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LIGHT SCATTERING STUDIES OF AN ELECTORHEOLOGICAL FLUID IN OSCILLATORY SHEAR

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ABSTRACT

We have conducted a real time, two-dimensional light scattering study of the nonlinear dynamics of field-induced structures in an electrorheological fluid subjected to oscillatory shear. We have developed a kinetic chain model of the observed dynamics by considering the response of a fragmenting/aggregating particle chain to the prevailing hydrodynamic and electrostatic forces. This structural theory is then used to describe the nonlinear rheology of ER fluids.

1. Introduction

The rheology of ER fluids at low to moderate volume fractions is due to the aggregation of particles into volatile chain-like structures whose size adjusts in response to the flow, fragmenting and aggregating as the shear rate increases or decreases. Understanding the size and orientation of particle structures has been the basis of the development of the microscopic droplet model¹ of electrorheology in steady shear, and light scattering² has proven useful in establishing many of the predictions of this model. Much less is known about ER fluid structure in oscillatory shear, where the orientational dynamics of chain-like aggregates is the key issue. Since an understanding of electrorheology in nonstationary flows is essential to modeling the behavior of ER devices, we have undertaken a light scattering study of chain dynamics in oscillatory shear.³

Light scattering enables us to determine both the orientation and size of chains as functions of time, revealing a class of nonlinear dynamics dominated by fragmentation/aggregation processes that occur throughout each shear cycle. We have developed a simple *kinetic chain model*³ that is in good agreement with the observed dynamics and that allows us to predict the nonlinear rheology. In fact, direct rheological measurements^{4,5} show that the framework of linear viscoelasticity- a phase-shifted stress proportional to an applied strain- is of limited utility for ER fluids, so a nonlinear theory is appropriate.

Previous light scattering and diffraction studies focused on the quiescent fluid and on steady shear. The kinetics of structure formation⁶ and the equilibrium state of the quiescent fluid⁷ have been reported, as has the manner in which the chain size and orientation increases with shear rate.² These latter measurements are in accord with earlier experiments and theory of the power-law shear thinning viscosity.¹

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2. Experimental

2.1. Sample and Apparatus

Our light scattering sample is a transparent model silica fluid developed for light scattering and electrorheology studies.⁶ The 700 nm spheres are coated with a silane coupling agent and dispersed in 4-methylcyclohexanol to 7.5 wt % silica. Aggregation is reversible by Brownian motion alone.

The scattering cell consists of an inner 40x2 mm circular disk electrode that is concentric to a 42 mm hole in an outer electrode, thus creating a radial electric field in a 1 mm gap. The outer electrode is sandwiched between plastic, and both are embedded between glass plates, with a fluid-filled 2 mm gap between the electrodes glass plates. The inner electrode is oscillated by a rod connected to a 25 mm lever on the electrode shaft, driven by an eccentric on a 300 oz.-in. microstepping motor.

The electric field is a 1 kHz square wave from a Trek™ power supply driven by Wavetek™ signal generator. Voltages are reported peak-to-peak.

Scattering data are captured by a Pulnix™ video camera, and stored on video tape. Data were then real-time digitized by a Perceptix™ frame grabber on a Macintosh Quadra 950™. Optical corrections were then made to the scattering data.⁶

A problem in this experiment is the phasing of the applied strain with the scattering data. We devoted a small corner of the scattering screen to an optical "strain phase clock" created by rotating a prism in synchrony with the stepping motor. The prism deflects a He-Ne laser beam that thus scribes a circle on the scattering screen, encoding the absolute strain phase on each image.

2.2 Data analysis

A scattering image contains a pair of scattering lobes⁶ and the strain phase clock. These scattering lobes are tilted relative to the orientation of the scattering lobes obtained for the quiescent fluid, which are *orthogonal* to the electric field. The orientation of the scattering lobes reflects the orientation of the chains.

