Dense Colloidal Suspensions under Time-Dependent Shear

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We consider the nonlinear rheology of dense colloidal suspensions under a time-dependent simple shear flow. Starting from the Smoluchowski equation for interacting Brownian particles advected by shearing (ignoring fluctuations in fluid velocity) we develop a formalism which enables the calculation of time-dependent, far-from-equilibrium averages. Taking shear-stress as an example we derive exactly a generalized Green-Kubo relation, and an equation of motion for the transient density correlator, involving a three-time memory function. Mode coupling approximations give a closed constitutive equation yielding the time-dependent stress for arbitrary shear rate history. We solve this equation numerically for the special case of a hard sphere glass subject to step-strain.

The constitutive equations of a material relate its stress tensor $\sigma(t)$ at time $t$ to its flow history, described by a strain-rate tensor $\kappa(t' \leq t)$. Dense suspensions of colloidal particles, close to the glass transition, show strongly viscoelastic behaviour and nonlinear shear response; their constitutive equations must be highly nontrivial. In this paper, we report first-principles work aimed at elucidating these equations theoretically.

Three alternative approaches to the rheology of glassy materials have recently been considered. The phenomenological soft glassy rheology (SGR) model mimics the glass transition by a one-particle hopping dynamics in a well chosen distribution of trap-depths. While the predictions of SGR are broadly consistent with experiments on many non-ergodic soft materials it does not capture the discontinuous jump in yield stress on glass formation observed in experiments on colloidal suspensions of hard spheres. The same is true of spin glass approaches which describe a different phenomenology akin to ‘power-law yielding materials’. The observed yield-stress is captured however by a first-principles approach to colloid rheology, based on Mode Coupling Theory (MCT), which has recently been formulated for systems under steady shear. The MCT has had considerable semiquantitative success in accounting for the interaction dependence of the static glass transition and the time dependence of light scattering correlators from microscopic starting points. MCT also gives sensible predictions for the viscoelastic spectrum $G^\ast(\omega)$ as measured in linear rheology.

In this Letter we develop a first-principles description of the far-from-equilibrium states of dense colloids under prescribed time dependent shear flow. For a system of interacting particles advected by the imposed strain rate $\kappa$ (this neglects velocity fluctuations and hence hydrodynamic interactions), we begin by developing a formalism which facilitates calculation of general time dependent averages. Using this formalism we derive formally exact generalized Green-Kubo equations, taking the shear stress as an example. These expressions can be approximated in terms of transient two-time density correlators. We find an exact equation of motion for the correlator which, for general strain rate, displays a remarkable three-time structure to the memory function. Finally, we make an MCT-based closure of this equation. To show that the theory yields sensible predictions for strongly time-dependent flows, we consider step-strain as a specific example. Our approach is valid for all homogeneous and incompressible flows which satisfy $\kappa(t)\cdot\kappa(t) = 0$ (this enforces homogeneous states with translationally invariant spatial correlations). For clarity of presentation we focus on the case of simple shearing with fixed axes (velocity along $x$, gradient along $y$), and an arbitrary time-dependent strain rate $\dot{\gamma}(t)$, so that $\kappa_{ij} = \dot{\gamma}(t)\delta_{ix}\delta_{jy}$.

Our findings highlight the formal importance of ‘integration through transients’ (ITT) in preparing the best ground for judicious application of MCT. Indeed, a somewhat simpler MCT-inspired approach to colloid rheology was developed in [12, 13], which for fluid states in steady shear gives broadly similar results to those of [6]. However, its recent (ad-hoc) extension to time dependent flows gives results quite different from ours; in particular, there is no sign of a third time in the memory function which we show to be an exact consequence of the Smoluchowski equation and which is preserved in our approximations. This feature (also missed in another recent simplified MCT approach) turns out to be crucial in capturing the nonlinear response, even for simple time-dependent flows. Our findings should also help guide the development of ‘fully schematic’ single-mode models. These models can address physics not considered here, such as shear thickening, so their extension to time-dependent flows is highly desirable. In future, such models may suggest improvements to the MCT factorizations used here, iterating towards a fully predictive theory of colloid rheology.

