

# COMPLEX FLUIDS

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Complex fluids and soft matter are materials intermediate between conventional liquids and solids, displaying fluid-like as well as solid-like behavior. Examples are polymeric melts or solutions, glasses, gels, foams and granular matter. Many of these systems are inherently disordered and strongly heterogeneous with large fluctuations on a wide range of length- and time-scales. Furthermore many complex fluids, such as glasses or gels, never relax to equilibrium, which makes a theoretical analysis difficult. In our group we aim to understand the cooperative behavior of complex fluids and soft matter on the basis of the underlying constituents and their mutual interactions. For example we want to know: What structures can be formed in and out of equilibrium? What are the underlying principles of self-organization and what are other emergent phenomena as observed in complex fluids?

## Biopolymer networks

Many important biopolymers, such as DNA, the cytoskeletal filaments as well as collagen in the extra cellular matrix are fluctuating macromolecules with a bending stiffness intermediate between that of a flexible random coil and a rigid rod. A variety of linker proteins is known, which bind two filaments together, thereby generating complex structures, such as bundles, fibrils and networks. One of the most important characteristics of these binding proteins is their lifetime, which sets the timescale for the crossover from elastic to viscous behavior of the cross-linked network. Two limiting cases are of particular interest: so called reversible cross-links which open and close a bond on the timescales of the polymers motion and irreversible crosslinks, which persist indefinitely once they have formed. Whereas the irreversible cross-links are responsible for the stability and persistence of shape of the structures, the reversible ones allow for a reconstruction of the network, which is e.g. required for a cell to move.

We are studying the elasticity of biopolymer networks with help of simulations [1] and analytical theory [2]. The biopolymers are modeled as semi-flexible chains which are characterized by a highly nonlinear force-extension relation and are cross-linked irreversibly. We perform simulations of large networks (an example is shown in Fig. 1) under different loading conditions and determine the linear and nonlinear response of the network. The elastic modulus,  $G$ , displays an intermediate super-stiffening regime as can be observed in Fig. 2. Here the modulus increases much stronger with applied stress  $\sigma$  than predicted by the force-extension relation of a single wormlike chain ( $G_{wlc} \sim \sigma^{3/2}$ ). We interpret this super-stiffening regime in terms of the reorientation of filaments with the maximum tensile direction of the deformation field. A simple model for the reorientation response gives an exponential stiffening,  $G \sim e^\sigma$ , in qualitative agreement with our

data. We are currently generalizing the model to include active elements, i.e. motors, and study their effects on the elastic properties of the network.



Fig. 1: Snapshot of a network of cross-linked semiflexible filaments.

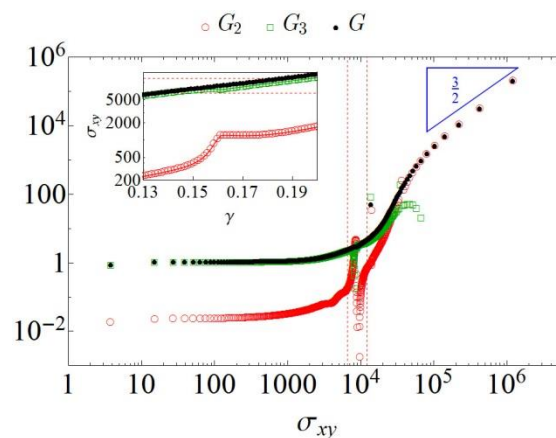


Fig. 2: Elastic modulus  $G$  as a function of applied shear stress;  $G$  is constant in the linear regime (small  $\sigma$ ) and increases like  $\sigma^{3/2}$  for large stresses; in between super-stiffening is observed; also shown are the contributions from particle ( $G_2$ ) and 3 particle interactions ( $G_3$ ) with  $G_3$  dominating for small  $\sigma$  and ( $G_2$ ) dominating for large  $\sigma$ .

