Chapter 14

From viscous fluids to elastic solids:
A perspective on the glass transition

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A theory for the non-local stress in liquids captures the crossover from viscous to elastic correlations upon supercooling. It explains the emergence of long-ranged stress fields in glass which originate from the coupling of shear stress to transverse deformations. The Goldstone mode in colloidal glass is shown to be diffusive.

1. Introduction

The most prominent distinction between a fluid and a glass is the response to a static shear stress: A fluid continues to flow as long as the shear is applied and hence its response is characterized by a finite shear viscosity. On the other hand, a glass or an amorphous solid displays a finite deformation in response to a small applied shear and is thus characterized by a finite elastic resistivity to shear deformations. One of the first to capture this fundamental difference was Maxwell\(^1\) who suggested that the transition from viscous to elastic behaviour is due to the divergence of a (single) relaxation time \(\tau\). He proposed the following simple relation between a shear stress, e.g. \(\sigma_{xy}\), and the corresponding velocity gradient

\[
(\partial_t + 1/\tau)\sigma_{xy} = \mu \partial_y v_x
\]

in terms of the shear modulus, \(\mu\), encoding the elasticity. In the solid \(\tau\) is infinite, implying an elastic response \(\sigma_{xy} = \mu \partial_y u_x\) in terms of the displacement, \(u_x\), which enters Eq. \(1\) via its time derivative, \(v_x = \partial_t u_x\). In the fluid, \(\tau\) is finite, so that in the hydrodynamic limit \(\sigma_{xy} = \eta \partial_y v_x\) with the shear viscosity given by \(\eta = \mu \tau\).

What is missing? We know from linear elasticity theory that stresses are long ranged in solids: A localised shear strain, \(\epsilon_{xy}\), generates far away stresses according to

\[
\sigma_{xy}(\mathbf{r}) = 2\mu \int d^3r' G(\mathbf{r} - \mathbf{r}')\epsilon_{xy}(\mathbf{r}')
\]

\[
G(\mathbf{r}) = \frac{3}{4\pi r^3} \left(r^2(x^2 + y^2) - 10x^2y^2\right) \propto r^{-3}
\]

Note that the Green function, \(G(\mathbf{r})\), is not only long-ranged, but also anisotropic, even though we have specialised to isotropic solids, such as glasses or amorphous solids.
The basic questions we want to address in this paper are the following: How do long range stress correlations build up at the glass transition? Are there precursors in the supercooled liquid? Can we formulate a unified hydrodynamic theory of liquids and glasses?

To answer these questions, we have computed the correlations of the local shear stress fluctuations

\[ C(q) = \frac{n}{k_B T} \langle \sigma_{xy}(-q,t) \sigma_{xy}(q) \rangle \]  

where the homogeneity of the system is conveniently exploited by Fourier transforming. The microscopic stress tensor that enters Eq. (3) is taken from Irving and Kirkwood which reads for the potential contribution:

\[ \sigma_{\alpha\beta}(r) = \sum_{j,k} r_{jk} U'(r_{jk}) a \int_0^1 ds \delta(r - r_k - s r_{jk}). \]  

The shortcoming of a single relaxation time approximation à la Maxwell is the neglect of slow dynamics in the local stress fluctuations, which cannot be captured by a single relaxation time and which will ultimately give rise to nontrivial stress correlations.

2. Emergence of long range stress correlations

The obvious candidates for slow relaxation in a Newtonian fluid are the conserved densities of particle number, momentum and energy. For simplicity, we consider an incompressible, isothermal system and refer to the literature for the general case. The only conserved field is thus the transverse momentum or velocity, defined as \( v^\perp(q) = q \times (q \times v(q))/q^2 \) with \( v(q) = \frac{1}{\sqrt{N}} \sum_{i=1}^N e^{iqr_i(t)}v_i \).

