Almost Ab Initio Nonlinear Rheology of Entangled Polymers

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We use a slip-link picture for entangled polymers to derive a set of integrated, well-defined mathematical models on varying levels of description. Each level is applicable to any chain architecture, molecular weight, or blend, and under any flow. For an atomistic basis we exploit primitive-path analysis [Everaers et al. Science (2004); Kröger Comp.Phys.Comm. (2005); Tzoumanekas and Theodorou Macomolecules (2006)], whereby one freezes the ends of the polymer chains in an atomistic simulation, and shrinks the length of all the chains while simultaneously preventing chain crossings. From the resulting statistics we are able to determine all but a single (monomeric friction) parameter in our most-detailed slip-link model. We then go through a series of coarse-graining steps to create a hierarchy of integrated slip-link models. This procedure produces a mathematical model whose calculations are 3 million times faster than the most-detailed level of description, and 20 billion times faster than atomistic-level calculations. Using any single member of the hierarchy, we can then fit our friction parameter to a dynamic equilibrium experiment of any chain molecular weight and chain architecture, and make predictions of the nonlinear rheology of any chain architecture, molecular weight, blends of these and in any flow field. Predictions of experiment are quantitative. More important than computational speed up is the dramatic reduction in the number of dynamic variables necessary to describe the system, which suggests a deep understanding of the physics of entangled polymers. Given that the time scales of the adjusted friction are order nanoseconds, truly ab initio rheology predictions of entangled homopolymers now seem possible.

Large scale Brownian dynamics simulations of complex viscoelastic Soft Matter

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In order to describe flow of soft matter in complex geometries detailed information is needed about how stresses depend on velocity gradients and concentration. Besides this, often compressible flow equations must be solved concomitantly with diffusion equations.

Since it is difficult to collect the appropriate information and to accurately represent it with a constitutive model, it is natural to develop particle based methods that can be applied to large portions of matter. In order to achieve this goal large, mesoscale objects must be represented by single particles, which move such that both the thermodynamic and the viscoelastic properties of the system are recovered. The latter usually result from a strong interplay between the dynamics at a large range of time and length scales of those degrees of freedom that have been eliminated in the coarse description. I will discuss a model in which the particles are dressed with additional variables which roughly reinstate the effects of the eliminated degrees of freedom.
I will describe the nature of the forces on the centers of mass of star polymers in a Kremer-Grest star polymer melt and present a model which is able to capture the global features.

In a second part I will present a model of deformable particles which is able to describe both the linear and the non-linear rheology of entangled polymer solutions.
Finally, I will present a Galilean invariant method to perform Brownian dynamics simulations of flowing soft matter in complex geometries.

Dynamic Phase diagram of soft colloids

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Soft colloids, e.g. polymer-coated silica particles, block copolymer micelles, star polymers etc., are hybrids between (linear) polymer chains and (hard sphere) colloids. Due to this hybrid nature, soft colloids macroscopically show interesting (phase) behaviour resulting from its unique microscopic structure. The combination of polymer-like properties, i.e. the formation of (transient) geometric constraints due to overlapping polymeric coronas and direct colloidal interactions due to the (hard) core in particular affects flow properties and non-equilibrium behaviour of soft colloids. Therefore soft colloids are frequently used in many technical applications (paints, shampoos, motor oils, polymer nano-composites etc.). The task of fundamental research on soft colloids is to investigate the basic principles of the so-called structure-property-relationship (SPR) that finally enables tailoring material properties for technical applications. Their macroscopic phase behavior and non-equilibrium flow properties are directly linked to the details of their unique microscopic structure.

