A Molecular Hydrodynamic Theory of Supercooled Liquids and Colloidal Suspensions under Shear

Kunimasa Miyazaki and David R. Reichman
Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA 02138

We extend the conventional mode-coupling theory of supercooled liquids to systems under stationary shear flow. Starting from generalized fluctuating hydrodynamics, a nonlinear equation for the intermediate scattering function is constructed. We evaluate the solution numerically for a model of a two dimensional colloidal suspension and find that the structural relaxation time decreases as $\gamma_\nu^\nu$ with an exponent $\nu \leq 1$, where $\gamma$ is the shear rate. The results are in qualitative agreement with recent molecular dynamics simulations. We discuss the physical implications of the results.

PACS numbers: 05.70.Ln,64.70.Pf

Recently, there has been an explosion of interest in understanding out of equilibrium properties in supercooled liquids. In general, the nonequilibrium behavior of a glassy system is characterized by a violation of the fluctuation-dissipation theorem and the absence of time translation invariance. In the particular case where the system is subjected to a homogeneous, steady shear flow, time translation invariance is recovered. This simpler nonequilibrium situation is of interest for two reasons. First, understanding the rheological properties of complex fluids such as colloidal suspensions and polymers at a microscopic level is important for the design and control of new materials. On a more fundamental level, it has recently been suggested that for supercooled liquids there are fundamental connections between the standard thermodynamic control variables of temperature and density in the equilibrium case and steady state shear out of equilibrium. A major goal of this work is to develop a theory that provides an explicit microscopic connection between the temperature, density and shear rate in a supercooled liquid.

Dense colloidal suspensions are known to exhibit weak shear thinning behavior. Such behavior is predicted for simple liquids as well, but the effect is too small to observe at temperatures well above the glass transition. For supercooled liquids, however, the situation is different. Recent numerical simulations have revealed anomalous rheological behavior in supercooled liquids. Yamamoto and Onuki and Berthier and Barrat have simulated supercooled liquids under strong stationary shear flow and observed a characteristic shear dependence of the structural relaxation time and the shear viscosity, $\tau_\alpha,\eta \propto \gamma^{-\nu}$, where $\tau_\alpha$ is the structural relaxation time, $\eta$ is the shear viscosity, $\gamma$ is the shear rate and the exponent $\nu$ is empirically found to range between 2/3 and 1. An abstract schematic approach based on the exactly solvable p-spin spin glass has been proposed and studied by Berthier, Barrat and Kurchan. This model predicts $\nu = 2/3$ in agreement with the lower bound found in the simulations of Berthier and Barrat. Since this model is schematic, it cannot be used to understand in detail the microscopic relationship between fluid structure and dynamics as a function of thermodynamic control variables and external driving.

In this letter, we shall generalize the mode-coupling theory developed to describe the fluctuations in an equilibrium state to that of a system under a stationary shear flow. Our starting point is generalized fluctuating hydrodynamics. Using several approximations, we obtain a closed nonlinear equation for the sheared generalization of the intermediate scattering function. In this letter, we shall consider both normal liquids as well as the overdamped Brownian behavior of a colloidal suspension in the absence of hydrodynamic interactions. Numerical results will only be presented for the Brownian case, but the more general results derived here could be used to make quantitative contact with recent molecular dynamics simulations.

Consider the shear flow given by

$$v_0(r) = \Gamma \cdot r = (\gamma y, 0, 0),$$

where $\Gamma_{\alpha\beta} = \gamma_\beta\delta_{\alpha\gamma}$ is the velocity gradient matrix. The hydrodynamic fluctuations for density $\rho(r, t)$ and the velocity field $v(r, t)$ obey the following set of Langevin equations:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho v),$$
$$\frac{\partial (\rho v)}{\partial t} + \nabla \cdot (\rho vv) = -\rho \nabla \frac{\delta F}{\delta \rho} - \zeta_0 (v - v_0) + f_R,$$

