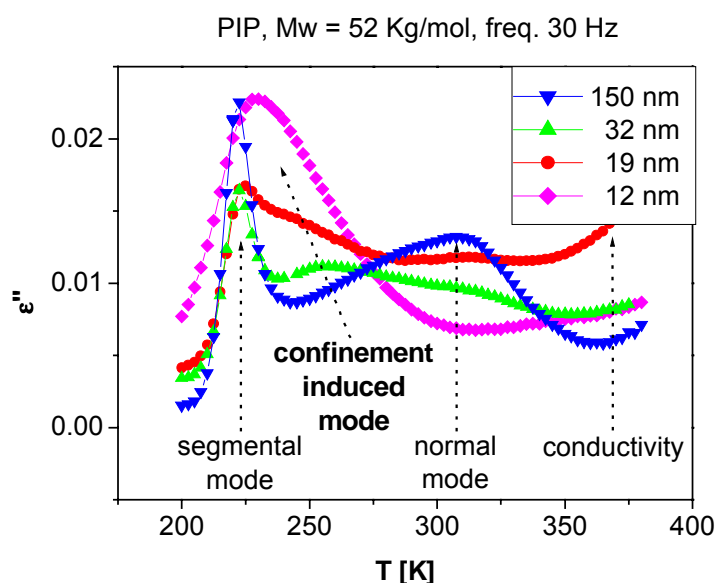

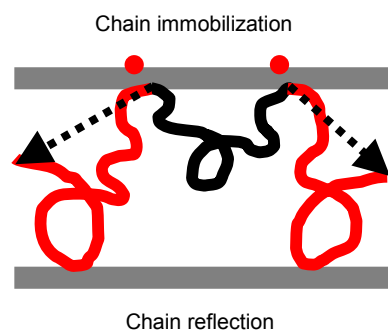Fig. 1: Dielectric loss versus temperature for different thicknesses

Fig. 2: Terminal subchains formed by immobilization of chain segments at an interface

References:
[1] A. Serghei, F. Kremer, *Phys. Rev. Lett.* **91**, 165702 (2003)
[2] A. Serghei, F. Kremer, W. Kob, *EJP* E **12**, 143 (2003)

Collaborators:
W. Kob (Universite Montpellier, France)

2.3 Glass transition and molecular dynamics in grafted and spin coated PDMS layers

F. Kremer, L. Hartmann

Thin polymer films are an ideal system to study the influence of finite size effects on the polymer dynamics [1-3]. We focus on measurements of dipole fluctuations by Broadband Dielectric Spectroscopy to reveal deviations from the bulk behaviour when reducing the film thickness. In case of poly(dimethyl siloxane) (PDMS) we have studied the influence of different preparation techniques (thin grafted and spin cast films [3]) on the molecular dynamics of this particular polymer besides that of mere variation of the film thickness [2].

In thin films of grafted PDMS of thickness d above and below the radius of gyration R_g we find bulk-like behavior for d=41nm>R_g whereas for $d<R_g$ the dynamic glass transition (α-relaxation) is by up to two orders of magnitude faster than in the bulk (Fig. 1). The latter finding is explained by an altered chain conformation compared to the bulk which presumably leads to an increased free volume as a consequence of the grafting procedure. The α-relaxation in spin cast films compares well with that of the bulk with respect to the thermal activation down to a film thickness d of 14 nm. However, in these films an additional relaxation shows up which is faster than any relaxation in the bulk. To explain this, we assume that in spin cast films only a part of the chains (close to the upper film surface) experiences an altered chain conformation leading to this faster relaxation. This interpretation is supported by the values obtained for the dielectric strength $\Delta\varepsilon$. In all films the α_c-relaxation related to fluctuations in the amorphous fraction of PDMS above crystallization has been observed showing no particular dependence of the geometric confinement.
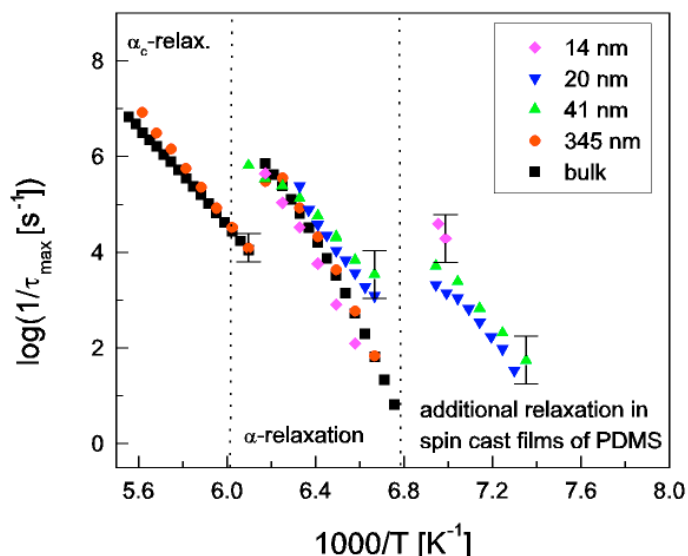
Fig. 1:
Activation plot for PDMS of a molecular weight of 1.4 10^5 g/mol in the bulk (black symbols) and as spin cast films (full colored symbols).

References:
[1] L. Hartmann, K. Fukao, F. Kremer,
    Chapter in book: "Broadband Dielectric Spectroscopy", p. 433, (Springer Verlag, Berlin, (2002), F. Kremer, A. Schönhals (Eds.)
[2] L. Hartmann, F. Kremer, P. Pouret, L. Léger, *J. Chem. Phys.* **118**, 6052 (2003).
[3] F. Kremer, L. Hartmann, A. Serghei, P. Pouret, L. Léger, *Eur. Phys. J.* E. **12**, 139 (2003)

Collaborators:
Prof. Dr. L. Léger (Collège de France, Paris, France)

