Fluctuation dissipation relations in stationary states of interacting Brownian particles under shear

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The fluctuation dissipation theorem (FDT) is studied close to the glass transition in colloidal suspensions under steady shear. Shear breaks detailed balance in the many-particle Smoluchowski equation, and gives response functions in the stationary state which are smaller at long times than estimated from the equilibrium FDT. During the final shear-driven decay, an asymptotically constant relation connects response and fluctuations, restoring the form of the FDT with, however, a ratio different from the equilibrium one.

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In thermal equilibrium, the response of a system to a small external perturbation follows directly from thermal fluctuations of the unperturbed system. This connection is the essence of the fluctuation dissipation theorem (FDT) which lies at the heart of linear response theory. In non-equilibrium systems, much work is devoted to understanding the general relation between fluctuation (correlator functions) and response (susceptibility $\chi(t)$) functions. It has been characterized by the fluctuation dissipation ratio (FDR) $X(t)$ defined via

$$\chi(t) = -\frac{X(t)}{k_B T} \frac{\partial}{\partial t} C(t).$$

It is unity close to equilibrium, $X^{(e)}(t) \equiv 1$, but deviates in non-equilibrium because the external perturbations act against non-vanishing currents (see Eq. (2) below); FDRs quantify the currents and signal non-equilibrium [1].

Colloidal dispersions exhibit slow cooperative dynamics at high concentrations and form glasses. These metastable soft solids can easily be driven into stationary states far from equilibrium by shearing with already modest flow rates. Spin glasses driven by nonconservative forces were predicted to exhibit nontrivial FDRs in mean field models [2]. Such behavior was observed in detailed computer simulations of sheared super-cooled liquids by Berthier and Barrat [3,4]. During the shear induced relaxation, the FDR for particle motion perpendicular to the shear plane is different from unity, but constant in time. This ratio was also found to be independent of observable, which led to the notion of an effective temperature $T = T_{\text{eff}}$ describing the non-equilibrium state. Further simulations with shear also saw $T_{\text{eff}} > T$ [5,6,7], and recently $T_{\text{eff}}$ was connected to barrier crossing rates [8].

On the theoretical side, much effort has been made on different spin-models, close to criticality. Universal FDRs were found under coarsening [9] and under shear [10], where at the critical temperature, a universal value of $X = \frac{1}{2}$ was found. Yet, the situation for structural glasses has not been clarified.

In this letter, we investigate FDT for colloidal suspensions close to a glass transition under steady shear starting from the $N$-particle Smoluchowski equation. While time dependent correlation functions are calculated in the integration through transients (ITT) approach [11,12], which is based on mode coupling theory, the connection to the corresponding susceptibilities will be derived for the first time here. We show that equilibrium FDT is violated, but can be restored in a well defined sense with a renormalized FDR at long times; however, the ratio depends on variable, contradicting the notion of an effective temperature. Moreover, we establish a connection to the concept of a yield stress, which gives a scenario quite different from mean field spin glass [2].

$N$ spherical Brownian particles of diameter $d$, with bare diffusivity $D_0$, and interacting via internal forces $F_i = -\partial_i U$, $i = 1, \ldots, N$, are dispersed in a solvent with a steady and homogeneous velocity profile $v(r) = \kappa \cdot r$, with shear rate tensor $\kappa = \dot{\gamma} \hat{x} \hat{y}$. Neglecting hydrodynamic interactions, the distribution of particle positions evolves according to the Smoluchowski equation [13]

$$\partial_t \Psi(t) = \Omega \Psi(t), \quad \Omega = \sum_i \partial_i \left[ \partial_i - F_i - \kappa \cdot r_i \right], \quad (1)$$