The rotation angle θ of the chains was determined by dividing the scattering image into 360 wedges, each subtending 1° of arc, and then integrating to find the average intensity in each wedge.² The orientation of the scattering lobes was then obtained by: locating the intensity maximum, θ_{max} ; or finding the median, θ_m , that divides the integrated scattered intensity into equal halves, so

$$\int_{\theta_m}^{90^\circ} I(\theta) d\theta = \int_{-90^\circ}^{\theta_m} I(\theta) d\theta.$$

The median is useful when the dynamics is strongly nonlinear, but gives an orientation angle about five times smaller than θ_{max} .

3. Measurements

At low strain amplitudes $\gamma_0 \ll 1$ the response of the orientation angle θ_{max} to the shear strain $\gamma = \gamma_0 \sin(2\pi\omega t)$ was nearly sinusoidal. This sinusoidal response is exemplified in Fig. 1, where clockwise Lissajous plots of $\tan(\theta_{max})$ against γ are shown to be nearly elliptical. At high frequencies the shear rate, $\dot{\gamma} = 2\pi\omega\gamma_0 \sin(2\pi\omega t)$, is large, and the chain orientation is nearly in phase with the fluid shear, since the hydrodynamic dominates electrostatic torque. Affine deformation is nearly achieved, as shown by the dashed line. At low shear frequencies the chain orientation leads the strain by 57° and thus lags the strain rate by 33° . In this regime electrostatic torque evidently dominates the hydrodynamic torque.

Figure 1: Clockwise Lissajous plots of $\tan(\theta_{max})$ against γ .

At higher strain amplitudes, Fig. 2, the sinusoidal motion becomes "clipped" as the chains fragment and aggregate during a cycle to maintain good field alignment, giving parallelogram Lissajous plots. At lower voltages we observe a highly nonlinear fluid response, as shown in Fig. 3. Starting at maximum positive strain, the chain half cycle can be described as follows. As the strain reverses, the chains co-move with the fluid, tilt to a maximum angle at half maximum strain, whereupon they fragment and undergo retrograde motion to realign with the electric field. Analysis shows that as they co-move with the

Figure 2: Lissajous plots at $\gamma = 0.5, 1.6$, and 3.2 have parallelogram shapes that indicate a "clipping" of the motion. Theoretical curves are computed in the limit of large k .

Figure 3: At low voltages a novel retrograde motion of fragmenting chains can be observed (dashed line is theory). The amplitude of motion is sensitive to the dipolar model and the method of data reduction.

shearing fluid, the chains aggregate, and indeed the scattering lobes brighten considerably during this time. These observations of chain motion have led us to propose the following model of ER fluid microstructure and rheology.

4. Chain Model

The salient features of experimental results we have shown can be understood in terms of a kinetic model of the dynamics of volatile chains. In this model we assume that dipolar interactions and hydrodynamic forces dominate thermal forces, which is certainly true in our experiments. This kinetic chain model differs from the elliptical droplet model, which minimizes a free energy and is thus an equilibrium model. Although it is not appropriate to give a full derivation of the model here, a brief description will aid the reader.

4.1. Equation of Motion

We consider a linear chain of $2N+1$ spheres of radius a in an oscillatory shear field. The chain has a rotational velocity $\dot{\theta}$ and makes an angle θ to the electric field. The hydrodynamic force the fluid exerts can be decomposed into a tangential component that causes chain rotation, and a radial component that causes tension or compression. The tangential force is a maximum at the chain center, where in low Reynolds number flow is balanced by the tangential component of the dipole-dipole interaction force. Balancing the tangential hydrodynamic and electrostatic forces at the chain center⁸ gives the damped oscillator equation

$$\dot{\theta} + \omega_d \sin 2\theta = \dot{\gamma} \cos^2 \theta, \quad \text{where} \quad \omega_d = \dot{\gamma} / 16MnN^2 \quad (1)$$

Here $Mn = \mu_0 \dot{\gamma} / 2\epsilon_0 \epsilon_c \beta^2 E_0^2$ is the Mason number, which expresses the ratio of hydrodynamic to electrostatic forces, β is the dielectric contrast factor $(\epsilon_p - \epsilon_c) / (\epsilon_p + 2\epsilon_c)$, ϵ_c and ϵ_p are the liquid and particle dielectric constants.⁹

