Supercooled liquids under shear: A mode-coupling theory approach

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Abstract. We generalize the mode-coupling theory of supercooled fluids to systems under stationary shear flow. Our starting point is the generalized fluctuating hydrodynamic equations with a convection term. The method is applied to a two dimensional colloidal suspension. The shear rate dependence of the intermediate scattering function and shear viscosity is analyzed. The results show a drastic reduction of the structural relaxation time due to shear and strong shear thinning behavior of the viscosity which are in qualitative agreement with recent simulations. The microscopic theory with minimal assumptions can explain the behavior far beyond the linear response regime.

Many complex fluids such as suspensions, polymer solutions, and granular fluids exhibit very diverse rheological behavior. Shear thinning is among the most-known phenomena. Recently, it was found by experiments[1] and simulations[2] that supercooled liquids near the glass-transition also show strong shear thinning behavior. They have observed that near the transition temperature, the structural relaxation time and the shear viscosity both decrease as \( \dot{\gamma}^\nu \), where \( \dot{\gamma} \) is the shear rate and \( \nu \) is an exponent which is less than but close to 1. For such systems driven far from equilibrium, the nonequilibrium parameter \( \dot{\gamma} \) is not a small perturbation parameter but plays a role more like an intensive parameter which characterizes the “thermodynamic state” of the system[3]. Such rheological behavior is interesting in its own right, but understanding the dynamics of supercooled liquids in a nonequilibrium state is more important because it has possibility to shed light on another typical and perhaps more important nonequilibrium problem, non-stationary aging. Aging is the slow relaxation after a sudden quench of temperature below the glass transition temperature. In this case, the waiting time plays a similar role to (the inverse of) the shear rate. Aging behavior has been extensively studied for spin glasses (see Ref.[4] and references therein). The relationship between aging and a system driven far away from the equilibrium was considered using a schematic model based on the exactly solvable p-spin spin glass by Berthier, Barrat and Kurchan[5] and its validity was tested numerically for supercooled liquids[6]. There are attempts to study the aging of structural glasses theoretically[7] but it has not been analyzed and compared with the simulation results[8].

In this paper, we investigate the dynamics of supercooled liquids under shear theoretically, by extending the standard mode-coupling theory (MCT). We start with generalized fluctuating hydrodynamic equations with a convection term. Using several approximations, we obtain a closed nonlinear equation for the intermediate scattering function for the sheared system. The theory is applicable to both normal liquids and colloidal suspensions in the absence of hydrodynamic interactions. Numerical results will be presented only for the colloidal suspensions, but generalization to liquids are straightforward. Some of the preliminary results have already been published in Ref.[9].

We shall consider a two dimensional colloidal suspension under a stationary simple shear flow given by

\[
\mathbf{v}_0(r) = \Gamma \cdot \mathbf{r} = (\dot{\gamma} y; 0);
\]

where \( \langle \dot{\gamma} \rangle_{a\beta} = \gamma \delta_{a\alpha} \delta_{b\beta} \) is the velocity gradient matrix. The hydrodynamic fluctuations for density \( \rho(r,t) \) and the velocity field \( \mathbf{v}(\mathbf{r},t) \) obey the following set of Langevin equations[10].

\[
\frac{\partial \rho}{\partial t} = \nabla \cdot (\rho \mathbf{v});
\]

\[
m \frac{\partial (\rho \mathbf{v})}{\partial t} + m \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \rho \frac{\delta F}{\delta \rho} \xi_0 \rho \cdot \mathbf{v}_0 + \mathbf{f}_R;
\]

where \( \xi_0 \) is the collective friction coefficient for colloidal particles. \( \mathbf{f}_R(\mathbf{r},t) \) is the random force which satisfies the
fluctuation-dissipation theorem of the second kind (2nd FDT):

$$\hbar f_R(\mathbf{r}, \tau) f_R(\mathbf{r}, \tau) = 2k_B T \rho(\mathbf{r}) \zeta(\mathbf{r})(\mathbf{r}^2 \delta \mathbf{\tau} - \mathbf{\tau}^2)$$