where $\zeta_0$ is the collective friction coefficient for colloidal particles and $f_R(r, t)$ is the random force. The $\zeta_0$ term is specific for the colloidal case. In the case of atomic liquids, the friction term should be replaced by a stress term which is proportional to the gradient of velocity field multiplied by the position dependent shear viscosities. Both cases, however, lead to the same dynamical behavior at long time scales. We neglect the weak $r$ dependence of the friction coefficient that could arise from hydrodynamic interactions between colloidal particles in.
the Brownian case. The first term in the right hand side of the equation for the momentum is the pressure term and $F$ 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:

$$\beta F \simeq \int dr \rho(r) \ln \rho(r) - \frac{1}{2} \int dr_1 \int dr_2 \rho(r_1) c(r_{12}) \rho(r_2),$$

where $\beta = 1/k_B T$ and $c(r)$ is the direct correlation function. Under shear, it is expected that $c(r)$ will be distorted and should be replaced by a nonequilibrium, steady state form $c_{\text{noneq}}(r)$, which is an anisotropic function of $r$. The effect of shear on the static correlation functions has been studied and is found that the distortion is characterized by the Péclet number is small, the above assumption is valid. In the presence of shear, transverse momentum fluctuations even if necessary, the full anisotropic steady state structure may be used. By linearizing eq. (2) around the stationary state as $\langle R \rangle$, where $R$ is a function of arbitrary fluctuations, an approximate expression; if necessary, the full anisotropic steady state structure may be used. By linearizing eq. (2) around the stationary state as $\langle R \rangle$, where $R$ is a function of arbitrary fluctuations, an approximate expression; if necessary, the full anisotropic steady state structure may be used.

$$\langle f_k(t) g_{k'}(0) \rangle = \langle f_k(t) g_{k'}(0) \rangle \times \delta_{k(k'),k'},$$

where $k(t) = \exp[i\mathbf{T}t] \cdot k = k + \gamma t k_x \hat{e}_x$, where $\mathbf{T}$ denotes the transpose of $\mathbf{T}$ and $\delta_{k,k'} \equiv (2\pi)^d V^{-1} \delta(k - k')$ for a system of volume $V$.

Eq. (6) states that the fluctuations satisfy translational invariance in a reference frame flowing with the shear contours. This approximation holds for long wavelengths where the direct interactions between particles are not important. On the other hand, for correlations between particles separated by molecular length scales, this is not generally true. The validity of this approximation for molecular length scales should be systematically examined in the future.

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

$$F(k,t) = \frac{1}{N} \langle \delta \rho_k(-t) \delta \rho_k(0) \rangle,$$

where $N$ is the total number of the particles in the system. Note that the wave vector in $\delta \rho_k(t)$ is now replaced by a time-dependent one $k(-t)$.

Eq. (4) has a nonlinear term

$$R_k(t) = -\frac{1}{m\beta S(k)} \int \mathbf{q} \cdot \mathbf{c}(\mathbf{q}) \delta \rho_{k-q}(t) \delta \rho_q(t).$$

This term can be renormalized with the definition of a generalized friction coefficient following the standard procedure of derivation of the mode-coupling equations.

To lowest order in the fluctuations, we have

$$\langle \frac{\partial}{\partial t} - k \cdot \mathbf{v} \rangle J_k(t) = - \frac{ik}{m\beta S(k)} \delta \rho_k(t) - \frac{1}{m} \int \mathbf{q} \cdot \mathbf{c}(\mathbf{q}) \delta \rho_{k-q}(t) \delta \rho_q(t) + f_{R_k}(t),$$

where $\mathbf{c}(\mathbf{q})$ is the Fourier transform of $c(r)$, $\mathbf{k} \equiv k/|k|$, $J_k(t) = \rho_0 k \cdot \mathbf{v} \delta k(t)$ is the longitudinal momentum fluctuation, and $f_{R_k}(t)$ is a corresponding random force. $\mathbf{c}(\mathbf{q})$ is given by the sum of the bare friction coefficient and the mode-coupling term as