2.4 Molecular dynamics in alternating maleimide copolymers as studied by Broadband Dielectric Spectroscopy

F.Kremer, J.Tsuwi

Structural segments consisting of alkyl and perfluoroalkyl groups covalently linked by a C-C bond are well known for their microphase separation resulting in highly ordered bulk structures. The use of such materials for surface modification is numerous because of the resulting low surface free energy. We are employing Broadband Dielectric Spectroscopy to study the molecular dynamics in a set of poly (alkene-*alt-N*-(perfluoro-)alkylmaleimide) copolymers with two types of side chains: alkyl or perfluoroalkyl. Generally, four relaxation regions are observed for copolymers with alkyl side chains (Fig. 1a), while three processes are observed for the perfluorinated copolymer systems (Fig. 1b).
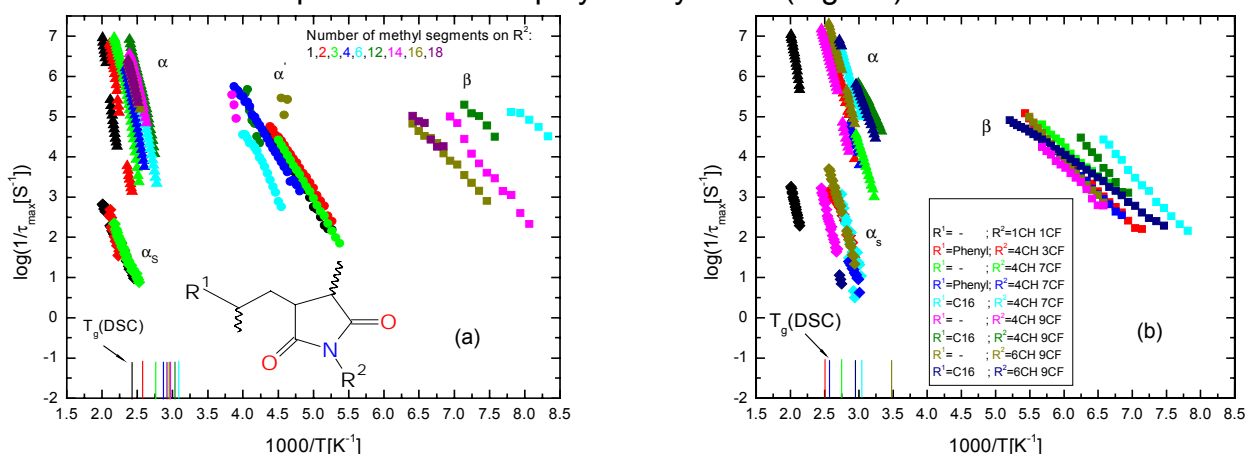

Fig. 1: (a) Activation plot showing four relaxation processes (β, α', α, α_s) for unfluorinated copolymer systems and inset: maleimide unit with two side chains R^1 and R^2. (b) Activation plot with three processes for perfluorinated copolymers.

The low temperature β-process is assigned to libration motion of CH_3 at the end of alkyl side chain, described by Arrhenius-type temperature dependence. The α'-process is assigned to an out-of-plane motion of the succinimide ring while the α-process is assigned to an in-plane fluctuation of one maleimide ring. The slowest α_s-process is assigned to fluctuations of 2-3 maleimide rings that constitute the helical superstructure of the copolymers. In contrast, the perfluorinated polymer systems show three relaxation regions only. The faster process at low temperatures is assigned to the librational motion of the CF_3 end group while the other two processes are the α- and α_s- processes assigned as earlier.

References:
[1] Song, K.,Twieg., J.R., Rabolt, J.F., *Macromolecules* **23**,3712 (1990)
[2] Bailey, J., Walker, S.M., *Polymer* **13**, 561 (1972)
[3] Block H., Lord, P.W., Walker, S.M., *Polymer* **16**, 739 (1975)
[4] Cubbon R.C.P, *Journal of Polymer Science: Part C* **16**, 387-392 (1967)
[5] Baltá-Calleja, F.J., Ramos J.G., Barrales-Rienda, J.M., *Kolloid-Z. und Z. Polymere* **250**, 474-481 (1972)
[6] Tsuwi, J., Appelhans, D., Kremer, F., to be submitted to *Macromolecules*

Collaborators:

D. Appelhans (IPF Dresden, Germany)

2.5. Dielectric relaxation of inverse miniemulsions

F.Kremer, J.Tsuwi

Miniemulsions are specifically formulated heterophase systems where stable nanodroplets of one phase are dispersed in a second continuous phase. These nanodroplets are envisaged to act as nanoreactors of polymer reactions resulting in polymer dispersions when appropriate reaction initiators are introduced. We focus on dielectric measurements of miniemulsions in the microwave frequencies to study nanodroplet stability.
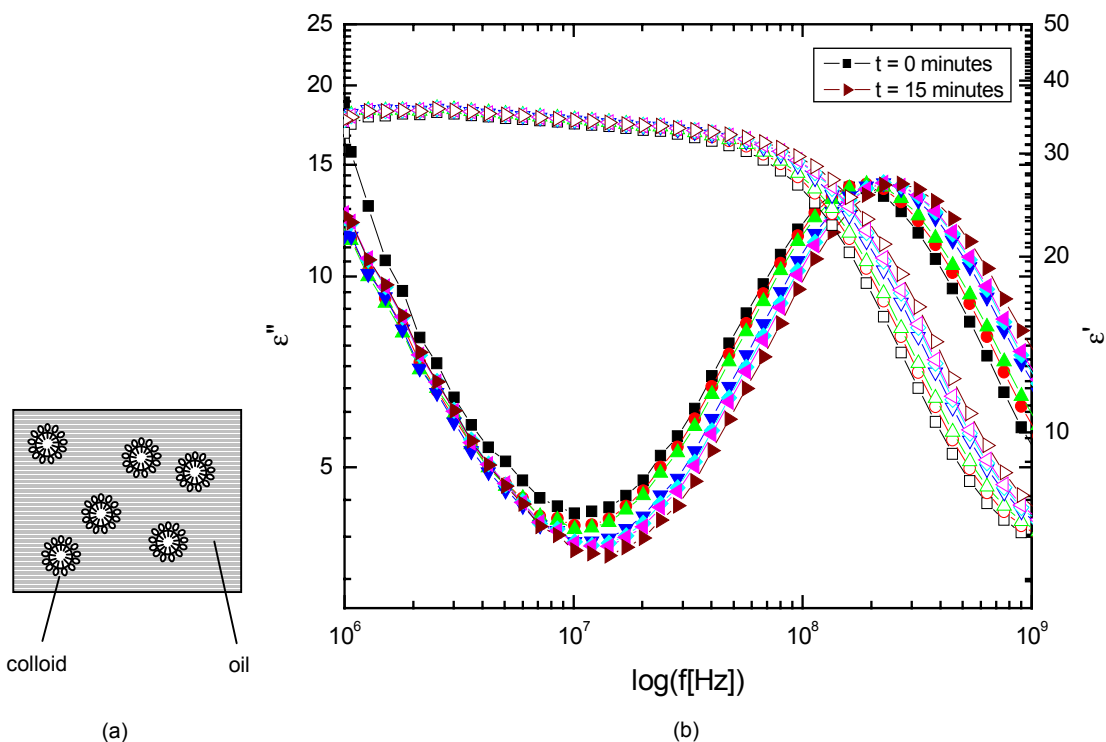