We start with a system of $N$ spherical Brownian particles of diameter $d$ interacting via internal forces $\mathbf{F}_i$, $i = 1, \cdots, N$, and dispersed in a solvent with a specified time dependent velocity profile $\mathbf{v}(\mathbf{r}, t) = \mathbf{\kappa}(t) \cdot \mathbf{r}$. The distribution function of particle positions evolves according to...
to the Smoluchowski equation \[ \partial_t \Psi(t) = \Omega(t) \Psi(t) \]
where \( \Omega(t) \) is the Smoluchowski operator and we have introduced dimensionless variables for length, energy and time, \( d = k_B T = D_0 = 1 \). Translational invariance of the sheared system leads to a coupling between a density fluctuation with pre-advanced wavevector \( \mathbf{q}(t, t') = \mathbf{q} - \mathbf{q} \cdot \frac{d}{dt} \int_{t}^{t'} ds \kappa(s) \) at time \( t' \) and another with wavevector \( \mathbf{q} \) at later time \( t \). Wavevector advection is how strain enters our formalism and accounts for the affine part of the particle motion in the imposed flow.

Integrating the Smoluchowski equation we obtain the following formal solution for the distribution function
\[
\Psi(t) = \Psi_e + \int_{-\infty}^{t} dt' \Psi_e \text{Tr}\left\{ \kappa(t) \sigma \right\} e^{\int_{t'}^{t} ds \Omega^\dagger(s)}, \tag{2}
\]
\[
\sigma(t) = \int_{-\infty}^{t} dt' \gamma(t') \left[ \frac{1}{V} \langle \sigma_{xy} e^{\int_{t'}^{t} ds \Omega^\dagger(s)} \sigma_{xy} \rangle \right], \tag{3}
\]
where the factor \([\cdot]\) can be identified formally as \( G(t, t', [\cdot]) \), a time-dependent shear modulus. Replacing \( \Omega^\dagger(t) \) with the quiescent-state operator recovers linear response. Eq. (3) opens a route to calculate \( \sigma(t) \) for a given flow history \( \gamma(t) \). The ITT method based on Eq. (2) also yields expressions for correlators, distorted structure factors and susceptibilities which will be detailed elsewhere.

To approximate our formally exact result \( \sigma \) we now project onto densities \( \rho_q = \sum_n e^{i q \cdot r_n} \) and density pairs (given by the square of the density in real space) \( \Omega(t) = \sum_i \partial_i \cdot (\partial_i - F_i - \kappa(t) \cdot r_i) \), \( \Omega(t) = \sum_i \partial_i \cdot (\partial_i - F_i - \kappa(t) \cdot r_i) \)
The resulting shear stress is given by
\[
\sigma(t) = \int_{t'}^{t} dt' \frac{k_B^2 k_y k_y(t, t') \Phi_k^2(t, t')}{k(k(t')^2) S_k(t', t') \Phi_k^2(t, t')}, \tag{4}
\]
where \( \Phi_k(t, t') \) is the transient density correlator which (in the absence of time translational invariance) is a function of two times, and \( S_k = d S_k / dk \) with \( S_k \) the equilibrium static structure factor. The projection onto density pairs means that the interparticle forces \( F_i \) are fully determined from \( S_k \) and density fluctuations. This MCT-based approximation is well-tested, although if the equal-time structure under shear deviates strongly enough from \( S_k \) to enter an anharmonic regime, improvements to it may be needed [14, 15]. In Eq. (4), the term \( \Phi_k^2(t, t') \) can be viewed as the ‘survival probability’ to time \( t \) of a stress contribution created by an initial step-strain applied at earlier time \( t' \); the remaining factor is the stress per unit initial strain. The transient density correlator required in Eq. (4) is defined as \( \Phi_k(t, t') = \left\langle \rho_i q^2 \exp \left[ \int_{t'}^{t} ds \Omega^\dagger(s) \right] \right\rangle / (N S_q) \) and is a key quantity within our approach. Note that it only contains information on the strain accumulated between the two correlated times \( t \) and \( t' \) and is independent of the strain history for times earlier than \( t' \).