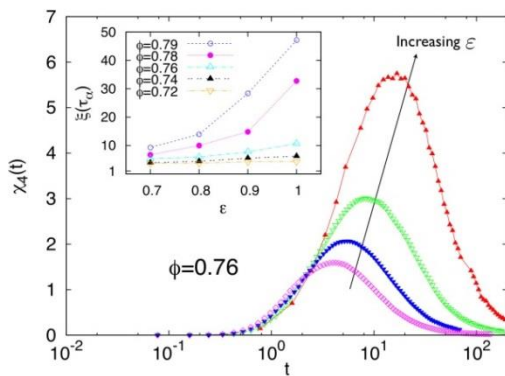
Other projects tackled with analytical theory are the bundling transition of reversibly crosslinked, grafted polymers [3], i.e. brushes, the phase diagram of cross-linked block-copolymers [4] and the tension induced binding of reversibly cross-linked filaments [5].

### Granular fluids

Granular media are an important and popular subject of current research which is owed partly to the striking phenomena which they reveal and partly to their ubiquity in nature and industry which makes a good understanding of their properties indispensable. Examples are sand, snow, gravel, and seeds to mention but a few. In fact the majority of industrial products are processed and handled in the form of granular media, such as powders. The materials are composed of macroscopic particles, which are big enough to render thermal agitation negligible. The interactions are in general dissipative, so that granular systems continuously loose energy unless they are externally driven to a stationary state.

#### Non-equilibrium glass transition

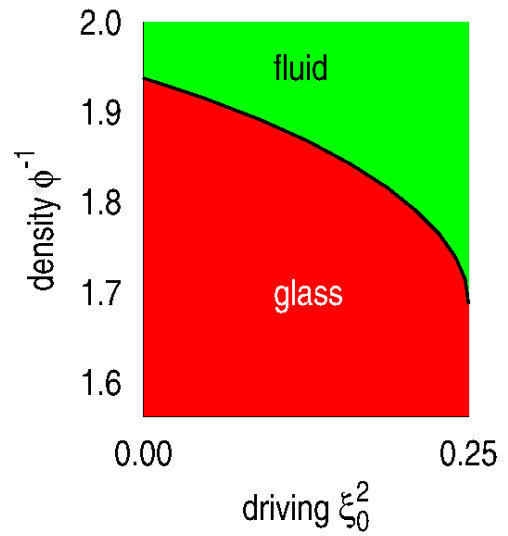
The glass transition has been studied extensively in thermal fluids and colloids – systems which are in equilibrium at high temperature or low density and fall out of equilibrium when the viscosity increases dramatically at the glass transition. We are interested in fluids which are inherently out of equilibrium, but nevertheless undergo a glass transition [6]. The prototype example is a granular fluid which is driven into a stationary state. As the dynamical arrest is approached, not only does the dynamics become dramatically slower, but it becomes increasingly heterogeneous. Large scale simulations of 2d driven granular fluids allow to determine spatial correlations via the four-point structure factor  $S_4(q, t)$ . The latter is shown to obey



**Fig. 3:** Four point susceptibility  $\chi_4(t)$  for various packing fractions  $\phi$ , revealing a strong increase as the glass transition is approached; inset: correlation length  $\xi$  as a function of the coefficient of restitution for several values of  $\phi$ .

scaling, which is remarkably universal with respect to the strength of dissipation. Both the dynamic susceptibility,  $\chi_4$ , and the correlation length,  $\xi$ , increase dramatically as a function of density and can be fitted to power law divergencies, see Fig. 3.

Mode-coupling theory is an analytical approach to the glass transition which can be generalized to non-equilibrium systems [7]. A phase diagram, shown in Fig. 4, can be derived in the plane of packing fraction,  $\phi$ , and driving strength,  $\xi_0^2$ . The glass transition in granular fluids is qualitatively similar to thermal fluids with, however, non-universal exponents.