4.2. Mechanical Stability

The oscillator frequency ω_d depends strongly on chain size. Physically acceptable values of N must correspond to mechanically stable chains or fragmentation will occur. The radial component of the hydrodynamic force is a maximum at the chain center, puts the chain in tension when $\theta \dot{\gamma} > 0$ and under compression when $\theta \dot{\gamma} < 0$. For the chain to be stable to fracture this hydrodynamically induced force must be smaller than the radial component of the electrostatic interaction.⁹ The maximum stable chain number is determined by balancing these forces at the chain center.

$$N_{\max} = \begin{cases} \sqrt{\frac{2}{Mn} \frac{3\cos^2 \theta - 1}{\sin 2\theta}} & \dot{\gamma}\theta \geq 0 \\ \infty & \dot{\gamma}\theta < 0 \end{cases} \quad (2)$$

$N_{\max}$ is dependent on chain orientation and strain rate, causing nonlinear response when driven by oscillatory shear $\dot{\gamma} = 2\pi\omega\gamma_0\cos(2\pi\omega t)$. The maximum stable chain length diverges when the chain is aligned with the field, when the instantaneous strain rate is zero, and when the chain is under compression.

4.3. Kinetics of aggregation and fragmentation

If a chain finds itself far from its maximally stable size then its size will adjust by aggregation or fragmentation. The kinetics of aggregation and fragmentation can be described by the phenomenological formula

$$\frac{dN(t)}{dt} = \frac{k}{N(t)} \left[1 - \frac{N(t)^2}{N_{\max}^2(t)} \right] \quad (3)$$

where because induced dipolar forces drive aggregation the rate constant $k=k_0(8\epsilon_0\epsilon_c\beta^2E_0^2/\mu_0)$ where k_0 is a concentration dependent constant. When the chain is at its maximum length no aggregation or fragmentation occurs since $dN(t)/dt=0$. When the chain is much smaller than its maximum stable length, the chain will aggregate according to $N(t) = \sqrt{N(0)^2 + 2kt}$, in agreement with the root time prediction of See and Doi.¹⁰ Thus aggregation is a slow power law growth process that is independent of the often divergent size $N_{\max}$. If the chain is much larger than its stable length, then it will fragment exponentially quickly according to $N(t) = N(0)\exp(-kt/N_{\max}^2)$. Note that the fragmentation rate $k/N_{\max}^2$ is proportional to the strain rate and is *independent* of the electric field.

Equations 1-3 are a set of coupled nonlinear equations that model the dynamics of chains in shear flow. There are four independent parameters in the system; Mn , ω , γ_0 , and k_0 . A reduction to a two-parameter model occurs by noting that solutions to the kinetic equation are of the form $N(t) = (\dot{\gamma}/16\omega Mn)^{1/2} n(\omega t)$. The two parameter (γ_0, k_0) model is a result of the rate equation we have chosen, and because the strain amplitude is fixed by experiment, this is really a single free parameter model.

4.4. Electrorheology

Before showing the behavior of these equations we would like to discuss the predicted rheology. The stress σ in the sample is the hydrodynamic torque

density, which equals the electrostatic torque density since inertia is small. In terms of the volume fraction ϕ of spheres this is

$$\sigma = 6\mu_0 N^2 \phi (\dot{\gamma} \cos^2 \theta - \dot{\theta}) = \frac{3}{4} \epsilon_0 \epsilon_c \beta^2 E_0^2 \phi \sin 2\theta. \quad (4)$$

This equation demonstrates that the stress is nearly proportional to the angle θ , and that light scattering is an indirect probe of stress.¹¹ Furthermore, it is apparent that when $\theta = 0$, the chain is comoving with the fluid so $\dot{\gamma} \cos^2 \theta = \dot{\theta}$.