Equation (4) gives the stress in terms of \( \Phi_k(t, t') \) which is itself dependent on flow history. Using Zwanzig-Mori type projection operator manipulations and applying the theory of Volterra integral equations, we obtain the following formally exact results:
\[
\frac{\partial}{\partial t} \Phi_q(t, t_0) + \Gamma_q(t, t_0) \left( \Phi_q(t, t_0) \right) = 0, \tag{5}
\]
\[
\int_{t_0}^{t} dt' m_q(t, t_0) \frac{\partial}{\partial t'} \Phi_q(t', t) = 0, \tag{6}
\]
\[
\Gamma_q(t, t_0) = -\frac{1}{S_q} \left\langle \rho_q \Omega_q(t, t_0) \rho_q \right\rangle
\]
\[
= \frac{S_q}{q} - q \cdot \kappa_{t_0} - \frac{1 + S_q}{S_q} + |q \cdot \kappa_{t_0}|^2
\]
\[
m_q(t, t_0) = -\frac{\left\langle \rho_q \Omega_q(t, t_0) U(t, t', t_0) Q_q \Omega_q(t, t_0) \rho_q \right\rangle}{S_q \Gamma_q(t', t_0) \Gamma_q(t, t_0)} \tag{7}
\]
In the equation of motion (5) for \( \Phi_k(t, t') \), the initial decay rate \( \Gamma_q(t, t') \) describes Taylor dispersion which enhances diffusion in the direction of flow [16]. For our chosen flow geometry, this can be calculated explicitly as given in Eq. (5), where \( Q_{t_0} = \int_{t_0}^{t} ds \kappa(s) \) is the shear strain accumulated between \( t_0 \) and \( t \). The memory function \( m_q(t, t_0) \) in Eq. (7) describes competition between shearing and the cage effect responsible for slow structural relaxation; strikingly, this is a function of three times, not two. It is useful to interpret \( m_q(t, t', t_0) \) as describing the decay of memory between times \( t' \) and \( t \), in the presence of shear, allowing for the coupling to stress in the system that is still relaxing from the strain accumulated between \( t_0 \) and \( t' \). The time \( t_0 \) enters the theory...
in a parametric fashion and is quite distinct in character from the two later times. Eq. (4) for $m_{q_0}$ involves the propagator $U(t,t',t_0) = \exp_0 \int^{t'}_t ds' Q_s \Omega_{s}^{irr}(s', t_0)$, where $Q_s^{irr}(t, t')$ is the single-particle-irreducible operator \cite{14} and $Q_s$ is an equilibrium projector orthogonal to density fluctuations. In deriving these formal results we introduced $\rho'_{q_0} = e^{iq \cdot r_x}$, the density of a single tagged particle, whose motion is described by $\Omega_{s}(t, t_0) = -i q \cdot \kappa(t) \cdot r_x - i q \cdot \kappa_{t_0} \cdot (2 \kappa_{x} + \kappa_{y}) + \Omega_{j}^{1}(t) - q \cdot \kappa_{t_0} \cdot \kappa_{t_0}^{*} \cdot q$. To close Equations (4) for the transient density correlation we now make an MCT-based approximation to the average in Eq. (4). Taking care to preserve translational invariance of $m_q(t, t', t_0)$, we obtain

$$m_q(t, t', t_0) = \frac{\rho}{16 \pi^3} \int d k \frac{S_{k} S_{p} V_{q,kp}^{(1)} V_{q,kp}^{(2)} \Phi_{k}(t, t') \Phi_{p}(t, t')}{S_{q} \gamma_{q}(t', t_0) \gamma_{q}(t, t_0)}$$

with $q_0 \rightarrow q, \beta$; $\rho_n = N/V$; $\rho_{q_0} = 1 - 1/S_q$. The wavevectors $q = q_0 - \kappa_{t_0}$, and $q = q_0 - \kappa_{t_0}$ contain shear strains accumulated over different temporal ranges.