$$\zeta(k,k',t) = \zeta_0 \times 2\delta(t) + \delta \zeta(k,k',t),$$

with the mode-coupling contribution given by

$$\delta \zeta(k,k',t) = \frac{m^2 \beta}{N} \langle R_k(t) R^*_k(0) \rangle.$$
This involves a four point correlation function. Using the Gaussian approximation, this can be decomposed into a product of two-point correlation functions as
\[
\langle \delta \rho_{k,-q}(t) \delta \rho_{q}(t) \delta \rho_{k,-q'}(0) \delta \rho_{q'}(0) \rangle \\
\simeq N^2 F(k(t) - q(t), t) F(q(t), t) \\
\times \left\{ \delta_{k(t),k'} \delta_{q(t),q'} + \delta_{k(t),k} \delta_{q(t),q'} \right\},
\]
where use has been made of the translational invariance, eq. (13).

Substituting eq. (19) back to eq. (22), we obtain
\[
\delta \zeta(k, k', t) = \delta \zeta(k, t) \delta(k(t), k'),
\]
with
\[
\delta \zeta(k, t) = \frac{\rho_0}{\beta} \int_q \left\{ k \cdot q c(q) + \hat{k} \cdot (k - q) c(k - q) \right\} \\
\times k(t) \cdot q(t) c(q(t)) F(k(t) - q(t), t) F(q(t), t)
\]
\[
= \frac{\rho_0}{2\beta} \int_q \mathcal{V}(k, q) \mathcal{V}(k(t), q(t)) F(k(t) - q(t), t) F(q(t), t),
\]
where \( \mathcal{V}(k, q) \) is the vertex function given by
\[
\mathcal{V}(k, q) = \hat{k} \cdot \{ q c(q) + (k - q) c(k - q) \}.
\]

From these results and eq. (10), the equation for the correlation function,
\[
C(k, t) \equiv \frac{1}{N} \langle J_{k(t)}(t) n_k^a(0) \rangle
\]
is given by
\[
\frac{dC(k, t)}{dt} = -\hat{k}(-t) \cdot \Gamma \cdot \hat{k}(-t) C(k, t) - \frac{ik(-t)}{m \beta S(k(-t))} F(k, t)
\]
\[
- \frac{1}{m} \int_0^t dt' \delta \zeta(k(-t), t - t') C(k, t').
\]

Note that in the above equation, the differential operator \( k \cdot \Gamma \cdot \partial / \partial k \) disappears because
\[
\frac{dC(k, t)}{dt} = \frac{\partial C(k, t)}{\partial t} - k(-t) \cdot \Gamma \cdot \frac{\partial}{\partial k(-t)} C(k, t).
\]

Likewise, the continuity equation (the first term in eq. (21)) can be written as
\[
\frac{dF(k, t)}{dt} = -ik(-t) C(k, t).
\]

This equation together with eq. (17) comprises the closed set of the mode-coupling equations for \( F(k, t) \) and \( C(k, t) \) under shear.

For colloidal suspensions the relaxation time of the momentum fluctuations is of the order of \( \tau_m = m/\zeta_0 \) and is much shorter than the relaxation time for density fluctuations which is of the order of or longer than \( \tau_d = \sigma^2 / D_0 \). For the time scale of interest, \( \hat{k}(-t) \cdot \Gamma \cdot \hat{k}(-t) \) as well as the inertial term can be neglected in the equation for the momentum fluctuations since \( \gamma \tau_m \ll 1 \) in realistic situations. Thus, the equation for the momentum fluctuations may be written as
\[
0 = -\frac{ik(-t)}{\beta S(k(-t))} F(k, t) - \zeta_0 C(k, t)
\]
\[
- \int_0^t dt' \frac{\partial C(k(-t), t - t')}{\partial t'} C(k, t').
\]