(3)

for $t = \tau^2$, where $\langle \cdot \rangle_0$ is an average over the unconditional probability for a fixed value of $\rho(\mathbf{r})$ at $t = \tau^2$. Note that the random force depends on the density and thus the noise is multiplicative. We assumed that the 2nd FDT holds even in nonequilibrium state since the correlation of the random forces are short-ranged and short-lived, and thus the effect of the shear is expected to be negligible. The friction term is specific for the colloidal case. In the case of liquids, it should be replaced by a stress term which is proportional to the gradient of the velocity field multiplied by the shear viscosity. Both cases, however, lead to the same dynamical behavior on long time scales. The first term in the right hand side of the equation for the momentum is the pressure term and $\mathcal{F}$ is the total free energy in a stationary state. Here we assume that the free energy is well approximated by that of the equilibrium form and is given by a well-known expression:

$$\beta \mathcal{F} = \sum_{\mathbf{r}} \left[ \frac{1}{2} \partial_\mathbf{r} \rho(\mathbf{r}) \ln \rho(\mathbf{r}) \right] \rho(\mathbf{r}) + g \left( \mathbf{v}_0 - \mathbf{v} \right)$$

(4)

where $\beta = 1/k_B T$ and $c(\mathbf{r})$ is the direct correlation function. Under shear, it is expected that $c(\mathbf{r})$ will be distorted and should be replaced by a nonequilibrium, steady state form $c_{ne}(\mathbf{r})$, which is an anisotropic function of $\mathbf{r}$. It is, however, natural to expect that this distortion is very small in the molecular length scale, which plays the most important role in the slowing down of the structural relaxation near the glass transition. We confirmed this by numerical simulation[11]. By linearizing eq.(2) around the stationary state as $\rho = \rho_0 + \delta \rho$ and $\mathbf{v} = \mathbf{v}_0 + \delta \mathbf{v}$, where $\rho_0$ is the average density, we obtain the following equations:

$$\frac{\partial}{\partial t} \mathbf{k} \Gamma \frac{\partial}{\partial \mathbf{k}} \delta \rho_k(\mathbf{r}) = i k J_k(\mathbf{r})$$

$$\frac{\partial}{\partial t} \mathbf{k} \Gamma \frac{\partial}{\partial \mathbf{k}} \mathbf{\dot{r}}_k(\mathbf{r}) + \Gamma \mathbf{\dot{r}}_k(\mathbf{r}) = \frac{i k}{m_B \beta} \delta \rho_k(\mathbf{r})$$

$$\frac{1}{m_B} \int_{\mathbf{q}} \left( \mathbf{q} \cdot \mathbf{\hat{r}}_k(\mathbf{r}) \right) \mathbf{q} \cdot \delta \rho_k(\mathbf{r}) + \frac{\zeta_0}{m_B} J_k(\mathbf{r}) + \mathbf{f}_{rk}(\mathbf{q})$$

(5)

where $c(q)$ is the Fourier transform of $c(\mathbf{r})$, $\mathbf{\hat{r}}_k = \mathbf{k} + \mathbf{q}$, $J_k(\mathbf{r}) = \rho_0 \mathbf{k} \cdot \mathbf{\hat{r}}_k(\mathbf{r})$ is the longitudinal momentum fluctuation, and $\mathbf{q} = 2\pi \mathbf{q}^2$. Note that our approximate equation does not contain coupling to transverse momentum fluctuations even in the presence of shear.

In order to construct equations for the appropriate correlations from the above expressions, an approximate symmetry is necessary. In the presence of shear, translational invariance is violated. In other words, correlations of arbitrary fluctuations, $f(\mathbf{r}, \mathbf{t})$ and $g(\mathbf{r}, \mathbf{t})$, do not satisfy $h f(\mathbf{r}, \mathbf{t}) g(\mathbf{r}, \mathbf{t}) g(\mathbf{r}, \mathbf{t})$ $h f(\mathbf{r}, \mathbf{t}) g(\mathbf{r}, \mathbf{t}) g(\mathbf{r}, \mathbf{t})$. Instead, it has the following symmetry[12]:

$$h f(\mathbf{r}, \mathbf{t}) g(\mathbf{r}, \mathbf{t}) g(\mathbf{r}, \mathbf{t}) = h f(\mathbf{r}, \mathbf{t}) g(\mathbf{r}, \mathbf{t}) g(\mathbf{r}, \mathbf{t})$$

(6)

or in wavevector space

$$h f_{\mathbf{k}}(\mathbf{q}) g_{\mathbf{k}}(\mathbf{q}) = h f_{\mathbf{k}}(\mathbf{q}) g_{\mathbf{k}}(\mathbf{q})$$