Fig. 1: (a) miniemulsion composed of nanodroplets (colloids) dispersed in a continuous medium of oil. (b) Real part (ε', closed symbols) and imaginary part (ε'', open symbols) of dielectric function versus frequency for time-dependence measurement of miniemulsion with 0.5% surfactant concentration.

The dielectric spectra of miniemulsions are analyzed by considering the relaxation behaviour of both the surfactant and the solvent that form the nanodroplets. In the analysis, the emulsions are modeled in the context of Effective Medium Theory to quantitatively determine the dielectric energy storage and loss behaviour.

References:

[1] Antonietti M.,Landfester K., *Prog. Polym.Sci.* **27**, 689 -757(2002)
[2] Baar, C., Buchner, R., Kunz, W., *J. physical chem*. B **105**, 2906-2913 (2001)
[3] Baar, C., Buchner, R., Kunz, W., *J. physical chem*. B **105**, 2914-2922 (2001)
[4] Buchner, R., Barthel, J., *Annu. Rep. Prog. Chem.* C **97**, 349-382 (2001)

Collaborators:

M. Antonietti (Max Planck Institute of Colloids and Interfaces, Golm, Germany)

2.6 Fourier Transform Infrared Spectroscopy on ferroelectric liquid crystal polymers

F. Kremer, M. Tammer

Time-resolved polarised Fourier Transform Infrared (FTIR) Spectroscopy is employed to analyse the structure and dynamics in ferroelectric liquid crystal (FLC) polymers and elastomers. The specifity of the IR-spectroscopy enables us to study for the different molecular moieties the response to external mechanical end electrical excitations. By that, subtle details of the microscopic motion such as angular excursion, reorientation time, order parameter, asymmetries in the reorientational behaviour or elastomeric memory effects can be unravelled for the system under study.

(a)   (b)
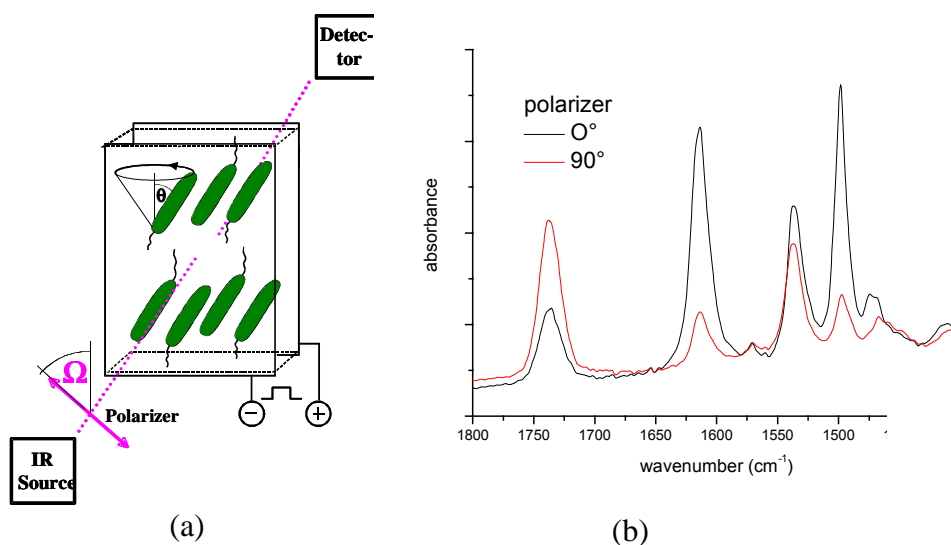
Fig. 1: (a) Setup of the polarized IR Spectroscopy. The liquid crystal is studied in bookshelf geometry: the layer normal of the smectic phase is perpendicular to the surface normal of the cell windows and the IR beam. (b) polarization dependent spectrum

(a)   (b)
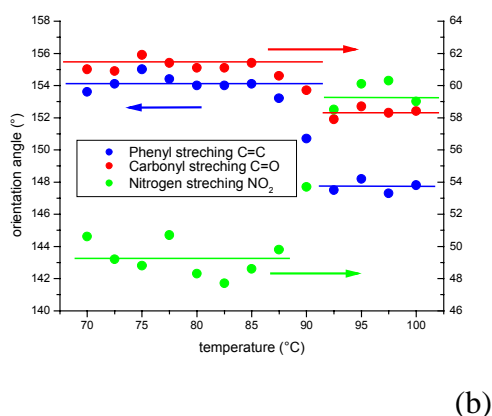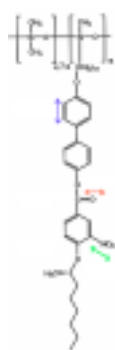
Fig. 2: (a) FLC polymer studied by FTIR. (b) Orientation angle for three different molecular groups of the FLC polymer in dependence of temperature. The change in orientation at the phase transition from SmC* to SmA is studied from these data.

