



Program and book of abstracts of the

Joint Symposium of the

Belgian Group of Rheology

German Rheological Society

ProcessNet-Subject Division „Rheology“

Rheology – 360°

March 19-20, 2018

University of Luxembourg, Campus Limpertsberg



City of Luxembourg (Wikipedia)

The focus of the joint symposium of the DRG and the BGR are the rheological properties of complex fluids in all its aspects. Colloidal dispersions, polymer solutions and melts, filled systems and life science fluids are characterised by complex flow behaviour. The objective of this symposium is to present novel results in the fields of theory & simulations, experiments and applications. Contributions from both academia and industry are welcomed in order to touch flow phenomena of a wide variety of complex fluids.

<https://www.kwt-uni-saarland.de/de/buchungen/rheology.html>



Organizers

A. Tobias (ULuxembourg, LU), J. Baller (ULuxembourg, LU), U. Handge (HZG, DE), C. Wagner (USaarland, DE), N. Willenbacher (KIT, DE), P. Roose (allnex, BE), C. Clasen (KUL, BE), E. van Ruymbeke (UCL, BE).

Scientific committee

P. Moldenaers (KUL, BE), N. Reddy (UHasselt, BE), E. van Ruymbeke (UCL, BE), J. Baller (ULuxembourg, LU), U. Handge (HZG, DE), N. Willenbacher (KIT, DE), C. Wagner (USaarland, DE).

Program

The scientific program will start Monday 9 am and will end Tuesday around 3 pm and there will be a poster session.

Amherst Rheology Course

The traditional Amherst Rheology Course will take place just after the Symposium on March 21-22 at the same location.

Conference fee

The regular conference fee for participants from academics (industry) is 120 € (240 €) including two lunches and one dinner buffet. Reductions for early bird registration and PhD students are available.

Travel

Luxembourg is well connected by fast trains to Paris, Brussel and Cologne and there is an international airport. If you travel by train from southern Germany, you might want to consider a connection via France.

Accommodation

A contingent of hotel rooms is reserved until 31/01/2018 and the youth hotel until 31/12/2017.

Social program

On Sunday afternoon March 18 a guided tour through the lovely, historic city of Luxemburg will be offered for free. On Sunday evening we will organize a conference dinner that can be booked separately.

Information and REGISTRATION to the symposium and/or the rheology course:

<https://www.kwt-uni-saarland.de/de/buchungen/rheology.html>

Please note that at the same location, the **German Liquid Crystal Conference** will take place directly after the rheology meeting: <http://www.glcc18lux.lcsoftmatter.com>



The symposium is kindly supported by



Program - talks

Monday

09:00	Ewoldt	Randy	Invited: Intrinsically-nonlinear rheometry
09:45	Handge	Ulrich	Extensional rheology of polystyrene- <i>block</i> -poly(4-vinylpyridine) diblock copolymers in the melt
10:05	Lehr	Claudius Moritz	Investigation of structure formation under shear by Brillouin Light Scattering
10:25	Pötschke	Petra	Melt rheological behavior of PC/SAN blends selectively filled with CNTs
10:45			coffee break
11:15	Brossard	Gabriel	Interfacial rheology of triglyceride lipid emulsion
11:35	Kostrzewa	Monika	Role of calcium ion concentration on the mechanical properties of sodium alginate hydrogels obtained via Diffusion
11:55	Meeus	Yannick	On the rheology of mixed dough systems: when wheat flour meets rye flour
12:15	Bindgen	Sebastian	Dynamic properties of capillary suspensions: A molecular dynamics study using ESPResSo
12:35			lunch
13:35	Darras	Alexis	Superparamagnetic colloid's droplets evaporation under field
13:55	Kihm	Alexander	A neural network-assisted approach for RBC classification
14:15	Lang	Christian	Rheology of morphologically ideal and non-ideal rod-like colloids
14:35	Lindner	Anke	Oscillatory surface rheotaxis of swimming E. coli bacteria
14:55	Massaro	Roberta	Role of polymer matrix architecture on the rheology and flow induced microstructure of colloidal dispersions
15:15	Pleiner	Harald	Dissipative versus Reversible Contributions to Macroscopic Dynamics of Passive and Active Systems
15:35			coffee break
16:05	Zhang	Peng	Shear-thinning behavior of phosphonium ionic liquids: the roles of chain length and fluorination
16:25	Fiscina	Jorge Eduardo	Dissipation in sheared wet and dry sand under confinement
16:45	Qi	Fenglei	Granular flow rheology in a cylindrical Couette cell
17:05	Saker	Assia	Quantification of formulation effect on powder flowability via powder rheology
17:25	Vandewalle	Nicolas	Compaction dynamics as a test for the rheology of powders and grains
17:45	Brebels	Johnny	Luxinnovation
18:05	Weis	Clara	DRG Preisvortrag: Untersuchung des Phasenverhaltens kolloidaler Dispersionen mit schwach attraktiven Wechselwirkungen
18:25			Poster and walking diner

Tuesday

09:00	Franck	Aloyse	Invited: Review of the latest techniques to characterize complex fluids with rotational rheometers
09:45	Laeuger	Joerg	A New Shear-Induced Polarized Light Imaging (SIPLI) Technique and its Applications
10:05	Lettinga	Pavlik	Tuning shear banding in entangled DNA-polymer hybrids
10:25	Brenn	Günter	Measuring polymeric time scales from linear drop oscillations
10:45			coffee break
11:15	Fischer	Peter	Effect of oil hydrophobicity on adsorption and rheology protein adsorption layers at oil-water interfaces
11:35	Holzapfel	Bjoern	Characterization of entangled networks of wormlike micelles by combining light scattering and rheological techniques
11:55	Recktenwald	Steffen M.	Elongational flow behavior of surfactant solutions at low concentrations
12:15	Bharati	Avanish	Routes to develop self-compatibilizing polymer blends
12:35	Poster prize		
			lunch
13:35	Scheid	Benoit	New insights on draw resonance in the fiber spinning process
13:55	Wagner	Manfred H.	The Interchain Tube Pressure and the Effect of Oligomeric Solvents
14:15	Shahid	Taisir	The fast flow dynamics of polymer melts and solutions: Is it possible to achieve a universal scaling?
14:35	Sharma	Ashwinikumar	Effect of polymer architecture on viscoelastic properties of Thermoplastic Elastomers
14:05	Zhuge	Flanco	Shear and uniaxial extensional rheology of supramolecular entangled polymers
15:15			closing coffee

Poster

Huysecom	An-Sofie	Inducing electrical conductivity by tuning the phase-separated morphology and carbon nanotube network in bi-phasic polymer blends with free and crafted (co)polymers
Koekoekx	Robin	Embedding quantum dots in polymer particles via electrospraying
Rehor	Martin	Preconditioners for viscoelastic flows in FEniCS
Szántó	Levente	Trimodal PE-blends and its viscoelastic properties
van Ruymbeke	Evelynne	Decoding the linear viscoelastic properties of model telechelic metallo-supramolecular polymers
Ghiassinejad	Sina	Understanding the Dynamics of developed palladium-based slide-ring gels
Sharma	Atul Kumar	Understanding the Dynamics of developed palladium-based slide-ring gels
Barabé	Blandine	Rheology of doped depletion gels
Wierschem	Andreas	Aqueous salt-free xanthan solutions at high shear rates
Fischer	Steffen	Simultaneous stress and weight measurements for particulate films made from capillary suspensions
Köhn	Oliver	Applying an Extended Kalman Filter to extract bacteria statistics
Potisk	Tilen	Rheological properties of a ferromagnetic nematic liquid crystal
Van Ammel	Helene	Effect of nanoparticles at the droplet interface on the dynamics of a droplet subjected to shear flow
Handa	Rishab	Rheologically Probing and Predicting the Non-Linear Behavior of Functional Powders
John	Thomas	A Model for the Transient Subdiffusive Behavior of Particles in Mucus
Ratzsch	Karl-Friedrich	Deformation-controlled low-field Rheo-NMR
Van Aeken	Jasper	A new filament stretching device and the exploration of its capabilities and complementarity to existing techniques
Formenti	Susanna	The effect of polymer degradation on the evaluation of short relaxation times in ROJER experiments
Natalia	Irene	Shear dependent network orientation in capillary suspensions
Thagipour	Hamid	Universal Relaxation Behavior of Entangled Star Poly(hydroxybutyrate) Melts in the Transient Shear Startup

Rheology of doped depletion gels

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Gel like products are omnipresent in foodstuff, building and geological material. Their solid like properties enable them to bear their own mass and those of fillers, that may be added to increase the overall elastic properties of those viscoelastic systems.

Successive shearing events may decrease, or even suppress, particle-bearing properties¹. This may be the case when shearing the gel irreversibly changes its structure. Such effects are not desirable for consumer products, in which fillers should stay homogeneous in solution during process and shelf life.

For this reason, model systems are sought in order to understand better the recovery of gel macrorheological properties in the presence of inclusion(s).

Such yield stress fluids are often composed of attractive isotropic subunits, such as casein micelles.

Gel-like model solutions of attractive beads were obtained by inducing depletion interaction between poly(methyl methacrylate) colloidal hard spheres through the addition of linear polymer chains^{2,3}. Homogeneously dispersed large non-Brownian inclusions stably created doped depletion gels which were studied under shear.

The rate of formation of a stable gel structure following preshear was studied as a function of inclusions content. The properties of obtained gels were probed in the linear regime by small amplitude oscillatory shear test (SAOS). The increase of the elastic modulus was compared with literature for density matched inclusions. Moreover the influence of inclusion concentration on the non linear response of the gels and their recovery properties will be presented.

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Routes to develop self-compatibilizing polymer blends

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We describe a novel approach to develop self-compatibilizing polymer blends. This has been achieved by employing short unentangled PS polymers or long-functionalized PMMA-SH polymers in solution mixed P α MSAN/PMMA and PS/PMMA blends. The compatibilization effectiveness of the various polymers was demonstrated by their ability to segregate to the blend's interface, established from the decrease in the interfacial tension and coalescence suppression of PMMA droplets in 85/15 P α MSAN/PMMA blends. The time evolution of the ratio of volume average radius (R_v) to interfacial tension (α) was obtained during the application of a low shear rate on a blend in which a fine droplet size was first created with a preshear. The flow was stopped intermittently to determine the dynamic moduli in small amplitude oscillatory shear, which were then fitted with the Palierne emulsion model. The results in Figure 1 allow to gauge at the coalescence evolution and by combining the rheological information with the droplet sizes from STEM images, α could be estimated. The compatibilization efficiency of PS was verified to be independent of its end-group functionalization. The compatibilization efficiency of short PS polymers, segregated at the blend's interface due to entropic repulsion, was strongly contingent on their molecular weight (M_w). With increasing M_w of PS polymers beyond the entanglement molecular weight (M_e) of both PS and P α MSAN, a monotonous decrease in the compatibilization efficiency followed by negligible effects were observed. This was owing to the increased miscibility of the PS polymers with the P α MSAN matrix. A similar dependence of the M_w of PS on its compatibilization efficiency was observed in immiscible PS/PMMA blends. For polymers with M_w higher than M_e , functionalization allows to obtain compatibilization. The -SH end groups of PMMA steered the long polymers to interfacially segregate at the blend's interface. Their ensuing ability to effectively entangle with the PMMA droplets resulted in a pronounced increase in the compatibilization efficiency. The effects of the compatibilizers on the phase separation thermodynamics and kinetics were also investigated. Our highly robust novel compatibilizing routes will facilitate blend compatibilisation and trigger the use of compatibilized blends.

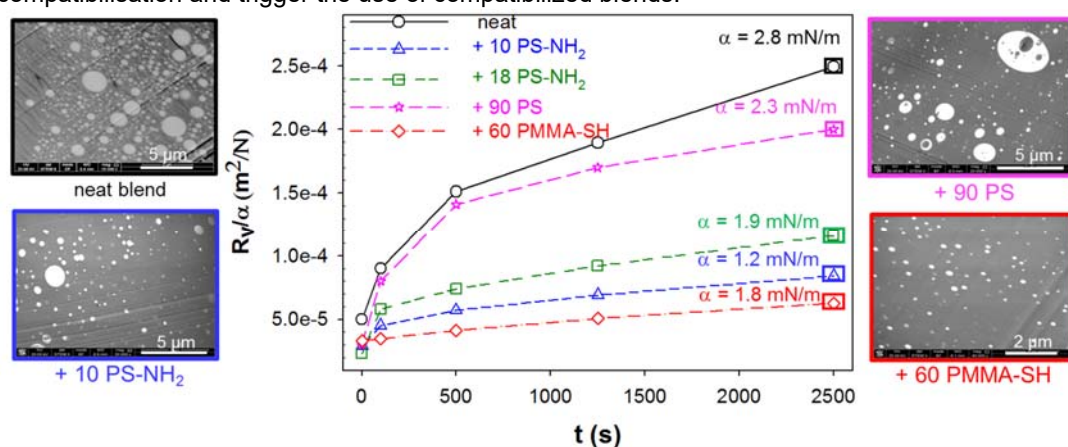


Figure 1: Dependence of the Palierne fitting parameter R_v/α (droplet radius/ interfacial tension) on the coalescence time for a neat bi-phasic 85/15 P α MSAN/PMMA blend and blends with 2 wt% short PS-NH₂ (10, 18 kg/mol), long PS (90 kg/mol) and long PMMA-SH (60 kg/mol). The number in the polymer name indicates its M_w . STEM images of the bi-phasic blends after the shear protocol are presented, as marked using color codes.

Dynamic properties of capillary suspensions: A molecular dynamics study using ESPResSo

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Capillary suspensions are a ternary liquid – liquid – solid system arising from the addition of a small amount of a second, immiscible liquid to a suspension. A sample spanning network is formed, which drastically alters the rheological properties of the suspension [1]. These properties can be tuned by adjusting the individual processing route as well as through the choice of the three components. Many in-vitro experiments have shown a strong influence of processing conditions on the rheological properties, implying a change in the micro- and network structure, however, a deterministic connection remains unknown [2][3]. Such a connection will open pathways for the rational design of materials with tunable properties.

We have developed a computational model for capillary suspensions in order to study the network formation process as well as the dynamic, rheological properties. Our model allows us to precisely tune microstructural parameters such as the liquid bridge volume and the ability of capillary bridges to rotate over the surface. We study the influence of these parameters on the resulting structure and shear moduli of the bulk material.

For our research, we use a model based on the open-source, coarse-grained, MD code ESPResSo [4], which includes rigid spheres and capillary interactions [5][6] as well as hydrodynamics. These hydrodynamic interactions are modelled via the lattice Boltzmann technique. A collision detection feature is used to construct the capillary bonds that connect individual spheres to form a network. Shear is introduced via Lees-Edwards (LE) boundary conditions [7][8]. The network analysis relies on both traditional techniques, e.g. the radial distribution function or the coordination number, and on new approaches derived from graph theory. We use the Python package networkx [9] for this purpose. We show that graph theory offers a new useful tool to quantify the interconnectivity of network sites via the clustering coefficient or the important sites for momentum flux by taking the minimum spanning tree into account.