where $\Omega$ is the Smoluchowski operator and we have introduced dimensionless units for length, energy and time, $d = k_B T = D_0 = 1$. The Smoluchowski operator for the system without shear ($\kappa = 0$) and the flow-part will be denoted $\Omega_e$ and $\delta \Omega = \Omega - \Omega_e$. We distinguish two time-independent distributions, $\Omega_e \Psi_e = 0$ without shear and $\Omega \Psi_s = 0$ for the stationary system. Averages are $\langle \ldots \rangle$ and $\langle \ldots \rangle^{(s)}$, respectively. Stationary correlation functions are $C_{\text{ab}}(r) = \langle \delta a^* e^{i \Omega t} \delta b \rangle^{(s)}$, where $\Omega^\dagger$ is the adjoint operator obtained by partial integrations [11,14]; a fluctuation equals $\delta a = a - \langle a \rangle^{(s)}$. Note that shear in Eq. (1) leads to a non-Hermitian eigenvalue problem [15]. The susceptibility $\chi_{\text{ab}}(t)$ describes the linear response of the stationary expectation value of $b$ to an external perturbation $h_e(t)$ shifting the internal energy $U$ to $U - a^* h_e(t)$,

$$\langle b \rangle^{(s,h_e)}(t) = \langle b \rangle^{(s)} + \int dt' \chi_{\text{ab}}(t-t') h_e(t') + O(h_e^2).$$

One finds $\chi_{\text{ab}}(t) = \langle \sum_i \frac{\partial a^*}{\partial r_i} \cdot \partial_i e^{i \Omega t} b \rangle^{(s)}$ [14]. In non-equilibrium, where detailed balance is broken and a nonzero stationary probability current $J^s_i = [-\partial_i F_i + \kappa \cdot r_i] \Psi_s$ exists, the equilibrium FDT is extended (with $j^s_i$ the adjoint of the current operator defined by $j^s_i = \gamma_i \Psi_s$),

$$\Delta \chi_{\text{ab}}(t) = \chi_{\text{ab}}(t) + \dot{C}_{\text{ab}}(t) = -\sum_i j^s_i \cdot \frac{\partial a^*}{\partial r_i} e^{i \Omega t} b \rangle^{(s)} \quad (2)$$
and a deviation of the fluctuation dissipation ratio (FDR)

\[ X_{ab}(t) = \frac{\chi_{ab}(t)}{-C_{ab}(t)} \]  

(3)

from unity, the value close to equilibrium, arises. While Eq. (2) has been known since the work of Agarwal [14], we will analyze it for driven metastable (glassy) states and show that the additive correction \( \Delta \chi_{ab}(t) \) [14, 17, 18] leads to the nontrivial multiplicative correction, i.e., a constant FDR at long times. For simplicity, we will look at auto-correlations (\( b = a \)) of \( x \)-independent fluctuations, \( \delta \Omega^i a = 0 \), where the flow-term in the current operator \( \Psi^i_t \) in (2) vanishes.

\( \Psi_s \) is not known and stationary averages are calculated via the ITT approach [11, 12].

\[ \langle \ldots \rangle^{\Delta t} = \langle \ldots \rangle + \dot{\gamma} \int_0^\infty ds \langle \sigma_{xy} e^{\Omega^i t} \ldots \rangle, \]

where \( \sigma_{xy} = -\sum_i F_e^x y_i \) is a microscopic stress tensor element. (Operators act on everything to the right, except for when marked differently by bracketing.) ITT simplifies the following analysis because averages can now be evaluated in equilibrium, while otherwise non-equilibrium forces would be required [13]. E.g. due to \( \dot{\partial}_t \Psi_e = F_e \Psi_e \), the expression (2) vanishes in the equilibrium average. The remaining term is split into three pieces containing \( \Omega^i \)

\[ \Delta \chi_a(t) = \frac{-\dot{\gamma}}{2} \int_0^\infty ds \langle \sigma_{xy} e^{\Omega^i t} \Omega^i a^* - a^* \Omega^i + (\Omega^i a^*) \rangle e^{\Omega^i t} a \].

