LETTER

An order parameter equation for the dynamic yield stress in dense colloidal suspensions

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Abstract. We study the dynamic yield stress in dense colloidal suspensions by analysing the time evolution of the pair distribution function for colloidal particles interacting through a Lennard-Jones potential. We find that the equilibrium pair distribution function is unstable with respect to a certain anisotropic perturbation in the regime of low temperature and high density. By applying a bifurcation analysis to a system near the critical state at which the stability changes, we derive an amplitude equation for the critical mode. This equation is analogous to order parameter equations used to describe phase transitions. It is found that this amplitude equation describes the appearance of the dynamic yield stress, and it gives a value of 2/3 for the shear thinning exponent. This value is related to $\delta$ in the Ising model.

Keywords: structural colloidal and polymer glasses (theory), colloids, rheology and rheophysics
1. Introduction

Soft glassy materials, such as dense colloidal suspensions and supercooled liquids, exhibit diverse rheological phenomena [1,2]. Typical examples are the decrease of the viscosity with increasing the shear rate, called shear thinning, and the increase of the viscosity with the shear rate, called shear thickening. These phenomena appear when the shear rate is beyond the Newtonian regime, that is, the regime in which the shear stress $\sigma_{xy}$ depends linearly on the shear rate $\gamma$, and hence the viscosity, $\eta = \sigma_{xy}/\gamma$, is independent of the shear rate. Interestingly, the Newtonian regime becomes narrower as the temperature decreases and the density increases, and eventually it disappears. In the case that there exists no Newtonian regime, the stress is finite in the limit $\gamma \downarrow 0$. This stress is called the dynamic yield stress. We seek to understand these rheological properties systematically on the basis of a microscopic description of the system.

Recently, the nonlinear rheology of soft glassy materials has been studied extensively through use of molecular dynamics simulations [3]–[5], analysis of random spin models [6,7], and mode coupling theory applied to systems under shear [8]–[10]. In particular, the mode coupling theory has predicted that the dynamic yield stress appears discontinuously at the glass transition point [8] and the results have been compared with a numerical simulation [11] and an experiment [12]. On the other hand, the power law $\eta \sim \gamma^{-2/3}$ has been observed for a shear thinning fluids [5,6].

Among theoretical approaches, one standard method for microscopic study of nonlinear rheology is based on the mode coupling theory. In this theory, the singular behaviour of the viscosity is described by the anomalous part of the time correlation function, using a generalized Green–Kubo formula [13]. As another approach describing the singular behaviour, one could focus on the shear stress. Here, let us recall that the shear stress $\sigma_{xy}$ is defined as the average of the $y$-component of the interparticle force acting on a plane transverse to the $x$-direction. When there exist only two-body forces among the particles, this average can be expressed in terms of the pair distribution function. Therefore, in this case, the rheological properties mentioned above can be accounted for through an analysis of the pair distribution function.

Employing an approach of the latter type, in the present letter, we first investigate the linear stability of the equilibrium pair distribution function. We find that this function is
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unstable in the regime of low temperature and high density. Next, applying a bifurcation
analysis to a system near a critical state at which the stability changes, we derive an order
parameter equation that describes the appearance of a dynamic yield stress in a simple
manner.

2. Model

We consider a system consisting of \( N \) spherical colloidal particles suspended in a solvent
under shear flow described by \( \mathbf{v}(\mathbf{r}) = (\gamma y, 0, 0) \). We denote the volume of the system by
\( V \) and the temperature by \( T \). Let \( \Gamma = (\mathbf{r}_1, \ldots, \mathbf{r}_N) \) represent the particle positions.
The time-dependent distribution function for \( \Gamma \), \( \Psi_N(\Gamma, t) \), satisfies the Smoluchowski
equation [1]

\[
\frac{\partial \Psi_N(\Gamma, t)}{\partial t} = \sum_{i=1}^{N} \nabla_i \cdot \left( \frac{T}{R} \nabla_i - \frac{1}{R} \mathbf{F}_i(\Gamma) - \mathbf{v}(\mathbf{r}_i) \right) \Psi_N(\Gamma, t).
\]  

