Enhancement of structural rearrangement in glassy systems under shear flow

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Abstract. – We extend the analysis of the mean field schematic model recently introduced [1] for the description of glass forming liquids to the case of a supercooled fluid subjected to a shear flow of rate $\gamma$. After quenching the system to a low temperature $T$, a slow glassy regime is observed before stationarity is achieved at the characteristic time $\tau_g$. $\tau_g$ is of the order of the usual equilibration time without shear $\tau_{0g}$ for weak shear, $\gamma \tau_{0g} < 1$. For larger shear, $\gamma \tau_{0g} > 1$, local rearrangement of dense regions is instead enhanced by the flow, and $\tau_g \simeq 1/(T\gamma)$.

Structural rearrangement in supercooled liquids and glassy systems is severely suppressed due to configurational restrictions, requiring a cooperative dynamics of correlated regions that involves many degrees of freedom [2]. This complex behaviour often results in a slow kinetics characterized by diverging relaxation times at the temperature of structural arrest $T_o$ [3] and strong non-equilibrium effects, such as aging. A glassy system above $T_o$ is generally observed to be off-equilibrium either because a modification of the control parameters, such as the pressure or the temperature, has been exerted or because it is driven mechanically. In the latter situation it is possible to show that the aging of some systems can be triggered by the external forcing and that they look younger if a larger drift is applied [4]. This is also witnessed by the modalities of the violation of the fluctuation dissipation theorem [5, 6]. In many cases, by injecting power there is the possibility to interrupt aging and stabilize the system into a power-dependent stationary state. This effect is observed, for instance, in gelling systems under an applied shear force [7].

In this letter we study the out of equilibrium evolution of a glassy system, such as a supercooled fluid, quenched above $T_o$ in the presence of a shear flow with rate $\gamma$ [8]. The analysis of the dynamics is carried out in the framework of a model [1] recently introduced for the description of the glassy behavior close to the dynamical transition. The approach
is simple enough to be handled analytically, allowing explicit calculations. Our main result is the observation of two regimes: a weak shear regime, where the flow does not practically affects the glassy behavior, and a strong shear situation, where the inner relaxation process is enhanced, because density fluctuations are convected by the flow, and aging is interrupted after a time $\tau_g \simeq 1/(T\gamma)$. For $t > \tau_g$ a shear-induced time-translational invariant steady state is entered where the decay of the two-time correlation function is characterized by the presence of inflection points.

When a macroscopic motion of the fluid is present, the mean field version of the model introduced in [1] is generalized by the following constitutive Equation

$$\frac{\partial \rho(\vec{r}, t)}{\partial t} + \vec{V} \cdot \rho(\vec{r}, t) \vec{V}(\vec{r}) = D(t) \nabla^2 \rho(\vec{r}, t) + \eta(\vec{r}, t)$$

(1)

where $\rho(\vec{r}, t)$ is a coarse grained particle density, and $D(t) = \langle M(\rho) \rangle$ is the average mobility of the particles. $\eta$ is a gaussianly distributed random field, representing thermal noise, with expectations $\langle \eta(\vec{r}, t) \rangle = 0$ and $\langle \eta(\vec{r}, t)\eta(\vec{r}', t') \rangle = -2T D(t) \nabla^2 [\delta(\vec{r} - \vec{r}')\delta(t - t')]$, where $\langle \ldots \rangle$ is the ensemble average and $T$ is the temperature of the bath. In Eq. (1) the second term on the l.h.s. is an advection contribute, due to the presence of the flow, which was not considered in [1]; $\vec{V}$ is the velocity of the fluid: for the case of a plane shear flow we consider $\vec{V}(\vec{r}) = \gamma y \vec{e}_x$, $\vec{e}_x$ being the unitary vector in the flow direction. Eq. (1) describes a system where the shear rate is homogeneous throughout the sample and applies therefore only to materials which can support such a flow (these are sometimes referred to as soft glassy materials, as opposed to hard glassy materials where strain localization or fractures are observed [10]).