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Measuring polymeric time scales from linear drop oscillations

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The oscillating drop method allows material properties of liquids to be measured from damped drop oscillations. The literature discusses, among others, the measurement of the liquid dynamic viscosity and the surface tension against the ambient medium, predominantly for Newtonian liquids. We use this method for measuring pairs of material properties of polymeric liquids. Pairs of properties may be measured, since the quantity measured is a complex frequency with a real and an imaginary part. For the measurements, individual drops are levitated in air by an ultrasonic levitator [1]. Amplitude modulation of the ultrasound drives shape oscillations of the levitated drop. When the modulation is switched off, with the levitating force maintained, the drop performs free oscillations which are damped due to the liquid viscosity. The density and the surface tension of the liquid are known. Our measurements intend to yield either two viscoelastic time scales with the zero-shear viscosity known, or one time scale and the zero-shear viscosity, with the other time scale known. The two time scales are the stress relaxation and the deformation retardation times. The latter is difficult to get for polymer solutions [2].

The drops are produced and placed in the acoustic levitator with an insulin syringe and imaged with a high-speed camera. The drop size is $O(2\text{mm})$, the oscillation frequencies excited by the ultrasound modulation are $O(120\text{Hz})$, close to the resonance frequency of the base-mode $m=2$ of the drops at their size, density and surface tension. After switch-off of the modulation, the drop returns to its equilibrium shape by damped oscillations. Aperiodic return of the deformed drop to the equilibrium shape of course cannot be a subject of our measurements. The data acquired from the images recorded are the angular frequency and the damping rate. For determining the pair of liquid properties, e.g. zero-shear viscosity and deformation retardation time, the frequency and damping rate are used as an input into the characteristic equation of the oscillating drop. These two properties of the drop oscillations are measured at the late stages of the damped motion, where deformations are small, so as to ensure linear flow accessible by the characteristic equation.

The present contribution presents results from a large set of measurements of the deformation retardation time. Liquids studied are aqueous solutions of poly(acryl-amides) of different degree of hydrolysis at varying concentration. The corresponding values of the zero-shear viscosity agree well with the values from shear rheometry. Values of the deformation retardation time differ substantially from the values commonly used in viscoelastic flow simulations. Furthermore, the measured values disagree with the predictions from the viscous-elastic stress splitting approach in linear viscoelasticity. With our study we will provide a consistent set of material properties for the Oldroyd-B model in linear viscoelasticity. This will be important for material modelling in viscoelastic spray simulations [2].

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Interfacial rheology of triglyceride lipid emulsion

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The interface of an emulsion is known to be complex by nature. Two non-miscible fluids have the tendency to reduce their interfacial area in order to minimize the overall system energy. Owing to surface active components this interfacial tension is reduced and colloidal interactions are imparted, leading to the stabilization of an emulsion and ensuring long term stability. For triglyceride lipid emulsions phospholipids and fatty acids compose the interface and provide stabilizing properties to the droplets. In the special case of Intravenous (I.V.) lipid emulsions used for parenteral nutrition, most of research on the cause of emulsion stability focused on the characterization of standard physicochemical properties such as surface tension, zeta potential and density (Komatsu, Kitajima, & Okada, 1995) (Yamaguchi, Nishizaki, Itai, Hayashi, & Ohshima, 1995). Such physicochemical properties are typically related to macroscopic quality attributes of the finished product, as an indicator for long term stability, but there are no absolute predictive rules. Currently, the tools to predict the stability and behaviour of an emulsion are limited, in particular when the interface is highly structured, and further interface characterization is required.

The aim of the present research is to explore the interfacial rheology of phospholipid based interfaces with triglyceride lipid oils. When a structured interface is formed, the linear viscoelastic properties reflect its microstructure (Fuller & Vermant, 2012). The viscoelastic properties of an interface have been shown to relate to interface stabilization as demonstrated by theoretical and experimental studies of several authors (Dicharry, Arla, Siquin, Graciaa, & Bouriat, 2006) (Krägel, Derkatch, & Miller, 2008) (Wang, et al., 2012). Viscoelastic properties provide resistance against the creation of pores as long as the interface remains saturated and thus impart resistance against coalescence. However, for I.V. lipid emulsions no information has been published on such interfacial rheological properties. In order to understand the I.V. lipid emulsion interface stabilization process, ageing experiments were performed to highlight the dynamics of the formation of a complex interface, using a double wall ring geometry (Vandebril, Franck, Fuller, Moldenaers, & Vermant, 2010). A screening of the key formulation factors was performed to evaluate the impact of temperature, time, surfactant concentration, presence of a co-surfactant and lipid formulation.

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Superparamagnetic colloid's droplets evaporation under field

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The evaporation of colloidal droplets is currently a topic of intensive research due to its wide range of potential applications, extending from blood analysis [1, 2] via inkjet printing, paint and polymers [3], up to and including nanotechnology [4]. The main feature of colloidal droplets evaporation is the so-called coffee-ring effect [5, 6]. This effect implies that particles tend to be deposited at the edge of the final dried pattern. However, several studies have shown various mechanisms preventing this effect. Notably, capillary interactions of ellipsoidal particles [7, 8] and the presence of surface-adsorbed polymers [9] allow a uniform coating of the particles. More recently, some researchers have shown that more complex deposits' structures can be achieved thanks to various concentration of liquid crystals [10]. In our research, we demonstrate how magnetic interactions between superparamagnetic colloidal particles can be used to control the properties of colloidal droplets' deposits. This actually requires the right chemical composition of the suspension. But then, a single suspension can result in various dried patterns. The actual pattern is selected from the application of an external magnetic field during the evaporation. To our knowledge, this is the first time that such a tunable control of evaporative deposits is described in the literature.

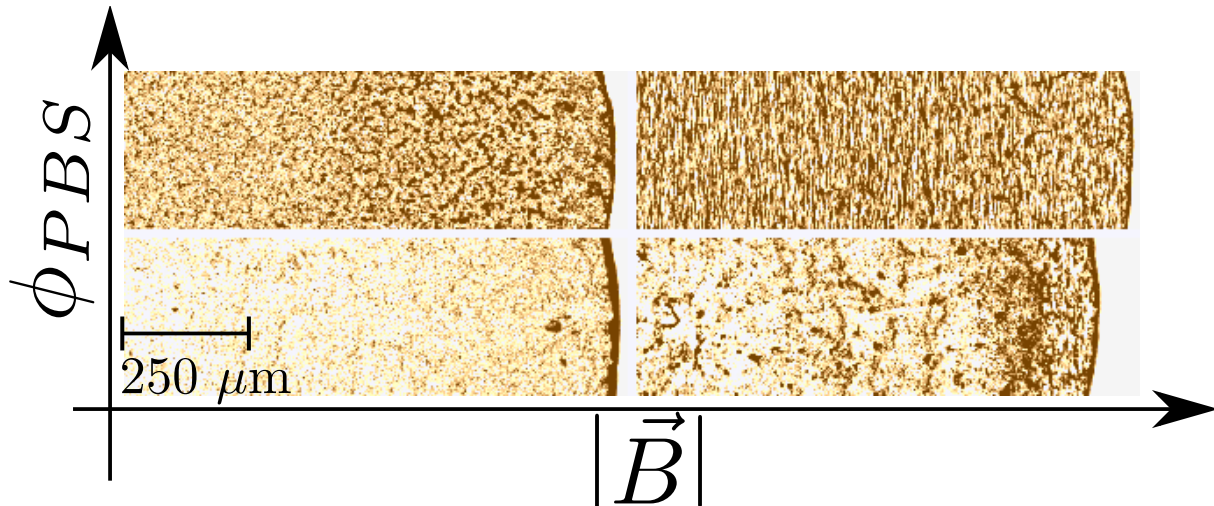


Fig. 1 : portions of dried drops deposits under different magnetic field, for different chemical compositions of the fluid.

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Intrinsically-nonlinear rheometry

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Nothing is truly linear. In rheology, linearity is only the first term of an infinite expansion. The higher order terms in this expansion are the intrinsic nonlinearities, which are present at any finite excitation. Here we acknowledge this for oscillatory rheometry. Although weakly nonlinear excitations are a fundamental characterization technique used in optics, acoustics, heat transfer, and other fields, rheometry methods have comparatively lagged in this area. This talk will review our contributions to intrinsically-nonlinear rheometry, also called medium-amplitude oscillatory shear (MAOS), a power-series expansion of large-amplitude oscillatory shear (LAOS). Recent progress has allowed for experimental and theoretical advances with significant implications for physical insight, structure-to-rheology understanding, microstructure inference, and constitutive model development.

Similar to linear viscoelasticity, i.e. small-amplitude oscillatory shear (SAOS), the four MAOS measures are functions of only frequency, not amplitude. Our theoretical contributions include complete definitions of all four MAOS signals and physical interpretations of these measures [1], derivations of universal aspects of their terminal regime signatures [2], and application to several microstructural classes of complex fluids and soft materials [3]–[8]. Experimentally, I will discuss best practices for measuring these properties and demonstrate methods of faster data acquisition using frequency sweeps [9]. As specific material examples, I will describe two cases: a supramolecular transient network polymer gel and a microgel suspension. In both cases, new models were developed to explain and fit data that no prior model could even qualitatively explain. The MAOS signature revealed the discrepancy, leading to new structure-to-rheology understanding.

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Effect of oil hydrophobicity on adsorption and rheology protein adsorption layers at oil-water interfaces

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The rheological behavior of protein layers at water-oil interfaces is critical to understand and predict emulsion formation and stability. Effects of ionic strength, pH, temperature and several pre-treatments are well-known. However, the oil phase has been regarded as exchangeable and its role in the protein adsorption mechanisms has been widely ignored. By measuring adsorption kinetic, dilatational and interfacial shear moduli, the influence of systematically selected oil interfaces of high purity on the formation and properties of β -lactoglobulin layers was evaluated [1]. A delayed protein solution injection enabled the measurement of the viscoelastic response of protein layer formation at an uncontaminated water-oil interface. It was found that depending on molecular size, flexibility, hydrophobicity, and polarizability of the oils, globular proteins adsorb distinctively. Stronger interactions of polar oils with the hydrophilic exterior of the native β -lactoglobulin lead to a decelerated protein unfolding [2]. This results in lower surface pressures and slower formation of viscoelastic networks. In addition, polar oils interact stronger with the protein network by hydrophilic bonding and thereby act as softening agents. The found effects of hydrophobic subphases on the adsorbed protein layers provide knowledge which promotes higher reproducibility in rheological studies and precise tailoring of interfacial films for an enhanced formation and stability of emulsions [3].

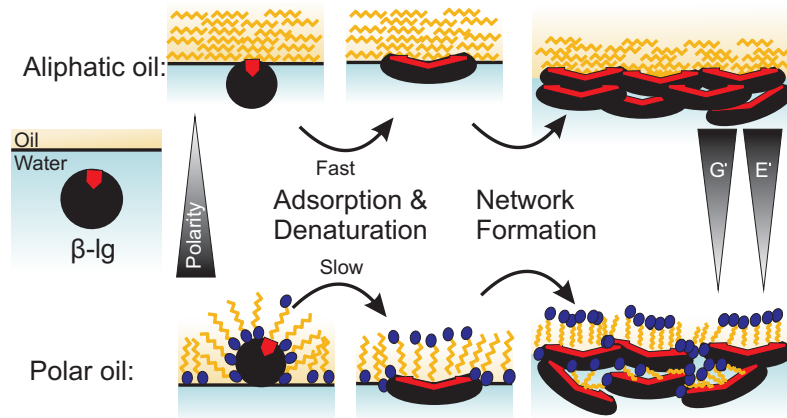


Fig. 1: Schematic of protein adsorption and denaturation at the interface of polar and aliphatic oils and its consequences on interfacial shear and dilatational rheology.

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Simultaneous stress and weight measurements for particulate films made from capillary suspensions

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Abstract for poster presentation

Cracking and particle mobility are a significant problem in the drying of films from hard sphere suspensions. One pathway to avoid these problems is by using capillary suspensions [1]. In the pendular state, the preferentially wetting secondary fluid forms capillary bridges between the particles. The capillary force from such bridges induces the formation of a sample-spanning particle network [2, 3], which limits the degree of particle motion during film drying, and the capillary force also counters the capillary force within pores generated by evaporation. Crack-free films can be produced at thicknesses much greater than the critical cracking thickness for a suspension without capillary interactions, and even persists after sintering. This method is applicable to a broad range of materials and can be easily implemented using well-established industrial methods.

A simultaneous weight and stress measurement of a drying film allows the direct correlation of changes in stress with the drying rate. The overall stress of a film can be measured using the cantilever deflection method [4] as the film dries in a temperature and humidity controlled chamber. Capillary suspensions, with a higher shear modulus, can lower the overall stress in the film while drying. Although no visible cracks occur in the films, a characteristic stress increase followed by relaxation occurs. Capillary suspensions change the shape of the stress profile from a slow stress rise followed by a rapid, uniform relaxation towards a more rapid rise followed by a two-stage relaxation, where the stress reduction in the second stage is significantly slower. When adding up to 2.5% water by volume as a secondary fluid, which increases the storage modulus by up to two orders of magnitude, the peak stresses are continuously decreased at various drying temperatures. Importantly, by increasing the chamber's relative humidity (RH) up to 20% the occurring peak stresses are generally lowered in the film. For the coatings made from capillary suspensions this can be explained by slower drying of the water bridges that restrict particle movement. Additionally, simultaneous weight measurements allow the calculation of the packing density of the drying film, which coincides with the peak stress. Films made with capillary suspensions show a more porous structure, directly correlating with a higher secondary fluid content i.e. more elastic suspensions.

The original particle volume fraction does not appear to have a significant impact on the peak stresses. At both high and low particle loadings, capillary suspensions can reduce these stresses over the pure suspension. The dry film density changes with particle loading, but is less densely packed for capillary suspensions.

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Dissipation in sheared wet and dry sand under confinement

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ABSTRACT

We investigated the stress strain behavior of sand with and without small amounts of liquid under steady and oscillatory shear. Since dry sand has a lower shear modulus, one would expect it to deform more easily. Using a new rheological technique to quasistatically push the sand through a tube with an enforced parabolic (Poiseuille-like) profile, we minimize the effect of avalanches and shear localization. We observe that the resistance against deformation of the wet (partially saturated) sand is much smaller than that of the dry sand, and that the latter dissipates more energy under flow. This is also observed in large amplitude oscillatory shear measurements using a rotational rheometer, showing that the effect is robust and holds for different types of flow.

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The effect of polymer degradation on the evaluation of short relaxation times in ROJER experiments

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Complementary to the CaBER technique, the Rayleigh Ohnesorge Jetting Extensional Rheometer (ROJER) is able to probe the extensional response of low-viscous weakly viscoelastic fluids [1], which are widely encountered in applications such as inkjet printing or spraying. A recent study has also pointed out that the thinning dynamics of weakly viscoelastic jets are governed by a slightly different force balance compared to static capillary bridges [2]. Hence, a scaling of $R \propto \exp(-t/2\lambda)$ has to be considered to determine the correct relaxation time in case of ROJER experiments, in contrast with the $R \propto \exp(-t/3\lambda)$ scaling classically employed in CaBER-type experiments. However, experimental results on dilute solutions of high molecular weight flexible polymers show even larger discrepancies between the relaxation times obtained from CaBER and ROJER experiments, which cannot be explained only by considering the different force balances.