Here, the Boltzmann constant is set to unity, \( R \) is the friction coefficient, and \( \mathbf{F}_i(\Gamma) \) is
the interaction force defined by \( \mathbf{F}_i(\Gamma) = -\nabla_i \sum_{j \neq i} V(|\mathbf{r}_i - \mathbf{r}_j|) \). In this work, we employ
the Lennard-Jones potential, with the explicit form \( V(r) = 4\epsilon[(r/\sigma)^{-12} - (r/\sigma)^{-6}] \). In
the treatment below, \( \sigma, \epsilon \) and \( R \) are set to unity, and all quantities are converted to
dimensionless forms.

From the \( N \)-particle distribution function \( \Psi_N(\Gamma, t) \), the pair distribution function
\( g(\mathbf{r}, t) \) is defined as

\[
g(\mathbf{r}, t) = V^2 \int d^3 \mathbf{r}_3 d^3 \mathbf{r}_4 \cdots d^3 \mathbf{r}_N \Psi_N(\Gamma, t),
\]  

where \( \mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2 \). Using this function, we can express the time-dependent shear stress
as [14]

\[
\sigma_{xy}(t) = \frac{\rho^2}{2} \int d^3 \mathbf{r} \mathbf{r}g(\mathbf{r}, t) \frac{x y \partial V(\mathbf{r})}{r^2} dV(\mathbf{r}),
\]  

where \( \rho \equiv N/V \) is the average number density of the colloidal particles, \( \mathbf{r} = (x, y, z) \), and
\( r = |\mathbf{r}| \). Here, we have ignored the hydrodynamic contribution to the shear stress.

It is useful to expand \( g(\mathbf{r}, t) \) in spherical harmonics, and we write

\[
g(\mathbf{r}, t) = f_I(\mathbf{r}, t) \text{Im} Y_{2,2}(\theta, \phi) + f_R(\mathbf{r}, t) \text{Re} Y_{2,2}(\theta, \phi)
+ \sum_{l \geq 0; |m| \leq l; (l,m) \neq (2,\pm 2)} G_{l,m}(\mathbf{r}, t) Y_{l,m}(\theta, \phi),
\]  

employing the spherical coordinate system \( (r, \theta, \phi) \). Hence, substituting equation (4)
into (3), we obtain

\[
\sigma_{xy}(t) = \sqrt{\frac{2\pi}{15}} \rho^2 \int_0^\infty dr r^3 \frac{\partial V(\mathbf{r})}{\partial r} f_I(\mathbf{r}, t).
\]  

This expression clearly indicates that if there is singular behaviour of the shear stress
\( \sigma_{xy} \), that of the pair distribution function can be observed. In particular, the existence
of a dynamic yield stress implies that the pair distribution function in the limit \( \gamma \searrow 0 \)

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An order parameter equation for the dynamic yield stress differs from the equilibrium one. This observation naturally leads us to conjecture that the dynamic yield stress is related to the instability of the equilibrium pair distribution function, $g_{eq}(r)$. For this reason, we carry out a linear stability analysis of $g_{eq}(r)$.

In order to determine the linear stability of $g_{eq}(r)$, we need to study the time evolution of the pair distribution function. This is described by the BBGKY hierarchy, and hence it is determined by the three-particle distribution function $g_3(r, r', t)$. In order to obtain a self-contained description, we truncate the BBGKY hierarchy by employing the Kirkwood superposition approximation, assuming the relation

$$g_3(r, r', t) = g(r, t)g(r', t)g(r - r', t)$$

This approximation has been used in the calculation of the pair distribution function for both an equilibrium system [16] and a non-equilibrium system under shear [17]. With this approximation, the evolution equation for the pair distribution function is derived as

$$\frac{\partial g(r, t)}{\partial t} = -\nabla \cdot J(r, t),$$

with

$$J(r, t) = -2T\nabla g(r, t) - 2\nabla V(r)g(r, t) - 2\rho \left( \int d^3r' \nabla V(r')g(r, t)g(r', t)g(r - r', t) \right) + \gamma y \frac{d}{dx} g(r, t).$$