In the hydrodynamic limit, its correlation function \( \langle v^\perp(q,t) \rangle \) describes diffusive momentum transport at long wavelengths; in the fluid phase the relaxation rate \( \eta q^2 \) diverges as the wavenumber goes to zero, reflecting the conservation law. This behaviour is captured in the following representation of the Laplace transform \( K_q(s) = \int_0^\infty dt e^{-st} K_q(t) \) in terms of a generalised shear modulus \( G_0(s) \). The main advantage of this representation is that it guarantees the correct treatment of the conservation law and allows for simple approximations of the modulus. For example, a single relaxation time approximation à la Maxwell, \( G_0(s) = (\mu \tau)/(1 + st) \), reproduces the diffusion of transverse momentum in the fluid (\( \tau \) finite) and (undamped) transverse sound modes in the solid (\( \tau \) infinite).

The conservation of transverse momentum gives rise to a slow component also in the relaxation of the stress correlation which can be isolated with help of the Mori-Zwanzig formalism. A projection operator \( P = \frac{m}{k_B T} v^\perp(q) \cdot (v^\perp(q))^* \) captures the
overlap between the transverse momentum and a fluctuation of the shear stress. Application of \( \mathcal{P} \) to the stress correlation, \( C(\mathbf{q}) \), yields the desired decomposition:

\[
C(\mathbf{q}, s) = G_0(s) - (q_x^2 + q_y^2 - 4q_x^2q_y^2/q^2) (G_0(s))^2 K_q(s) (6)
\]

into a hydrodynamic contribution and local dynamics entailed in \( G_0(s) \). In a straightforward generalization of the Maxwell model, we use a single relaxation time approximation for \( G_0(s) = (\mu\tau)/(1 + s\tau) \), allowing for a divergence of the structural relaxation time \( \tau \) at the glass transition.

What are the predictions of the generalised Maxwell Model? First, the result of Maxwell is reproduced for the global stress in a fluid, \( C(\mathbf{q} = 0, s) = \eta \) with shear viscosity \( \eta = \mu\tau \). Second, stress correlations are strongly \textit{anisotropic} in the isotropic fluid, characterized by finite \( \tau \):

\[
C(\mathbf{q}, s) = \eta - (q_x^2 + q_y^2 - 4q_x^2q_y^2/q^2) \frac{\eta^2}{nms + \eta q^2}. \quad (7)
\]

Local stresses do not decay quickly, but display long-lived diffusive behaviour. The distance to the glass transition is controlled by \( \tau \), or equivalently \( \eta \), which is known to increase dramatically as the glass transition is approached. Here, we follow Maxwell and consider an ideal glass transition with a true divergence of \( \tau \). The increasingly slow dynamics implies increasingly \textit{long-ranged} stress correlations as the glass transition is approached, i.e. \( \tau \rightarrow \infty \). The spatial extent of stress correlations is quantified by a correlation length \( \xi \) which diverges as the glass transition is approached,

\[
\xi^2 = \frac{\mu\tau^2}{mn}. \quad (8)
\]

The glass resists static shear deformations and the above static correlations are equivalent to Eshelby’s response function in Eq. \( \text{[2]} \). Shear deformations in the glassy phase are propagating sound modes as reflected in the connected correlation: \( C(\mathbf{q}, s) - C_\infty(\mathbf{q}) = \frac{\mu s}{s^2 + q^2c^2} \) for \( q_x = 0 \) and with speed of sound \( c^2 = \mu/(mn) \). Fourth, with the above definition of the correlation length we can write the stress correlation in scaling form:

\[
C(\mathbf{q}, t) = \frac{4q_x^2q_y^2 + q_x^2q_y^2}{q^4} \mu. \quad (9)
\]
3. Goldstone modes of a colloidal glass

The momentum of colloidal particles in suspension is not conserved in contrast to the Newtonian fluid discussed above.13 The interaction with the solvent is conveniently approximated by a constant friction coefficient $\zeta_0$, ignoring hydrodynamic interactions. Consequently, velocity correlations

$$K_q(s) = \frac{k_B T/m}{s + q^2 m C_0(s) + n \zeta_0}$$

(9)

decay on microscopic timescales in the hydrodynamic regime and, due to symmetry, there are no conserved fields which could give rise to slow shear stress fluctuations. However, we expect that correlations of the transverse displacement, $u^\perp$, are long ranged also in colloidal glasses. To capture these long range fluctuations in a unified hydrodynamic theory of supercooled liquids and glasses including suspensions, we separate the dynamics of stress fluctuations into a part in the subspace of $u^\perp$, or rather its time derivative $v^\perp = \partial_t u^\perp$, and the rest. In other words we use the same decomposition as for the Newtonian case with however different velocity correlations (Eq. 9).

