Towards an Understanding of the Rheological Response and Microstructure of Electro-Rheological Fluids and Concentrated Particulate Suspensions

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Some recent advances in our understanding of the mechanisms governing the flow behaviour of electro-rheological fluids and concentrated particulate suspensions are reviewed. For both systems an overview is presented of theoretical models based on interparticle forces and assumed microstructure, as well as of recent experimental studies which highlight features to be incorporated in future models, such as the effect on electro-rheological fluids of mixing particles with different sizes or electrical conductivities. It is apparent that models based on simplified microstructures can illuminate many of the physical mechanisms of these complex fluid systems.

Key Words: Electro-rheological fluid/ Particulate suspension/ Constitutive model/ Microstructure

1. INTRODUCTION

The modelling of particulate suspensions under flow is a complex matter. Not only do particle interactions affect the rheological response, but depending on the nature of the interactions, there can be structures (e.g. aggregates) formed by the particles which have a spatial extent considerably larger than the individual particle size (i.e., mesoscopic inhomogeneities in the sample). Theoretical models of the flow behaviour of such inhomogeneous systems pose many challenges, and significant modifications are required if single-phase continuum approaches are to be employed. Overviews of the advances in the theoretical modelling of hard sphere suspension systems are available in monographs.1,2 In this work we will focus on just two of the possible theoretical approaches to modelling such systems. It should be kept in mind that we are seeking to model not just non-interacting hard spheres, but also particles which may have strong interaction forces (as occurs, for example, in electrorheological fluids) with possibly the additional complication of being strongly anisotropic and separation-distance dependent. Although the focus of this discussion is on the development of theoretical constitutive models, it is acknowledged that computer simulations also play a most important role in exploring in detail the types of microstructure that form and their relation to the rheological response.

The two general modelling approaches we will focus on are described below. It should be emphasized that, in both approaches, the stress is assumed to be determined by the instantaneous configuration of the particles and the corresponding interaction forces between the particles. Hence the temporal evolution of the stress (rheological response) will be determined solely by the particle positions as they evolve with time. For simplicity we will assume we are dealing with spherical particles which are several microns in size, so we can ignore Brownian motion effects.

Approach 1: The particles are assumed to have formed into a particular microstructure; for example, as aggregates containing many particles, the size and internal configuration of these being determined by some fundamental physical rules. The important point is that the presence of these structures often renders the overall system spatially inhomogeneous over length scales much larger than individual particles, and anisotropic. In the systems we will discuss it will be assumed that the interparticle interaction forces depend on the instantaneous configuration of the particles, and do not depend, for example, on their relative velocities. When a strain is macroscopically applied, the microstructures are modeled to deform in a corresponding fashion. The forces between the particles in this deformed aggregate will give rise to an overall mechanical resistance to the deformation, which is measured macroscopically as shear stress, for example. Let us consider a
volume \( V \) containing many of these particles and aggregates, and consider a particle \( i \). We write \( \mathbf{r}_i \) for the position vector of particle \( i \), and \( \mathbf{F}_i \) for the (non-hydrodynamic) interaction force vector experienced by particle \( i \) due to the rest of the particles. The contribution of the interparticle interactions to the macroscopic stress tensor \( \tau_{\alpha\beta} \) will be given by the stress equation.

\[
\tau = -\frac{1}{V} \sum_i \mathbf{r}_i \mathbf{F}_i
\]

The above is based on the Kirkwood formulation\(^3\) – see for example Doi and Edwards\(^4\) for a derivation. It should be emphasized that we have assumed that the microstructure has been built up from many small point-like elements. In fact, the particles we deal with have finite size, and this will lead to complex hydrodynamic interaction effects as they move through the flow field, but for simplicity these effects are often ignored (“free-draining” limit). This approach has been used for developing models of electrorheological fluid, as will be seen in section 2.1.1 below. It has also been used to develop theoretical models of flocculated suspensions.\(^5\)

As mentioned, we will focus in this discussion on the case where the particles have arranged themselves in a prescribed microstructure - this facilitates calculation of the response under a prescribed strain. In reality, the particles may arrange themselves into a variety of structures - that is, the system has spatial inhomogeneities with an imprecisely defined microstructure, in combination with anisotropic interparticle interactions. Clearly it is difficult to model such systems theoretically (the focus of the present discussion), although it should be noted that many attempts have been made to study the nature of the variety of microstructures through molecular dynamic computer simulations - for example, in electrorheological fluids\(^6\) or flocculated particulate suspensions.\(^7,8\)

The above formulation has focussed explicitly on the interparticle interaction forces to calculate the stress tensor. It should be noted that it is also possible to obtain a useful expression for the stress tensor using a less microscopic approach, but still retaining the anisotropic and inhomogenous nature of the material. An example dealing with ERF will be discussed in section 2.1.2.1.