Collaborators:
R. Zentel (University of Mainz, Germany), H. Finkelmann (University of Regensburg, Germany)

2.7 Optical tweezers as a tool to unfold RNA-aptamers

F. Kremer, M. Salomo, M. Struhalla, J. Reinmuth, W. Skokow

Optical tweezers are commonly used to manipulate microscopic particles, with applications in cell manipulation, colloid research, manipulation of micromachines and studies of the properties of light beams. With their extraordinary resolution in space (~2 nm) and force (~1 pN) they became an irreplaceable tool for such purposes.

In our projects we want to use them to study folding and unfolding mechanisms of nucleic acid structures. One project deals with the unfolding of RNA-aptamers. We want to immobilize a single aptamer molecule between two polystyrene particles. One of them is fixed with a femtotip. The other one is hold in the beam by the optical tweezers. To realize the necessary distance between the two colloids the aptamer-RNA was elongated by 500 bases on both ends. The immobilization between the two particles is then realized by DNA/RNA-hybrids (Fig. 1). With the use of this experimental set-up it is possible to apply forces in the range of piconewtons on the folded RNA-sequence. The aim of these experiments is to investigate the behaviour of two aptamers that have specific binding partners, an aptamer that binds to the antibiotic Moenomycin A and a second one that has thrombin as binding partner. We want to investigate the differences in their folding behaviour in absence and presence of their binding partners. So far we have synthesised all necessary components for the pulling experiment (ssDNA handles, RNA aptamers) and are now about to assemble and measure the system.
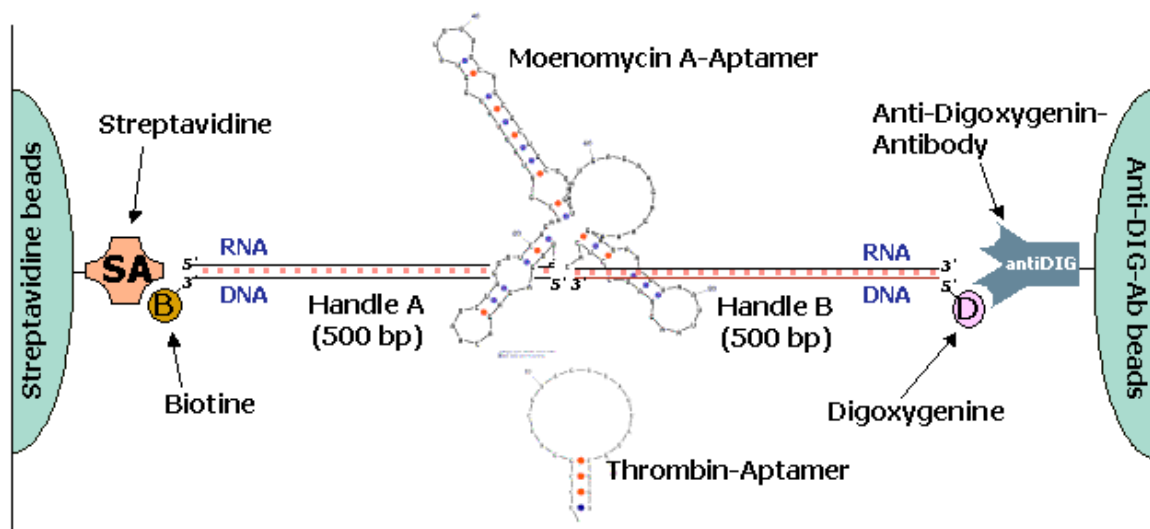

Fig. 1: Schematic representation of the molecule arrangement between the two beads.

References:
[1] J. Liphardt et al., *Science* **292**, 733-737 (2001)

Collaborators:
Prof. Dr. U. Hahn (University of Hamburg, Germany), Prof. Dr. A. Beck-Sickinger (University of Leipzig, Germany)

2.8 Investigating DNA-binding proteins with optical tweezers

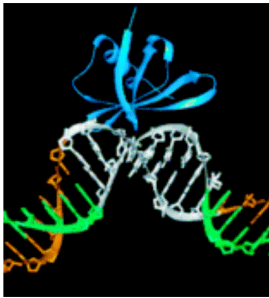F. Kremer, M. Salomo, M. Struhalla, J. Reinmuth, W. Skokow

Fig. 1: Model of the binding mechanism of the Sac7d protein (blue) to a DNA helix.
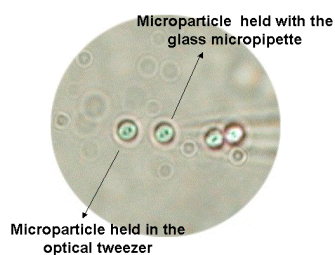

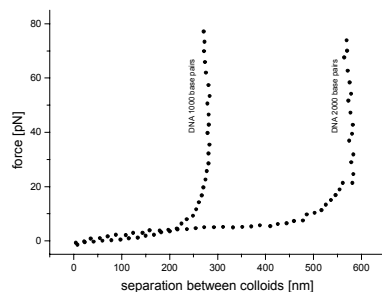Fig. 2: Two beads (∅ 2.2 µm) of which one is hold by a femtotip while the other fluctuates in the photonic

Fig. 3: Force-extension curves for 1000 base pairs (bp) and 2000 bp dsDNA.

Sac7d belongs to a class of small chromosomal proteins identified in the hyperthermophilic archaeon *Sulfolobus acidocaldarius*. It is extremely stable to heat, acid and chemical agents and binds strongly to the minor groove of DNA, causing a sharp kinking of the DNA helix leading to a shortening of the DNA (Fig. 1). Our project has the aim to investigate the influence of this DNA-binding protein on a DNA-double helix immobilized between two particles. We want to use the optical tweezers to measure the dimension of shortening. The protein should bind to the DNA every 3 bp leading to a theoretical compaction ratio of ~1.2. The first aim of our project was to overproduce the sac7d protein. For this purpose we used an *E. coli* based expression system. The protein purification was done via affinity chromatography. The combination of these two methods enabled us to isolate the protein in sufficient amount with a very high purity. The second step was to establish a suitable experimental setup to measure the shortening of DNA after Sac7d has bound. For that we immobilized a DNA-double helix between two polystyrene particles and we were able to establish a system as shown in Fig. 2. One particle is fixed by a glass micropipette, the other one is hold in the optical tweezers. Via Streptavidin/Biotin- and Digoxigenin/Anti-Digoxigenin interactions we were able to immobilize a single DNA-molecule between this particles. We immobilized DNA with different lengths (1000 bp – 4000bp) between the two particles and recorded force extension curves as shown in Fig. 3.