This paper introduces an experimental study focusing on a possible reduction of molecular weight due to the high shear rates that polymer chains are subjected to in the jetting nozzle. Choosing high molecular weight dilute solutions suitable for both ROJER and CaBER experiments allows to compare the relaxation times obtained from jetting rheometry with static capillary breakup experiments performed both on fresh solutions and samples recovered after undergoing the jetting process. Systematic changes in the relaxation times are correlated to a decrease in molecular weight in the solutions after jetting as determined through gel permeation chromatography. In particular for the highest molecular weights, relaxation times calculated from ROJER experiments show a significant reduction compared to CaBER experiments on fresh samples, while they match CaBER results obtained on the solutions recovered after jetting. This degradation phenomena will be related to critical stresses experienced in the nozzle.

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Review of the latest techniques to characterize complex fluids with rotational rheometers

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Mid last century, the rheological characterization of complex fluid systems such as emulsion, suspensions, etc. was limited to steady shear measurements using rotational viscometers. The yield stress determination was based on modeling the steady state viscosity as a function of shear rate^{1,2}. In the seventies, controlled stress rheometers revolutionized the characterization³ of complex fluids. By means of an air-bearing, supported rotating motor shaft, it was possible to measure and control very small torques - thus a direct measurement of the yield stress became possible. Also with the introduction of real time correlation techniques, a major hurdle was removed allowing the evaluation of small amplitude oscillation measurements. Oscillation strain and frequency sweeps turned into key test method to characterize complex systems⁴. The next major development in rheometry came along with the need to analyze and understand the non-linear material response in LAOS (Large Amplitude Oscillation Shear) experiments. Fourier transform (FT) rheology is based on the analysis of the harmonic response to a simple sinusoidal strain or stress input^{5,6}. Other approaches are studying the time response of stress and/or strain directly⁷. From an experimental standpoint the challenge is to minimize the feedback of the non-linear material response on the input strain or stress. This effect is quite important for low viscosity fluids where instrument inertia correction is essential.

The latest technique developed and implemented in the rheometer for analyzing complex fluids is the orthogonal superposition (OSP) of a small amplitude oscillation shear on a continuous shear deformation. Small amplitude shear is used to characterize the underlying material structure changes as a function of time and shear rate^{8,9}. Orthogonal superposition poses real challenges to the instrument manufacturer. Currently the shear rate is applied in the angular direction and the small amplitude oscillation deformation in the axial direction of a modified double wall cylinder. Critical from an experimental standpoint is the axial force resolution (small signal) and cross talk between force and torque (decoupling the angular and axial direction). The advantage of the OSP technique is the fact, that a linear viscoelastic characterization is used to monitor material structure changes in the non-linear flow regime. When applying oscillatory deformations in both angular and axial directions, anisotropy in the sample can be probed while swiping the main deformation direction in the 2D deformation plane from the angular to the axial direction¹⁰.

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Understanding the Dynamics of developed palladium-based slide-ring gels

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The main objective in this project is to create, analyze and model slide-ring gels where the mobility and the density of the sliding cross-links can be finely controlled. In such gels, the polymer chains are held together by linked macrocycles (rings) forming a 8-shape, each of these rings having a polymer chain threaded into its cavity. Thus, the cross-links have the strength of covalent bonds but are mobile since the rings can slide along the polymer chains. Moreover, this will enable us to modify the sliding mobility of the rings by controlling the ring-thread interactions. To this end, a step by step synthesis protocol is followed in order to incorporate macrocycles (rings) along copolymers of linear poly(ethylene glycol) containing bulky end-groups in order to prevent the rings from unthreading[1].

In addition, in order to understand the dynamics of such systems, preliminary rheological studies were done. The viscoelastic properties of the samples obtained at each stage are then determined and analyzed with the help of the TMA (Time Marching Algorithm) tube model, in order to understand the role of the different components (chain extender, bulky end groups, rings etc) on the dynamics of the chains[2].

Starting from the experimental results, we then modify the tube model for linear entangled polymers in order to account for the influence of ring mobility, and possible ring associations on the dynamics of these systems toward our final goal to characterize and model the viscoelastic behavior of well-defined slide-ring gels.

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Rheologically Probing and Predicting the Non-Linear Behavior of Functional Powders

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Granular systems, often considered as the most used material in the industries, have attracted significant number of researchers. Correspondingly, powders have been given extensive commercial importance but lacks of fundamental research contribution. In this study, we have experimentally investigated the relationship between microstructural changes and the relative non-linear rheological response of dry and wet functional powders using large amplitude oscillatory shear (LAOS) rheometry. We have chosen three different powder systems; DynoSeeds-Silicon Oil, Lactosa (hydrophilic and hydrophobic), and Sand-Water. We show that wet and dry functional powders when deformed at large amplitude which is similar to industrial processing operation conditions, can undergo systematic internal microstructural changes. Further analyzing the contribution of higher harmonics (of LAOS response) to non-linear stress-strain response using Pipkin space, sheds light on flow induced microstructures. Such topological changes can significantly adjust the energy dissipation rate, allowing powders to exhibit dynamically rich flow characteristics, for example, dry powder flow slower than wet powder. Tuning non-linear structural relaxation of powder systems brings up myriad of possibilities to extend their processing limits and applications, significantly impacting on the qualitative and quantitative attributes.

Extensional rheology of polystyrene-*block*-poly(4-vinylpyridine) diblock copolymers in the melt

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The rheological properties of polymer melts in extensional flows are crucial for a variety of processing procedures such as polymer foaming, film blowing and blow moulding. Consequently, a series of investigations has focused on the flow properties of polymers in melt elongation, both from a theoretical and an experimental point of view. Strain-hardening of polyolefins in melt elongation is a prominent example how the molecular architecture influences the elongational viscosity of the melt. Whereas a series of works has been devoted to homopolymers, only a very limited number of publications has focused on the properties of microphase-separated block copolymers in extensional flows.

In this study, the properties of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymers in melt elongation are investigated [1]. In order to analyse the influence of block copolymer morphology on the flow properties, three different PS-*b*-P4VP block copolymers with a similar number average of the molecular weight were synthesised using the technique of anionic polymerisation. The weight ratio of PS and P4VP was varied such that the synthesised block copolymers were associated with three different types of morphology (spherical, cylindrical and lamellar). The analysis of the dynamic moduli (linear regime) reveals the appearance of composition (superposition of moduli) and interfacial effects caused by microphase separation. In stress-growth experiments, the measured transient shear and extensional viscosities agree with a value of three for the Trouton ratio within experimental scatter. Strain-softening appears for the diblock copolymers with a cylindrical and a lamellar morphology. For the diblock copolymer with a spherical morphology, respectively, strain-softening is only observed to a lesser extent. Our experimental data show that strain-softening of diblock copolymer melts can be adjusted by the composition of the diblock copolymer. In conclusion, microphase-separated diblock copolymers are characterised by strain-softening in melt elongation which is a counterpart to the well-known strain-hardening of polyolefins.

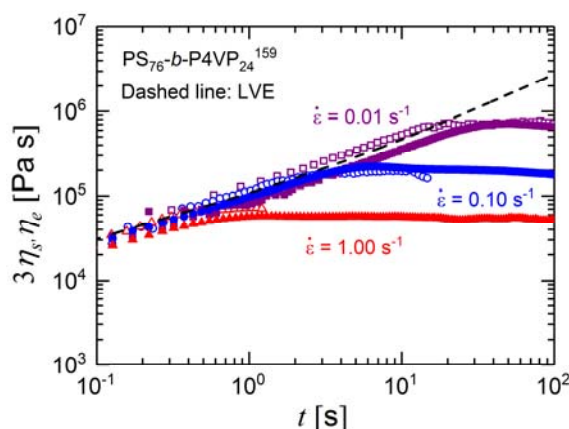


Fig. 1 Transient shear (multiplied by a factor of three) and elongational viscosity $3\eta_s$ and η_e of a PS-*b*-P4VP diblock copolymer (76 wt% PS, 24 wt% P4VP, $M_n = 159$ kg/mol) as a function of time t . The measurement temperature was 240 °C. The Hencky strain rate $\dot{\epsilon}$ is indicated. LVE means linear viscoelastic prediction.

Characterization of entangled networks of wormlike micelles by combining light scattering and rheological techniques

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Viscoelastic surfactants and their rheological properties in solution have been of considerable interest in recent decades. This is mainly due to the formation of entangled networks of wormlike micelles, which exhibit striking viscoelastic properties. Because micellar networks are, in contrast to polymer solutions, continuously breaking and reforming again, these surfactant solutions provide ideal model systems for advanced studies of fundamental principles of flow.

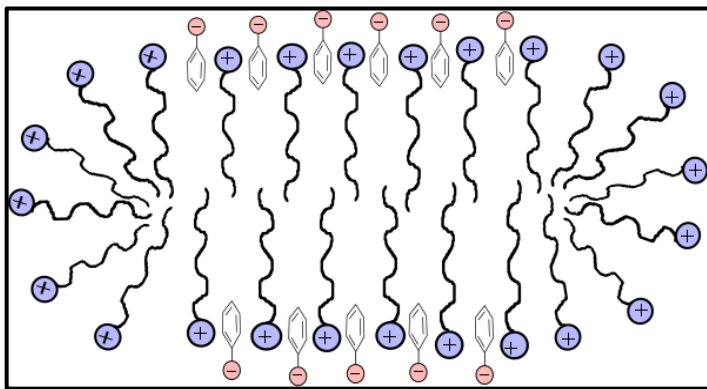


Figure 2 Stabilization of a rodlike micelle by benzoic acid derivate cosurfactants

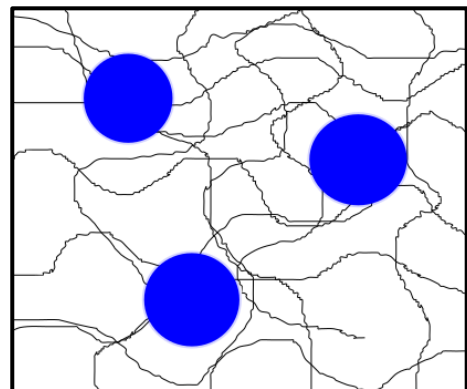


Figure 1: Tracer Particles trapped in entangled micelles

In a series of experiments we investigated different aqueous solutions of Cetylpyridiniumchloride at various Sodiumsalicylate concentrations. Commercially available micro-rheology software was used to evaluate values for the storage and loss moduli. In these experiments, we added tracer particles to the samples and observed the diffusion process of these particles. Furthermore we studied the autocorrelation function of the quiescent surfactant solutions which allowed further insights into the stress relaxation properties of these solutions. We also determined the zeta potentials for a series of co-surfactant concentrations in order to describe the elastic properties as a function of the ionic strengths and the salt concentration. We finally compared all these measured values with the rheological results obtained in commercial rheometers.

Inducing electrical conductivity by tuning the phase-separated morphology and carbon nanotube network in bi-phasic polymer blends with free and grafted (co)polymers

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We present novel routes to tune the phase-separated morphology and the percolated network of multiwalled carbon nanotubes (MWNTs) in 60/40 PMMA/PaMSAN LCST blends. The rheological and dielectric properties were monitored during phase separation to probe the morphological development and the MWNT network build-up. The steady-state microstructure of the phase-separated blends was verified by (S)TEM imaging. By altering the sample preparation method from melt to solution mixing, the improved dispersion of MWNTs reduced the rheological and electrical percolation threshold from 2 wt% in melt mixed blends to 0.5 wt% in solution mixed blends. Different novel compatibilizers were employed in order to stabilize and refine the blend morphology, including short PS-Br polymers, long SH-functionalized PMMA polymers and short PS-PMMA block-copolymers with distinct molecular weight and asymmetry. The interfacial segregation of the (co)polymers during phase separation resulted in different morphologies based on the ability of the (co)polymer to entangle with the blend components, the presence of steric hindrance and the (co)polymer asymmetry compared to the curvature of the blend interface. The kinetic competition between the migration of the (co)polymers to the blend interface and the migration of the MWNTs to the energetically preferred PaMSAN phase governed the MWNT localization. They ended up either in the continuous PaMSAN phase, at the blend interface or in the dispersed PMMA phase, thereby giving rise to different paths for charge transfer. Irrespective of the compatibilizer type, the electrical percolation threshold of solution mixed blends was further reduced from 0.5 wt% to 0.15 wt% in presence of 2 wt% of compatibilizer. As an alternative, chemically grafting the different compatibilizers onto the surface of the MWNTs further tuned the localization of the MWNTs and the formation of conductive pathways in one of the phases or along the blend interface. This allowed the formation of a percolated 0.15 wt% MWNT network at reduced compatibilizer concentrations of 0.1 wt% or less without severely affecting the intrinsic conductivity of the MWNTs. However, the limited amount of compatibilizer, combined with the interfacially localized MWNTs, exhibited less refinement ability as compared to 2 wt% of isolated compatibilizer (see Figure 1). Our novel routes could steer the development of polymer blends with tailor-made morphologies and highly specific percolated networks of conductive nanofillers at ultra-low concentrations.

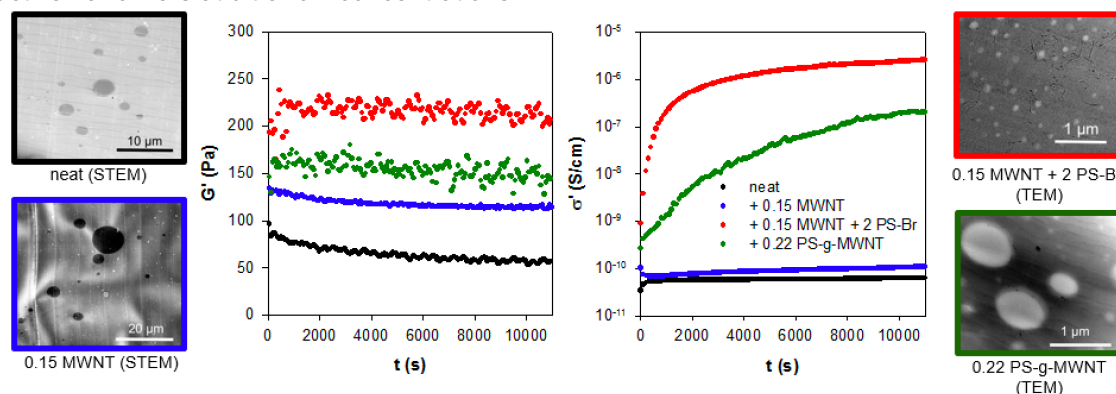


Figure 1: The elastic modulus G' (at 0.1 rad/s) and the conductivity σ' (at 1 Hz) versus time t during phase separation for a neat 60/40 PMMA/PaMSAN blend, a blend with 0.15 wt% MWNT, a blend with 0.15 wt% MWNT and 2 wt% short PS-Br (6 kg/mol) and a blend with 0.22 wt% PS-g-MWNT (equivalent to 0.15 wt% MWNT and 0.07 wt% PS). (S)TEM images of the steady-state morphology after phase separation are marked using color codes. The darkest phase represents PaMSAN.