Approach 2: Here the particles are not considered as separate entities, but the particulate system is assumed to be smeared out i.e., spatially homogeneous, although not necessarily isotropic. The concept of particles is usually introduced in an intermediate stage, however, to produce an expression for the microstructural field. Often in this calculation a mean field approach is taken whereby the distribution of particles around an arbitrary particle is considered, taking into account the interactions between the test particle and its neighbours. In this way an expression is obtained for the microstructural field, which also needs to be coupled to the flow or deformation field in a particular way (this must be specified in the model as well). This approach will be discussed below in section 2.1.2.2, in the context of a newly developed model of electrorheology, and in section 3.3 in the context of concentrated particulate suspension.

In the rest of this paper, we consider two specific systems within the above modelling framework for particulate suspensions: electro-rheological fluids (section 2) and concentrated particulate suspensions (section 3). In addition to the modelling aspects, for both systems we will review some recent experimental results: Some of these results support the basic predictions of the models, while others indicate new important trends which cannot be explained by present models and thus give us directions for future model development.

## 2. ELECTRO-RHEOLOGICAL FLUIDS (ERFs) : MICROSTRUCTURE AND RHEOLOGICAL BEHAVIOUR

ERFs are suspensions of micron-sized semi-conducting solid particles dispersed in an insulating carrier liquid. An ERF shows a dramatic increase in flow resistance when an external electric field is applied. The basic mechanism is thought to be that the external field induces electric polarization within each particle relative to the carrier fluid, and the resulting electrostatic interaction forces between the particles lead to the formation of aggregates aligned in the direction of the field.

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Fig.1 A schematic diagram illustrating the aggregate microstructure in an electrorheological fluid (ERF) undergoing shear flow. Note that particle size has been greatly exaggerated for clarity (typically particles are several microns and the gap ~ 1mm). The external electric field \( E \) induces polarization in each particle, indicated by the arrows within the particles. Interaction between the polarized particles leads to the formation of elongated aggregates or particle chains, which cause the increase in shear stress.
The basic idea is shown schematically in Fig 1. There are several recent review papers available. These materials are currently the object of intense research attention, as well as considerable applications development work in industry (e.g. tunable vibration damping systems) which utilize the adjustable flow properties. The behaviour under steady shearing is often modeled as a Bingham fluid as follows

$$\tau = \tau_y + \eta \gamma$$

(2)

where \(\tau\) is the shear stress, \(\gamma\) the shear rate, \(\eta\) the plastic viscosity, \(\tau_y\) is the yield stress, which is usually a function of the electric field strength \(E\) - this relationship is expressed as \(\tau_y \propto E^b\), with \(b\) measured to take on values of 1.5 up to 2.2.

Within the framework of this paper, it is noted that ERF is a good example of a suspension of interacting particles showing complex rheological behaviour, due to the large and highly anisotropic aggregate structures formed under the electric field. It is a major challenge to produce a predictive model which relates this microstructure to the rheological properties, and indeed there is much ongoing research in this area. Below we will describe, within the context of the general approaches discussed previously in section 1, some simple models of these systems. We will then describe some experimental studies of ERF which reveal new layers of complexity in these materials - these measurements are helping to point the direction for future research activity.

2.1 Theoretical studies

2.1.1 Chain model for arbitrary flow fields

For the case of simple shear flow, a microstructural model that has been extensively used to date is the single-width chain model, whereby the increased shear viscosity is attributed to the chain-like aggregates of particles. These aggregates form due to the interactions between the induced electric dipoles in the particles (Fig 1). Clearly this “chain model” falls into the category of modelling approach 1 discussed in section 1.

Recently this technique has been extended to the general case of a uniform flow field described by the velocity gradient tensor \(\mathbf{\kappa}_{\mu\nu}\) to produce a broader constitutive framework. In this calculation, the chains are linear and for simplicity assumed to be straight with the orientation of a chain expressed by the unit vector \(\mathbf{u}\). The presence of the electrodes will not be considered – we assume an infinite sea of fluid undergoing shear. The relationship between \(\mathbf{u}\) and \(N\), the number of particles in the chain, is determined from the balance of the electric torque which acts to align each chain with the electric field, and the hydrodynamic torque which tends to rotate each chain in the imposed flow field. This formulation enables the calculation of the stress tensor for flow fields and electric fields of different geometries. A key simplifying assumption is that all of the particles in the system belong to one of these chains, which are all of equal length. A simple overview of this general constitutive formulation will now be presented.