The present model aims to describe the main features of the out-of-equilibrium dynamics above $T_g$. It is schematic in spirit and, in order to be generic, leaves aside as much system specific details as possible. The basic assumptions is that a good deal of the complex behavior of glassy systems can be encoded into the conventional convection-diffusion [9] equation (1) by means of a suitably chosen particle mobility $M(\rho)$. In [1] a quickly vanishing function of the density, $M(\rho) = \exp\{v[\rho - 1]^{-1}\}$ was proposed on phenomenological grounds; here $v$ is a (temperature dependent) parameter and the particle density has been rescaled so that $\rho = 1$ is the point of dynamical arrest. This form of the mobility has been obtained in different approximations by several authors in apparently heterogeneous contexts as the free-volume theory of the glass transition [2] or in "car parking" problems in one dimension [11]. In the mean field version of the model, expressed by Eq. (1), $M(\rho)$ is replaced by its average value that can be computed as

$$D(t) = [2\pi S^2(t)]^{-1/2} \int_0^1 M(\rho)e^{-(\bar{\rho} - \rho)^2/2S^2(t)}\,d\rho$$

(2)

where $\bar{\rho} = \langle \rho \rangle$ and $S^2(t) = \langle (\rho - \bar{\rho})^2 \rangle$, since the density distribution is gaussian [1].

From Eq. (1), by transforming into momentum space, the following formal solution for the two-time correlator $C(\vec{k}', \vec{k}, t_1, t_1 + \Delta t) = \langle \rho(\vec{k}', t_1)\rho(\vec{k}, t_1 + \Delta t) \rangle = C(\vec{k}, t_1, t_1 + \Delta t)\delta[\vec{k}(\Delta t) + \vec{k}']$ is found, with

$$C(\vec{k}, t_1, t_1 + \Delta t) = \chi[\vec{k}(\Delta t), t_1] \exp \left[ - \int_0^{\Delta t} \mathcal{K}^2(s)D(t_1 + \Delta t - s)\,ds \right]$$

(3)

where $\mathcal{K}(s) = k_x s \vec{e}_y$, $\vec{e}_y$ being the unitary vector in the shear direction. Notice the presence of the delta function $\delta[\vec{k}(\Delta t) + \vec{k}']$, as opposed to the usual $\delta[\vec{k} + \vec{k}']$, due to the distortion induced by the flow [12]. $\chi(\vec{k}, t) = C(\vec{k}, -\vec{k}, t, t)$ is the structure factor that, with a
high temperature disordered initial condition \( \chi(\vec{k}, 0) = \Delta \), evolves according to

\[
\chi(\vec{k}, t) = (\Delta - T) e^{-2 \int_0^t \kappa^2(s) D(t-s) ds} + T
\]

From Eq. (3) the average density fluctuations can be computed through

\[
S^2(t) = (2\pi)^{-d} \int_{|\vec{k}| < \Lambda} \chi(\vec{k}, t) d\vec{k}, \quad \text{where} \quad \Lambda \text{ is a phenomenological momentum cutoff.}
\]

For sufficiently long times the integral of the exponential terms in Eq. (4) can be extended to the whole \( \vec{k} \)-plane (letting \( \Lambda = \infty \)) because the support of \( \chi \) shrinks towards the origin (see Fig. 1), yielding

\[
S^2(t) = \frac{\pi^{-\frac{d}{2}}}{2^d} (\Delta - T) R_0(t)^{\frac{d-2}{2}} \cdot \left\{ R_0(t) - \gamma^2 \left[ \frac{R_2(t)}{R_0(t)} - R_2(t) \right] \right\}^{-\frac{1}{2}} + qT
\]

where \( q = (\Sigma_d / d) \Lambda / (2\pi)^d \), \( \Sigma_d \) is the surface of the \( d \)-dimensional unitary hypersphere and \( R_n(t) = \int_0^t z^n D(t-z) dz \). Eqs. (2,5) are closed coupled equations which allow the computation of \( D(t) \) and hence the whole evolution of the model, through the correlator (3).