A Model for the Transient Subdiffusive Behavior of Particles in Mucus

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In this study we have applied a model to explain the reported subdiffusion of particles in mucus, based on the measured mean squared displacements (MSD). The model considers Brownian diffusion of particles in a confined geometry, made from permeable membranes. The applied model predicts a normal diffusive behavior at very short and long time lags, as observed in several experiments [2,3]. In between these time-scales, we find that the “subdiffusive” regime is only a transient effect, $MSD \propto \tau^\alpha$; $\alpha < 1$. The only parameters in the model are the diffusion-coefficients at the limits of very short and long times, and the distance between the permeable membranes L . Our numerical results are in agreement with published experimental data for realistic assumptions of these parameters. Finally, we show that only particles with a diameter less than 40 nm are able to pass through a mucus layer by passive Brownian motion.

This work was published as

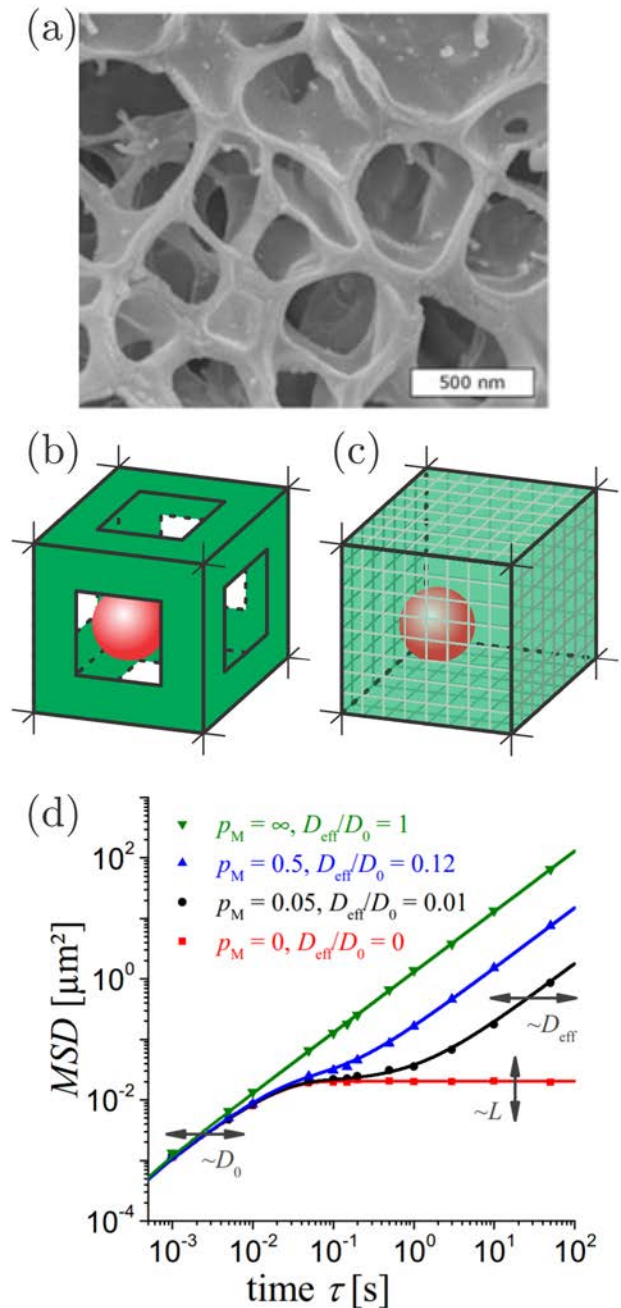
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Fig. 1(a) Scanning electron microscopic image of horse pulmonary mucus [1]. (b) single cube with reflecting walls and open windows. (c) simplification a cube with permeable membranes. (d) predicted $MSD(\tau)$ with a transient subdiffusive behavior for increasing membrane permeabilities, from free diffusion down to fully reflection (upper to lower).



On the macro and micro rheology of supramolecular self-assembled new bi-component system

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We present a new low molecular weight bi-component gelator system which self-assemble, via supramolecular interactions in water to furnish gel behavior. This gel possess unusual viscoelastic behavior which might be useful for tissue engineering or can be used for soft electronics as tactile or heat sensors. At lower concentration this gel exhibits shear thickening behavior and with the increase in concentration this shear thickening behavior diminish and at 5% wt/vol it shows typical shear thinning behavior. Also it was found that upon increase in concentration of equimolar bi-component gelator from 1.5% wt/vol to 7%wt/vol E moduli increases form ~ 100 Pa to ~ 1000 Pa. Alongside zero shear viscosity η_0 and modulus calculations form rheological data also found to be concertation dependent which is from ~ 100 Pa.s to 100000 Pa.s and ~ 20 Pa to 6000 Pa respectively, this happens due to unique micro structure of gel shown in figure 1. Also Optical Micro rheology is used to determine the microstructure and micro rheological properties of gels at different concentration. Morphology of gel was determined via cryo-sample preparation SEM, found to contains pores lamella stacked over each other interconnected via filaments or ribbons. Gels obtained from alteration of composition of bi-component at fix concentration 5%wt/vol provides different type of morphology and rheological properties with different responses overs stress. In the end we use ^1H NMR to determine the molecular interactions in gel which was responsible for such unique morphology and rheology.

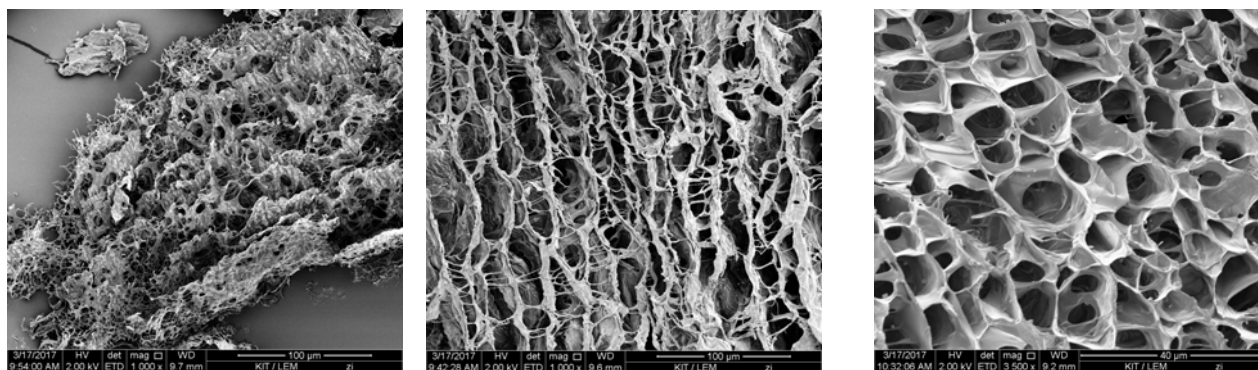


Figure 1: SEM images of bi-compoenet hydrogel showing pores lamella stacked over each other and interconnected via filaments and ribbons

A neural network-assisted approach for RBC classification

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Over the past decades, neural networks (NN) have proven to be a mighty tool for object classification issues. Although omnipresent in technical signal processing (such as e.g. recognition of traffic signs), it is not widespread in life science disciplines. We therefore present an NN-based approach for classifying biological cells, specifically red blood cells, in flow. Our experimental setup consists of in-vitro microcapillaries, being a ubiquitous tool for mimicking human capillary red blood cell (RBC) flow. These microcapillaries are linear channels with a length of 4cm and a cross-section of ca. $10\mu\text{m} \times 12\mu\text{m}$. A dilute suspension of erythrocytes is injected in these channels with a varying pressure drop, imposing different flow regimes, as in [2]. For a discrete set of pressure gradients, image sequences are recorded and post-processed with a particle-tracking algorithm. Further, we crop a picture for each flowing single cell and classify their shape into three categories: Slippers, croissants, and others. Slippers are characterized by an elongation in flow direction and an offset from the channel-axis. Croissants, in contrast, are symmetric shapes, their center being on the channel-axis. Others are all cells distinct from these two classes.

The huge amount of collected data demands for an automated analysis of images, and due to the complexity of the problem, we decided the use of NNs. Therefore, valuable training data, i.e. perfect slippers and perfect croissants have to be chosen to receive a performant NN in the end. We present a phase diagram of flowing RBC, performed by an eminent automated analysis and evaluated by reference on manual classification. However, the final neural network can be used for further tasks in classification of living cells.

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Embedding quantum dots in polymer particles via electrospraying

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Quantum dots (semiconductor nanocrystals) gain large research interest in the last decade due to their exceptional electronic and optical properties such as very narrow but tunable fluorescence spectra, high brightness and strong resistance to photobleaching. This makes them an excellent solution for a multitude of applications ranging from replacements for dyes to new types of displays. Due to the nature of their building blocks (in this case CdSe core and CdS shell), quantum dots generally exhibit negative properties like cytotoxicity, low stability in an oxygen-rich environment and poor biocompatibility, which limits their current use. One way of solving those issues, is to embed a certain amount of QDs in polymer micro-/nanoparticles, which shields them from their surroundings. Electrospraying is an effective one-step method to produce such particles due to its relative simple setup and high encapsulation efficiency. The main principle of this technique involves the addition of surface charge to a polymer solution jet to induce a forced break-up into droplets, resulting in micro- to nanometer-sized particles after fast solvent evaporation during the droplet trajectory towards an oppositely charged collector. Maximizing the polymer load for an effective encapsulation while maintaining and controlling the flow properties of this process requires, however, an understanding of the rheological properties of the nano-particle/polymer solution/suspension.

In this paper, a block-copolymer of polystyrene endblocks and a large polyethylene-butylene midblock (SEBS) was selected as carrier due to its favorable interaction with the CdSe/CdS quantum dots, which results in final particles where the quantum dots are well dispersed. The applied solvent system is of extreme importance for the morphology of the final product. SEM imaging reveals completely different particle shapes when SEBS in a single solvent is electrosprayed or in a double solvent system, where a fraction of DMF is added. The mechanism responsible for this transition in morphology has been investigated by inspecting the elongational properties of the solutions by the recently developed dripping-onto-substrate (DOS) method. Finally, the fluorescence characteristics of the final quantum dot embedded polymer particles have been investigated by spectrophotometry.

Applying an Extended Kalman Filter to extract bacteria statisticsO Köhn¹, T John¹, C Wagner¹¹AG Wagner, Universität des Saarlandes, 66123, Saarbrücken, Germany

Bacteria tend to swim in liquids in absence of food facilitated by creation of flagella. The trajectories are determined by slightly curved lines (running states) and randomly interrupted by short intervals with strong direction changes (tumbling state)[1]. This behavior seems to be efficient in finding food in unknown environments. We assume an intrinsic randomness in the running states as well in the appearance of the tumbling intervals.[1] Furthermore in real experiments the extracted positions are influenced by a detection noise. Estimating the stochastic trajectory properties requires the distinction between bacteria intrinsic randomness and the measurement noise. From the engineers it is known that the Kalman filter algorithm provide this in an optimal way [2]. We adapted and implemented this filter for simulated as well as measured bacteria trajectories.

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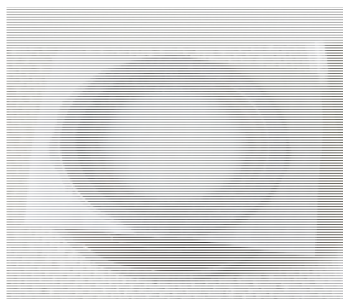
ROLE OF CALCIUM ION CONCENTRATION ON THE MECHANICAL PROPERTIES OF SODIUM ALGINATE HYDROGELS OBTAINED VIA DIFFUSION

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Efficient separation of proteins from urine is crucial for early diagnosis of kidney diseases. Gel permeation chromatography using alginate hydrogels as membranes is an established method for protein separation. Asymmetric flow field fractionation is a cheap alternative. However, due to the low reproducibility, this hydrodynamic separation method is not widely employed. The separation efficiency, however, may be greatly improved by placing an alginate hydrogel layer as an additional membrane in the flow channel. The gelation of alginate can be carried out in an extremely mild environment using non-toxic reactants such as the divalent cation Ca^{+2} . However, due to the very rapid and irreversible binding of the calcium ions, it is impossible to obtain a homogenous gel by simply adding Ca^{+2} to the alginate solution. Using the diffusive way of alginate crosslinking (Fig 1a), we prepared alginate hydrogels at different calcium concentrations, characterized by smooth and uniform surfaces (Fig. 1b). These hydrogels were rheologically characterized using an Anton Paar MRC 502 rheometer. Small amplitude oscillatory shear measurements were carried out using a plate-plate configuration with sandblasted surfaces. We found that the dynamic moduli are largely frequency insensitive, indicating weak gel-like behavior. Furthermore, their magnitudes are proportional to the calcium ion concentration. Additionally, the swelling behavior was examined in buffer solutions with varying salt concentrations and under the presence of an electric field. The swelling ratio defined as the relative change in dry weight after immersion [1] gives information about the inertial structure of the formed hydrogels (i.e., crosslink density) and the interactions between the polymers chains and the solvent. Interestingly, the swelling behavior of the alginate hydrogels strongly depends on the ratio of Ca^{+2} to monovalent ions present in the buffer solutions. The maximum swelling was attained at an ion ratio of 0.7. Moreover, the electric field affected the swelling behavior of the alginate hydrogel showing a relationship between the swelling ratio and the applied current. In summary, intact alginate hydrogel layers with a high swelling ratio could be formed via diffusion. Current research focuses on the application of such layers in asymmetric flow field fractionation with and without the presence of an electric field.

a)



b)



Fig 1. Gelation of alginate hydrogel via diffusion using a saturated with Ca^{2+} filter paper (a) and the final gelled homogenous alginate (b)

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A New Shear-Induced Polarized Light Imaging (SIPLI) Technique and its Applications

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Rheological methods reveal information on macroscopic material properties. However, the mechanical material properties are strongly dependent on the underlying microstructure. Therefore information on the microstructure is often valuable for a better understanding of the rheological behavior. Simultaneous use of rheological and optical techniques, i.e. of rheo-optical methods, is helpful to gain a better understanding of the dependencies between the microstructure and the mechanical properties of complex fluids. Different optical methods such as small angle light scattering, microscopy (polarized, fluorescence, confocal), spectroscopy (NIR, IR, Raman), birefringence and dichroism, as well as pure visualization techniques have been employed. In this paper, applications of a new rheo polarized imaging techniques will be discussed [1]. SIPLI (shear induced polarization light imaging) combines a visualization technique with measurements of local stresses through the detection of the birefringence. By employing parallel-plate geometries, different shear rates exist throughout the sample, from a maximum shear rate at edge of the sample to a zero shear rate in the center of the plate. With SIPLI the whole plate is observed and the birefringence can be displayed over the full range of shear rates within one single experiment. The figures show the schematic, a photo of the SIPLI setup and as an application a strain sweep on a gel like DNA-solution with the corresponding images. As the strain exceeds the limit of the linear region the molecules are stretched leading to a birefringence which can be detected by the SIPLI technique as can be seen in Figure 3.