Because the dynamics of chain orientation $\theta(s)$ is independent of electric field and shear frequency, we conclude that the stress scales purely as the square of the electric field. In steady shear it is readily shown that $\sin 2\theta = 2\sqrt{6}/5$, so the the *inherent* viscosity is given by the Bingham plastic form

$$\mu_I \equiv \frac{\mu - \mu_\infty}{\phi \mu_0} = \frac{1}{5} \left(\frac{3}{2} \right)^{5/2} Mn^{-1}. \quad (5)$$

Note that we have subtracted off the infinite shear rate viscosity and divided by the liquid viscosity: at low volume fractions these viscosities are virtually equal and the lhs of Eq. 5 is the conventional definition of the inherent viscosity.

The shear thinning result $\mu \propto \dot{\gamma}^{-1}$ has been obtained in many experiments, including those conducted on our silica fluid.¹ However, for the silica fluid at low fields we find $\mu \propto \dot{\gamma}^{-2/3}$, a result consistent with the droplet model.

4.5. Numerical Results

The nature of the nonlinear response is illustrated in Fig. 4 (small strains give a sinusoidal response). For $k = 0$ the oscillator reorientation rate ω_d is constant, and the remaining nonlinearities in Eq. 1 are small enough that a nearly elliptical response is observed. As k increases, the chains fragment and aggregate to achieve mechanical stability while trying to maximize their length, and Lissajous plots approach a parallelogram, as in Fig. 2. Finally, for intermediate values of k an interesting crossover to retrograde motion is observed. This is observed in our data at low fields, as illustrated in Fig. 3.

4.5. Chain Size

It is clear from the model that chain size variations due to aggregation and fragmentation are the dominant factors driving the nonlinear dynamics. The predicted dynamics of fragmentation, which occurs at twice the oscillation frequency, is shown in Fig. 5. Chain aggregation is very pronounced just as the electrode is about to return to zero angle, with chains reaching a maximum size

Figure 4: Lissajous plots change unexpectedly as the rate constant k is varied. For $k = 0$ the oscillator reorientation rate ω_d is constant, and the nonlinearity is small. For large k Lissajous plots approach a parallelogram, whereas for intermediate k values retrograde motion is observed.

just after the maximum strain. During this time interval the chain is more or less comoving with the flow. Fragmentation occurs much before the electrode returns to zero angle because the chain is nearly 90° ahead of the strain and thus is already at its maximum tilt angle in the opposite direction. The power law aggregation and exponential fragmentation leads to a decided asymmetry in the chain size peaks.

Large aggregate structures give rise to intense light scattering, so we decided to revisit the data to see if there is any experimental evidence that would directly support the chain model. At each time we determined the wedge integrated maximum intensity I_{max} (as opposed to the peak position θ_{max}) and plotted this versus time in Fig. 6. We were frankly surprised at the close correspondence between these data and the prediction of the kinetic chain model. The peak position relative to the applied strain is about right, and even the peak asymmetry, due to slow aggregation and fast fragmentation, can be seen. Moreover, this pattern was observed in all of the data sets, except those taken at a strain amplitude of 0.25, despite the tremendous variations in Lissajous plots.

Fig. 5 The kinetic chain model predicts chain size fluctuations during each cycle, the magnitude of these fluctuations increases with the rate constant k .

Fig. 6 Light scattering measurements indicate that the predicted chain fluctuations do occur. Note the asymmetry between the aggregation and fragmentation.

5. Conclusions

We have conducted light scattering studies that show that ER fluids can have strongly nonlinear behavior in oscillatory shear. The dipolar kinetic chain model gives a qualitative account of the nonlinearities observed in our data, without generating behaviors that we have not observed. However, it makes a number of quantitative predictions that are not correct, such as predicting chain angles that are too large and not accounting for residual field/frequency trends in the data. It is easy to modify the theory to give much better fits to the data, but only at the expense of introducing arbitrary parameters. What are the problems? Multipolar interactions actually increase the chain angle.¹² However, the distribution of chain sizes has been ignored, yet light scattering samples all chains and thus *underestimates* the maximum chain orientation. Nonetheless, we feel that this model provides a framework that captures the essence of the observed dynamics.

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