References:

[1] H. Robinson et al.; *Nature* **392**, 202-205 (1998)
[2] J.G. McAfee et al.; *Bioch.* **34**, 10063-10077 (1995)
[3] D. Kulms et al.; *Biol. Chem.* **378**, 545-551 (1997)

2.9 Nano- and microfluidics using optical tweezers with fast single particle tracking

F. Kremer, K. Kegler

Optical tweezers with fast single particle tracking are microscopic (~ 1 µm) rheometric tools with nanometer resolution in space and subpico-newton resolution in force. The proposed project has two intentions (i) to contribute to basic questions in colloid- and polymer-research and (ii) to address technological problems of micro- and nanofluidics.In detail the following experiments are planned: 1.) Measurements of the force-distance-dependence between two isolated *single* colloids of which one is hold by a micropipette (Ø ~ 0.4 µm) and the other by an optical tweezer.
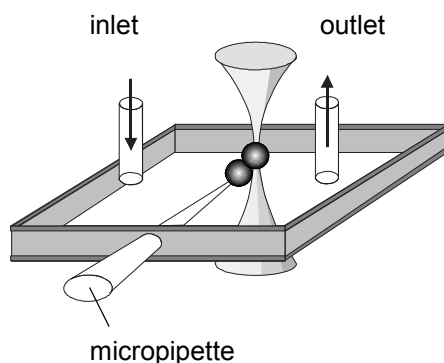

inlet   outlet

micropipette

Fig. 1 Scheme of the sample cell to measure forces between two separated colloids

The separation between the colloids can be varied in nanometer steps. 2.) Measurement of the force-distance-dependence between a *single* colloid and a wall in the steady state and in fluid flow for coated and uncoated surfaces. 3.) Measurement of depletion forces between *single* colloids in the steady state and in flow for polymer solutions of varying concentration and for polymers of different topology. 4.) A fluctuation analysis of the Brownian motion of a colloid in an optical trap enables one to deduce the local *tensor* of viscosity. By that inhomogeneous microscopic structures like microchannels or living biological systems can be explored. 5.) Measurement of the flow profile of homogeneous and heterogeneous liquids in small (~ µm) confining geometries like plates with micrometer separation, microchannels, etc. with – and without surface modifications (e.g. hydrophobization).

This project will be part of the DFG-Schwerpunktprogramm "Nano- und Mikrofluide: Von der molekularen Bewegung zur kontinuierlichen Strömung".

2.10 Time-resolved in-situ GISAXS measurements of thin films of lamellar diblock copolymers

Ch. M. Papadakis, P. Busch

High molar mass polystyrene-polybutadiene (PS-PB) diblock copolymer thin films have been found to spontaneously form patterned surfaces related to a perpendicular orientation of the lamellae [1,2]. Non-equilibrium structures are notorious in such systems because of the low mobility of the polymers in thin film geometry. Exposure to solvent vapor is therefore frequently used in order to drive the films towards equilibrium. The mechanisms for reorientation have not been elucidated yet, though.

By means of Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) the mesoscopic structures within the films can be studied [2]. At low incident angles of the X-ray beam (slightly above the critical angle of total external reflection), a substantial portion of the incident and scattered radiation is reflected by the substrate, resulting in high recorded intensity and low measuring times (a few seconds), which enables time-resolved studies. The intensity due to the substrate reflection can be understood in terms of the distorted-wave Born approximation. Our in-situ studies of a high molar mass PS-PB film during treatment with toluene vapor show that the lamellar orientation changes within minutes but the perpendicular orientation is regained after the solvent is removed (Fig. 1, Ref. 3).
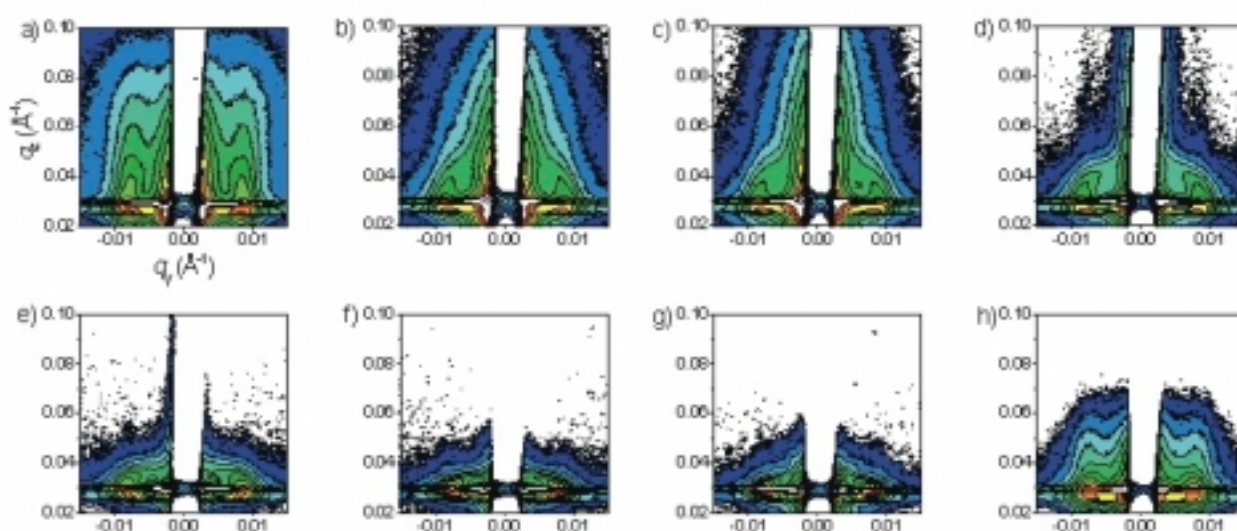

Fig. 1: 2D GISAXS maps of a high molar mass film (183 kg/mol, lamellar thickness 836 Å). (a) In the dry state. (b) 1 min, (c) 2 min, (d) 4 min, (e) 8 min, (f) 17 min, and (g) 33 min after the injection of toluene into the sample chamber. (h) 5 min after removal of toluene. Incident angle = 0.21°. The straight Bragg rods in (a) indicate the presence of perpendicular lamellae, the bending in (b-g) indicates reorientation of the lamellae.