Applications of the method are presented including simultaneous SIPLI and the rheology of the oriented lamellar phase of block copolymers, liquid crystals, cellulose and block copolymer solutions, as well as a study of the thermally-induced reversible transformation of worm-like micelles to spherical micelles.

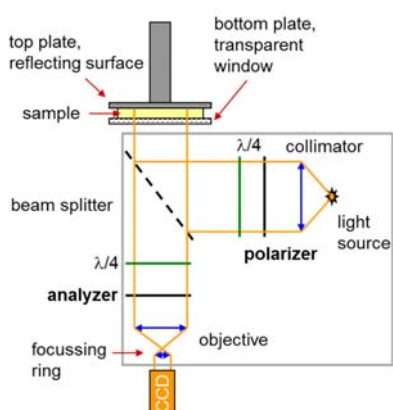


Figure. 1. Schematic of SIPLI setup

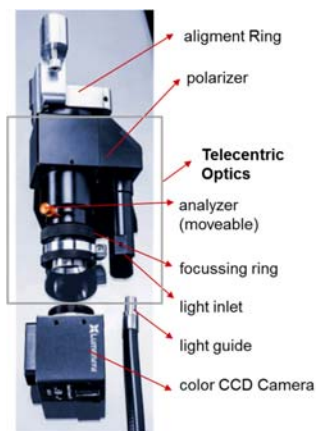


Figure. 2. Optical parts of SIPLI setup

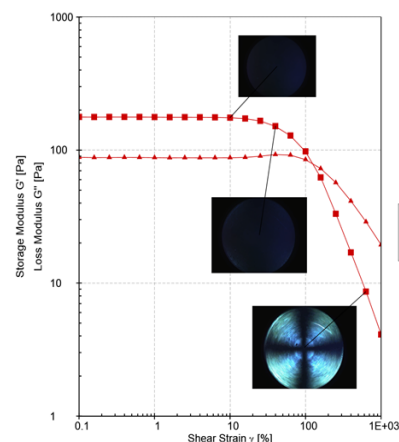


Figure. 3. Strain Sweep and corresponding SIPLI images

Rheology of morphologically ideal and non-ideal rod-like colloids

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Non-spherical nanoparticles are abundantly present in nature, e.g. in the form of F-actin constituting the cytoskeleton, and play a significant role for many industrial applications such as strong fibers and structured consumer products.

The mechanical properties of complex fluids containing rod-like colloidal particles are hugely affected by flow via the particle orientation. The morphology of rods, thereby, plays a key role in the microscopic behavior which leads to the macroscopic rheological response.

We will present the linear and nonlinear rheological behavior of such rod-like colloidal suspensions with differing well-controlled morphology. For this purpose, a library of naturally monodisperse rod-like bacteriophages, ranging from 0.33-2.1 μm in contour length, from 6.6-18 nm in thickness and 1.2-9.1 μm in persistence length is used. The rheological characteristics in steady state shear flow are measured using a combination of rheology and small angle neutron scattering [1]. We resolve the orientational ordering of rods during steady state shear flow in 3 dimensions, allowing for an in depth comparison with Smoluchowski theory [2]. Figure 1 shows orientational (a) and rheological (b) master curves for all systems. Parts of the relaxation time spectrum for colloidal rods in the semi-dilute concentration regime are revealed by small angle oscillatory shear, comparing well with Morse theory [3]. Capillary breakup extensional rheometry is used to determine the flexibility and concentration dependent Trouton ratio of rod-like colloidal suspensions in the high flow rate regime. Results of the elongational rheology agree well with the theories by Batchelor [4] as well as Shaqfeh and Fredrickson [5].

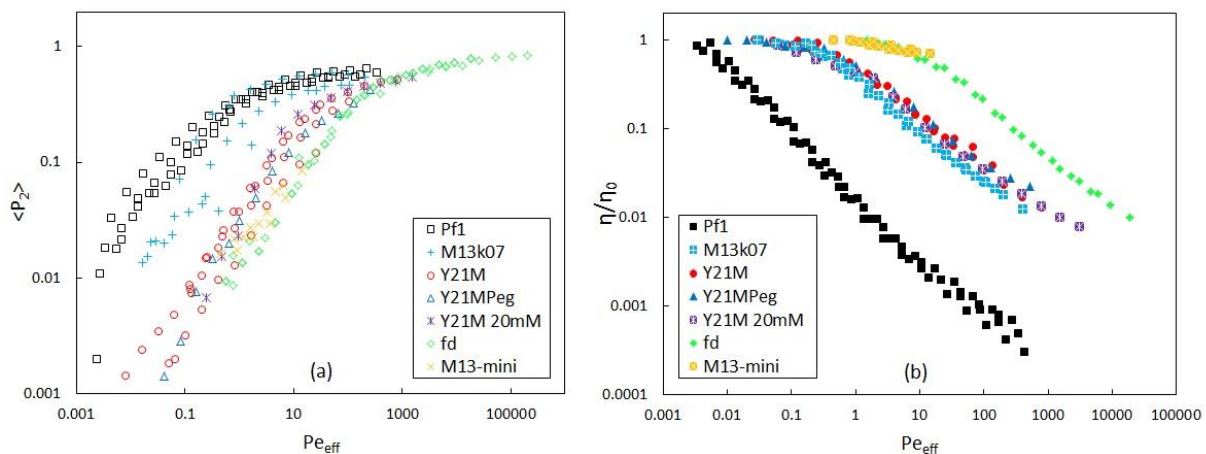


Fig. 1 (a) Orientational order parameter and (b) relative shear viscosity as a function of effective Peclet number.

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Investigation of structure formation under shear by Brillouin Light Scattering

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Many materials such as polymers, liquid crystals or suspensions which show isotropy in macroscopic physical quantities build up internal structures when exposed to a shear field. These internal structures lead to anisotropic macroscopic properties which can e.g. be observed in the dependency of the elastic moduli or the complex viscosity on the applied shear stresses. Classical rheology alone does not allow to link changes in complex viscosity to the formation of internal structures. Polarizing Light Microscopy, Dynamic Light Scattering and Small Angle X-Ray or Neutron Scattering are often combined with rheology to shed light on this relationship. With this contribution we present a new approach to assess the formation of structure under shear: Brillouin Light Scattering. In our setup, elastic moduli are measured at high frequencies simultaneously to the application of shear stress to a viscoelastic sample. Brillouin Spectroscopy is a contactless technique which allows to determine the full elastic tensor of liquid, viscoelastic or even solid samples. In this contribution, the experimental technique as well as very first measurements are presented.

Tuning shear banding in entangled DNA-polymer hybrids

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Shear banding, where a sheared fluid separates in regions of different shear rate and viscosity, is ubiquitous in complex fluids, but the molecular mechanisms underlying this behaviour only partly understood. In entangled polymer system, for example, the existence of shear banding would overturn the well-known Tube theory [1]. Moreover, there is considerable debate whether shear banding observed in entangled polymers can be considered as a steady state [2].

We report here that the flow behaviour changes from well-defined banded flow to almost linear flow for entangled poly-electrolyte system, by tuning the interaction between chains. To this end, we perform velocity profiling experiments on xanthan[3] and DNA as a function of the ionic strength. Moreover, we grafted short PNIPA (Mw=3k) chains on the DNA backbone at a relatively low grafting density, thus being able to tune attraction by increasing the temperature around the Lower Critical Solution Temperature (LCST). The grafting PNIPA does not change the flow behavior of DNA at temperature lower than its LCST. At higher temperature than LCST, where the PNIPA undergoes coil-to-globule conformation change, the velocity profile becomes almost linear. We observe this suppressed shear banding also when adding salt to the bare poly-electrolytes. These observations suggest that shear banding in polymers is suppressed by retraction force and we show how this is connected to a widening of the interface between bands.

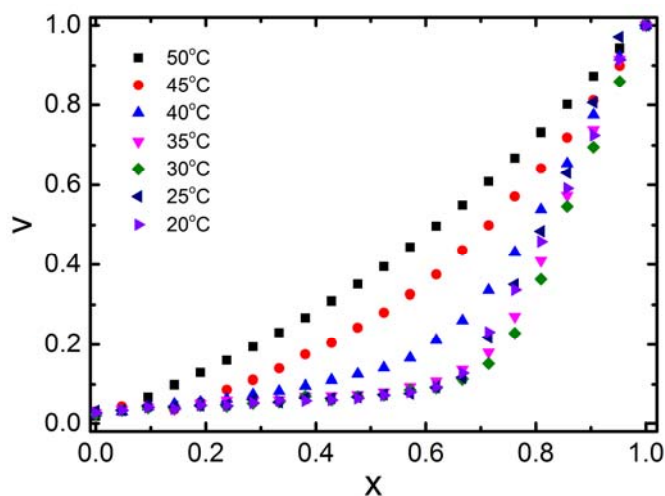


Fig. 1 Velocity profiles of PNIPA coated DNA at the same shear rate of 50s^{-1} at different temperatures

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Oscillatory surface rheotaxis of swimming *E. coli* bacteria

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We demonstrate experimentally and theoretically the existence of oscillatory rheotaxis by *E. coli* bacteria at surfaces under flow. Three transitions are identified with increasing shear rate: From circular to straight upstream motion, the emergence of oscillations at tuneable frequencies, and finally coexistence of rheotaxis along the positive and negative vorticity directions. We develop a model to explain these transitions and predict the corresponding critical shear rates. Our results shed new light on bacterial transport in flow networks and strategies for contamination prevention.

Role of polymer matrix architecture on the rheology and flow induced microstructure of colloidal dispersions

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The balance of hydrodynamic and interparticle forces determines the microstructure of colloidal dispersions and their macroscopic behavior under flow. When the suspending medium is a polymer melt, polymer-mediated forces between particles such as depletion and bridging must be taken into account. Both are attractive and lead to the formation of flocs and, eventually, to percolation and gel formation at higher concentrations. Flow can induce structural changes, which manifest in a variable viscosity that, if reversible and time dependent, leads to a thixotropic behavior of the system. The time scales associated with this structuration are typically longer than the classical viscoelastic time scales of the components but faster than other slow phenomena as ageing or degradation. In many relevant thixotropic systems, the suspending medium is viscoelastic. In that case there will be a competition between the time scale associated with the particulate network and the time scale associated with the inherent viscoelasticity of the matrix. The role of a viscoelastic medium was investigated here experimentally by studying model colloidal particles in polymeric media of different architecture. First, the initial states of the dispersions were quantified based on the high frequency rheometry to measure the effective hydrodynamic volume fraction of the aggregates. Second, a high speed rheo-confocal microscope, equipped with structured illumination optics, was used to study the structural evolution during steady state and transient flows. By using a counterrotating rheometer mounted onto the confocal the changes in microstructure as well as the rheology could be followed. In this manner the contributions to the stress of the different components in dispersions in polymeric matrices have been studied as a function of polymer matrix architecture.

On the rheology of mixed dough systems: when wheat flour meets rye flour

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As a large part of the population worldwide is being confronted with a variety of dietary health problems, time has come to tackle these problems by providing people with the possibility to improve their daily nutrition. The development of highly nutritious breads, e.g. containing a substantial fraction of rye, could play a pivotal role in facing these diet-related health problems, due to the significant contribution bread has to the human diet.

This study investigates the rheological (flow) behavior of dough blends consisting of wheat and rye flour. It aims at obtaining doughs with a high breadmaking potential and a satisfactory nutritional profile. In addition, wheat flour, which basically consists of starch granules and gluten proteins, was diluted with starch to gain insight in the effect of a pure decrease in wheat gluten content and the resulting changes in rheological behavior. Small-amplitude-oscillatory-shear measurements and uniaxial extensional measurements characterize the linear and the non-linear rheological behavior of the dough respectively.

It was observed that with an increasing percentage of rye flour in the blend the consistency of the doughs was increased, represented by an upward shift of the dynamic moduli in the oscillatory measurements. In a similar manner, the linear viscoelastic envelope observed during the extensional tests was moved upwards with increasing rye content. The extensional tests also showed that the transient extensional viscosity at a maximum strain of 2.9 was not influenced by the ratio of wheat to rye flour. Despite these observations, a dough blend consisting of 60% rye and only 40% wheat still produced strain hardening behavior. In contrast to the replacement of wheat by rye flour, it was found that as wheat was systematically replaced by pure starch the transient extensional viscosity at maximum strain decreased. The results show how uniaxial extensional measurements can be used to evaluate the rheological behavior of blended dough systems with non-wheat grains. Furthermore, the study clearly demonstrates that as wheat becomes diluted by non-wheat grains as in multi-cereal dough blends, other dough components can compensate for the decrease in wheat gluten content and the accompanying changes in rheological behavior. Future research aims at identifying these dough components, one possibility being the arabinoxylan fraction.

Shear dependent network orientation in capillary suspensions

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The addition of small amounts of an immiscible secondary fluid to a suspension can dramatically change the rheological behavior of the suspension by inducing particle gelation or by reinforcing a weak network [1]. This transition is caused by strong attractive capillary force between the particles and two fluids producing a sample-spanning network. Capillary suspensions exist in two states: a pendular state when the secondary fluid preferentially wets the particles, and a capillary state when the bulk fluid is preferentially wetting.

These capillary suspension networks demonstrate a negative normal stress difference, from re-orientation of the flocs into the vorticity direction during shearing. Typically, systems with negative normal stress differences have either high volume concentrations ($\phi \sim 58\%$) and are shear thinning, or are shear thickening with very low particle concentrations ($\phi \sim 0.09\%$) [2, 3]. In contrast, the capillary suspensions we report here have a 25% solid concentration and are shear thinning; a combination that has never before been reported in literature.

To investigate the network build-up systematically, we use strain rate sweep measurement with decreasing shear rate and report the corresponding normal stress differences. In the pendular state, the system undergoes a transition from a positive normal stress differences at the high shear rates to negative normal stress at the low shear rates. This phenomenon occurs due to the motion of particle networks, where the hydrodynamic force dominates and the flocs break-up at high shear rates. The remaining dimers and trimers tumble in the flow-gradient plane (Jeffrey orbits) and experience friction as they come into contact due to the capillary force. The network reforms and the size of the flocs grow as the shear rates decreases. The long, asymmetric flocs rotate to reorientate in the vorticity direction and this leads to a negative normal stress differences. Furthermore, we compare the rheological properties and images from confocal microscopy during shearing to gain insight into the network microstructure.

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Dissipative versus Reversible Contributions to Macroscopic Dynamics of Passive and Active Systems

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We discuss the time-reversal behavior of dynamic cross-couplings among various hydrodynamic degrees of freedom in passive and active liquid crystal systems. Using a standard hydrodynamic description including linear irreversible thermodynamics we show that the distinct thermodynamic requirements for reversible and irreversible couplings lead to experimentally accessible differences. We critically compare our descriptions with those of existing standard continuum mechanics theories [1] and popular active system models [2,3], where time-reversal symmetry is not adequately invoked.