In the case with no flow it has been shown \([1]\) that when \( \gamma \) is close to the critical value \( \gamma = 1 \) a cage effect produces a transient pinning phenomenon characterized by the constancy of the main observables, namely \( C, \chi, D \) and \( S \). Then, for longer times, less dense regions start evolving, but yet high density regions are almost frozen and evolve slower, producing a glassy behavior characterized by the existence of many time scales and aging. The evolution of the system in this regime is characterized by a decay of \( C \) slower than the usual diffusive behavior with an exponential damping of the correlations. Aging is eventually interrupted after a characteristic time \( \tau_g \) and an equilibrium state is entered where time translational invariance is recovered. For dense systems \([13]\), equilibration is induced by thermal fluctuations which shake the frozen regions of the system.

When shear is applied to the fluid a similar situation occurs. In the following we describe the main results of the analytical solution. We refer to a deep quench (low \( T \)) with a high density \( (\gamma \approx 1) \). Initially the cage effect is observed, as discussed in \([3]\); this is reflected in Fig. 2 by the constancy of \( D \) for small times. For longer times the evolution starts and the glassy regime is entered, as for \( \gamma = 0 \). The behavior of the structure factor in this time domain is shown in Fig. 1 where the anisotropic character of the correlations is evident. We consider the situations relative to different ranges of the strain \( \gamma t \).

**Small strain.** For sufficiently small \( \gamma t \), neglecting the terms proportional to \( T \) and \( \gamma \) in Eq. (5) one can solve Eqs. (2,5) obtaining

\[
D(t) \sim t^{-1} (\ln t)^{\delta-1},
\]

where \( \delta = 6/d \), as without flow. This is shown in Fig. 2 where it is seen that the curves for \( D(t) \) initially collapse onto the \( \gamma = 0 \) line. Inserting the expression for \( D \) into Eq. (3) one finds that the terms proportional to \( \gamma \) are negligible and \( C \) falls isotropically as an enhanced power law. Time translational invariance is lacking and the system ages. Shear induced effects become relevant at the crossover time \( \tau_c \), when the terms proportional to \( \gamma \) and \( T \) cannot be neglected in Eq. (5). From the analysis of Eq. (3) we obtain

\[
\tau_c = \min\{\tau_g^0, \gamma^{-1}\}
\]

and \( \tau_g^0 \), the time at which aging is interrupted in the corresponding undriven system, is computed in \([1]\). In the weak shear regime, with \( \tau_g^0 \ll \gamma^{-1} \), the glassy evolution is ended at \( t \approx \tau_g^0 \), due to the thermal fluctuations, and the presence of the flow only affects the
asymptotic dynamics that will be discussed below. For the choice of parameters of Figs. 1, 2 one has $\tau_g^o \approx 10^8$ (this is the time at which $D$ approaches the asymptotic constant value) and so, from Eq. (3), we expect the curves of $D$ to depart from the $\gamma = 0$ case for $\gamma \leq 10^{-8}$, as shown in Fig. 2.

**Large strain.** For large strain and values of $\gamma$ in a strong shear regime with $\gamma^{-1} < \tau_g^o$, the glassy behavior is changed for $t > \tau_c$ by the motion of the fluid. By keeping only terms proportional to $\gamma$ in Eq. (3) we find

$$D \sim e^{-(t/t_o)^{1/3}},$$

(8)

where $t_o$ is a constant. In this glassy regime the convergence to the asymptotic stationary state is enhanced by the shear. One can check that the term $qT$ is negligible on the r.h.s. of Eq. (3) up to $\tau_g = (T \gamma)^{-1}$, when aging is interrupted. The dependence of $\tau_g$ on $\gamma$ is shown in the inset of Fig. 2, showing that $\tau_g = \tau_g^o$ for small $\gamma$ while it approaches a $\tau_g \sim \gamma^{-1}$ law for larger values of the shear. This completes the description of the pre-asymptotic glassy stage.