The key parameters of the model are as follows. The particles are spheres of radius \(a\) and are assumed to have a constant electric conductivity of \(\sigma_p\). Since the particles used in ERF are often a few microns in size, Brownian motion effects can be ignored. The particle volume fraction is \(\phi\). The carrier fluid is a Newtonian liquid with viscosity \(\eta_c\), dielectric constant \(\epsilon_r\), and electric conductivity \(\sigma_c\) (with \(\sigma_c \ll \sigma_p\)). A uniform dc electric field \(E\) is applied, which induces an electric dipole in each particle (vector \(\mathbf{P}\)), due to the mismatch in conductivities of the carrier fluid and particle material. It is assumed that the electric current through the system reaches steady state practically instantaneously. Further, it is assumed that the field is strong compared to the imposed flow strength - this condition can be expressed as follows.

$$\frac{\epsilon_0 \epsilon_r}{\eta_c} \left[\frac{(\sigma_p - \sigma_c)}{\sigma_p + 2\sigma_c}\right]^2 E^2 / (\eta_c \xi) \gg 1$$

(3)

Here \(\eta_c\) is the viscosity of the carrier liquid, \(\epsilon_r\) is the permittivity of free space (\(\epsilon_0 = 8.85 \times 10^{-12}\) C\(^2\) / J m\(^{-1}\)). The quantity \(\xi\) is a measure of the rate of deformation of the imposed flow field having units of \(s^{-1}\); for example \(\xi = [\kappa / \kappa]^{1/2}\). The inverse of the non-dimensional quantity appearing on the left hand side of this equation is often called the Mason number in the literature (symbol \(Mn\)), and it naturally drops out of the equations of motion. As later calculations will show, the weak flow assumption implies that the number of particles in each chain is large i.e., \(N > 20\). Details of the calculations will be omitted here, but the main steps in the formulation are

1. Stress equation - This represents the contribution of the dipole-dipole interactions between the particles to the stress tensor. The following equation is found:

$$\tau_{\alpha\beta} = \left(\frac{3}{4}\right)^2 \frac{1}{4\pi^2 a^6 \epsilon_0 \epsilon_r} \phi u_{\mu} P_\mu u_\alpha P_\beta$$

(4)

(2) Torque balance condition:

$$u_\alpha \left[ N^2 T \mathbf{\kappa}_{\mu\nu} \mu_\mu u_\nu + (u_\mu P_\mu)^2 \right] = N^2 T \mathbf{\kappa}_{\alpha\mu} u_\mu + (u_\mu P_\mu) P_\alpha$$

(5)

(3) Chain rupture condition:

$$N^2 = [3(u_\mu P_\mu)^2 - 1]/[3T \mathbf{\kappa}_{\mu\nu} u_\mu u_\nu]$$

(6)
The Einstein summation convention over repeated indices has been used in the above equations. The quantity \( T = \pi \eta_s a^2 / F_i \) is the viscous relaxation time associated with two interacting particles, with \( F_i = 3 / 2 \pi \epsilon_0 \epsilon_r a^2 \left[ (\sigma_p - \sigma) / (\sigma_p + 2 \sigma) \right]^2 E^2 \) (characteristic magnitude of the interaction force). For the case of shear flow, \( \kappa_{xy} = \gamma / (\sigma_p - \sigma) \), and the above equations can be solved analytically to yield \( u = 1 / \sqrt{3} \delta_x + \sqrt{2} / \sqrt{3} \delta_y \), where \( \delta_x, \delta_y \) are unit vectors in x, y directions. The particle-contributed shear stress is found to be

\[
\tau_{xy} = 3 \sqrt{2} / 2 \phi \epsilon_0 \epsilon_r \left[ (\sigma_\rho - \sigma_c) / (\sigma_\rho + 2 \sigma_c) \right]^2 E^2 \tag{7}
\]

As can be seen, the above expression predicts that the particle-contributed shear stress is independent of the shear rate. This result supports the notion that ERF can be modeled as a Bingham fluid type material with a yield stress. Further, it shows a quadratic dependence on \( E \), as observed in many experiments. Not unexpectedly, the above shear stress result agrees with other calculations performed in shear flow. Discussion of the behaviour of this model in other deformation geometries is presented elsewhere.