For passive system this concerns the dynamics of Lehmann-type effects in chiral liquid crystals. If both, the direct and the inverse Lehmann effect is measured for the same system, one can verify that these effects are based on the irreversible, rather than the reversible part of the dynamics [4]. A second example is the dynamic magneto-electric response in ferromagnetic nematics [5], where the different behavior under time reversal of the nematic director and of the magnetization leads to characteristic, experimentally detectable features that have not been found by a continuum mechanics approach.

Macroscopic descriptions of active nematic systems show a direct coupling of the stress tensor with the order parameter, often called “active term”. Recently, we showed [6] that such terms can occur in active as well as passive systems, depending on whether the variables that give rise to those cross-couplings in the stress tensor, are driven internally, or externally, or not at all. In any case, however, they are reversible and come with a counter term that ensures zero entropy production. Therefore, they cannot drive the system. On the other hand, if counter terms are neglected, the “active term” leads to non-zero entropy production and acts as an additional, albeit dubious driving force.

In active polar systems the existence of a finite velocity in the stationary state is a clear indication of the non-equilibrium situation due to the internal driving force. The active transport term reflects non-equilibrium, but, like any transport term, cannot drive the system out of equilibrium, since it is reversible with zero entropy production [7]. In the literature, e.g. in the Toner-Tu model as presented in [3], dynamic polar order is often described by a polarization vector, which is even under time reversal. Thereby, the active transport becomes dissipative and leads to a non-zero entropy production that drives the system. The physical origin of this additional, inadvertent driving force is dubious.

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Rheological properties of a ferromagnetic nematic liquid crystal

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It has long been known that suspensions of ferromagnetic nanoparticles in a nematic liquid crystal could induce a ferromagnetic liquid crystal phase [1]. Only recently this phase was successfully experimentally realized [2]. In Refs. [3] and [4], the measurements of the statics and the dynamics were modeled using the existing theory first presented in [5].

The ordering in a ferromagnetic nematic liquid crystal is described by two fields: the director field $\mathbf{n}$, which describes an average orientation of the molecules of the liquid crystal and the magnetization field $\mathbf{M}$, describing an average orientation of the magnetic moments of the magnetic particles. Unlike for usual nematics, the ferromagnetic phase is sensitive to very small magnetic fields.

To understand the complete dynamic behavior of a ferromagnetic nematic one needs to measure rheological properties of the system. We study the case of a simple shear flow in a sample of a ferromagnetic nematic confined between two parallel plates. A magnetic field is applied perpendicularly to the plates and the so called effective viscosity is calculated. This viscosity is defined as the difference of the shear stresses across the top fluid-glass interface at the upper plate divided by the shear rate. We observe that for the material parameters used, the effective viscosity increases by a factor of at least two and saturates, when the magnetic field is increased from zero to 20 mT. A similar behavior was observed experimentally in [6]. Increasing the magnetic field even further, the viscosity starts to increase again and saturates at fields of order 1 tesla, when the director and the magnetization point along the magnetic field direction.

Generally, the measured viscosity of the system depends on the magnitude of the shear rate. To circumvent this dependence, simple experiments were proposed in [7], where the orientation of the molecules is fixed by an external electric or a strong magnetic field. This way, one can introduce in an ordinary nematic liquid crystal three different Miesowicz viscosities. In a ferromagnetic nematic the presence of the magnetization leads to additional dynamic cross-couplings [5]. As a result, the three Miesowicz viscosities for an ordinary nematic are replaced in a ferromagnetic nematic by nine viscosities.

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Melt rheological behavior of PC/SAN blends selectively filled with CNTs

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Polycarbonate (PC) based composites and co-continuous PC / poly(styrene-acrylonitrile) (SAN) blends with carbon nanotubes (CNTs) were prepared by a melt mixing approach. By using two sets of mixing parameters (PM), different states of filler dispersion in the premixtures and in the blends are obtained. Thereby, multiwalled carbon nanotubes were premixed in the thermodynamically preferred polycarbonate component and for the selectively filled blends subsequently mixed with the SAN. A higher mixing speed combined with a longer mixing time (PM2) resulted in better filler dispersion than a lower speed with shorter mixing time (PM1). However, with increasing CNT dispersion, an increase in electrical resistivity near the percolation threshold is observed for the PC-CNT composites and the (PC+CNT)/SAN blends. This suggests that the higher mixing energies - required for better dispersion - also result in a more severe reduction of the CNT aspect ratio. This effect was proven by CNT length measurements. Melt rheological studies showed higher reinforcing effects for composites with worse dispersion. The Eilers equation (1), developed in 1941 by H. Eilers for filled emulsion describing the melt viscosity as function of filler content [1], was used to fit the data.

$$\eta_r = \left(1 + \frac{0,5 * [\eta] * \varphi}{1 - \varphi / \varphi_{max}}\right)^2 \quad (1)$$

with $[\eta]$ the intrinsic viscosity, φ_{max} maximum volume content, at which the viscosity diverges and where a fully elastic behavior of the composite is expected.

The equation was used to obtain information about an apparent aspect ratio change in the PC composites, which was in accordance with the measured CNT length reduction. Such fitting could be also transferred to the blends and serves for a qualitatively based discussion.

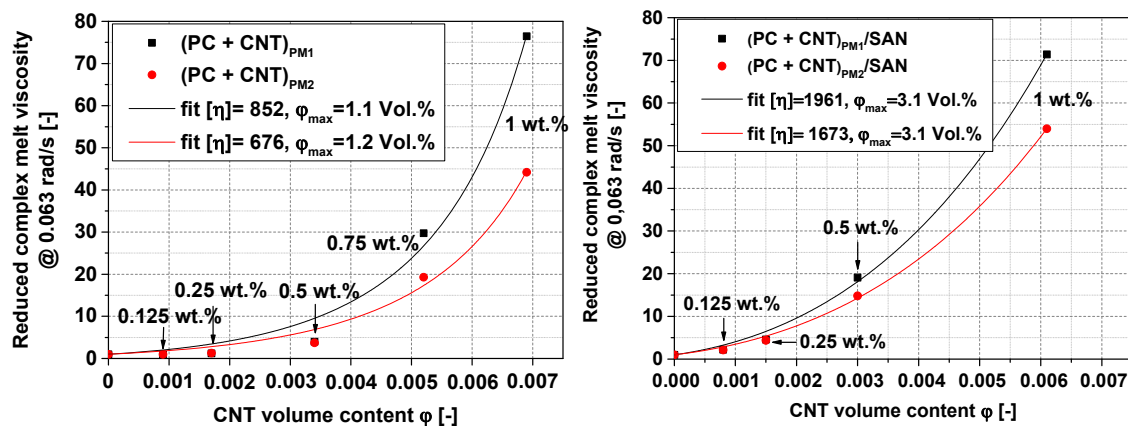


Fig. 1: Reduced complex melt viscosity for PC-CNT (left) and selectively filled (PC+CNT)/SAN composites (right) shows a non-linear increase as a function of filler volume content and good agreement with theoretical model-fit according to equation (1)

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Granular flow rheology in a cylindrical Couette cell

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Abstract

Handling of granular matters is often encountered in industrial sections such as food processing and production, pharmaceutical manufacturing, coal-based power generation, ore reduction and cement production. In spite of its ubiquity, understanding of granular flow behaviors in all kinds of facilities is far from satisfaction. One of the limiting factors in correctly predicting granular flow behaviors is the inadequacy of the granular flow rheology model which reflects the relationship between shear stress and shear strain rate in the flow, and thus attracts a lot of research interests. In this research, we adopted Discrete Element Method (DEM) to numerically simulate the granular flow in a cylindrical Couette cell which has heterogeneous stress distribution as reported in the literature and confirmed in this study. Statistical analysis of particle-scale interactions reveals the relationship between non-dimensional shear stress parameter μ and non-dimensional strain rate parameter I in the granular flow. The prediction has a good agreement with experimental measurements at quasi-static flow regime. Comparisons of μ vs I was also carried out between DEM simulations and predictions using the proposed $\mu(I)$ -rheology model and non-local rheology models based on the fluidity concept in the literature. The velocity profiles from the DEM simulation and continuum approach with rheology models was also compared. Analysis is given for the limitations of current continuum approach.

Acknowledgement

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Deformation-controlled low-field Rheo-NMR

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The in-situ combination of additional methods like SAXS or NMR into a rheometer allows to directly relate the respective measurement results to a mechanical deformation and therefore rheological properties, without concerns about temperature calibration or identical sample history and geometry arising from the use of separate instruments. NMR, being sensitive to molecular structure and mobility, is an especially promising goal for such a hyphenated technique, as it can bridge the gap between the time and length scales of the rheological measurement, and those at the microscopic foundations of the observed macroscopic material properties.

In a recent paper [1], we described the first integration of a 0.7 T (30 MHz proton resonance) time-domain NMR magnet system into a commercially available strain-controlled shear rheometer. This allowed to assess the time-dependent phase composition of a crystallising isotactic polypropylene, and relate it to the development of the dynamic moduli of the sample. The use of a sophisticated rheometer makes it possible at the same time to apply nonlinear shear deformation, and measure the sample response, e.g. normal forces, overtones, or shear induced crystallization.

We would like to present our latest developments on this novel time-domain Rheo-NMR setup, which now, apart from technical improvements in the magnet design, temperature control, and NMR probe specifications, also includes the possibility to synchronise the pulsed NMR experiment to a specific point in the time dependent deformation $\gamma(t)$ of a (dynamic) shear experiment. The transient ordering of amorphous polymeric samples under shear flow gives rise to observable changes in the nuclear magnetic relaxation behavior [2]. We would like to show preliminary results from the application of this new deformation-controlled Rheo-NMR scheme to polymer melts and rubbers under large amplitude oscillatory shear.

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ELONGATIONAL FLOW BEHAVIOR OF SURFACTANT SOLUTIONS AT LOW CONCENTRATIONS

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Self-assembling surfactants that form wormlike micelles (WLM) are widely used as drag reduction agents, personal care products, and as fracture fluids in enhanced oil and gas recovery. These applications often involve complex flows with strong shear and extensional components that can induce structural changes, thus leading to a dramatic change of the flow behavior [1]. Therefore, understanding the flow behavior of WLM solutions in complex flow fields is crucial for optimizing their application.

We characterize aqueous micellar solutions of a mixture of cetyltrimethylammonium bromide (CTAB, cationic surfactant) and sodium salicylate (NaSal, organic hydrotropic salt) covering a broad range of surfactant concentration c_s and salt/surfactant ratio R . We employ a combination of classical shear rheometry, uniaxial extension through capillary breakup elongational rheometry (CaBER), and planar elongation of the solution using an optimized-shaped cross-slot extensional rheometer (OSCER). In steady shear experiments, samples with a low salt concentration exhibit a Newtonian-like regime at low shear rates with a zero shear viscosity of $\eta_0=2.3\text{mPa}\cdot\text{s}$, followed by a sudden increase in the shear viscosity by around one order of magnitude indicating shear-induced structure (SIS) buildup above a critical shear rate.

During filament thinning in CaBER, long filament lifetimes are observed for samples at low R , indicating the formation of elongation-induced structures (EIS) [2]. These long lasting filaments are reproducible in CaBER experiments in oil, as well as in falling drop and filament stretching experiments. Particle image velocimetry (PIV) on horizontal surfactant filaments of these EIS-forming fluids reveals a heterogeneous velocity distribution, with flow in both axial directions in the filament cross-section. This unique flow behavior stems from a competing flow from the reservoirs into the filament and vice versa which explains the long filament lifetimes for these solutions. Increasing c_s and R of the solution results in a more uniform flow profile as expected for viscoelastic fluids [3].

In an effort to shed light on the underlying mechanism of EIS formation for solutions with low salt content, we further perform PIV and flow induced birefringence (FIB) measurements in planar elongation using a microfluidic OSCER device [4]. Flow velocimetry exhibits steady Newtonian-like flow behavior for small flow rates. Increasing the flow rate, and hence the elongation rate in the cross-slot, leads to a time-dependent transition from a Newtonian-like to an asymmetric flow resembling elastic instabilities previously reported for polymer solutions [4]. The time required for the onset of this large-scale symmetry-breaking decreases with increasing elongation rates, with the critical total strain remaining constant. Preliminary FIB imaging shows the development of a localized birefringent strand at intermediate rates, indicating micellar orientation. This strand oscillates laterally with increasing flow rates, similarly to the spatio-temporal fluctuations of the asymmetric flow field.

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Preconditioners for viscoelastic flows in FEniCS

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Keywords: *Viscoelastic flow simulations, Iterative solvers, Block preconditioning, Discrete elastic-viscous stress splitting (DEVSS), High performance computing (HPC).*

In this contribution we present an efficient strategy for numerical solution of viscoelastic flow problems the mathematical formulation of which involves the Oldroyd-B type constitutive models. The viscoelastic problem is discretized using the DEVSS method, originally developed in [5], based on the mixed finite element formulation involving three unknown fields (velocity, pressure and viscous polymer stress). The arising algebraic systems of equations are tackled using iterative solvers of the Krylov subspace type with a certain type of block preconditioning strategy following the ideas from [4] and [6].

Motivated by the large scale problems encountered in rubber industry, we aim to provide the implementation suitable for deployment on HPC systems. We build on top of the FEniCS Project [1], revisiting the implementation of the DEVSS approach in Rheagen [7], and we implement the preconditioning strategy using the state-of-the-art algorithms available in PETSc [2] by extending the ideas previously applied in FENaPack [3].

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Quantification of formulation effect on powder flowability via powder rheology

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Keywords: Cohesive powder, nanoparticles, rheology, flowability.

Fine powders are often cohesive in nature, thus they naturally tend to form agglomerates with bad flowing properties. The poor ability of fine powders to flow could be explain by the presence of interparticles forces which dominate gravitational forces [1]. In industry, the manipulation of powders with poor flow leads to blocking or dosage problems and thus affect the final products quality. Therefore, to guarantee a good process, it is essential to control, monitor and ensure a good flowability during production.

In order to improve the bulk flow behavior, a dry submicrometre material called “flow regulator” or “glidant” playing a role of reducing the interparticles forces between particles is frequently added to the powder [2]. In order to select the best additive and to optimize the quantity, it is important to quantify with accuracy the additive effect on flowability.

For this purpose a rheological approach has been chosen. Bulk and tapped densities were measured and compared with measurements obtained with a stress-imposed rheometer. Thereby, rheograms were obtained in both steady-state and dynamic regime and can be interpreted respectively in terms of viscosity, elastic and viscous moduli allowing to assess and quantify the effect of silica particles on the flow properties of lactose powder.