The most surprising results of the generalised Maxwell model refer to the colloidal glass. The static elasticity, as described by $C_{\infty}(q)$, is the same as for the Newtonian model as one would expect. However, frequency dependent transverse deformations propagate diffusively

$$C(q, s) - C_{\infty}(q) = \mu \left( \frac{q_x^2 + q_y^2}{q^2} - 4 \frac{q_x^2 q_y^2}{q^4} \right) \frac{\zeta_0}{s \zeta_0 + q^2 \mu/\rho}$$

(10)

We identify this diffusive mode with the Goldstone excitations of an amorphous solid. Localisation of the particles implies a spontaneous breaking of the translational symmetry of the system. In contrast to crystalline systems, the symmetry is restored on a macroscopic level, because the particles are localised at random positions.14 Nevertheless, a uniform translation of all particles leaves the energy invariant and the energy of an almost uniform translation goes to zero as the wavelength of the perturbation grows. In a phenomenological approach, we start from the elastic free energy
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\[ F = \frac{\mu}{2} \int d^d q \; q^2 \; u^\perp(q) \cdot u^\perp(-q) \] and assume purely relaxational dynamics

\[ n\zeta_0 \frac{\partial}{\partial t} u^\perp(q) = -\frac{\delta F}{\delta u^\perp(-q)} = -\mu q^2 \; u^\perp(q). \]

The relaxation of \( u^\perp(q) \) is diffusive in perfect agreement with the diffusive pole \( s = -q^2 \mu/(n\zeta_0) \) observed in Eq. (10).

Precursors of this diffusive mode can be observed in supercooled colloidal suspensions, which are well described by Eq. (10) in the large damping limit, ignoring inertial terms. The frequency dependent spectra are strongly anisotropic in \( q \)-space, as already observed for the Newtonian case. Choosing \( q \) along one of the axis, say \( q = (q, 0, 0) \) we find:

\[
C(q, s = -i\omega) = C'(q, \omega) - iC''(q, \omega) \\
C''(q, \omega) = \mu \left( \frac{\omega^2}{(q^2 + 1)^2 + \omega^2} \right) \xi^2 \\
C'(q, \omega) = \mu \left( \frac{\omega^2}{(q^2 + 1)^2 + \omega^2} \right) \xi^2
\]

Here we have introduced the correlation length \( \xi^2 = \mu \tau/(n\zeta_0) \), which diverges as \( \xi \propto \sqrt{\tau} \) in contrast to the Newtonian case. For sufficiently large \( q\xi > 1 \), the peak in the loss spectrum is located at \( \omega \tau \sim q^2 \xi^2 \).

4. Conclusions

We have computed the nonlocal stress correlations for both, Newtonian as well as colloidal fluids. A generalised Maxwell model connects the emergence of long range stress correlations in the viscous fluid to the elasticity of glasses. In Newtonian fluids, the range of stress correlations is charcterized by a correlation length \( \xi \propto \tau \), which grows approaching the glass transition, whereas in colloidal fluids \( \xi \propto \sqrt{\tau} \). In the colloidal glass, transverse deformations propagate diffusively in contrast to transverse sound in the Newtonian case.

The nonlocal stress correlations can equivalently be computed from purely hydrodynamic considerations, decomposing the flow field into the externally imposed flow and a fluctuating part. The response function to the externally imposed flow is related via the fluctuation-dissipation theorem to the correlation function, discussed here. Several extensions of the simple model are possible; we have already analysed compressible systems including longitudinal sound. Another extension refers to a computation of the generalised modulus, going beyond the single relaxation time approximation.
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