

# 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?

## Gels and glasses

If the molecules in a polymeric melt or dense solution are sufficiently crosslinked, a gel transition is observed, when a macroscopic cluster of connected molecules forms for the first time (Fig.1).

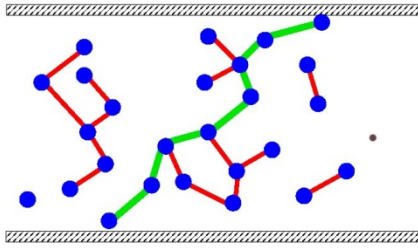


Fig. 1: Spanning cluster (green) of crosslinked molecules

Whereas in the fluid or sol phase at low crosslinking the molecules explore all the available volume, in the gel or amorphous solid phase the particles are localized at random positions and perform finite thermal excursions. Furthermore the fluid is characterized by a viscous response to a shear flow with a shear viscosity that diverges as the gel point is approached, indicating structural arrest. The amorphous solid has a finite stiffness to static shear deformations, which is lost at the gel point as indicated by a vanishing of the shear modulus. The experimental findings are sketched schematically in Fig.2 where  $c$  denotes the concentration of crosslinks.

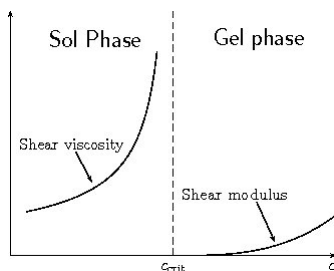


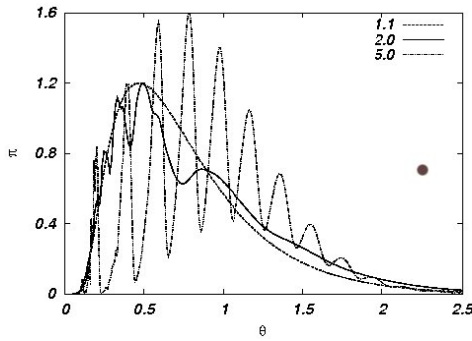
Fig. 2: Shear viscosity and shear modulus as a function of crosslink concentration  $c$ ; gel transition at  $c = c_{crit}$

In the past we have computed the viscoelastic response near the gel transition and in the highly crosslinked limit, using the methods of statistical mechanics.

Another interesting question is how to characterize the structure of an amorphous solid. What is the right order-parameter for the transition from the fluid to the amorphous solid or glassy state? On the basis of a snapshot of the glass, one cannot distinguish a fluid from a glassy state because both are disordered. On the other hand taking a second snapshot at a much later time and asking for the correlation between the two snapshots will reveal drastic differences between fluid and glassy phases. Whereas in the fluid the two disordered arrangements of the particles are completely uncorrelated, - in the amorphous solid or glass, the arrangements will be highly correlated, in fact perfectly correlated if thermal motion were suppressed. Hence an adequate order parameter is the long time limit of the incoherent scattering function

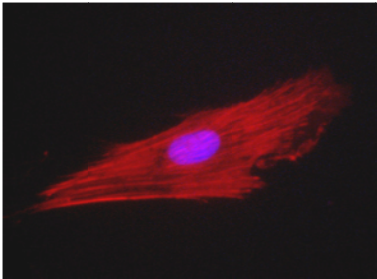
$$\begin{aligned} \Omega(\vec{q}) &= \lim_{t \rightarrow \infty} \left[ \langle e^{i\vec{q} \cdot (\vec{r}_i(t) - \vec{r}_i(0))} \rangle_i \right] \\ &= \begin{cases} e^{-Dq^2 t} \rightarrow 0; & \text{fluid} \\ [e^{-q^2 \xi^2}] \neq 0; & \text{glass} \end{cases} \end{aligned}$$

where the localization length  $\xi$  is a measure for the extent of thermal motion. In a disordered system this quantity fluctuates from site to site, so that the main structural characteristic of an amorphous solid is the distribution of localization length:  $P(\xi^2)$ . It can be computed analytically within mean field theory and some results are shown in Fig. 3. Close to the transition ( $c = 1.1$ )  $P(\xi^2)$  is a universal function. In the highly crosslinked limit ( $c = 5.0$ ) the distribution consists of a set of peaks, each associated with a given coordination number.



**Fig. 3: Distribution of inverse localization length  $w(\theta)$  ; near the gel point ( $c = 1.1$ ) and in the highly crosslinked limit  $c = 5$ .**

We are presently generalizing these theories to anisotropic gels, displaying long range orientational order as well as glassy states. These systems show a variety of interesting new phenomena due to the coupling of stress and strain to oriental degrees of freedom which are easy to manipulate. For example, shape changes can be induced by temperature or external fields opening the route to a variety of applications such as artificial muscles. Anisotropic gels are also prominent in biological systems such as cells (Fig. 4), yet their viscoelastic properties are only poorly understood.