3. Linear stability analysis

First, the equilibrium pair distribution function $g_{eq}(r)$ for this model is obtained as the isotropic solution of the equation $J = 0$ with $\gamma = 0$. This equation is called the Born–Green equation [15], which has been solved numerically [16]. Then, writing

$$g(r, t) = g_{eq}(r)(1 + h(r, t)),$$

we substitute equation (8) into equations (6) and (7) and obtain the form

$$g_{eq}(r) \frac{\partial}{\partial t} h(r, t) = \mathcal{L}(h(r, t)) + \mathcal{N}(h(r, t)) + \gamma \mathcal{G}(h(r, t)),$$

where $\mathcal{L}$ is a linear operator and $\mathcal{N}$ contains only second-order and third-order polynomials in $h(r, t)$.

Because the equilibrium pair distribution function $g_{eq}(r)$ is non-negative, it is linearly unstable if and only if the linear operator $\mathcal{L}$ has a positive eigenvalue. Therefore, in order to determine the linear stability of $g_{eq}(r)$, we could numerically compute the eigenvalues of $\mathcal{L}$. However, due to the three-dimensional spatial dependence of $h(r, t)$, the computation of these eigenvalues is not simple. Therefore, to simplify the problem, we assume perturbations $h(r, t)$ of the form $h(r, t) = \psi(r, t) \text{Im} Y_{2,2}(\theta, \phi)$. Such an assumption is reasonable, because the equilibrium pair distribution function is expected to be unstable with respect to perturbations of the form $\text{Im} Y_{2,2}(\theta, \phi)$ in the regime characterized by low temperature and high density. (See equations (4) and (5).) Then, using the explicit form
of $\mathcal{L}$, we can rewrite $\mathcal{L}(h(r, t))$ in equation (9) as

$$\mathcal{L}(h(r, t)) = \text{Im} Y_{2,2}(\theta, \phi) M(\psi(r, t)).$$

(10)

To solve the linear stability problem, we seek the eigenvalues of $\mathcal{M}$.

The eigenvalues of the operator $\mathcal{M}$ are computed numerically in the following way. We first restrict the spatial domain of $\psi(r, t)$ to the interval $[0, l]$, with the boundary conditions $\partial\psi(r, t)/\partial r = 0$ at $r = 0$ and $l$. We next approximate the linear operator $\mathcal{M}$ as a matrix $\mathcal{M}$ by using a difference method with a spatial mesh size $\delta x$ [18]. We calculated the eigenvalues of $\mathcal{M}$ for many values of $(\rho, T)$.

In figure 1, we display the stability diagram obtained numerically. It is seen that the pair distribution function $g_{\text{eq}}(r)$ is unstable in the low-temperature, high-density regime. Note that the form of the boundary between the two regimes is qualitatively similar to the curve representing the glass transition in the $(\rho, T)$-plane calculated using mode coupling theory [19], though at each density the value of the temperature on the boundary in the present case is approximately twice that in the glass transition case. This overestimate of the temperature might be caused by the inaccuracy of the equilibrium pair distribution function $g_{\text{eq}}(r)$ calculated with the Kirkwood superposition approximation. Indeed, it has been known that the maximum of $g_{\text{eq}}(r)$ obtained by this approximation is less pronounced and is shifted towards smaller interparticle distances than that obtained by Monte Carlo simulations.