References:
[1] P. Busch, D. Posselt, D.-M. Smilgies, B. Rheinländer, F. Kremer, C.M. Papadakis, *Macromolecules* **36**, 8717 (2003).
[2] P. Busch, D.-M. Smilgies, D. Posselt, F. Kremer, C.M.Papadakis, *Macromol. Chem. Phys.* **204**, F18 (2003), invited contribution.
[3] D.-M. Smilgies, P. Busch, D. Posselt, C.M. Papadakis, *Synchr. Rad. News* **15**, 35 (2002), invited contribution.

2.11 A model of the GISAXS intensity of thin films of lamellar diblock copolymers in the framework of the DWBA

Ch. M. Papadakis, P. Busch

Block copolymer thin films offer an opportunity for patterning of surfaces on the sub-micrometer scale. By combining atomic force microscopy with Grazing-Incidence Small-Angle X-ray Scattering (GISAXS), we have investigated the lamellar orientation in thin films of symmetric, lamellae-forming polystyrene-polybutadiene (PS-PB) diblock copolymers [1,2]. GISAXS measurements were performed in dependence of the incident angle α_i. Fig. 1a shows a two-dimensional GISAXS map of a film with lamellae oriented parallel to the substrate surface. Distinct peaks are visible in the vicinity of the beam stop as marked by the arrow. The dependence of the q_z-positions of these peaks on α_i cannot be understood in the context of the Born approximation (BA), where only single scattering is considered. We have modeled the scattering within the distorted wave Born approximation (DWBA) which additionally takes into account the refraction of the X-rays by the film surface and the reflection by the substrate. The peak positions expected from this model are in excellent agreement with the experimental data (Fig. 1b).
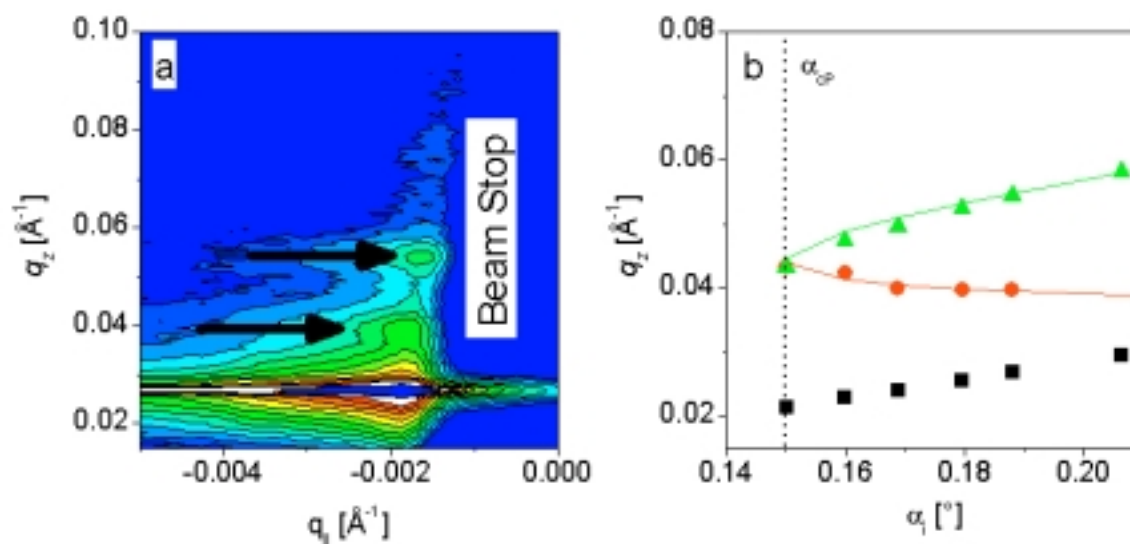

Fig. 1: (a) 2D GISAXS map of a thin film of PS-PB having a molar mass of 22.6 kg/mol, a lamellar thickness of 197 $\pm$ 4 Å and a film thickness of 1750 $\pm$ 30 Å at α_i = 0.19°. (b) Experimental q_z-positions of the specularly reflected beam (squares) and the non-specular peaks in dependence of the incident angle α_i (triangles, circles). The solid lines are the positions expected from DWBA theory. The dotted line denotes the critical angle of the polymer film.

References:

[1] P. Busch, D. Posselt, D.-M. Smilgies, B. Rheinländer, F. Kremer and C.M. Papadakis, *Macromolecules* **36**, 8717 (2003).
[2] D.-M. Smilgies, P. Busch, D. Posselt and C.M. Papadakis, *Synchr. Rad. News* **15**, 35 (2002).

Collaborators:

2.12 Aggregation behavior of amphiphilic diblock copolymers studied using fluorescence correlation spectroscopy and dynamic light scattering

Ch. M. Papadakis, T. B. Bonné

In aqueous solution, amphiphilic block copolymers have been found to spontaneously aggregate into micellar solutions and lyotropic phases reminiscent of the structures encountered in low molar mass surfactants and lipids [1]. The aim of our study is to elucidate the diffusion mechanisms in such systems. Poly(oxazolin) based polymers constitute a very versatile model system. They have the advantage that their architecture (homopolymers, diblock and triblock copolymers) as well as the degree of hydrophobicity of the blocks can readily be varied, and they can be fluorescence labeled.

We have used Fluorescence Correlation Spectroscopy (FCS) in order to study the self-diffusion of fluorescence-labeled poly(methyloxazolin)-poly(nonyloxazolin) diblock copolymers in aqueous solution. The fluorescence-labeled polymers were used as tracers in aqueous solutions of otherwise identical, non-labeled polymers. In this way, a large concentration range could be accessed without oversaturating the FCS detector. By identifying the diffusion coefficients of the unimers and the micelles, the critical micelle concentration was identified (Fig. 1).