Equations (4) and (5) form a closed set of equations to predict the shear stress for arbitrary time-dependent shear flows of the form $\kappa = \gamma(t) \cdot h_x \delta y$. Otherwise than $\gamma(t)$, the only required inputs are density $\rho$ and the static structure factor $S_{k}$ in the unstrained state. The parametric nature of $t_0$ is made explicit in the MCT approximation \cite{15} where all three times enter the vertex functions $V^{(1,2)}$ but only $t'$ and $t$ enter the correlators. For $\gamma = 0$ our equations reduce to those of quiescent MCT \cite{16} and for steady shear to those of \cite{17}.

In developing nonlinear constitutive equations it is helpful to study nonlinear step-strain as a benchmark. In an idealized step-strain experiment the shear rate is given by $\gamma(t) = \gamma_0 (t - t_0)$, which provides a demanding test of any constitutive equation. For step-strain our approximate Green-Kubo relation \cite{17} reduces to

$$\sigma(t) = \int d k \left\{ \frac{\gamma}{16 \pi^3} \frac{k_{x} k_{y} k_{z} S_{k} S_{k}'}{\gamma_{k}} \right\} \left( \Phi_{k}(t, t_0) \right)^2,$$

where $t > t_0$ and $k_{\gamma} = (k_{x}, k_{y}, 0 - \frac{1}{2} \gamma k_{x}, k_{z})$. We have included an additional superscript on the correlator to make explicit the strain dependence. The initial decay rate becomes independent of time, $\Gamma_{k} = q^2 / S_{q} + q_{x} q_{y} \gamma (1 + S_{q}) / (2 S_{q}) + 2 q_{x}^2 \gamma^2 / 4$, as the time $t_0$ drops out in an explicit $\gamma$ dependence. A similar reduction occurs for the memory function, leading us to modify the notation, $m_{q}(t, t_0) \rightarrow m_{q}^{(2)}(t, t')$. The memory function \cite{15} is thus given in step-strain by

$$m_{q}^{(2)}(t, t') = \frac{\rho}{16 \pi^3} \int d k \frac{S_{k} S_{p} V_{q,kp}^{(1)} V_{q,kp}^{(2)} \Phi_{q,kp}(t, t') \Phi_{p}(t, t')}{S_{q} \gamma_{q}^{(2) k_{\gamma}^{(2) q}}}$$

with $q_0 \rightarrow q$, hatted variables made unhattred, and $\kappa_{t_0} \rightarrow \gamma \delta_{l}, \gamma \delta_{y}$ in the vertex expressions of Eq. (5). The strain is zero in the two correlators since there is no strain imposed between $t'$ and $t$; these are quiescent MCT correlators. Thus all the $\gamma$ dependence in the memory function stems from the presence of $t_0$ in Eq. (5). In Eq. (10) the forces represented by the vertices are strain-dependent but relaxation of the structure is $\gamma$-independent \cite{15}. We thus obtain a simplified equation of motion for the correlators needed in \cite{17}. At statepoints for which quiescent MCT predicts a glass, the memory function remains non-ergodic for all values of $\gamma$. The equation of motion for $\Phi_{q}(t, t_0)$ is a linear equation in $\Phi_{q}(t, t_0)$ with given non-Markovian memory function. Due to the zero duration of the applied strain we can make the replacements $\Phi_{q}(t, t_0) \rightarrow \Phi_{q}(t - t_0), m_{q}^{(2)}(t, t') \rightarrow m_{q}^{(2)}(t - t')$ without further approximation.