(4)

We start with the first term in the square brackets (without the factor \( \frac{1}{2} \)) which can be integrated over \( s \) directly giving

\[ \dot{\gamma} \langle \sigma_{xy} \delta a^* e^{\Omega^i t} \delta a \rangle = \frac{\partial}{\partial t_w} C_a(t, t_w) \bigg|_{t_w=0}, \]

(5)

where from now on we consider fluctuations from equilibrium \( \delta a = a - \langle a \rangle \); (the constant \( \langle a \rangle \) cancels in (2)). Intriguingly, in Eq. (5) the two time correlator enters,

\[ C_a(t, t_w) = \langle \delta a^* e^{\Omega^i t} \delta a \rangle + \dot{\gamma} \int_0^\infty ds \langle \sigma_{xy} e^{\Omega^i s} \delta a^* e^{\Omega^i t} \delta a \rangle, \]

(6)

where the rheometer has been shearing for a period \( t_w \) before the correlation measurement is started. It is one of the central quantities in the spin-glass theory of aging [2]. While the transient correlator \( C_a(t) = C_a(t, 0) = \langle \delta a^* e^{\Omega^i t} \delta a \rangle \) describes the dynamics after switch on of the rheometer, the stationary correlator \( C_a(t) = C_a(t, \infty) \) is observed after waiting long enough; it measures fluctuations in the stationary state.

Our approximation for \( \Delta \chi_a(t) \) in Eq. (2) rests on the observation that it contains the product of a fluctuation \( \delta a \) and the stationary current. We expect current fluctuations to always decay to zero, even in possible non-ergodic situations, and thus search for a coupling of \( \Delta \chi_a(t) \) to derivatives of \( C_a(t) \) as they cannot be non-ergodic. Partial integration can be used to show

\[ \frac{\partial}{\partial t_w} C_a(t, t_w) \bigg|_{t_w=0} = \dot{C}_a(t) - (\Omega^i a^*) e^{\Omega^i t} \delta a, \]

where

\[ \dot{C}_a(t) - C_a(t)(t) \approx \int_0^\infty ds \langle \sigma_{xy} e^{\Omega^i s} \sigma_{xy} \rangle \frac{\partial C_a(t, t_w)}{\partial t_w} \bigg|_{t_w=0}, \]

(8)

where we used \( t_w = \infty \), and factorized the appearing two-time average with the projector \( \sigma_{xy} \langle \sigma_{xy} \sigma_{xy} \rangle^{-1} \langle \sigma_{xy} \rangle \). A small parameter \( \delta \equiv \dot{\gamma} \int_0^\infty ds \langle \sigma_{xy} e^{\Omega^i s} \rangle \langle \sigma_{xy} \rangle^{-1} \langle \sigma_{xy} \sigma_{xy} \rangle \) arises which contains as numerator the stationary shear stress

\[ \dot{\gamma} \int_0^\infty ds \langle \sigma_{xy} e^{\Omega^i s} \sigma_{xy} \rangle \]

FIG. 1: \( C(t) \) from the \( F^{(5)} \)-model [22] and \( \chi(t) \) via Eq. (9) for a glassy state \( (\varepsilon = 10^{-8}) \) and \( \dot{\gamma} = 10^{-2} \) with \( n = 1...4 \). Shown are integrated correlation, \( 1 - C(t) \) and response \( \chi'(t) = \int_0^\infty \chi(t')dT' \). Inset shows additionally the normalized transient correlator \( C(t) \) for comparison and the \( X^{(uni)} = \frac{1}{2} \) susceptibility for \( \dot{\gamma} = 10^{-8} \). The latter term contains the equilibrium derivative \( \Omega^i a^* \). It is not conserved and decorrelates quickly as the particles loose memory of their initial motion even without shear. The latter term is the time derivative of the equilibrium correlator, \( C^{(e)}(t) = \langle \delta a^* e^{\Omega^i t} \delta a \rangle \). A shear flow switched on at \( t = 0 \) should make the particles forget their initial motion even faster, prompting us to use the approximation \( e^{\Omega^i t} \approx e^{\Omega^i t} Pe^{-\Omega^i t} e^{\Omega^i t} \) with projector \( P = \delta a \langle \delta a^* \delta a \rangle^{-1} \langle \delta a^* \rangle \). It is then assured to decay faster than in equilibrium. This leads, together with an analogous approximation in \( \langle \delta a^* e^{\Omega^i t} \delta a \rangle \), to

\[ \frac{\partial}{\partial t_w} C_a(t, t_w) \bigg|_{t_w=0} \approx \dot{C}_a(t) - C_a(t)(t) \]

(7)

The last term in (7) will be identified as short time derivative of \( C^{(e)}(t) \), connected with the shear independent decay, while \( \frac{\partial}{\partial t_w} C_a(t, t_w) \bigg|_{t_w=0} \) will turn out to be the long time derivative of \( C_a(t) \), connected with the final shear driven decay. This is our main result. It captures the additional dissipation provided by the coupling to the stationary probability current in Eq. (2).