(7)

where we defined the time-dependent position and wave vector by $\mathbf{r}(t) = \exp[\mathbf{r}(\tau)] \mathbf{r} = \mathbf{r} + \tau \mathbf{v}(\mathbf{r})$, where $\mathbf{v}(\mathbf{r})$ is an unit vector oriented along the $x$-axis and $\mathbf{k} = \mathbf{k} + \tau \mathbf{v}(\mathbf{r})$, where $\mathbf{v}(\mathbf{r})$ denotes the transpose of $\mathbf{v}$ and $\delta \mathbf{k}_{\mathbf{k'}(\mathbf{t})} = (2\pi)^2 \mathbf{v}(\mathbf{t}) \mathbf{\delta} \mathbf{k}(\mathbf{t})$ for a system of volume $V$. Using this approximation, it is straightforward to construct the mode-coupling equations for the appropriate correlation functions. We shall derive the equation for the intermediate scattering function defined by $F(\mathbf{k}, \mathbf{t})$ and $N^{-1} \int_{\mathbf{k}_0} m_B \beta \delta \rho_{\mathbf{k}_0}(\mathbf{r}, \tau) \delta \rho_{\mathbf{k}_0}(\mathbf{r}, \tau)$, where $N$ is the total number of the particles in the system. Note that the wave vector in $\delta \rho_{\mathbf{k}_0}(\mathbf{r}, \tau)$ is now replaced by a time-dependent one $\mathbf{k}(\mathbf{t})$.

Eq.(5) has a quadratic nonlinear term in $\delta \rho_{\mathbf{k}_0}(\mathbf{r}, \tau)$. This term can be renormalized to give a generalized friction coefficient or the memory kernel following the standard procedure of derivation of the mode-coupling equation[13]. To the lowest order in the loop expansions, we obtain the equation for the velocity-density correlation $C(\mathbf{k}, \mathbf{t})$ and $N^{-1} \int_{\mathbf{k}_0} m_B \beta \delta \rho_{\mathbf{k}_0}(\mathbf{r}, \tau) \delta \rho_{\mathbf{k}_0}(\mathbf{r}, \tau)$:

$$\frac{\partial C(\mathbf{k}, \mathbf{t})}{\partial \mathbf{t}} = \Gamma(\mathbf{t}) C(\mathbf{k}, \mathbf{t}) = \frac{ik(\mathbf{t}) F(\mathbf{k}, \mathbf{t})}{m_B \beta(\mathbf{k}, \mathbf{t})}$$

$$\frac{1}{m_B} \int_{\mathbf{q}} \left( \mathbf{q} \cdot \mathbf{\hat{r}}_k(\mathbf{r}) \right) \mathbf{q} \cdot \delta \rho_k(\mathbf{r}) + \frac{\zeta_0}{m_B} J_k(\mathbf{r}) + \mathbf{f}_{rk}(\mathbf{q})$$

(8)

Note that in the above equation, the differential operator $\mathbf{k} \Gamma \partial \mathbf{k}$ disappears and $\mathbf{k}$ is replaced by $\mathbf{k}(\mathbf{t})$. $\mathbf{\delta}_{\mathbf{k}_0}(\mathbf{t})$ is the generalized friction coefficient. $\mathbf{\delta}_{\mathbf{k}_0}(\mathbf{t})$ is given by the sum of the bare friction coefficient and the mode-coupling term as

$$\mathbf{\delta}_{\mathbf{k}_0}(\mathbf{t}) = \zeta_0 + \delta \mathbf{\zeta}(\mathbf{k}, \mathbf{t}) \mathbf{\delta}_{\mathbf{k}_0}(\mathbf{t})$$

(9)

with the mode-coupling contribution given by

$$\delta \mathbf{\zeta}(\mathbf{k}, \mathbf{t}) = \frac{\rho_0}{2 \beta} \mathbf{q} \cdot \mathbf{\hat{r}}_k(\mathbf{q}) \mathbf{\hat{r}}_k(\mathbf{q})$$

$$F(\mathbf{k}, \mathbf{t}) \mathbf{q}(\mathbf{t}) F(\mathbf{q}, \mathbf{t})$$

(10)
The wavevectors were chosen to be expressions derived by Baus change by increasing the grid number. However, the qualitative behaviors does not large enough to give the right transition density which is the derivative of $C(\mathbf{k}, \tau)$. In the overdamped limit, we may neglect the time derivatives as well as correlation functions[13] are natural introduced. The 1st FDT makes it possible to eliminate the propagators in favour of the correlation functions. In the overdamped limit, we may neglect the time-derivative of $C(\mathbf{k}, \tau)$. The second term on the left hand side is also neglected if Péclet number $Pe= \gamma \sigma^2 D_0 (\sigma$ is the diameter of the particle and $D_0 = k_b T = \xi_0$ is the diffusion coefficient) is small. Therefore, combining the first equation of eq.(5), one may eliminate $C(\mathbf{k}, \tau)$ from the above equations and arrive at the closed equation for $F(\mathbf{k}, \tau)$:

$$\frac{dF(\mathbf{k}, \tau)}{d\tau} = \frac{D_0 k_\perp(0, \tau)}{S_k(t)} F(\mathbf{k}, \tau)$$  \(\zeta\) \(\frac{1}{0} M(\mathbf{k}, (t)) F(\mathbf{k}, \tau)\), where

$$M(\mathbf{k}, \tau) = \frac{\rho_0 D_0 k / k_\perp}{2} \frac{d}{d\tau} \frac{1}{0} M(\mathbf{k}, (t)) F(\mathbf{k}, \tau)$$