### 2.1.2 Continuum models

#### 2.1.2.1 Layered model

A layered model of electro-rheological fluid under shearing, proposed by Klingenberg and Zukoski, has been extended by See and Saito to estimate the variation of electric current with shear rate in addition to predicting the rheological behaviour. This model focussed on the role of the conductivities of the particles and carrier fluid. The basic idea behind the model was that the increase in shear viscosity of the ERF is due to a layered structure between the electrodes, comprised of the remnants of particle chains adhering to the electrodes by electrostatic image forces, and a freely flowing central liquid layer where all the shear flow is concentrated giving rise to the apparent increase in viscosity (Fig 2). As the shear rate is raised the central liquid layer increases in thickness. Such layered structures have been observed experimentally, and this model would appear to be appropriate for reasonably concentrated ERF under moderate to high shear rates. The difference between this model and the “particle chain” approach discussed previously is that the individual particle chains are now replaced by a “smeared out” layered structure, but this approach still retains the non-homogenous and anisotropic nature of the system. Within the context of the general modeling strategies discussed in section 1, it is clear that this approach is another example of approach 1.

Although the details of the calculations will be omitted here for brevity (see the paper), the essential features are as follows. A force balance calculation on a test particle at the interface between the solid and liquid layers will lead to an equation for the thickness of the central liquid layer. Since we assume that all the shear flow is concentrated in this layer the macroscopically measured shear stress can then be estimated (shear stress and layer thickness will of course strongly depend on shear rate and electric field strength). The end result of this calculation is the following formula for the particle-contributed shear stress:

\[
\tau_{xy} = \epsilon_0 \epsilon_r \left[ (\sigma_\rho - \sigma_c) / (\sigma_\rho + 2 \sigma_c) \right]^2 E^2 \left[ \eta(\phi) - \eta_c \right] / \eta_c \tag{8}
\]

Here \( \eta(\phi) \) is the overall viscosity of the suspension, assuming that the particles were non-interacting and uniformly dispersed with volume fraction \( \phi \).

Observe the similarity between this result (8) and that obtained from the chain model (7). This is not unexpected since both approaches essentially focus on the relative magnitudes of (i) the electric dipole forces which tend to keep neighbouring particles together, and (ii) the forces due to the imposed flow field which tend to pull neighbouring particles apart. The layered model approach, however, does readily permit additional modelling calculations to be performed: for example it enables us to estimate the dependence of electric current on shear rate (an important engineering consideration), as well as the change in shear stress due to the mixing of higher conductivity particles. These two aspects will now be briefly discussed.

The variation of electric current with shear rate was determined by See and Saito using this layered model. A key feature of the calculation was the use of effective medium theory to estimate the overall conductivity through the liquid...
layer, which was assumed to be an instantaneous random network of conducting spheres. The calculation predicted a distinct drop in electric current as shear rate is raised, in qualitative agreement with the experimental observations of Chen and co-workers. The calculations showed there is a minimum value of the shear rate above which the electric current will drop with increasing shear rate, until an upper value \( \dot{\gamma}_{\text{max}} \) is reached. Above \( \dot{\gamma}_{\text{max}} \) it was predicted that the current would level off, since the entire gap would have become filled by the free flowing liquid layer. A substantial drop in electric current was predicted with increasing shear rate, in agreement with the experimental observations, although the crudity of the model did lead to considerable over-estimation. Note that this model assumed that the electric field is held constant and that the increasing shear rate causes the changes in the layer microstructure and electric current - the electric field dependence of the current was not predicted.

In another calculation, the layered model has been extended to take into account the drop in field-induced shear stress when particles of different conductivities are mixed. This phenomena has been observed experimentally (as will be described in more detail in section 2.2.1) and is a potentially very serious problem for the large scale manufacture of ERF.

The layered model of ERF was extended in the following way: an approximate treatment was developed of the non-uniformities of the electric current (field) when high conductivity particles (conductivity \( \sigma_b \)) are randomly introduced into the middle of the solid region where the bulk of the particles have a conductivity \( \sigma_p \). Writing the volume fraction of the higher conductivity particle as \( \phi_b (<<1) \), the following result was obtained using the layered model for the relative reduction in shear stress \( \Delta \tau/\tau_0 \) due to the non-uniformity

\[
\Delta \tau/\tau_0 = (\phi_b)^{2/3} \left[ 4\beta_{hp} - \frac{1}{2} (\beta_{hp})^2 \right]
\]

Here \( \tau_0 \) is the shear stress in the case of no high conductivity particles being present, and \( \beta_{hp} = (\sigma_b - \sigma_p)/(\sigma_b + 2\sigma_p) \) reflects the mismatch of electrical conductivities between the two particle types. It was found that this model showed reasonable qualitative agreement with the experimental data.