We consider now the behavior of the system in the asymptotic domain ($t > \tau_g$). Since $R_n(t) \to \infty$, one has $S(t) \simeq qT$ so that $D(t) = D(\infty) = \text{const.}$. This can be seen in Fig. 2. Hence one time quantities do not depend on $t$ and two time observables, such as the correlator (3), are functions of the difference $\Delta t$ alone

$$C(\vec{k}, \Delta t) = T \exp\{-D(\infty)[2\Delta tk^2 + \gamma(\Delta t)^2k_xk_y + \frac{\gamma^2}{3}(\Delta t)^3k_x^2]\}$$

(9)

Time translational invariance is then recovered. For $\gamma = 0$, from Eq. (3), $C$ has a simple exponential form. When the shear is present, on the other hand, the decay is faster for large $\Delta t$ (except at $k_x = 0$), indicating that the relaxation of fluctuations is enhanced by the flow. Actually the behavior of $C$ is more complex, as shown in Fig. 3. In this picture the behaviour of $C(\vec{k}, \Delta t)$ is plotted at $\gamma = 10^{-2}$ for different $\vec{k}$. In the sectors $k_xk_y > 0$ all the coefficients of the polynomial form in the argument of the exponential in Eq. (3) are positive. Then $C$ is depressed with respect to the case $\gamma = 0$ for any $\Delta t$. On the other hand, $C$ develops inflections in the sectors with $k_xk_y < 0$. From the comparison with the case $\gamma = 0$ one sees that this effect causes correlations to be initially (for $\gamma \Delta t < -3k_y/k_x$) enhanced by the shear and only successively damped.

Integrating the expression of Eq. (3) over the space of wave vectors we obtain the behaviour of the autocorrelation function

$$A(\Delta t) = \int_{k<\Lambda} \frac{d\vec{k}}{(2\pi)^d} C(\vec{k}, \Delta t) = \frac{T}{2\pi^{d/2} \left[D(\infty)\Delta t\right]^{d/2} \left[1 + \frac{7}{16}(\Delta t)^2\gamma^2\right]}$$

(10)

For $\Delta t < \Delta t^* = 4/(\sqrt{7}\gamma)$ shear is ineffective and $A$ decays as for $\gamma = 0$. At large strain the term proportional to $\gamma$ in Eq. (10) prevails so that $A \sim \gamma^{-1}(\Delta t)^{-1+2/3}$. Correlations are then suppressed by the flow for $\Delta t > \Delta t^*$. A relaxation time proportional to $\gamma^{-1}$ is also found in molecular dynamics simulations of supercooled liquids in shear flow [14].

In this paper we have studied the behavior of a quenched glassy system under the effect of an applied shear flow. The analysis has been carried out analytically in the framework of the mean field model recently introduced in [3]. Two shear regimes can be distinguished which behave differently. While for weak shear the off-equilibrium evolution is unaffected by the flow, for strong shear the evolution towards the stationary state is enhanced and aging is interrupted after a time $\tau_g = 1/(T \gamma)$ by the flow itself. We have also described how the properties of the time correlation function in the stationary state are modified by the flow. These predictions are amenable of experimental checks; it would be interesting to know if similar feature can be observed in real glassy systems such as hard spheres or colloidal suspensions.
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Fig. 1. – Four snapshots of the structure factor $\chi(\vec{k}, t)$ are shown for $d = 2$ at times $t = 2, 7, 20, 60$ for $\rho = 0.95, T = 10^{-4}$ and $\gamma = 1$. $k_x$ increases from left to right ($k_x = 0$ is in the middle); $k_y$ increases towards the upper part of the figure.
Fig. 2. – $D(t)$ is shown in $d = 2$ for $\rho = 0.95$, $T = 10^{-4}$ and different values of $\gamma$ ($\gamma = 1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-8}, 0$) from left to right. The curves with $\gamma = 10^{-8}$ and $\gamma = 0$ are not distinguishable in this plot. The finite final value $D(\infty)$ is very small for high densities and practically coincides with the $t$ axis in this picture. In the inset the characteristic time $\tau_\gamma$ when aging is interrupted is plotted against $\gamma$. The solid line is the $\gamma^{-1}$ law.
Fig. 3. – The two-time correlator $C(\vec{k}, \Delta t)$ in the stationary state is plotted against $\Delta t$ for $\gamma = 10^{-2}$, $k_y = 1$ and different values of $k_x$ and $k_z$ as indicated in the legend. Solid lines refer to wavevectors in the sector with $k_x k_y < 0$ whereas dashed lines correspond to the region $k_x k_y > 0$. 