4. Nonlinear analysis

Next, we focus on systems near the critical state at which the stability changes. If we fix the density, then we find that there exists a critical temperature $T_s$ below which the equilibrium pair distribution function $g_{\text{eq}}(r)$ is unstable. Let $\psi_*(r)$ be the critical eigenfunction of the operator $\mathcal{M}$ at $T = T_s$. Then, we write a perturbation $h(r, t)$ in the form

$$h(r, t) = A(t)\psi_*(r) \text{Im} Y_{2,2}(\theta, \phi) + s(r, A(t)).$$

(11)

Here, $s(r, A(t))$ represents the contribution to $h(r, t)$ that is not from the critical mode, and we have assumed that its time dependence is restricted to that of the amplitude.
A. This is a reasonable assumption because the amplitudes of non-critical modes decay quickly to the values determined by $A$.\footnote{We found numerically that in the neighbourhood of the stability boundary, the largest non-critical eigenvalue is less than $-0.5$.}

Then, using a bifurcation analysis (see [20] as a review), from equations (9) and (11) we perturbatively obtain the evolution equation for $A(t)$ in the form

$$\frac{d}{dt} A(t) = (T_s - T) a A(t) + G(A(t)) + \gamma H(A(t)), \quad (12)$$

where $a$ is a positive constant, and the functions $G(A)$ and $H(A)$ can be calculated from equation (9) [21]. In this letter, we do not calculate $G(A)$ and $H(A)$. Instead, considering the general forms of these functions, we qualitatively describe the singular behaviour of the shear stress.

First, because the system possesses symmetry with respect to the simultaneous transformation $x \rightarrow -x$ and $\gamma \rightarrow -\gamma$, $G(A)$ must be an odd function and $H(A)$ an even function. We therefore expand them as

$$G(A) = b_3 A^3 + b_5 A^5 + \cdots, \quad (13)$$

$$H(A) = c_0 + c_2 A^2 + \cdots. \quad (14)$$

Next, let $A_*(\gamma)$ be a stable stationary solution of equation (12). Then, from equations (5) and (11), the shear stress for systems near the critical state $T = T_s$ and $\gamma = 0$ can be approximately expressed as

$$\sigma_{xy} \simeq A_*(\gamma) \sqrt{\frac{2\pi}{15}} \rho^2 \int_0^\infty dr r^3 \frac{\partial U(r)}{\partial r} g_{eq}(r) \psi_*(r), \quad (15)$$

because $s(r, A(t))$ in equation (11) contains no terms linear in $A$, as we have confirmed. Thus, the value of $A_*(\gamma)$ determines the behaviour of the shear stress near the critical state. In this sense, the amplitude of the critical mode can be regarded as an order parameter describing the appearance of the dynamic yield stress.

Now, we investigate equation (12). For $\gamma = 0$, this equation possesses the trivial stationary solution $A_* = 0$. This solution is stable only when $T > T_s$. The non-trivial stationary solutions depend on the form of $G(A)$. First, let us consider the case that $b_3 < 0$ in equation (13). (We conjecture that $b_3 < 0$ for the model we study.) Then, for $T \simeq T_s$ and $\gamma \simeq 0$, $A_*$ satisfies $(T_s - T) a A_* + b_3 A_*^3 \simeq -\gamma c_0$. Here, we note that the term $\gamma c_2 A_*^2$ is neglected, because one can always choose a share rate in such a way that $|\gamma c_2 A_*^2| \ll |b_3 A_*^3|$ for the case $T < T_s$ and $|\gamma c_2 A_*^2| \ll |(T_s - T) a A_*|$ for the case $T > T_s$. Thus, in the limit $\gamma \searrow 0$, the shear stress is obtained as a function of the temperature near $T = T_s$. The qualitative form of this function is displayed in the left-hand side of figure 2. It is seen that the dynamic yield stress increases continuously from zero as $T$ decreases from $T_s$. By contrast, when $T = T_s$ and $\gamma > 0$, we obtain