In this study, a lactose polydisperse powder ($d_{43}= 56 \mu\text{m}$) with poor flowability properties was studied for the evaluation of additives effect. Several types of silica nanoparticles playing the role of flow regulator were used in order to observe how the flow properties of the pure lactose powder can be changed. Effects of size, quantity and hydrophilicity of silica nanoparticles were also considered. Furthermore, a link between local study of the role of the flow regulator and improvement of flow properties in the global scale was implemented and completed by morphologic and granulometric analysis.

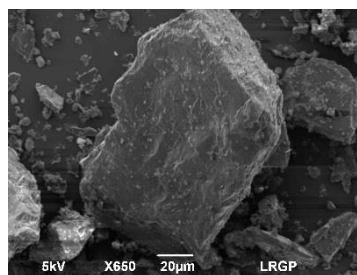


Figure 1: SEM picture of lactose powder covered by flow regulator

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New insights on draw resonance in the fiber spinning process

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In fiber spinning processes, molten material is extruded through a die and taken up by a spinning wheel (see Fig. 1). If the draw ratio Dr , i.e., the ratio of outlet to inlet velocity, exceeds a critical value, Dr_c , both fiber diameter and flow velocity exhibit steady oscillations, which is commonly known as draw resonance. In practical application, these oscillations lead to inhomogeneous product properties and a possible breakdown of the process. In this work, we analyze the linear stability of the process using a one-dimensional slender fiber model including gravity, inertia and surface tension effects simultaneously. Applying an alternative scaling (introduced in [1]) yields the dimensionless fluidity F , inlet velocity Q and a surface tension number S as control parameters, and enables the visualization of the stability behavior in stability maps of practical relevance (see Fig. 2). The interplay of the destabilizing effect of surface tension and the stabilizing effects of inertia and gravity lead to non-monotonous stability behavior with respect to the control parameters, and local stability minima and maxima can be found. Moreover, regions of unconditional stability caused by inertia effects and unconditional instability caused by surface tension effects are revealed. In particular, the destabilizing mechanism of surface tension, reminiscent to the Rayleigh-Plateau instability, is shown to reinforce the draw resonance instability, an effect that had largely be disregarded so far in literature. We finally show new results on the destabilizing role of viscoelasticity on draw resonance.

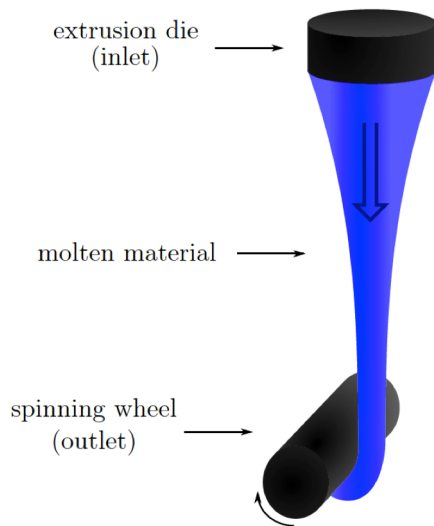


Figure 1 Sketch of the fiber spinning process. The flow direction is indicated by the arrow.

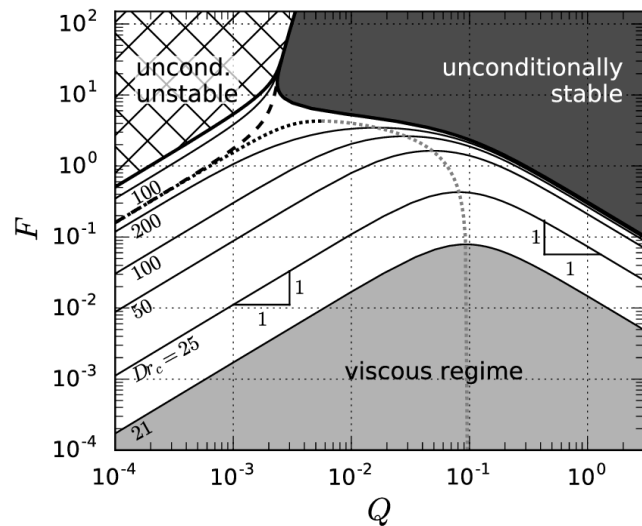


Figure 2 Stability map with isolines of constant critical draw ratio Dr_c with respect to dimensionless inlet velocity Q and dimensionless fluidity F for a constant surface tension number $S = 10^{-3}$. Dashed and dotted lines guide the eyes towards local stability maxima and minima.

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The fast flow dynamics of polymer melts and solutions: **Is it possible to achieve a universal scaling?**

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Previous elongational non-linear experiments on entangled polymer melts and solutions demonstrated qualitatively different behaviors. While the polymer melts show a monotonic thinning behavior for all applied strain rates ^{1,2}, polymer solutions exhibit an initial thinning followed by a strong thickening trend ³. Recently, it was shown that polymer melts and solutions with the same number of entanglements exhibit an identical linear behavior, however, this was not observed for nonlinear behavior ^{4,5}. This raises the following question: is it actually possible to achieve a universal scaling between polymer melts in non-linear flows?

We designed and investigated a new set of polymer solution systems where a high molecular weight polystyrene is diluted in a styrene oligomer at several concentrations from concentrated to diluted solutions. Using these and literature data, we are able to show that it's possible to obtain universality between melts and solutions by explicitly normalizing them in the non-linear regime. This understanding can help us to develop a model that can predict non-linear elongational behavior of both polymer melts and solutions under one framework.

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Effect of polymer architecture on viscoelastic properties of Thermoplastic Elastomers

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Key words - Thermoplastic Elastomers, H-bonds, Dumbbell TPEs

Thermoplastic Elastomers (TPEs) are one of the important class of segmented block copolymers, particularly for industrial applications due to their tunable engineering properties. TPEs consist of hard segments (HS) and soft segments (SS) whereby, Hard segment capable of making supramolecular interactions/physical crosslink via Hydrogen bonding e.g.- bisureas, amides and soft segment comprise of groups which are amorphous and shows low T_g. These materials shows phase separated morphology and behaves as rubbers at room temperature while being melt-processable above their order-disorder transition temperature. Recently, we investigating the viscoelastic properties of four linear well-defined segmented block copolymers composed of poly-TetraHydroFuran (polyTHF) (SS) and T4T (HS) segments (5, 10, 15 and 20%). We concluded that the viscoelastic properties of these material are strongly dependent on their thermal and deformation history, as well as chain composition. Apart from this the soft segment entanglement trapped between associating HSs plays important role in liquid to solid sharp transition. The fast association of HSs leads to formation of stable crystallites with large plateau modulus, which remains unaffected by thermal history. Consequently the important contribution of soft segment entanglements on their dynamics at intermediate or high temperature was understood via the HS association/dissociation process. Entanglements trapped between associated HSs were found to be responsible for the sharp liquid-to-solid transition of the samples during cooling. The fast HS association at low temperatures lead to the formation of strong and stable crystallites with large plateau modulus, which was unaffected by the thermal history. However, the stability and melting temperature of these HSs domains have been found to correlate with the protocol of crystallite formation and, more specifically, the potential ability of HSs to avoid being trapped into metastable HSs domains.

In order to understand the effect of soft segment entanglement and position of the supramolecular group in the polymer chain, we synthesized the dumbbell architecture copolymers, keeping the chemical composition same as that of segmented copolymers i.e. poly-TetraHydroFuran (polyTHF) (SS) and T4T (HS) segments. We have also varied the terminal HS densities (3,5 and 20%) in dumbbell architecture, making three samples different in SSs length (M_n – 11, 12 and 3K g/mol) Therefore in this work we address the effect of SS entanglements and chain architecture effect on the viscoelastic properties in terms of association/dissociation of HSs at terminal position and relaxation of SSs entanglements. We believe the dumbbell TPEs should show the better association of HS and crystals formation and delayed terminal relaxation due to increased SSs entanglements. Our previous study on segmented copolymer enables us to have a systematic comparative study and will be presented.

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Understanding the Dynamics of developed palladium-based slide-ring gels

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The main objective in this project is to create, analyze and model slide-ring gels where the mobility and the density of the sliding cross-links can be finely controlled. In such gels, the polymer chains are held together by linked macrocycles (rings) forming a 8-shape, each of these rings having a polymer chain threaded into its cavity. Thus, the cross-links have the strength of covalent bonds but are mobile since the rings can slide along the polymer chains. Moreover, this will enable us to modify the sliding mobility of the rings by controlling the ring-thread interactions. To this end, a step by step synthesis protocol is followed in order to incorporate macrocycles (rings) along copolymers of linear poly(ethylene glycol) containing bulky end-groups in order to prevent the rings from unthreading[1].

In addition, in order to understand the dynamics of such systems, preliminary rheological studies were done. The viscoelastic properties of the samples obtained at each stage are then determined and analyzed with the help of the TMA (Time Marching Algorithm) tube model, in order to understand the role of the different components (chain extender, bulky end groups, rings etc) on the dynamics of the chains[2].

Starting from the experimental results, we then modify the tube model for linear entangled polymers in order to account for the influence of ring mobility, and possible ring associations on the dynamics of these systems toward our final goal to characterize and model the viscoelastic behavior of well-defined slide-ring gels.

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Trimodal PE-blends and it's viscoelastic properties

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There is a high demand for polyethylene (PE) possessing superior mechanical properties (i.e. high tensile strength, impact resistance, Young's modulus and abrasion resistance) and being easily processable. Therefore, ultrahigh molecular weight PE (UHMWPE) with a molecular weight higher than 10^6 g/mol used as a low-concentration additive for conventional PE improves mechanical properties [1]. Unfortunately, UHMWPE is characterised by extremely high viscosities and melt-blending with PE, containing high amount of UHMWPE, leads to heterogeneous blends with inferior mechanical properties [2]. In contrast, ethylene polymerization using multisite catalysts produces bimodal reactor blends containing of 40 wt.% UHMWPE (RB40) or 50 wt.% of UHMWPE (RB50) and the corresponding amount of PE wax [1]. The RB is later melt-blended with high density PE (HDPE) to obtain trimodal PE blends with high amount of UHMWPE (Fig. 1). It is well known, that the presence of extremely long chains and very high molar-mass dispersity ($\bar{M}_w$) significantly influence the rheological properties [3-5]. Thus, rheological measurements were carried out to investigate the influence of extraordinary long chains and high $\bar{M}_w$, in the range of up to 10^3 , on the molecular dynamics of different tri-modal PE blends.

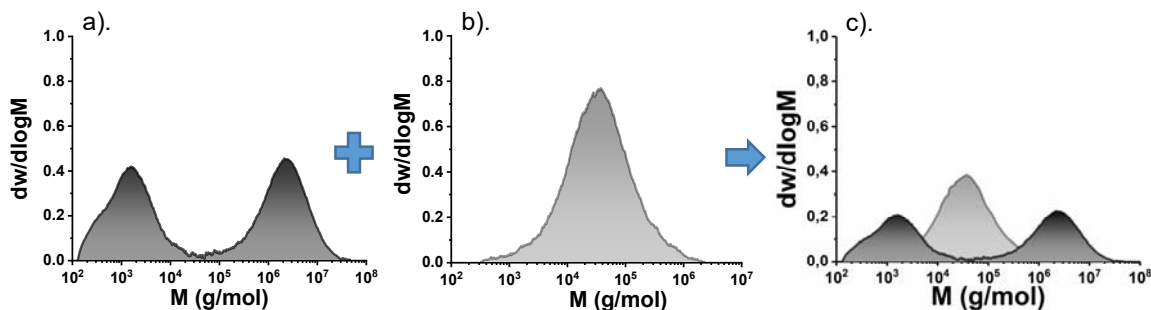


Fig. 1. HT-GPC curves of RB40 (a), HDPE (b) and 50RB40 trimodal PE blend, which contains 50 wt.% of RB40 (c).

Linear viscoelastic characterization was performed by dynamic- and creep shear experiments (Fig. 2). Furthermore, uniaxial extensional measurements were carried out to describe the non-linear viscoelastic behaviour (Fig. 3). The obtained results significantly contribute to determine the influence of UHMW-content on the viscosity, terminal relaxation time, and strain hardening behaviour of these blends.

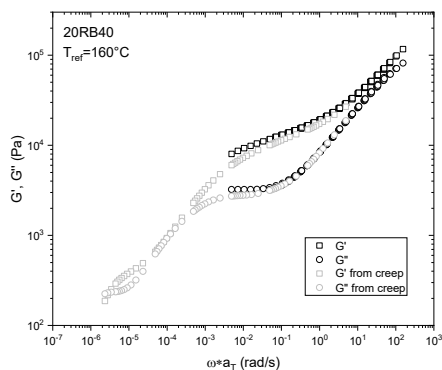


Fig. 2. Master curve of 20RB40 trimodal PE blend, which contains 20 wt.% of RB40

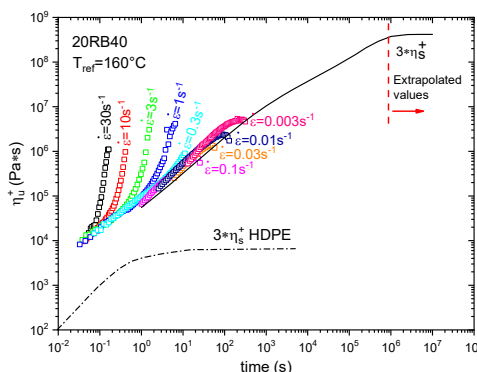


Fig. 3. Uniaxial extensional viscosity

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Universal Relaxation Behavior of Entangled Star Poly(hydroxybutyrate) Melts in the Transient Shear Startup

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Nonlinear viscoelastic stress response for Poly(hydroxybutyrate) star polymers are compared to typical constitutive equations, such as the Graham, Likhtman, McLeish and Milner (GLaMM)¹ and the Mead, Larson, Doi (MLD)² models. This requires modifying these models, which were described for entangled solutions and melts of linear chains, to systems which cannot relax by reptation.

At significantly low shear rates (smaller than the inverse reptation time) a reasonable agreement is found between the data of the startup and the linear viscoelastic envelope measured in a cone partitioned plate geometry. However, at moderately high Weissenberg number, the shear stress growth coefficient doesn't increase monotonically but pass through a maximum indicates a full alignment of the arms along the shear direction.

At significantly high shear rates (larger than the inverse Rouse time) the arms undergo stretch and fast retraction process following by local convection of the total constraints around the arm's extremities which eliminate the deep fluctuation effects on the relaxation process.

We compare the predictions of the two mentioned tube models and comment on their performance; we also highlight similarities and/or differences, which we explain in terms of the underlying molecular physics and the way the latter have been implemented in the models.