2.1.2.2 Models assuming homogeneity

In addition to the above particle-particle interaction approaches, an alternative approach to formulate models of ERF behavior is to assume some kind of smeared-out continuum to replace the particle aggregate structure altogether. Although the author has not been involved in this field, it is appropriate to briefly summarise recent developments here as well, as part of our larger discussion on modelling strategies of ERF. Within the context of the general modelling approaches discussed in section 1, these methods would fall into the category of approach 2, whereby the entire system is assumed to be uniform (not necessarily isotropic), and an equation for the stress tensor is determined.

A calculation along these lines based on equilibrium thermodynamics, has recently been advanced by Shkel and Klingenberg, whereby the entire fluid is replaced by a uniaxial anisotropic continuum. The strain dependence of the dielectric tensor is calculated via electro-striction coefficients, enabling the field-induced stresses to be determined from the free energy. Since this is an equilibrium approach, the model is restricted to calculating the small strain response of these systems (essentially the yield stress) and in its present formulation assumes a linear material response to the field (i.e., low fields). The advantage of these continuum techniques is that, in principal, they open up the possibility of efficient prediction of the behavior under any deformation or sample geometry, without detailed information of the microstructure of the particle aggregates.

It is appropriate at this point to summarise the discussion in this sub-section 2.1. Clearly the above theoretical approaches have managed to capture many of the essential features of ERF behaviour, such as the increased flow resistance under large electric fields, the Bingham type behaviour under shearing etc.

However, it is a fact that there are still many experimental phenomena which cannot be explained by these simple models. Indeed, these experiments are signposting the directions where future modeling efforts will need to be channeled, if we are to eventually obtain a general, predictive constitutive framework for these materials. Some of these key experimental studies will now be presented.

2.2 Experimental studies

2.2.1 Blending of particles with different conductivities

Recent studies have highlighted the importance of uniformity in the particles’ electrical properties. Sakurai and co-workers carried out a series of measurements using carbonaceous particles dispersed in silicone oil. Here particles of a higher conductivity were deliberately blended into a system consisting of standard uniform particles. The ratio of conductivities was 10 and this was the only difference between the two particle types, since the particle shape, size distribution and dielectric constant were the same for both systems. For all measurements the total volume fraction was kept at 0.3, but the proportion of the higher conductivity particles was varied systematically. Under a 2kV/mm dc electric field and 100s−1
steady shearing, the system composed entirely of standard particles produced a shear stress of 245Pa, whereas the system of only higher conductivity particles produced a somewhat higher shear stress of 340Pa, as would be expected. However, for blends of the two particle types, the shear stress did not follow a “linear law of mixtures” between these two values, but showed a dramatic dip with a minimum value of just 70Pa occurring for the blend with 20% standard and 80% higher conductivity particles. On the other hand, the electric current showed the expected monotonic increase as more higher conductivity particles were added. This large decrease in the field-induced shear stress with the addition of only a small amount of higher conductivity particles, is clearly of great importance from a manufacturing viewpoint: to achieve optimal electrorheological performance we must have a high degree of uniformity in the particle conductivity. In another paper, Sakurai and co-workers\textsuperscript{24}\textsuperscript{24} reported that if the shear rate is increased, the dip becomes relatively less pronounced. This dip phenomena is illustrated in Fig 3 for different values of the shear rate. Our understanding of the mechanism behind this dip phenomena is still very rudimentary, although there has been an attempt to model this using the layered model, as mentioned in section 2.1.2.1 - the qualitative agreement obtained is encouraging.\textsuperscript{24}\textsuperscript{24}

2.2.2 Effect of particle size distribution on ERF behaviour

The effect of mixing particles of different sizes on the electrorheological response of suspensions under steady shear flow has recently been investigated. Two sizes, 15µm and 50µm, of monodisperse spherical sulfonated poly (styrene-co-divinylbenzene) particles were used (kindly provided by Nihon Shokubai Co. Ltd). Several electrorheological fluids were made containing different proportions of small and large particles dispersed in silicone oil, but with constant overall particulate concentration. It was found that the mixed size system produced the highest electrorheological response under the shear rates used.\textsuperscript{29}\textsuperscript{29} This is the opposite trend to previous studies of bimodal systems with larger size ratios.\textsuperscript{30}\textsuperscript{30} Presently, efforts are being made to extend models of ERF to a level where phenomenon involving particle size distributions can be explained or predicted.\textsuperscript{31}\textsuperscript{31}

