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# Electrorheological Fluids



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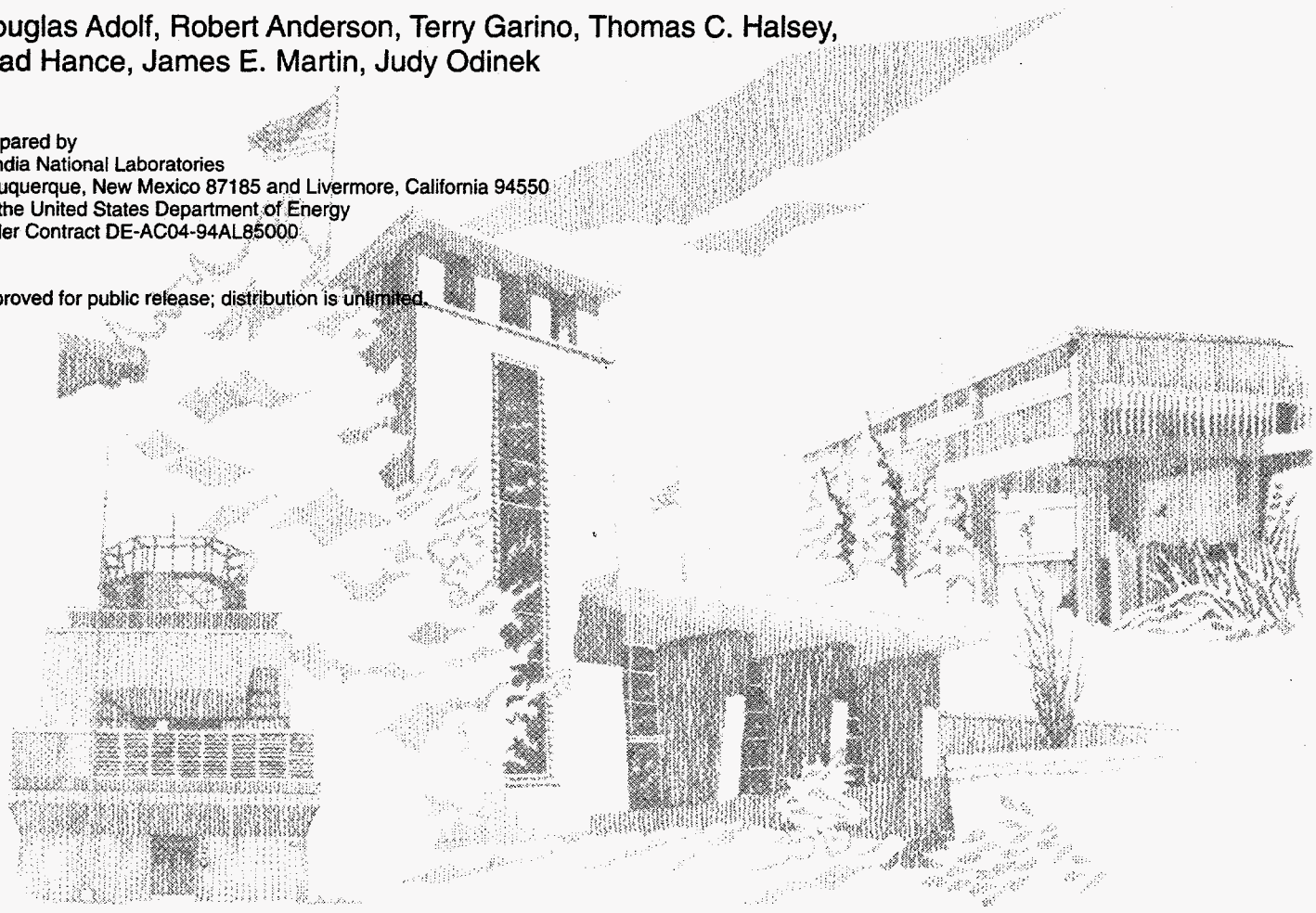