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Effect of nanoparticles at the droplet interface on the dynamics of a droplet subjected to shear flow

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Immiscible polymer blends still increase in importance in industry and in our daily life. By using polymer blends, high performance materials can be achieved which meet stringent customer demands. The complex interplay of droplet deformation, retraction, breakup and coalescence during processing determines the blend morphology, and hence the final product properties. Nanoparticles are often added to a polymer blend to manipulate the blend morphology as nanoparticles localized at the interface stabilize and refine the blend morphology by substantially suppressing coalescence [1]. Insight in the fundamental mechanisms by which nanoparticles affect other aspects of structure development, in particular droplet deformation and breakup, are nevertheless still lacking. The goal of the presented research is to understand the impact of nanoparticles localized at the droplet interface on droplet deformation and breakup as well as to correlate the observed droplet dynamics to the interfacial viscoelastic properties. To gain fundamental insight, the droplet dynamics is studied in-situ and time-resolved in a counter-rotating shear cell combined with an optical microscope. A model system consisting of a Newtonian PDMS droplet in a Newtonian PIB matrix is used in all experiments. Partially hydrophobic silanized spherical nanoparticles with a diameter of 50 nm localize at the PDMS-PIB interface, as shown by SEM images. At high particle concentrations, an interfacial particle network is formed. This particle network suppresses the droplet deformation substantially (Figure 1) and stabilizes the droplet against breakup. In addition, the elastic particle network has a clear effect on the droplet breakup behavior, resulting in irregular droplet shapes. The observed droplet dynamics clearly indicate the importance of the interfacial viscoelastic properties. Therefore, interfacial shear rheology experiments are performed to elucidate the relation between interfacial rheological properties and droplet dynamics. The results confirm that an elastic particle network is built up which can be broken down by shear. However, the results do not quantitatively match with the observed droplet dynamics, which suggests that the dynamics are dominated by interfacial dilatational properties rather than interfacial shear properties.

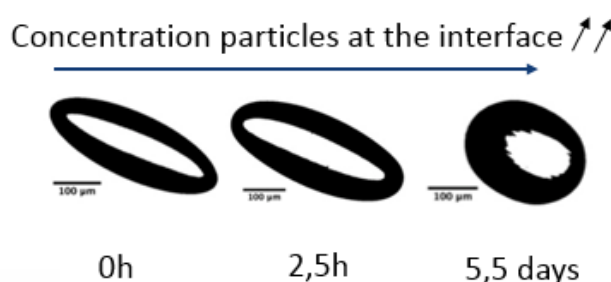


Fig. 1 Particles at the droplet interface substantially suppress the droplet deformation (droplet deformation in the velocity– velocity gradient plane, $Ca_{eff} \approx 0.5$).

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Decoding the linear viscoelastic properties of model telechelic metallo-supramolecular polymers

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This work focuses on the linear viscoelastic properties of entangled telechelic bulk metallo-supramolecular polymers. The latter are based on linear and star poly(n-butyl acrylate)s functionalized with a terpyridine ligand at each chain extremity, in the presence of transition metal ion of varying nature. The systems are investigated both experimentally and theoretically using small amplitude oscillatory shear and a modified version of the tube-based time marching algorithm (TMA), respectively.

The experimental data reveal that sample relaxation depends on both disentanglement and association dynamics, with the respective importance of these two processes depending on the nature of the metal ion and on the temperature. A good description of the data is achieved using the modified TMA(Time Marching Algorithm) tube model, provided that dissociation events of metal-ligand complexes occur via ligand exchange. The model contains two fitting parameters, i.e., the fraction of unassociated stickers and the longest time needed in order to ensure that all the chains were dissociated at least once. This latter time is found to be independent of the chain architecture and is well described by an Arrhenius equation, which allows the derivation of the related activation energy.

This work provides the necessary framework to explore other metallo-supramolecular networks, built from different chain architectures, and exploit the large richness of their dynamics.

A new filament stretching device and the exploration of its capabilities and complementarity to existing techniques

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The determination of extensional flow properties of complex fluids is a challenging task, and only recently instruments have been commercialized to quantitatively investigate extensional material properties. For higher viscous systems, this includes filament stretching devices as SER and EVF fixtures or the VADER, which are usually limited in the maximum applicable strain and rates which they can probe. For lower viscous fluids capillary thinning devices as CaBER or contraction flows can act as indexers that are, however, not capable of applying defined deformation rates or strains. In this light, we want to present in this paper a novel filament stretching device that is capable of delivering constant strain rates that are sufficiently high to measure intermediate viscous systems that have capillary thinning and breaking time scales that are not accessible with current filament stretching devices.

In this paper, the working principles of the newly built device are introduced and the operating limits explored with a set of Newtonian PDMS test fluids covering several orders of magnitude in viscosity as well as PIB based Boger fluids. The first objective of this paper is to validate the newly built set-up by this comparison and explore the limitations of the hardware components and accuracy. This is coupled to the optimization of the instrument control and software development with a focus on optimal control loop design. A second objective of this paper is then to identify the limits of the available device and to demonstrate its complementarity and the possible parameter space that is now available to be explored.

Compaction dynamics as a test for the rheology of powders and grains

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When a column of grains or a glass tube filled by a powder is submitted to a series of taps, the material is seen to densify [1]. This phenomenon is called compaction. We give a review about compaction dynamics of granular materials and powders when submitted to mechanical vibrations or taps. Experiments show that the dynamics of compaction is extremely slow, similar to glassy dynamics and crystalization [1,2]. Models are proposed for describing the slow reorganization of grains in a packing [3]. They give some clues to link the flowability of powders to compaction measurements [4]. We show that this kind of measurements is able to discriminate the flowing properties of powders and grains [5].

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The Interchain Tube Pressure and the Effect of Oligomeric Solvents

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In a tube model with variable tube diameter, chain stretch and tube diameter reduction are related, and at deformation rates larger than the inverse Rouse time, the chain is stretched and its confining tube becomes increasingly anisotropic. Tube diameter reduction leads to an interchain pressure in the lateral direction of the tube, which is proportional to the 3rd power of stretch. In the extended interchain pressure (EIP) model, it is assumed that chain stretch is balanced by interchain tube pressure in the lateral direction, and by a spring force in the longitudinal direction of the tube, which is linear in the stretch. The EIP model allows for quantitative agreement between highly nonlinear viscoelastic experiments in elongation and predictions for polystyrene (PS) melts and concentrated solutions of polystyrene in 1, 2, and 4 kg/mol oligomeric styrene [1]. Interestingly, recent experimental data on poly(methyl methacrylate) with molar weight of 86kg/mol (PMMA-86k) and 270kg/mol (PMMA-270k) dissolved in 2.1 and 3.5kg/mol oligomeric MMA (denoted as 20k and 40k) show elongational viscosities resembling melt behaviour [2]. Possible reasons will be discussed.

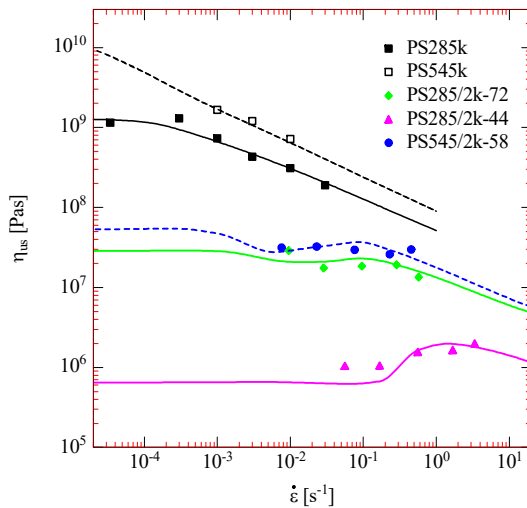


Fig. 1 Steady-state elongational viscosity of PS melt and PS solutions

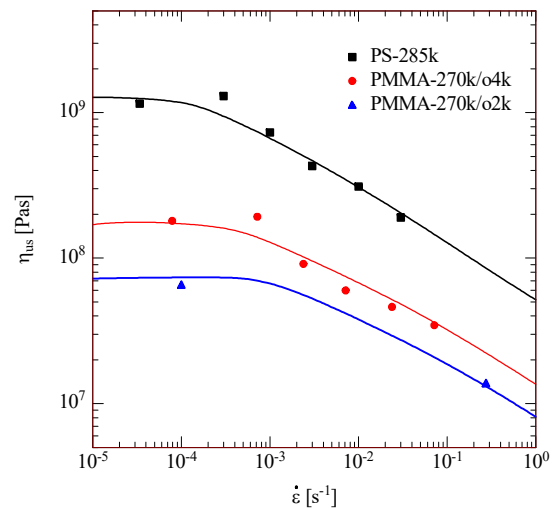


Fig. 2 Steady-state elongational viscosity of PS melt and PMMA solutions

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Aqueous salt-free xanthan solutions at high shear rates

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We study aqueous xanthan solutions with a narrow-gap rheometer [1] at gap widths of 20 μm and shear rates up to 10^5 s^{-1} . The gap-width precision is better than $\pm 1 \mu\text{m}$. At these shear rates, salt-free solutions show a second Newtonian branch. Depending on the xanthan concentration, we find two different regimes that we identify by their scaling laws. Up to a concentration of about 0.2 wt.%, we find a linear dependence of the specific viscosity in the second Newtonian branch. Beyond that concentration, the specific viscosity is approximately proportional to the square root of the concentration. We also measure the normal-stress differences and discuss their implications at the high shear rates studied.

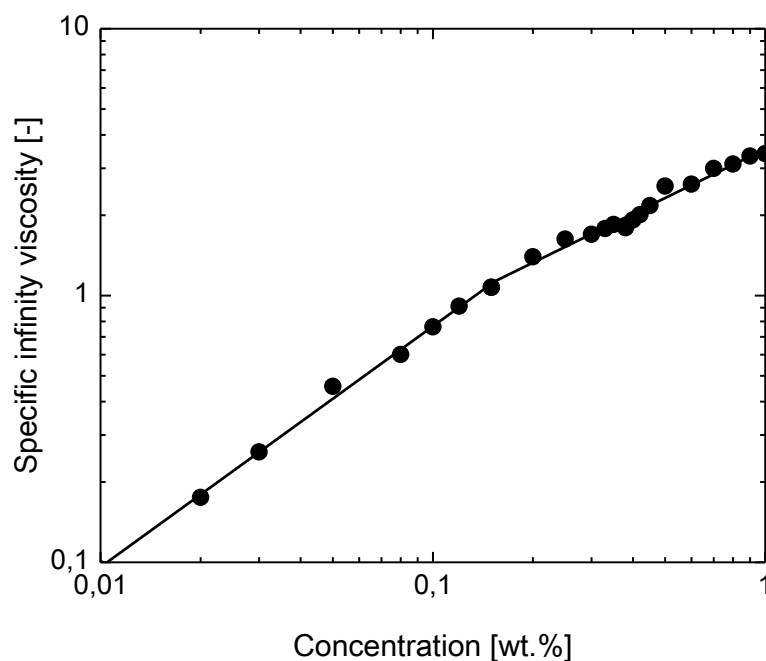


Fig. 1 Specific-viscosity of the second Newtonian branch as a function of the xanthan concentration. The straight solid lines are power-law fits to the data.

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Shear-thinning behavior of phosphonium ionic liquids: the roles of chain length and fluorination

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Ionic liquids (ILs) exhibit tunable properties that are due to their supramolecular structure. We synthesized a series of alkylated and fluorinated phosphonium dicyanamide ILs to study the relation between molecular and supramolecular structure and rheology with a focus on the roles of cation chain length and fluorination.¹ Small angle X-ray scattering indicated a lamellar structure with long-range order for all fluorinated ILs, while the corresponding alkylated ILs exhibited no order beyond the alternating of polar ionic and a nonpolar alkyl zones that is typical for ILs. “Fluorophobic” interactions caused microphase segregation of perfluorinated and other molecular segments, “fluorophilic” interactions among the perfluorinated segments stabilized the microphase structure, and the balance between Coulombic and van der Waals interactions led to a stable mesophase structure. We show that the lamellar structures strongly affect the rheology of the ILs. Fluorinated ILs had higher viscosities and exhibited non-Newtonian shear thinning; the alkylated ILs of the same length had an order of magnitude lower viscosities and were purely Newtonian. We propose that the disruption of lamellar structure in the shear flow causes the non-Newtonian flow behavior, as illustrated in Fig. 1.

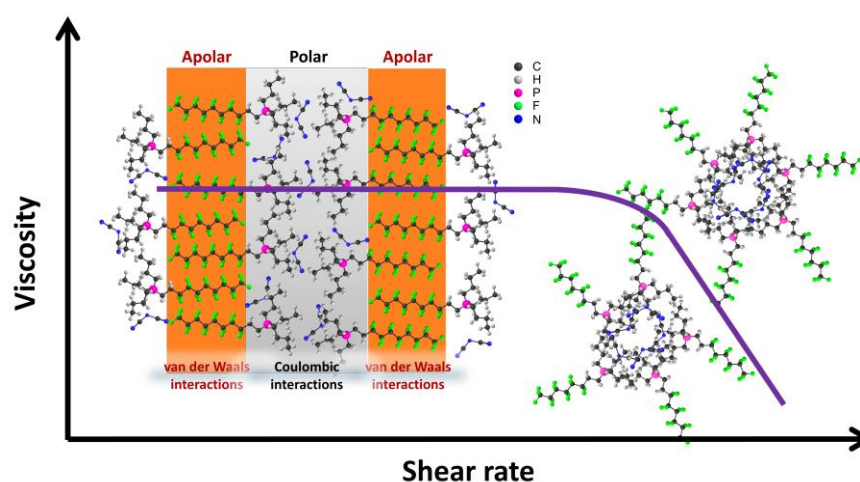


Fig. 1 Schematic illustration of shear-thinning in fluorinated ILs through the disruption of lamellar supramolecular order.

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Shear and uniaxial extensional rheology of supramolecular entangled polymers

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The advent of dynamic metal-ligand coordination in the last decades has emerged as a powerful strategy for the design of various types of self-assembled materials with stimuli-responsive features.¹ Among them, reversible polymeric networks obtained by functionalizing flexible polymer chains with metal-ligand coordination are a promising avenue to engineer soft materials with tunable mechanical properties.² In this work, we study the nonlinear shear and uniaxial extensional viscoelasticity of low-polydispersity (below 1.3) entangled poly (*n*-butyl acrylate) chains functionalized with 2,2';6',2"-terpyridine ligands.³ Upon self-assembly, the telechelic four-arm star precursors form model networks with minimum fraction of defects. Most of the chain segments participate in the entangled network, contrary to networks originating from linear chains with metal binding ligands along their backbone, which contain a large proportion of dangling chain ends or loops.

These model systems are therefore perfect to investigate how the dynamics of metallo-supramolecular bulk networks (MSBNs) is affected by both the dissociation kinetics of metal-ligand complexes and the disentanglement process, and how these two mechanisms are coupled. The measurements are performed on a filament stretching rheometer and on a strain controlled rotational rheometer equipped with a cone-partitioned plate geometry. In extension the MSBNs show strain hardening at extension rates ($\dot{\epsilon}$) below their respective terminal relaxation times τ_{rel} . Since the transient viscosity of MSBNs is measured at low $\dot{\epsilon}$ the strain hardening is attributed to the physical cross-links which comprise metal-ligand coordination. On the other hand, strong shear thinning behavior is observed at similar deformation rates in nonlinear shear flow. Then, by altering the temperature, we systematically vary the relative importance of the metal-ligand complexes, which allows us to determine their specific contribution to the network properties. Moreover, the properties of these systems can be finely tailored with varying the type or the nature of metal ions.⁴

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