Substituting this back into eq. (19), we arrive at
\[
\frac{dF(k, t)}{dt} = -\frac{D_0 k(-t)^2}{S(k(-t))} F(k, t)
\]
\[
- \int_0^t dt' M(k(-t), t - t') \frac{dF(k(t), t')}{dt'},
\]
where
\[
M(k, t) = \frac{\rho_0 D_0}{2} \frac{k}{k(t)} \int_q \mathcal{V}(k, q) \mathcal{V}(k(t), q(t))
\]
\[
\times F(k(t) - q(t), t) F(q(t), t).
\]

Eqs. (21) and (22) are the major result of this letter. In the absence of the shear, they reduce to the conventional mode-coupling equations (10).

In order to study the shear thinning effect in the supercooled state, we shall solve eqs. (21) and (22) numerically. Solving this equation is more difficult than solving the corresponding equation in the equilibrium case because the wave vectors are distorted by shear and the system is not isotropic. For simplicity, we shall consider a hypothetical two-dimensional colloidal suspension which is simple to handle numerically but still undergoes an ergodic-nonergodic transition below a certain density. The shear flow occurs in the \( x \) direction. We have chosen the following form of the static structure factor \( S(k) \):
\[
S(k) = S_{PY}(k + k_0, \alpha \rho_0) f(k - k_c),
\]
where \( S_{PY}(k, \rho) \) is the static structure factor for a hard-sphere system at the density \( \rho \) obtained from the Percus-Yevick closure, \( k_0 \) and \( \alpha \) are parameters which were chosen in such a way that \( S(k) \) is short-ranged and has a broader peak. \( f(k - k_c) \) is a cut-off function which makes \( S(k) \) approach unity smoothly for wave vectors larger than the cut-off \( k_c \). The choice of \( S(k) \) mimics the shape of \( S(k) \) of real systems although it does not satisfy sum-rule restrictions. In our calculation, we chose \( k_0 = 4.0 \), \( \alpha = 32 \) and \( k_c = 4.0 \). For this system, the ergodic-nonergodic transition occurs around a “density” \( \rho_0 \sigma^2 \simeq 1.2 \times 10^{-2} \) in the absence of shear. In Figure 1,
we show the behavior of $F(k,t)$ for $\rho \sigma^2 = 1.15 \times 10^{-2}$, slightly below $\rho_c$. The wave vector is $k = (0, 2\pi)$. Since $k_x = 0$, the expression for $F(k,t)$ is equivalent to that in the quiescent state, $F_{eq}(k,t) = N^{-1} \langle \delta \rho_k(t) \delta \rho_k^*(0) \rangle$. Thus, there is no direct effect from the convection term but, due to the nonlinear coupling through the mode-coupling term $M(k,t)$, a strong shear dependence of the relaxation time can be seen. The dependence of the coupling term $\tau_{M}(\hat{\gamma})$ on the shear rate $\hat{\gamma}$ is estimated from the value where $F(k,\tau_{M}) = e^{-1}$. For the particular case of $\rho \sigma^2 = 1.15 \times 10^{-2}$ we find the power law $\tau_{M} \approx \hat{\gamma}^{-\nu}$ with $\nu \approx 0.8$ for $Pe \geq 10^{-3}$ and $\tau_{M}$ saturates to the equilibrium value at $Pe \leq 10^{-3}$. This is similar to the behavior reported in recent molecular dynamics simulations. For values of $\rho \sigma^2 > 1.2 \times 10^{-2}$ (not shown), we find that the exponent $\nu$ saturates at a higher value, in agreement with the simulations of Berthier and Barrat [3].