$$\sigma_{xy} \simeq \gamma^{1/\delta}, \quad (16)$$

with $\delta = 3$. This $\delta$ corresponds to that appearing in the relation $M \simeq H^{1/\delta}$ describing critical phenomena for magnetic materials, and the value $\delta = 3$ is the mean-field value for the Ising model. Note that equation (16) yields $\eta \simeq \gamma^{-(1-1/\delta)}$. The exponent $1 - 1/\delta$ is
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Figure 2. Shear stress in steady states in equation (13). Here, the value plotted is that obtained in the limit \( \gamma \downarrow 0 \). The solid curve represents stable states, and the dashed line unstable states. The inset compares the dependence of \( \sigma_{xy} \) on \( \gamma \) in the three cases \( T > T_s \), \( T = T_s \) and \( T < T_s \). Left: the case that \( b_3 < 0 \). Right: the case that \( b_3 > 0 \) and \( b_5 < 0 \).

called the *shear-thinning exponent*, and we find it to be \( 2/3 \) in this analysis. We also find that when \( T > T_s \), a Newtonian regime appears near \( \gamma = 0 \). This regime is connected to the power-law regime that exists for higher shear rates. As seen in the inset of the left-hand side of figure 2, this behaviour corresponds to shear thinning.

Next, we consider the case \( b_3 > 0 \) and find that, here, a qualitatively different form of the stress is obtained. (We expect that there do exist models in which \( b_3 > 0 \), although we believe that the model studied here is not one of these.) One physically plausible situation is that in which \( b_5 < 0 \), where we have the form displayed in the right-hand side of figure 2. In this case, as the temperature is decreased, the dynamic yield stress increases discontinuously from zero to a finite value at some temperature \( T_c ( > T_s ) \), as shown in the right-hand side of figure 2. Furthermore, it is easily confirmed that shear thickening exists when \( T > T_c \).

5. Conclusion

The main finding of this letter is that the order parameter equation given in equation (12) provides a simple description of the nonlinear rheological phenomena exhibited by the systems considered here. We note that the order parameter in our model is defined to be the amplitude of the critical mode of the pair distribution function, which is related to the equal-time correlation function of the density. This contrasts with the situation for the critical phenomena of liquid–gas phase transitions, for which the order parameter is defined in terms of the critical mode of the density. Consideration of this difference might help elucidate the essence of the glass transition.

We conjecture that the coefficient \( b_3 \) is negative for the model we study. This indicates that the dynamic yield stress appears continuously from 0 at the transition point. This result is different from that obtained by the mode coupling theory that predicts the discontinuous appearance of the dynamic yield stress. Note that the recent result in [12] might support the discontinuous onset, while the power-law behaviour consistent with our result is still observed in the range \( 10^{-4} < \gamma < 10^{-1} \) in this report. Our simple theory in the present version might miss some important physical effects. We will study further in order to understand this discrepancy.

Finally, we present remarks regarding the two assumptions we employed in our analysis. First, the perturbations to \( g_{eq}(r) \) are assumed to be restricted to the form

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\[ h(\mathbf{r}, t) = \psi(\mathbf{r}, t) \text{Im} Y_{2,2}(\theta, \phi) \] for simplicity. Here, we note that we already performed the analysis without this restriction and obtained the same stability diagram [21]. In this analysis, the five critical modes, which correspond to \( \sigma_{xy}, \sigma_{yz}, \sigma_{zx}, \sigma_{xx} - \sigma_{yy}, \) and \( \sigma_{zz} - (\sigma_{xx} + \sigma_{yy})/2, \) appear simultaneously at \( T = T_s \) as the result of the rotational symmetry. Then, five order parameters are defined in association with these critical modes. We will report the result in another paper.

Second, with regard to the Kirkwood superposition approximation, we consider that it has some analogy with a mean-field theory for critical phenomena. Therefore, we expect that the time evolution of the five order parameter fields (that depend on the spatial coordinate) under the influence of noise can describe rheological phenomena more precisely. This extension might modify the critical exponent \( \delta, \) and also it might play an important role in the description of phenomena for the case \( T < T_s. \) We wish to develop such a theory as a natural extension of our analysis in this letter.

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