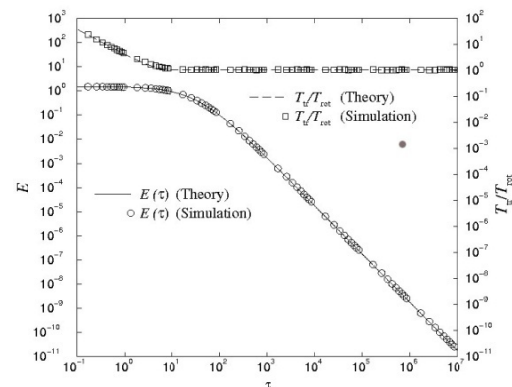


**Fig. 4: Mesenchymal cell on a gel with actin (red) and cell nucleus (purple) (courtesy of F. Rehfeldt).**

### Collective dynamics of granular fluids

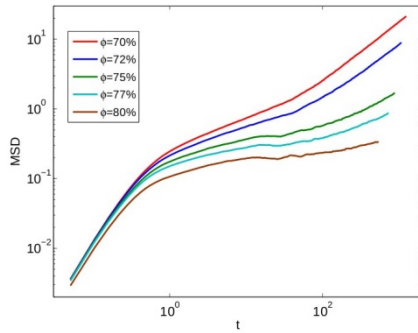
Granular media are an important and popular subject of current research which is owed partly to the striking phenomena which they reveal and partly to their ubiquity in nature and industry which makes a good understanding of their properties indispensable. Examples are sand, snow, gravel, and seeds to 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 lose energy unless they are externally driven to a stationary state.

We are doing basic research in our group and hence focus on simple model systems, such as hard, spherical particles which collide inelastically. The simplest problem is to understand, how a gas of such inelastically colliding particles cools down as a function of time. This problem has been investigated intensively for smooth granular particles ignoring frictional forces in collisions. Our focus is on particles with rotational degrees of freedom and friction, such that in collisions translational energy is transferred to rotational motion and vice versa. In the past we have shown that free cooling proceed such that the ratio of translational to rotational energy relaxes quickly to a constant value which is not only different from equipartition, but depends on the details of the collision rules and the particles' properties (Fig. 5). We have also shown that the direction of the linear velocity is in general correlated with the axis of rotation such that the granular particles move in some systems predominantly like sliced tennis balls in other systems like cannon balls.



**Fig. 5: Decay of the translational ( $T_t$ ) and rotational ( $T_{rot}$ ) energy for a freely cooling gas of frictional particles.**

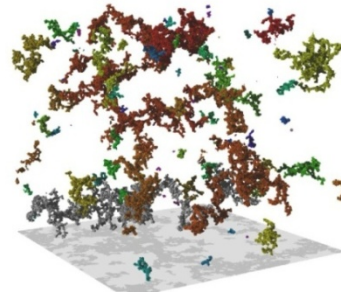
At present we are investigating the question, whether a driven granular gas undergoes a glass transition and if so, how the transition as well as the glassy state differ from an undriven, elastic glass-forming fluid. We perform event driven simulations and try to derive a mode-coupling theory, generalizing the results of molecular fluids to granular ones far from equilibrium. In the simulations we observe strong precursors of structural arrest: cage effects in the mean square displacement (Fig. 6), backscattering effects in the velocity autocorrelation and a strong decrease of the diffusion constant.



**Fig. 3: Mean square displacement of a driven granular fluid in two dimensions; volume fraction  $\phi$  is increasing from  $\phi = 70\%$  up to  $\phi = 80\%$ .**

Adding a small amount of liquid to a granular medium changes its properties dramatically, as is well known to everyone who has built sand castles. The difference in macroscopic behavior is reflected in the microscopic interactions. Wetted grains are covered by thin liquid films which merge, when the particles touch forming a liquid bridge. As the particles move apart the bridge is stretched and ultimately ruptures, provided the particles have enough kinetic energy. Rupture of a bridge gives rise to dissipation of a fixed amount of energy. In

collaboration with the group of Prof. Herminghaus at the MPI for Dynamics and Self-organization, we study the dynamics and structure formation in wet granular gases. We have formulated an event driven algorithm which allows simulating large assemblies for a long time. A particularly important aspect of cooling in cohesive gases is aggregation, which sets in when the kinetic energy falls below the bond-breaking energy. The resulting clusters, an example is shown in Fig. 7, are very loosely packed but stable structures with interesting fractal properties.



**Fig. 4: Aggregated clusters in a freely cooling cohesive granular gas.**

#### Selected publications

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