We present a comprehensive study employing several experimental techniques covering micro-, meso- and macroscopic length and time scales (like SANS, DLS and rheology), which enables us to take the first step forward in establishing an generalized view in terms of structure property relationship (SPR) and structural dynamics of soft colloids. Using "frozen" block copolymer micelles as tunable model systems of the latter ones, we varied/tuned its aggregation number (N_{agg}), and consequently its softness, by changing the (solvophilic-solvophobic) block ratio $m{:}n$ (Fig. 1) from a symmetric to a highly asymmetric regime. Based on a simple and general coarse-grained model of the (micelle-micelle) interaction potential, we verify the significance of the interaction length σ_{int} as generic feature for this class of colloids, and elaborate a comprehensive comparison between theoretical [1,2] and experimental information [3-5] describing both structure and dynamics, without requiring adjustable parameters, and covering a broad range of volume fractions and regimes from soft star-like to hard sphere-like colloids.
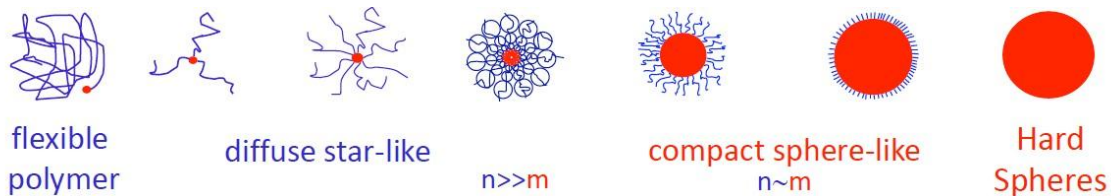

Fig. 1: Schematic representation of morphological evolution of star-like block copolymer micelles in selective solvent, from polymer-like Gaussian coil (N_{agg} = 1,2) to colloid like hard sphere ($N_{agg}\rightarrow\infty$). **n** and **m** denote the number of repetitive units for the solvophilic (blue) and the solvophobic (red) blocks, respectively.

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Thermodynamics of reductions in multiscale modeling

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Let $\mathcal{L}_1, \mathcal{L}_2, \mathcal{L}_3$ be three well established (i.e. well tested with experimental observations)
levels of description ordered from the most mi- croscopic to the least microscopic. By
comparing solutions to the time evolution equations $\mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3$ on all three levels we
can find relations $\mathcal{L}_1 \rightarrow \mathcal{L}_2 \rightarrow \mathcal{L}_3$ and $\mathcal{L}_1 \rightarrow \mathcal{L}_3$. Such relations give us: (i) relations
$\mathcal{E}_1 \rightarrow \mathcal{E}_2 \rightarrow \mathcal{E}_3$ and $\mathcal{E}_1 \rightarrow \mathcal{E}_3$, (ii) relations $\mathcal{P}_1 \rightarrow \mathcal{P}_2 \rightarrow \mathcal{P}_3$ and $\mathcal{P}_1 \rightarrow \mathcal{P}_3$, where $\mathcal{P}$
stands for material parameters, i.e. the parameters with which the individual nature of
the system under consideration is expressed, and (iii) six entropies, namely
$s^{(1\rightarrow2)}, s^{(1\rightarrow3)}, s^{(2\rightarrow3)}$ and $S^{(3\leftarrow1)}, S^{(3\leftarrow2)}, S^{(2\leftarrow1)}$. The entropies $s^{(i\rightarrow j)}$, $i < j$ are
potentials generating the approach (as time goes to infinity) of the level $\mathcal{L}_i$ to the level $\mathcal{L}_j$
and $S^{(i\leftarrow j)}$, $i > j$ are the entropies $s^{(j\rightarrow i)}$ evaluated at the states on the level $\mathcal{L}_i$ that
are reached in the approach $\mathcal{L}_j \rightarrow \mathcal{L}_i$. These six entropies represent the multiscale
thermodynamics corresponding to the sequence of levels $\mathcal{L}_1, \mathcal{L}_2, \mathcal{L}_3$.