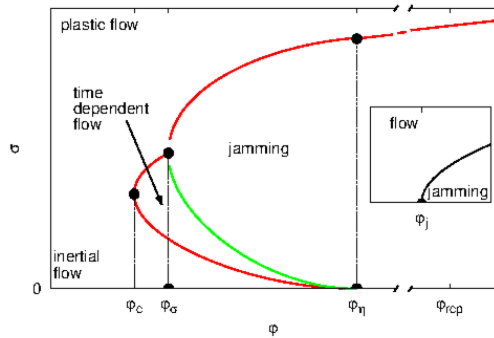


**Fig. 4:** Phase diagram of a driven granular fluid displaying a glassy phase; the origin of the graph lies at random-close packing.

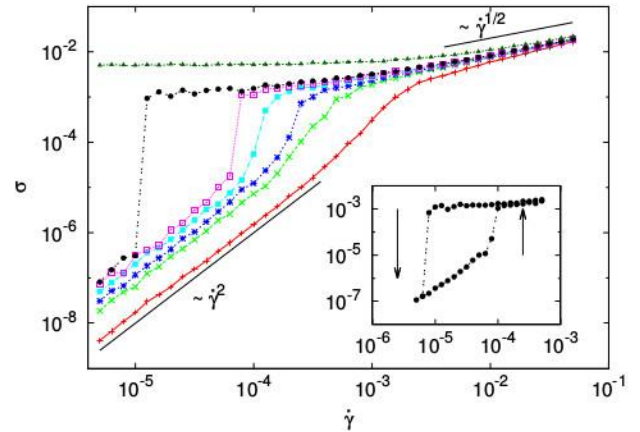
#### Rheology

Whereas jamming of frictionless particles has attracted a lot of interest and is reasonably well understood, the effects of friction are less clear, even though almost all experimental realizations of granular fluids involve frictional forces between the grains. The phase diagram of frictional grains, see Fig. 5, is substantially different from the frictionless case. It resembles an equilibrium first order phase transition [8] with a nonzero yield stress at jamming and reentrance as a function of applied stress  $\sigma$ . Small systems ( $N \leq 20.000$  in 2d) show discontinuous shear thickening and hysteresis as a function of the applied strain rate, see Fig. 6. For large systems on the other hand, there is a region in phase space where neither stationary flow nor a jammed state is observed. Instead the system displays rheological chaos with time-dependent heterogeneous flow. We are currently trying to understand microscopic mechanisms of shear thickening and frictional

granular matter. These projects are done in collaboration with Dr. Claus Heussinger, who is leading a junior research group funded by the Emmy-Noether program of the DFG.



**Fig. 5:** Phase diagram of frictional granular matter as a function of packing fraction  $\phi$  and shear stress  $\sigma$ .



**Fig. 6:** Flow curves  $\sigma(\dot{\gamma})$  for different packing fractions  $\phi = 0.78, 0.7925, 0.795, 0.7975, 0.79875, 0.80, 0.82$  (from bottom to top). Main part: Flow curves obtained by decreasing  $\dot{\gamma}$ . Inset: Example of a hysteresis loop for  $\phi = 0.80$ .

#### Selected publications

- [1] H. E. Amuasi, C. Heussinger, R. Vink, and A. Zippelius: *Nonlinear and heterogeneous elasticity of multiply cross-linked networks*, New J. Phys. **17**, 083035 (2015).
- [2] P. Benetatos and A. Zippelius: *Anisotropic random networks of semiflexible polymers*, Phys. Rev. Lett **99**, 198301 (2007).
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- [4] A. von der Heydt and A. Zippelius: *Phase diagram of selectively cross-linked block copolymers show chemically microstructured gel*, J. Chem. Phys. **142**, 054901 (2015).
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- [6] K. E. Avila, H. E. Castillo, K. Vollmayr-Lee, and A. Zippelius: *Strong dynamical heterogeneity and universal scaling in driven granular fluids*, Phys. Rev. Lett. **113**, 025701 (2014).
- [7] T. Kranz, M. Sperl, and A. Zippelius: *Glass transition for driven granular fluids*, Phys. Rev. Lett. **104**, 225701 (2010).
- [8] M. Grob, C. Heussinger, and A. Zippelius: *Jamming of frictional particles: A nonequilibrium first order phase transition*, Phys. Rev. E **89**, 050201 (2014).