In order to proceed, the difference between the stationary and the transient correlators needs to be known. We will comment below on the interesting result for the FDR following from the simplest approximation to set them equal. Going beyond this leading approximation can be done via Eq. (6).
measured in 'flow curves' as function of shear rate \[11\]. For hard spheres, the instantaneous shear modulus \(\langle \sigma_{xy}\sigma_{xy} \rangle\) diverges \[13\] giving formally \(\dot{\sigma} = 0\) and that transient and stationary correlator agree. In recent simulations of density fluctuations of soft spheres \[20\], the difference between the two correlators was found to be largest at intermediate times, and \(\mathcal{C}_s(t) \leq \mathcal{C}_a(t)\) was observed. Both properties are fulfilled by Eq. \[8\].

After the discussion of the first term in \[4\], we turn to the correction containing the last two terms in \[4\]. It has vanishing initial value and in a mode coupling approximation in ITT for the case of density fluctuations, the two terms almost cancel each other at long times making their sum a small correction. Here, we proceed by ignoring it until a future presentation. We hence find

\[
\mathcal{X}_a(t) \approx - \mathcal{C}_a(t) + t \left( \mathcal{C}_a(t) - \mathcal{C}_a(\tau) \frac{\mathcal{C}_a(t)}{\mathcal{C}_a(\tau)} \right). \tag{9}
\]

In the limit of small shear rates for glassy states, the correlators exhibit two separated relaxation steps \[12, 21\]. During the shear independent relaxation onto the plateau of height given by the non-ergodicity parameter \(f_a\), we have \(\mathcal{C}_a(t) \approx \mathcal{C}_a^\tau(t)\), and the equilibrium FDT holds. During the shear-induced final relaxation from \(f_a\) down to zero, i.e., for \(\dot{\gamma} \to 0\), and \(t \to \infty\) with \(\dot{\gamma} t = \text{const.}\), the correlator without shear stays on the plateau and its derivative is negligible. A non-trivial FDR follows. Summarized we find in the glass

\[
\lim_{\dot{\gamma} \to 0} \mathcal{X}_a(t) = \begin{cases} -\dot{\mathcal{C}}_a(t), & \dot{\gamma} t \ll 1, \\ -\mathcal{C}_a(t) + \frac{1}{2} \mathcal{C}_a(t), & \dot{\gamma} t = \mathcal{O}(1). \end{cases}
\]

It is interesting to note that approximating stationary and transient correlator to be equal \[12\], \(\mathcal{C}_a^\tau(t) \approx \mathcal{C}_a(t)\), we find \(\mathcal{X}_a(t) = -\frac{1}{2} \mathcal{C}_a(t)\) for long times. The FDR in this case takes

the universal value \(\lim_{\dot{\gamma} \to 0} \mathcal{X}_a(t \to \infty) = \hat{X}^{(univ)}(\dot{\gamma} t) = \frac{1}{3}\), independent of \(a\). This is in good agreement with the findings in \[3\]. The initially additive correction in Eq. \[2\] hence turns then into a multiplicative one, which does not depend on rescaled time during the complete final relaxation process.