Additional temperature-resolved Dynamic Light Scattering (DLS) experiments showed that dissolution at room temperature results in a metastable state containing very large aggregates. Only after heating to ~90°C, the micelles assume their equilibrium size of ~12 nm. Comparison of the hydrodynamic radii obtained using DLS with those from FCS on annealed samples showed that the hydrodynamic radius of the micelles can reliably be determined using FCS (Fig. 1). In the future, we wish to extend our dynamic studies to triblock copolymers as well as to lipopolymers.
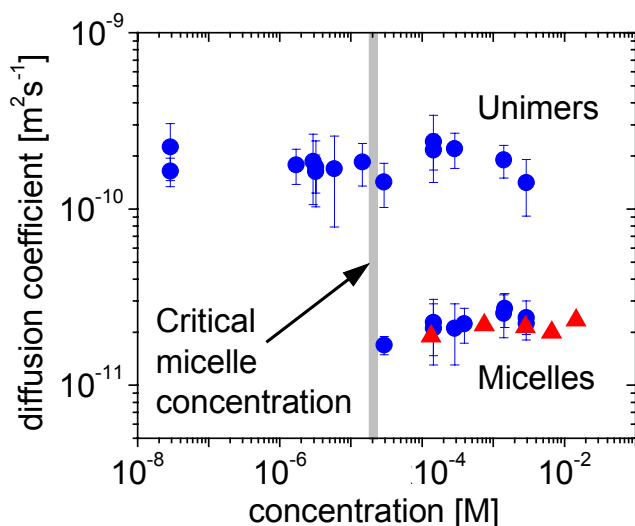

Fig. 1: Concentration dependence of the diffusion coefficients of aqueous solutions of a low molar mass poly(methyloxazoline)-poly–(nonyloxazoline) (PMox-PNox) diblock copolymer (molar mass 4796 g/mol, weight fraction of PMox 56%) with the fluorescence label TRITC attached to the end of the PMox block. The solutions were annealed prior to measurement. Blue symbols: results from FCS, red symbols: results from DLS.

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Collaborators:

2.13 Isotropic droplets in freely suspended smectic films

R. Stannarius, H. Schüring

Besides the well-known layer-by-layer thinning, droplet nucleation, as a phase transition phenomena in freely suspended smectic films, came into the focus of interest over the last years. Isotropic inclusions that form in the vincinity of the bulk smectic-isotropic phase transition are investigated my means of reflection microscopy. From their shapes and dynamics in the film plane, interface tensions between smectogens in different phases can be derived. Basing on the assumption of a surface phase transition from the isotropic phase to a smectic surface interphase, a model has been developed that considers the relevant interface tensions and the surface tension of the smectic phase. The latter can be easily determined by use of the earlier established bubble method. Thus, interphase tensions $< 10^{-3}$ N/m between isotropic and smectic phases can be accessed by an analysis of the droplet shapes. An extension of the model to inhomogeneously thick films explains the spontaneous arrangement of droplets at film thickness steps (Fig. 1) as well as the capillary force driven motion of droplets in the direction of the film thickness gradient.

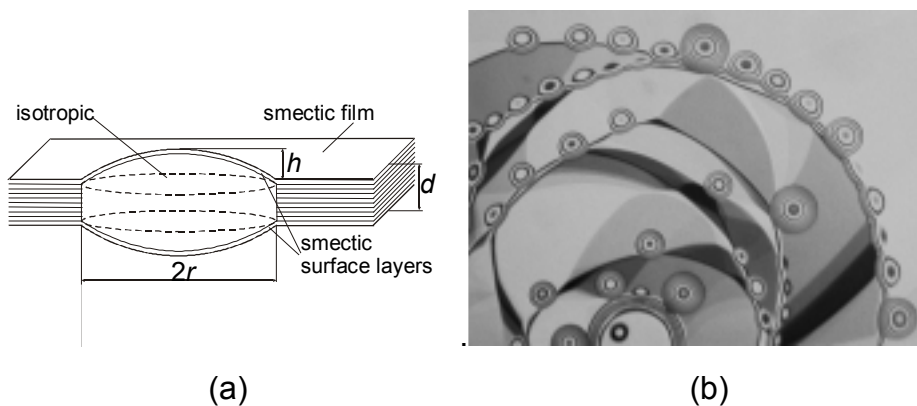(a)   (b)

Fig. 1: Model of an isotropic droplet in a homogeneous smectic film (a) and arrangement of isotropic droplets at film thickness steps, observed by reflection microscopy under monochromatic illumination (λ=630 nm), image size: 260 µm × 190 µm (b).

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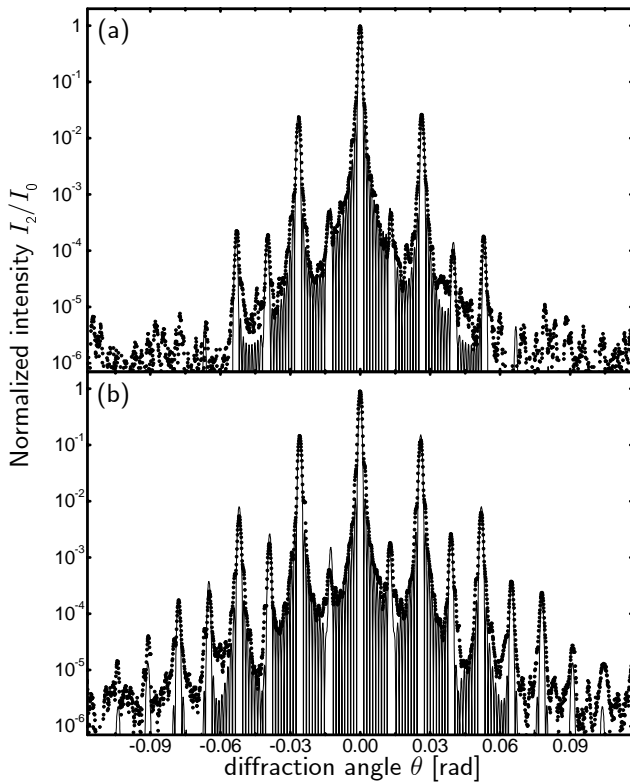
Collaborators:
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2.14 Laser diffraction by periodic dynamic patterns in anisotropic fluids