In practice the presence of anisotropy still poses difficulties for numerical computation; specializing to the case of hard spheres we have therefore solved Eq (9) for the shear stress $\sigma(t)$ within the isotropic approximation \cite{18,21}. The $S_{k}$ input is taken from the Percus-Yevick (PY) theory, which yields a glass transition at $\phi_{mct} = \pi d^3 \phi / 6 = 0.516$ with our present numerical discretization \cite{22}. In Figure 1 we show the long time stress $\sigma(\infty)$ as a function of strain $\gamma$ for a hard sphere glass just above the MCT glass transition ($\phi = 0.52, \varepsilon = (\phi - \phi_{c}) / \phi_{c} = 0.008$) following a step-strain. The dashed line is the linear response result and the solid line is $\sigma(\infty)$ calculated using the isotropic approximation \cite{21}. The inset shows the decaying shear as a function of time following the step for $\gamma = 0.2, 0.3, 0.4$ (full lines, bottom to top) and $\gamma = 0.5, 0.6$ (broken lines, top to bottom).

![FIG. 1: The long time stress $\sigma(\infty)$ as a function of strain $\gamma$ for a hard sphere glass just above the MCT glass transition ($\phi = 0.52, \varepsilon = (\phi - \phi_{c}) / \phi_{c} = 0.008$) following a step-strain. The dashed line is the linear response result and the solid line is $\sigma(\infty)$ calculated using the isotropic approximation \cite{21}. The inset shows the decaying shear as a function of time following the step for $\gamma = 0.2, 0.3, 0.4$ (full lines, bottom to top) and $\gamma = 0.5, 0.6$ (broken lines, top to bottom).](image-url)
becomes questionable. The inset shows $\sigma(t)$ for various values of $\gamma$. In contrast to polymer melts following a step-strain, $\sigma(t)$ for the present hard sphere system is not strain factorable [17].

The results (Fig. 1) are in qualitative agreement with recent step-strain experiments on suspensions of PMMA particles above the glass transition [23]. The experimental data show a peak and a region of negative slope in $\sigma(\infty)$ in accord with our findings [24]. The isotropic approximation is known to underestimate the effects of shearing [4]; a fuller treatment might shift the peak in $\sigma(\infty)$ from $\gamma \approx 0.4$ closer to the experimental results [25], which peak at $\gamma \approx 0.1$. Note also that in the experiments the strain is ramped up over some short finite interval, during which additional plastic rearrangement may occur. Our general expressions (4,5,6,8) should capture this although (9,10) clearly do not.

To summarize, for interacting Brownian particles advected by a non-fluctuating shear flow, we have generalized the integration through transients formalism of [4] to address arbitrary far-from-equilibrium, time-dependent shearing. When complimented with mode-coupling approximations this provides a route to calculating time de-
shearing. When complimented with mode-coupling ap-
proaches this predicts first a linear regime followed by plastic deformation of the glass with a maximum in the long-time stress, as seen experimentally.

The formalism excludes extensional flow, and we assumed a spatially homogeneous strain rate $\dot{\gamma}(t)$. Nonetheless, the work goes far beyond linear response [11]: applying the theory to the case of oscillatory shear would predict strain dependent storage and loss moduli including ‘higher harmonic’ contributions [1,22]. Efficient numerical algorithms to tackle the anisotropy and loss of time translation invariance are currently under development. Meanwhile the formal developments presented here form a secure starting point both for more complete theories, in which the MCT assumptions might be partially relaxed, and for schematic models that simplify the algebra but add extra physics such as anhar-
monicity, shear-thickening and jamming [17]. We acknowledge the Transregio SFB TR6, EPSRC/GR/S10377 and DFG Vo 1270/1-1 for financial support. We thank Stefan Egelhaaf, Marco Laurati and Martin Greenall for helpful discussions.