2.2.3 Effect of rheological properties of matrix

The influence of the viscoelastic properties of the matrix on the electrorheological behaviour is of great practical interest. A recent investigation has looked at the ER properties of dispersions of semi-conducting particles in oils and elastomers.\textsuperscript{32}\textsuperscript{32},\textsuperscript{33}\textsuperscript{33} The tests focussed on how the dynamic mechanical properties measured under oscillatory shearing change with the viscosity of the oil or the elasticity of the elastomer. The dependence on electric field and strain amplitude were also investigated. It was found that the largest increment of the mechanical properties under electric fields was obtained when using oils of low viscosity and elastomers of low elasticity. It was found that these results could be interpreted in terms of a model based on the competition between the dipole-dipole electrostatic interaction (which acts to maintain neighbouring particles together) and the shearing force due to the deformation of the matrix (which acts to separate the particles). This series of measurements revealed that there are many parallels between the electrorheological behaviour of particles dispersed in elastomers (these materials are often called “ER elastomers”) and the behaviour of particles dispersed in oils. ER elastomers have been the focus of much industrial interest since they essentially represent a mechanically tunable rubber, which has many potential applications in vibration damping.\textsuperscript{34}\textsuperscript{34} Despite this potential importance, the viscoelastic nature of the carrier matrix has yet to be incorporated into models of the electro-rheological response, with almost all treatments up to now focussing on the case of a Newtonian carrier liquid.

2.2.4 Effect of distribution of electrical properties within each particle

A recent series of experiments have examined the possibility of using particular types of carbonaceous spherical particles for use in electrorheological fluids, which consist of a semi-conducting inner core and an outer layer of lower electrical conductivity.\textsuperscript{35}\textsuperscript{35} When these particles were dispersed in silicone oil, the resulting fluid showed a large electrorheological effect under steady shear and dc electric field. However the electric current was found to be substantially lower than that of a suspension of homogeneous

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{The dependence of shear stress (under 2kV/mm dc field) on the proportion of high conductivity particles. The curves correspond to different shear rates: 1000s\textsuperscript{-1} (open circle), 366s\textsuperscript{-1} (triangle), 100s\textsuperscript{-1} (open square) and 10s\textsuperscript{-1} (filled square).}
\end{figure}
semi-conducting particles. Measurements of the dielectric permittivity were also carried out, and the Maxwell-Wagner model of interfacial polarisation was used to estimate the distribution of the electrical properties through the particle cross-section. Presently, models have not been developed to a level where details of the particle’s internal microstructure can be accounted for. The simplest way to go about this would be to retain the essential dipole-dipole interaction formulation, but modify the force magnitude depending on the nature of the particle’s internal composition.

2.2.5 Experiments on analogous field-responsive materials - Magnetic systems

Magneto-rheological suspensions (MRS), which are the magnetic analogs of ERF, have been the focus of much research interest worldwide, primarily due to the very high field-induced yield stresses that can be attained (see recent review articles[36,37]). As part of the overall research effort into field-responsive (or “smart”) fluids, the group at the University of Sydney has commenced studies of the fundamental rheological behavior of MRS. This work will be briefly introduced here as it provides interesting comparisons with the ERF systems, which are the focus of the present paper. A recent work has experimentally studied the different responses of the activated MRS at the start-up of shear flow. The rheological tests were carried out using laboratory prepared magneto-rheological samples and a modified controlled stress rheometer, the Paar Physica MCR300 (parallel plates, diameter 20mm, typically 1mm gap). The particles were carbonyl-iron powder (average particle size 4 µm), manufactured by ISP Corp (grade S3700). These were dispersed in a 0.1 Pas silicone oil (Dow Corning). The rheometer had been modified so that a uniform magnetic field can be applied to the sample (perpendicular to the plates) which is produced by an electromagnet under the bottom plate. We studied the transient response after shear start-up under slow constant shearing (yielding behaviour) with shear rates in the range ~ 0.01 to ~ 1 s⁻¹. A typical yielding curve is shown in Fig 4.

It is observed from Fig 4 that the material shows an elastic type response as the strain is first increased, but then the stress values roll over and reach a plateau value which corresponds to the steady state shear stress at that shear rate. The transition to the plateau is thought to correspond to yielding type behaviour, and presently we are exploring the comparison between the observed strain dependence and that predicted theoretically (for example using the magnetic analog of the single-width chain model, as discussed in section 2.1.1 for ERF).

3. CONCENTRATED PARTICULATE SUSPENSIONS: MICROSTRUCTURE AND RHEOLOGICAL BEHAVIOUR

Concentrated particulate suspensions are another class of industrially important materials where there is expected to be a strong interaction between the material microstructure and the macroscopic rheological response. Reviews discussing developments in modeling the rheology of concentrated suspensions are available.[1,2,38] Below we discuss some advances made in this research area. We will take the reverse order to the previous section and will first present some key experimental work, followed by an introduction to a theoretical model and its predictions.