R. Stannarius, T. John, U. Behn

We describe the application of a laser diffraction technique to the study of electroconvection in nematic liquid crystal cells. It allows a real-time quantitative access to pattern wave lengths and amplitudes. The diffraction profile of the spatial periodic pattern is calculated and compared quantitatively to experimental intensity profiles. For small director tilt amplitudes $\varphi(t)$, the phase grating generated in normally incident undeflected light and the first order term correction from light deflection is derived analytically. It yields an $I(t) \propto \varphi(t)^4$ dependence of the diffracted intensity I on the amplitude of director deflections. For larger director tilt amplitudes, phase and amplitude modulations of deflection of light in the inhomogeneous director field are calculated numerically. We apply the calculations to the determination of the director deflection and measure growth and decay rates of the dissipative patterns under periodic excitation. Real time analysis of pattern amplitudes under stochastic excitation is demonstrated.

Fig. 1: It is shown the comparison of numerical calculated diffraction profiles (solid line) and measured intensities (dots), normalized to the primary beam intensity. The measured profile at excitation voltage U = 28.79 V (a) and U = 28.90 V (b) corresponds to the calculation with amplitudes φ = 7.4° (a) and φ = 12.6° (b). The pattern wave length λ = 48 µm, cell thickness 48.5 µm, critical voltage for onset of electroconvection U_c = 28.73 V.

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Collaboration:
Prof. Dr. U. Behn (ITP Leipzig, Germany), Dr. T. Scharf (Neuchatel, Germany)

3 Publications

[1]   Serghei, A.; F. Kremer
      "A novel confinement-induced relaxation process in thin films of cis-polyisoprene"
      Phys. Rev. Lett. **91**, 165702-1-165702-4 (2003)

[2]   Hartmann, L.; F. Kremer, P. Pouret, L. Léger
      "Molecular dynamics in grafted layers of poly(dimethylsiloxane) (PDMS)"
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[3]   Doxastakis, M.; D.N. Theodorou, G. Fytas, F. Kremer, R. Faller, F. Müller-Plathe, N. Hadjichristidis
      "Chain and local dynamics of polyisoprene as probed by experiments and computer simulations"
      J. Chem. Phys. **119**, 6883-6894 (2003)

[4]   Serghei, A.; F. Kremer, W. Kob
      "Chain conformation in thin polymer layers as revealed by simulations of ideal random walks"
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      "Molecular dynamics in thin grafted and deposited polymer layers"
      Eur. Phys. J. E **12**, 139 (2003)

[6]   Kremer, F.; A. Huwe, A. Gräser, St. Spange and P. Behrens
      "Molecular dynamics in confined space"
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[7]   Stannarius, R.; J. Li and W. Weissflog
      "A ferroelectric smectic phase formed by achiral straight core mesogens"
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      "Hydrogen Bonded Ferroelectric Liquid Crystal Gels in Freely Suspended Film Geometry"
      Phys. Chem. Chem. Phys. **5**, 916-923 (2003)

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      "Laser diffraction by periodic dynamic patterns in anisotropic fluids"
      Europhys. J. B **35**, 267-278 (2003)

[10] Das, B.; S. Grande, W. Weissflog, A. Eremin, M. W. Schröder, G. Pelzl, S. Diele, and H. Kresse
      "Structural and conformational investigations in SmA and different SmC phases of new hockey stick-shaped compounds"
      Liquid Crystals **30**, (2003)

[11] Busch, P.; D. Posselt, D.-M. Smilgies, F. Kremer and C. M. Papadakis
      "Diblock copolymer thin films investigated by tapping mode AFM: Molar mass dependence of surface ordering"
      Macromolecules **36**, 8717-8727 (2003)

[12] Busch, P.; D.-M. Smilgies, D. Posselt, F. Kremer, C. M. Papadakis
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Proceedings of the Makromolekulares Kolloquium Freiburg, Feb.~2003, *Macromolecular Chemistry and Physics* **204**, F18 (2003) (invited contribution)

[13] Das, B.; S. Grande, W. Weissflog, A. Eremin, M.W. Schröder, G. Pelzl, S. Diele, H. Kresse
"Structural and conformational investigations in SmA and different SmC phases of new hockey-stick shaped compounds"
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[14] Köhler, R.; R. Stannarius, Ch. Tolksdorf and R. Zentel
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Liq. Cryst., accepted for publication (2003)

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[17] Papadakis, C.M.; F. Rittig, K. Almdal, K. Mortensen, P. Štěpánek
"Collective dynamics and self-diffusion in a diblock copolymer melt in the body-centered cubic phase"
subm. to *Eur. Phys. J. E.* (2003)

[18] John, T.; U. Behn, R. Stannarius
"Laser diffraction by periodic dynamic patterns in anisotropic fluids"
subm. to *Europhys. J. B* (2003)

4 Financial support

5 Graduations

Habilitation:

Dr. Christine Papadakis
27.10.2003
"Inner and outer interfaces in soft matter systems"

Promotions:

Dipl.-Chem. Peter Busch
17.11.2003
"Lamellare Orientierung in dünnen Diblockcopolymerfilmen – Strukturen an der Filmoberfläche und im Filminneren"

Dipl.-Phys. Heidrun Schüring
12.01.2004
"Mechanische und optische Untersuchungen freitragender smektischer Filme"

6 Visitors

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Moscow M. V. Lomonosov University, Russia
01.06. – 31.08.2003

7 Industry collaborations

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Hundsangen, Germany

Comtech GmbH
München, Germany

ISTAG AG
Research&Development Center
Egliswil, Switzerland

Freudenberg Dichtungs- und Schwingungstechnik KG
Weinheim, Germany

8 Patent application

Deutsches Patentamt, Nr.: 10 03 05 110.4-52
"Verfahren zur Feststellung wenigstens eines Zustandsparameters eines Dichtungssystems sowie Dichtungssystem"