In the absence of the shear, they reduce to the conventional mode-coupling equation[14].

Solving eqs.(12) and (13) numerically is more demanding than the equations in the equilibrium state because the wavevectors are distorted by shear and the system is not isotropic. We have considered a two dimensional colloidal suspension consisting of hard disks. For the static correlation function $c(\mathbf{k})$ and $S(\mathbf{k}, \tau)$, the analytic expressions derived by Baus et al.[15] were used. We have divided the two dimensional wavevector space into $N_k$ grids for each direction. The cut-off wavevector was chosen to be $k_c \sigma = 10 \pi$. For the self-consistent calculation of the mode-coupling equation, we have used the algorithm developed by Fuchs et al.[16]. In the following results, we have used the grid number $N_k = 55$, for which the ergodic-nonergodic transition occurs at the volume fraction $\phi_c = \pi \sigma^2 \rho_0 = 0.0665$. Apparently, $N_k$ is not large enough to give the right transition density which is 10% smaller. However, the qualitative behaviors does not change by increasing the grid number.

In Figure 1, we show the behavior of $F(\mathbf{k}, \tau)$ for $\phi = \phi_c = 0.10 \pi$. For various shear rate $Pe=10^{10}$ to $10$. The wavevectors were chosen to be $\mathbf{k} \sigma = (0, 3)$ and $M(\mathbf{k}, \tau) = (\mathbf{k} \sigma = (3, 0), (\mathbf{k} \sigma = (0, 3)$. In the absence of the shear, they reduce to the conventional mode-coupling equation[14].

$$\frac{dF(\mathbf{k}, \tau)}{d\tau} = \frac{D_0 k_\perp(0, \tau)}{S_k(t)} F(\mathbf{k}, \tau)$$

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where $\eta_0$ is the viscosity of the solvent alone. The integral can be implemented for the set of $F(\kappa, \mu)$ evaluated using eq.(12). Shear rate dependence of the reduced viscosity $\eta_R(\gamma') = \eta(\gamma') / \eta_0$ is plotted in Figure 2 for various densities around $\phi_c$. The strong non-Newtonian behavior is observed at high shear rate and large densities, which is again in qualitative agreement with the simulation results for liquids. Slightly above $\phi_c$, the plastic behavior which implies the presence of the yield stress is also observed. The shear thinning exponent is extracted from this plot between $10^{-10} < Pe < 1$ and we obtained $\eta_R(\gamma') \propto \gamma^{\nu'}$ with $\nu' = 0.99$. For the larger shear rate, $Pe > 1$, the exponent becomes smaller. In this regime, it is expected that other mechanisms such as the distortion of structure $c(\kappa)$ and $S(k)$ by shear becomes important.

The mode-coupling theory developed in this paper is far from complete. The most crucial approximation is the use of the 1st FDT, which was employed when we close the equation in terms of the correlation functions alone. It is already known that the 1st FDT is violated for supercooled systems under shear as well as during aging[6]. Without the 1st FDT, one has to solve simultaneously the set of mode-coupling equations for the propagator and correlation function, which couple each other through the memory kernels. Research in this direction is under way. Another important approximation was to neglect the small distortion of the structure, $c(\kappa)$ and $S(k)$, due to shear. The construction of the equation for such an equal-time correlation functions might be more subtle and should be considered in future. It is surprising, however, that despite of these approximations, the theory reproduces the major features which was seen in simulations; the drastic reduction of the relaxation time, the isotropic nature of the dynamics, and plastic-like strong shear thinning.

An analogous effort has been made by Fuchs and Cates[18]. They have derived a mode-coupling expression for $F(\kappa, \mu)$ using a projection operator for the Smoluchowski equation for $N$-particle colloidal suspensions. They have observed similar shear thinning behavior for approximated expressions, for an isotropic model, where the anisotropy hidden in the equations are neglected.

The details of analytical and numerical calculations for results given in the present paper are given elsewhere[11].

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