In my talk I will illustrate this multiscale thermodynamics (and pro- vide some of its
applications) on the example of $\mathcal{L}_1 \equiv$ level of description of complex fluids on which
inertia of the internal structure is taken into account , $\mathcal{L}_2 \equiv$ level of description of
complex fluids without the inertia, and $\mathcal{L}_3 \equiv$ equilibrium thermodynamics of complex
fluids.

A materials genome approach to engineering functional suprabiomolecular nanotubes

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Nanoscale biomolecular building blocks have unique chemical and structural features that may help overcome some of the persistent challenges in designing tough nanocomposites and separation membranes inspired from biology. However, it remains costly and time-consuming to uncover the hierarchical self-assembly principles and emergent properties of these novel systems through experimental trial-and-error. In pursuit of an accelerated pathway towards discovering novel biomolecular materials through computer simulations, this talk will summarize recent advances in predicting the assembly, mechanofunctionality, and transport capabilities of hybrid nanocomposites that blend the best aspects of biomolecules and engineering polymers. This talk will focus on polymer-conjugated cyclic peptide nanotubes (pc-CPNs) that self-assemble into biomimetic artificial nanochannels in polymer membranes. Predictive analytical relationships validated by both simulation and experiments will be presented to explain the breaking mechanisms and growth processes of pc-CPNs at the kinetic and thermodynamic limits. These discussions will culminate in a concept model that illustrates how the entropic forces arising from polymer conjugation could be utilized in directing the self-assembly of macrocycles towards nanochannels with spatially tunable interiors and thus engineered transport properties. More broadly, phase diagrams and kinetic growth models obtained provide general insight into the physics and mechanics of functional low-dimensional assemblies of soft nanoscale building blocks.

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Self-regulation in structure formation

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Understanding and predicting structure development during flow is key in the processing of semi-crystalline polymers. It is well known that subjecting a polymer melt to a channel flow below the melting point, relevant for e.g. injection molding, yields a non-homogeneous microstructure in the sample after cooling. Most notably, a layer with high orientation appears in the high shear rate region near the walls [1]. The crystalline structure in this shear layer contains a high density of so-called shish-kebabs, consisting of a fibrous backbone (the shish, diameter of ~20 nm, length in access of 1 μm, inter-shish distance ~100 nm) with lamellar overgrowth (kebabs). It has been shown that this effect has a dramatic effect on the final properties of injection-molded products [2].

In this work we study the formation of shish-kebabs. To this end, experiments were performed at the European Synchrotron Radiation Facility to probe crystallization kinetics in a well-defined slit flow with high shear rates (~1000 s^{-1}) with in-situ Wide-Angle X-Ray Diffraction. Simultaneously the rheology is probed by means of a pressure drop measurement over the channel. It is shown that due to formation of shish, the viscosity of the polymer melt is strongly increased, freezing the crystalline structure in at a certain density, thus placing an upper limit on the shish density.

These findings are incorporated in a model to describe the flow-induced crystallization process. Formation of crystalline structures is governed by deformation on a continuum level. Rheological properties depend on crystalline structure. The model is extensively validated with experimental data. The coupling between continuum rheological properties and crystalline structure on the microscale proves to be a vital ingredient for modeling structure formation in polymer melts.

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Local stress calculations in biomembranes: importance of force decomposition

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We present a molecular dynamics study of the microscopic stress in biomembranes. The microscopic stress in lipid bilayers has been a subject of profound studies due to its connections with protein function and different elastic properties, as predicted by thermodynamic approaches [1]. It also exemplifies the link between continuum and atomistic models through the so-called Irving-Kirkwood-Noll (IKN) procedure [2,3].
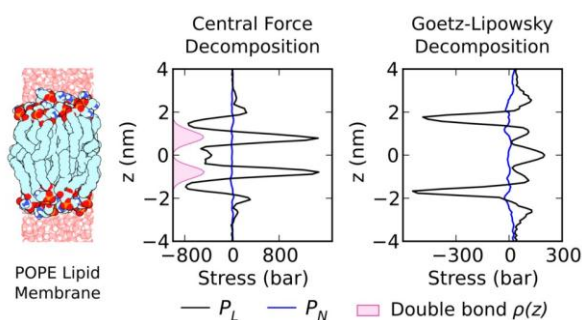

Figure 1: A comparison between lateral (P_L) and normal (P_N) stress profiles for a POPE bilayer with two different force decompositions.