The physical picture that emerges from the molecular hydrodynamic theory developed here is simple. The shear flow perturbs and randomizes the coupling between different modes. Physically, this perturbation dissipates the cage that transiently immobilizes particles. Mathematically, this is reflected through the time dependence of the vertex, which vanishes as $t \to \infty$. This simple picture illustrates the essence of the mode-coupling approach to the shear thickening effect in simple supercooled systems. Note that even for fluctuations orthogonal to the direction of flow, thinning occurs due to the coupling of fluctuations in all directions. In this sense, the picture of cage breakup in a supercooled liquid due to external flow is quite different from that of dynamic critical phenomena under shear, in which the faster relaxation occurs solely because the fluctuations are stretched out by the shear flow and pushed to larger wave vectors where faster relaxation occurs.

In this letter, we have derived an approximate mode-coupling theory for a supercooled liquid under steady shear flow. The most important assumption is the use of approximate translational invariance, eq. (4). This allows one to derive a nonlinear integro-differential equation for $F(k,t)$ similar to the one for the equilibrium state. The numerical analysis for a hypothetical two-dimensional colloidal suspension has been carried out and a typical behavior of $F(k,t)$ was shown to be consistent with recent simulations. The relaxation time is found to have the strong shear dependence. More systematic and thorough analysis of the numerical solutions of the mode-coupling equations are left for future work [11].

The authors acknowledge support from NSF grant #0134969. The authors would like to express their gratitude to Dr. Ryoichi Yamamoto for suggesting this problem during his stay at Harvard, and for useful discussions.

---

*Electronic address: miyazaki@fas.harvard.edu
†Electronic address: reichman@fas.harvard.edu

[1] A. J. Liu and S. R. Nagel, Nature 396, 21 (1998).
[2] R. Yamamoto and A. Onuki, Phys. Rev. E 58, 3515 (1998); R. Yamamoto and A. Onuki, J. Chem. Phys. 117, 2359 (2002).
[3] L. Berthier and J.-L. Barrat, J. Chem. Phys. 116, 6228 (2002).
[4] L. Berthier, J.-L. Barrat, and J. Kurchan, Phys. Rev. E 61, 5464 (2000).
[5] T. R. Kirkpatrick and J. C. Nieuwoudt, Phys. Rev. A 33, 2651 (1986).
[6] A. V. Indrani and S. Ramaswamy, Phys. Rev. E 52, 6492 (1995). In their paper, the convection term in the momentum equation is neglected.
[7] A. Onuki and K. Kawasaki, Ann. Phys. 121, 456 (1979); A. Onuki, J. Phys.: Condens. Matter 9, 6119 (1997).
[8] D. Ronis, Phys. Rev. A 34, 1472 (1986).
[9] R. Zwanzig, Nonequilibrium Statistical Mechanics (Oxford University Press, Oxford, 2001).
[10] W. Götze and L. Sjögren, Rep. Prog. Phys. 55, 241 (1992).
[11] As this manuscript was being written for publication, we became aware of a parallel effort by Fuchs and Cates [cond-mat/0204628, cond-mat/0207520]. While the omission of several details in their calculation make a detailed comparison between the two approaches impossible at this time, there are many similarities in the final expressions, and the physical picture is also quite similar. Differences do exist in the expressions, which most likely lead to different estimates of the exponent $\nu$. It will be most useful in the future to make a detailed comparison of the two theories since the differences in approach (fluctuating hydrodynamics verses the projection operator formalism) and the final results may lead to a better understanding of the limitations of several assumptions used to here and by Fuchs and Cates to describe how an external flow disrupts jamming.
FIG. 1: Normalized $F(k,t)$ for $k = (0, 2\sigma)$ for various shear rates $\dot{\gamma}$. The "density" is $\rho \sigma^2 = 1.15 \times 10^{-2}$. From the right to the left, $Pe = \dot{\gamma} \sigma^2 / D_0 = 0, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}$, and 1. The results for $Pe= 0$ and $10^{-4}$ are almost indistinguishable. The time $t$ is scaled by $\sigma^2 / D_0$. 

FIGURE CAPTIONS