3.1 Effect of matrix viscoelasticity on particle properties

Many composite materials involve particles dispersed in polymer matrices, and an understanding of the basic mechanical properties is essential for their optimal usage. Measurements have been performed of the response under small amplitude oscillatory deformations of a suspension of non-Brownian spheres dispersed in a viscoelastic fluid. A preliminary report of this work is available.[39] On the theoretical side, the correspondence principle of linear viscoelasticity was used to derive a simple constitutive model from a model for a suspension in a Newtonian liquid - the basis of this model is briefly described in section 3.3 below. The theory predicted that for a specific particulate system the concentration dependence of the viscoelastic properties $G'(\phi), G''(\phi)$ should collapse to a single master
curve when the values are normalised with those of the carrier fluid alone (for example, when we plot $G''(\phi)/G''(\phi=0)$ at various oscillation frequencies against $\phi$).

The measurements involved small amplitude oscillatory squeeze flow on two suspensions of monodisperse sized particles suspended in polymeric fluid and in silicone oil. The theoretically predicted master curve was indeed verified from the experimental tests (Fig 5), which were obtained using polyethylene spheres of 80µm diameter dispersed in 3% Separan polymer solution. The points plotted on Fig 5 cover the range of oscillation frequencies used (5Hz to 100Hz). The good data collapse indicates that the quantity $G''(\phi)/G''(\phi=0)$, representing the increment in viscoelastic properties due to the particles, is indeed determined essentially by the particle volume fraction.

3.2 Transient behaviour after shear reversal in particulate suspensions

A series of experiments have been carried out which examined the transient stress response under shear flow of concentrated suspensions of non-Brownian spheres.\(^{(40)}\) The focus of the experiment was on the stress behaviour after the shearing is momentarily stopped and re-started in the opposite direction – this type of test was originally studied by Gadala-Maria and Acrivos.\(^{(41)}\) It was found that the normalised stress recovery curves for different values of the initial and subsequent shear rates could be collapsed quite well if plotted against the strain. It was also found that the transient behaviour of the normal stress difference showed similar data collapse. Further, there appeared to be little qualitative difference in the behaviour of particulate systems with a high degree of size monodispersity and those more polydisperse.

3.3 Overview of the theoretical model

We now briefly introduce the key points of the constitutive model for concentrated suspensions of monodisperse spheres in a Newtonian carrier fluid. This model has recently been developed by Phan-Thien and co-workers.\(^{(42-44)}\) The essential idea is that the motion of a neighbouring pair of generic spheres in the suspension is modelled by a single pair of force-free and torque-free spheres, which tumble along with the imposed flow field. It is convenient to introduce $\mathbf{r}$, the unit vector field directed along the line of centres. Since the suspension is concentrated, each sphere experiences interactions with surrounding spheres, and this effect is modelled by an anisotropic diffusion-like process, with the magnitude of the diffusion tensor $\mathbf{D}$ assumed to be proportional to the imposed rate of strain. The following formula for the instantaneous particle-contributed stress tensor is obtained \(^{(43)}\):

$$\tau_p = \mu(\phi)[(1 - \bar{\xi})\mathbf{D} \cdot \mathbf{A}_2 + \gamma (\mathbf{K} \cdot \mathbf{A}_2 + \mathbf{A}_2 \cdot \mathbf{K} + \text{tr}(\mathbf{K})\mathbf{A}_2 - 2\mathbf{K} : \mathbf{A}_4)]$$  \( (10) \)

Here $\mu(\phi)$ is a scalar viscosity depending on the volume fraction $\phi$ - this can be separated as $\mu(\phi) = \mu(0)\Phi(\phi)$ where $\mu$ is the viscosity of the Newtonian carrier liquid and $f(\phi)$ is a function of the particle volume fraction (assuming monodisperse spheres). Further, $\bar{\xi}$ is a hydrodynamic interaction factor ($\bar{\xi} = 0.63$ for highly concentrated monodisperse spheres), $\mathbf{D}$ is the strain rate tensor and $\gamma$ is a positive measure of the rate of strain $\gamma = \sqrt{2\text{tr}^2(\mathbf{D} \cdot \mathbf{D})}$. $\mathbf{K}$ is a dimensionless tensor, which plays the constitutive role of describing the degree of anisotropy of the diffusion process - it is assumed $\mathbf{D} = \gamma \mathbf{K}$. $\mathbf{A}_2$ and $\mathbf{A}_4$ are tensors which describe the system microstructure: $\mathbf{A}_2 = <\mathbf{pp}>$ and $\mathbf{A}_4 = <\mathbf{pppp}>$ where $<...>$ denotes an ensemble average.