[1] G. Petekidis, D. Vlassopoulos and P. N. Pusey, Faraday Discussions 123, 287–302 (2003); J. Phys. Cond. Mat. 16, S3955 (2004), and references therein.
[2] P. Sollich et al, Phys. Rev. Lett. 78, 2020 (1997); S. Fielding, P. Sollich and M. E. Cates, J. Rheol. 44, 323 (2000); M. E. Cates and P. Sollich, J. Rheol. 48, 193 (2004).
[3] J.-P. Bouchaud, J. Physique Paris I, 2, 1705 (1992).
[4] S. D. Holdsworth, Trans. Inst. Chem. Eng. A 71, 139 (1993).
[5] L. Berthier, J.-L. Barrat and J. Kurchan, Phys. Rev. E 61, 5464 (2000).
[6] M. Fuchs and M. E. Cates, Phys. Rev. Lett. 89, 248304 (2002); M. Fuchs and M. E. Cates, J. Phys. Cond. Mat. 17, S1681 (2005); M. E. Cates et al, in Unifying Concepts in Granular Media and Glasses ed. A. Coniglio et al (Amsterdam, Elsevier, 2004) p203.
[7] W. Götzs and L. Sjöegren, Rep. Prog. Phys. 55, 241 (1992).
[8] K. N. Pham et al, Science 296, 104 (2002).
[9] W. van Megen and S. M. Underwood, Phys. Rev. Lett. 70, 2766 (1993); W. van Megen and S. M. Underwood, Phys. Rev. E 49, 4206 (1994); T. Eckert and E. Bartsch, Faraday Discussions 123, 51 (2003).
[10] W. Götzs, Liquids, Freezing and Glass Transition ed. J.-P. Hansen, D. Levesque and J. Zinn-Justin (Amsterdam: North-Holland, 1991) p287.
[11] G. Nägele and J. Bergenholtz, J. Chem. Phys. 108, 9893 (1998); M. Fuchs and M. R. Mayr, Phys. Rev. E 60, 5742 (1999).
[12] K. Miyazaki and D. R. Reichman, Phys. Rev. E 66, 050501(R) (2002); K. Miyazaki, D. R. Reichman and R. Yamamoto, Phys. Rev. E 70, 011501 (2004).
[13] K. Miyazaki et al, cond-mat/0509121.
[14] V. Kobelev and K. S. Schweizer, Phys. Rev. E 71, 021401 (2005).
[15] C. B. Holmes et al, J. Rheol. 49, 237 (2005).
[16] J. K. G. Dhont, An Introduction to the Dynamics of Col-
loids, (Amsterdam, Elsevier, 1996).
[17] M. Doi and S. F. Edwards, The Theory of Polymer Dyn-
amics, (Oxford University Press, 1989).
[18] Normal stresses can be found the same way by choosing $f = (\sigma_{xx} - \sigma_{yy})/V$, etc. and deriving analogs to Eq. 4.
[19] B. Cichocki and W. Hess, Physica A 141, 475 (1987).
[20] Note that the approach of [14] neglects the strain accumulated between $t_0$ and $t^*$ and gives a strictly linear stress-strain relation when applied to step-strain.
[21] In the isotropic approximation we replace both the nu-
merator and denominator in [14] by the average over $q$ to obtain an isotropic memory function $m_q(t,t^*)$. If we also isotropize the initial decay rate then we obtain an isotropic correlator. This is then used in Eq. 9.
[22] We employ the same numerical discretization as T. Fran-
osch et al, Phys. Rev. E 55, 7153 (1997).
[23] K. N. Pham et al, Europhys. Lett. 75, 624 (2006); W. C. K. Poon (private communication).
[24] Note that $d\sigma/d\gamma < 0$ for an elastic system would cause a mechanical (static shear-banding) instability. However, since $\gamma$ denotes an initial strain and $\sigma(\infty)$ a final stress, this might not arise under plastic flow conditions. No shear banding is reported in [23].
[25] M. Wilhelm, Macromol. Mater. Eng. 287, 83 (2002).