Despite being and old field, the theory of the microscopic stress is not fully settled [4]. A key step in the IKN procedure is the decomposition of forces from multibody potentials. However, different decompositions lead to possibly different stresses differing by a divergence-free field [4,5]. Moreover, some force decompositionslead to non-symmetric stresses that are difficult to interpret from the continuum mechanics of simple bodies. Only recently have a force decomposition, the so-called central force decomposition (CFD), been presented that produces symmetric stresses from first principles [5].

In a recent work [6], we compared stress profiles from the CFD and another common decomposition [7] in lipid bilayers. This common decomposition produces non-symmetric stresses for chiral lipids and very different stress profiles compared to those of CFD. This unsettling subjectivity of stress profiles calls for a reexamination of the physical grounds of the different force decompositions. An alternative approach to the IKN procedure based on equilibrium statistical mechanics may show that only the CFD leads to a valid stress from a thermodynamic viewpoint.

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Rheology and shear-induced diffusion in dense suspensions of red blood cells

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While the relaxation dynamics and rheological properties of hard sphere colloidal suspensions is rather well understood, a full theoretical understanding of these issues in the case of soft objects is still lacking. Deformability introduces additional time scales and degrees of freedom and thus makes a theoretical description more complicated [1].

This talk addresses this issue. A new effective medium theory is presented that takes accounts of effects arising from the deformability of a single object. The theory is then applied to a suspension of red blood cells (RBC). It is shown via computer simulations that the theory correctly describes the rheological response of the RBC suspension over a wide range of packing fractions and shear rates [2]. Moreover, shear-induced diffusion which becomes prominent at high concentrations is also investigated. A simple argument based on dissipation balance is used to predict the dependence of diffusion on imposed shear rate and packing fraction. These predictions are found to be in good agreement with results obtained from simulations [3].
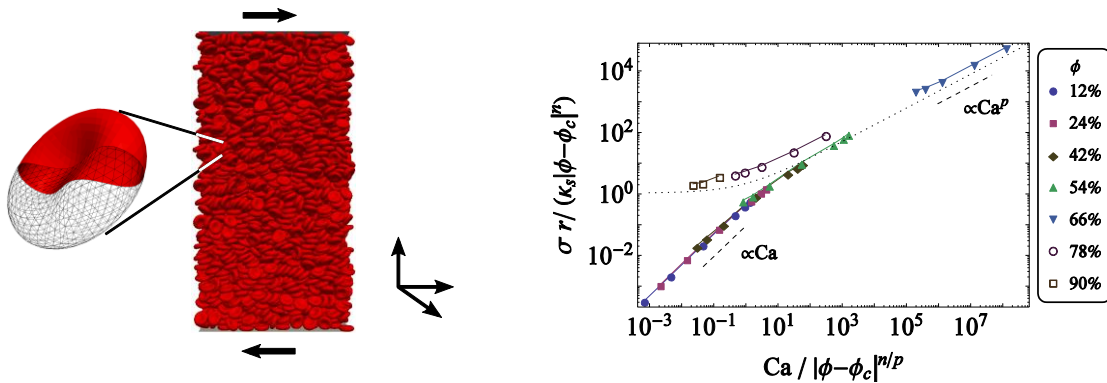

Figure 1: Left: A snapshot of the simulation box and a sketch of the surface mesh of a red blood cell. Right: Critical scaling plot of the suspension stress versus capillary number. Our data are in line with a critical jamming scenario with a critical packing fraction of $\phi_c = 0.66$. Figures adopted from [2].

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