For a more precise investigation of the FDR, we have to consider the difference between the transient and the stationary correlator in Eq. \[8\]. We turn to the schematic \(F_{12}^{(\tau)}\)-model of ITT \[22\], which has repeatedly been used to investigate the dynamics of quiescent and sheared dispersions \[12\], and which provides excellent fits to the flow curves from large scale simulations \[22\]. It provides a normalized transient correlator \(\mathcal{C}_a(\dot{\gamma} t)\), as well as a quiescent one, representing coherent, i.e., collective density fluctuations. The corresponding stationary correlator \(C\) is calculated in a second step via Eq. \[8\]. Fig. 1 shows the resulting \(C\) together with \(C\) for a glassy state at different shear rates. For short times, the equilibrium FDT is valid, while for long times the susceptibility is smaller than expected from the equilibrium FDT, this deviation is qualitatively similar for the different shear rates. For the smallest shear rate, we also plot \(\chi\) calculated by Eq. \[7\] with \(\mathcal{C}_a(\dot{\gamma} t)\) replaced by \(\hat{C}_a\), from which the universal \(\hat{X}^{(univ)}(\dot{\gamma} t) = \frac{1}{3}\) follows. In the parametric plot (Fig. 2), this leads to two perfect lines with slopes \(-1\) and \(-\frac{1}{2}\) connected by a sharp kink at the nonergodicity parameter \(f\). For the other (realistic) curves, this kink is smoothed out, but the long time part is still well described by a straight line, i.e., the FDR is still almost constant during the final relaxation process. We predict a non-trivial time-independent FDR \(\hat{X}_a(\dot{\gamma} t) = \text{const.}\) if \(\mathcal{C}_a(\dot{\gamma} t)\) (and with Eq. \[8\] also \(\mathcal{C}_a\)) decays exponentially for long times, because \(\Delta \mathcal{X}_a\) then decays exponentially with the same exponent. The line cuts the FDT line below \(\dot{\gamma} \to 0\). All these findings are in excellent agreement with the data in \[3\]. The FDR itself is of interest also, as function of time (in-

![FIG. 2: Parametric plot of correlation \(C(t)\) versus response \(\chi'(t) = \int_0^t \chi(t')dt'\) for a glassy state \((\varepsilon = 10^{-3})\) from the \(F_{12}^{(\tau)}\)-model \[22\] together with constant non-trivial FDR (straight lines) at long times. The vertical solid line marks the plateau \(f\). Inset shows the FDR \(X(t)\) as function of strain for the same susceptibilities.]

![FIG. 3: Long time FDR as function of shear rate for glassy \((\varepsilon \geq 0)\) and liquid \((\varepsilon < 0)\) states in the \(F_{12}^{(\tau)}\)-model \[22\], when approaching the glass transition for \(\varepsilon = \pm 10^{-1}, \pm 10^{-2}\). Inset: \(\lim_{\varepsilon \to 0} \mathcal{X}_a(t \to \infty)\) as function of wavevector \(q\) for incoherent density fluctuations at the critical density \((\varepsilon = 0)\) \[23\].]
set of Fig. 2. A rather sharp transition from 1 to $\frac{1}{2}$ is observed when $C(t) \approx C$ is approximated, which already takes place at $\dot{\gamma} t \approx 10^{-5}$, a time when the FDT violation is still invisible in Fig. 1. For the realistic curves, this transition happens two decades later. The huge difference is strikingly not apparent in the parametric plot.

Fig. 5 shows the long time FDR as a function of shear rate for different densities above and below the glass transition, determined via fits to the parametric plot in the interval [0 : 0.1]. In the glass $X(t \to \infty)$ is nonanalytic while it goes to unity in the fluid as $\dot{\gamma} \to 0$, where we verified that the FDT-violation starts quadratic in $\dot{\gamma}$ as is to be expected due to symmetries. Our analysis also allows to study the interesting question of the variable dependence of the FDR, for which we consider incoherent, i.e., single particle fluctuations [22] which were most extensively studied in [3]. The FDR is isotropic in the plane perpendicular to the shear direction but not independent of wavevector $q$, contradicting the idea of an effective temperature, which was developed for ageing and driven mean field models.

That Eq. (9) is nevertheless not in contradiction to the data in Ref. [3] can be seen by direct comparison to their Fig. 11. For this, we need the quiescent as well as the transient correlator as input. $C_q^{(e)}$ has been measured in Ref. [21] suggesting that it can be approximated by a straight line beginning on the plateau of $C_q(t)$. In Fig. 3 we show the resulting susceptibilities. There is no adjustable parameter, when $C_q(t) \approx C_q$ is taken, for the other curve, we calculated $C_q(t)$ from Eq. (8) using $\dot{\sigma} = 0.01$ (in LJ units) as fit parameter. The agreement is striking. In the inset we show the original $C_q$ from Ref. [3] together with our construction of $C_q^{(e)}$ and the calculated $C_q(t)$, which appears very reasonable comparing with recent simulation data on $C_q(t, t_w)$ [20].