In transient flows the system microstructure develops through the time evolution equations for $\mathbf{A}_2$ and $\mathbf{A}_4$. For example, the equation describing the change in $\mathbf{A}_2$ is

$$\frac{d\mathbf{A}_2}{dt} = (L - 3\gamma \mathbf{K}) \cdot \mathbf{A}_2 + \mathbf{A}_2 \cdot (L - 3\gamma \mathbf{K})^T - 2(L - 3\gamma \mathbf{K}) : \mathbf{A}_4 + 2\gamma \mathbf{K} - 2\gamma \text{tr} (\mathbf{K})\mathbf{A}_2$$  \( (11) \)

where $L$ is an equivalent velocity gradient tensor $L = L - \zeta \mathbf{D}$, with $L$ the velocity gradient tensor of the imposed flow field.
and ζ a hydrodynamic parameter (ζ=0.13). Note that the righthand side of eq.(9) involves the fourth-order tensor Aβ - to analytically deal with this equation a closure approximation is often employed (e.g. quadratic closure Aβ ≅ Aβ Aβ).

We observe that the righthand side of eq.(11) is linear in the rate of strain $\dot{\gamma}$. This means that during transient response, the timescales for structural evolution and hence the stress tensor evolution must be inversely proportional to $\dot{\gamma}$ - in other words, the microstructure and stresses evolve only as a function of the imposed strain. This was indeed observed experimentally.

The extension of this model (which assumes a Newtonian carrier liquid) to small amplitude oscillatory flow of a suspension in a viscoelastic matrix is carried out with the help of the correspondence principle of linear viscoelasticity.43 This principle states that, under a small amplitude oscillatory deformation of frequency $\omega$, the solution to a boundary value problem (i.e. prescribed forces/displacements on the spatial boundaries) for a viscoelastic material can be obtained from the corresponding Newtonian solution (eq (10) here). Since the strain amplitudes applied are small, the microstructure will be assumed to be the equilibrium isotropic state and unchanging. Hence we set $A_{2\nu\nu}=1/3 \delta_{\alpha\nu}$ and $A_{\alpha\beta\nu\nu}=1/15(\delta_{\alpha\nu}\delta_{\beta\nu}+\delta_{\alpha\nu}\delta_{\nu\beta}+\delta_{\nu\beta}\delta_{\alpha\nu})$. The end result of this analysis will be the following equation for the stress tensor which is now a sinusoidally varying, complex quantity 40:

$$\tau_p = \tau^* \rho e^{i\omega t} = kG^* f(\phi) \hat{D} e^{i\omega t}$$ (12)

where $k$ is a dimensionless numerical constant, $G^{*}$ the complex modulus of the matrix, and the tensor $\hat{D} e^{i\omega t}$ represents the oscillatory strain applied. Clearly, from this result, the increment in the viscoelastic properties due to the presence of the particles is contained in the function $f(\phi)$, and thus quantities such as $G^{*}(\phi)/G^{*}(\phi=0)$, which were discussed in section 3.1, are predicted to depend only on volume fraction $\phi$ and not on frequency $\omega$, etc. Indeed, the prediction is that $G^{*}(\phi)/G^{*}(\phi=0)=f(\phi)$. Thus we see that the model is able to capture the key features of the behaviour of the particles dispersed in a viscoelastic matrix.

4. CONCLUSIONS

This paper has briefly described some advances recently made in our understanding of the fundamental mechanisms behind the rheological behaviour of electro-rheological fluids and concentrated particulate suspensions. In general, it is apparent that much insight can be gained if we consider the mechanical behaviour of these complex materials in terms of the mechanical interactions between structural sub-units which comprise the material (e.g. chain-like particle aggregates in the case of ERF and MRS). This is the so-called microstructural approach. More specifically, two approaches to theoretically modeling these systems were considered: assuming an idealized microstructure which contains interacting particles in prescribed locations; or modeling the material as a continuum with the interparticle interactions reflected, for example, in the anisotropy and magnitude of the material’s mechanical response.

It should be pointed out that the models presented all assume a spatially homogenous deformation field (e.g. shearing) or that very small strains are applied. The response to non-uniform large strain fields needs to be understood before a widely applicable constitutive framework can be realized, enabling explanation of such phenomena as flow-induced migration of particles.40 A further complication with the electrorheological fluids is the effect of non-uniform electric field - the particles will experience an electromotive force tending to push them into regions of highest field intensity. Almost all modelling of electrorheology up to now has assumed a uniform external field. These issues should provide a rich environment for future investigations.

Although the advances described in this paper represent only a tiny fraction of the enormous volume of work carried out worldwide, it is hoped that they will serve to stimulate further research work into these fascinating and technologically important materials.

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