In summary, shear flow drives metastable Brownian dispersions to a stationary non-equilibrium state with a multiplicative renormalization of the FDR at long times, which is (almost) independent of rescaled time. It nearly agrees for variables not advected by flow and takes the universal value $\hat{X}_q(\dot{\gamma} t) = \frac{1}{2}$ in glasses at small shear rates in leading approximation. Corrections arise from the difference of the stationary to the transient correlator, and depend on the considered variable. They alter $\hat{X}_q$ to values $\hat{X}_q \leq \frac{1}{2}$ in the glass. We show a new connection between $\Delta \chi(t)$ and $\hat{C}_q(t, t_w)$, see Eq. (5), which can be tested directly in simulations.

The derived FDRs characterize the shear-driven relaxation at long times, which, according to the ITT approach, is also the origin of a (dynamic) yield stress in shear molten glass [11]. This view captures extended simulations [3, 23] and broad-band experiments [24], establishing shear molten glass as model for investigating non-equilibrium. Our finding of values close to the universal $\hat{X}_q(\dot{\gamma} t) = \frac{1}{2}$ points to intriguing connections to critical systems [3, 10]. Open questions concern establishing such a connection and to address the concept of an effective temperature, which was developed for ageing and driven mean field models.

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This supplementary material summarizes the known ITT models for transient correlators used to evaluate the stationary fluctuation functions and susceptibilities presented in the main text.

**SCHEMATIC MODEL**

In the schematic $F_{12}^{(\gamma)}$ model of ITT, a normalized transient correlator $\Phi(t) = C(t)$ is considered which represents collective density fluctuations. It obeys the equation of motion [12],

$$0 = \dot{\Phi}(t) + \Phi(t) + \int_0^t dt' m(\dot{\gamma}, t-t') \dot{\Phi}(t'),$$

with initialization $\Phi(t \to 0) \to 1 - t$. We use the much studied values $v_2^c = 2, v_1^c = v_2^c (\sqrt{4/v_2^c} - 1)$ with the glass transition at $\varepsilon = 0$, and take $m(0, t)$ in order to calculate quiescent ($\dot{\gamma} = 0$) correlators [25]. For the corresponding stationary correlator $C(t)$, we additionally have to estimate the normalized shear stress $\tilde{\sigma}$. In the $F_{12}^{(\gamma)}$-model, the shear modulus is described by the transient correlator and we insert a factor of $\frac{1}{3}$ to account for the different plateau heights of the two normalized functions. $\tilde{\sigma}$ is hence estimated as

$$\tilde{\sigma} = \frac{1}{3} \int_0^\infty dt \, \Phi(t) \frac{G_{\infty}}{f},$$

with $G_{\infty}/f \approx \frac{1}{\gamma}$. Additionally we approximate the normalizations for $C^{(t)}(t)$ and $C(t)$, i.e., the respective structure factors, to be equal. For incoherent fluctuations, this is exact.

**WAVEVECTOR DEPENDENCE**

To derive the long time FDR as function of wavevector $\mathbf{q}$ for incoherent, i.e., single particle density fluctuations, we use the normalized transient correlator from the ISHSM-model [12]. In glassy states, it approximately equals at long times

$$C_q^{(t)}(t) \approx f_q \exp \left( -\frac{\gamma h_q}{f_q} t \right),$$

where $f_q$ is the $q$-dependent nonergodicity parameter and $h_q$ is another coefficient which as well as $f_q$ follows from equilibrium properties. The quiescent correlator is constant at long times, $C_q^{(e)}(t) = f_q$. The long time FDR then follows from Eqs. (3, 7-9) with $\tilde{\sigma}$ estimated as above.

[25] W. Götze, Z. Phys. B 56, 139 (1984).