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# ELECTRORHEOLOGICAL FLUIDS

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## Abstract

An Electrorheological (ER) fluid is normally a low-viscosity colloidal suspension, but when an electric field is applied, the fluid undergoes a reversible transition to a solid, being able to support considerable stress without yield. The commercial possibilities for such fluids are enormous, including clutches, brakes, valves, shock absorbers, and stepper motors. However, performance of current fluids is inadequate for many proposed applications. Our goal was *to engineer improved fluids* by investigating the key technical issues underlying the solid-phase yield stress and the liquid to solid switching time. Our studies focused on the field-induced interactions between colloidal particles that lead to solidification, the relationship between fluid structure and performance (viscosity, yield stress), and the time evolution of structure in the fluid as the field is switched on or off.

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A study of the evolution of structure in a quiescent electrorheological fluid [1,2] was undertaken to understand the solidification process. We reported a real-time, two-dimensional light scattering study of the evolution of structure in a concentrated electrorheological fluid during the 'liquid-solid' phase transition. We found that after particle chaining along the electric field lines, strong light scattering lobes appeared at a finite scattering wavevector $q$ orthogonal to the field lines, and then brightened as they move to $q = 0$. This indicates the existence of an unstable concentration fluctuation that signifies the segregation of chains into columns. In fact, the observed growth kinetics of the characteristic length, as well as the form of the structure factor, are qualitatively similar to two-dimensional spinodal decomposition in a system with a conserved order parameter.

The evolution of structure in a quiescent ER fluid of highly polarizable ceramic particlulates was studied by measuring the increase in the static permittivity as a function of time and applied field strength [3]. The zero-time permittivity agreed well with theoretical predictions for randomly dispersed colloidal suspension. As time progressed, the permittivity increased as the anisotropic structure evolved, and the rate of increase in permittivity at early times depended on the square of the applied field. For low particle loadings and high fields, the measured permittivity at long times agreed with predictions for dense columnar aggregates. Under lower applied fields or in more concentrated suspensions, however, the intermediate time coarsening process was quenched, and the corresponding final structure was less compact resulting in a lower permittivity than predicted.

An experimental and theoretical study [4,5] of the steady and oscillatory shear viscoelasticity of a model electrorheological fluid led to an understanding of the complexities of ER fluids when subjected to flow. Viscosity measurements were made on a model fluid consisting of monodisperse, spherical, silica spheres

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immersed in a dielectric liquid using a parallel annulus electrorheometer built at Sandia. The shear-thinning viscosity $\mu$ showed a power-law dependence $\mu \sim \dot{\gamma}^{-\Delta}$ on the inverse strain rate $\dot{\gamma}$, with $\Delta$ in the range 0.68-0.93. Likewise, the frequency-dependent viscosity $\mu(\omega)$ showed a power-law dependence $\mu(\omega) \sim \omega^{-\bar{\Delta}}$ with $\bar{\Delta}$ in the range 0.73-1.0. A theoretical treatment of steady-state cluster formation in applied electric and shear fields predicted the observed power-law dependences of the steady and oscillatory shear viscosities at low voltages, albeit with exponents $\Delta = \bar{\Delta} = 2/3$.

We reported a real-time, two-dimensional light scattering study of the structure of an electrorheological fluid under steady shear [6,7]. When an electric field is applied to the quiescent fluid, particles chain along the electric field lines and cause strong light scattering lobes to appear at a finite scattering wavevector $q$ orthogonal to the field lines. We found that when the sample is subjected to steady shear a steady state scattering pattern emerges with lobes that are rotated in the direction of fluid vorticity. The angle of rotation was found to increase as the cube root of the shear rate, in agreement with the theoretical prediction of the steady state structure of fragmenting particle droplets.

The structure of highly polarizable ceramic particlulates under steady and oscillatory shearing flow was also studied by measuring the increase in the static permittivity as a function of shear rate and applied field strength [8]. Under steady shear flow, a unique relationship defined the dependence of permittivity on viscosity for suspensions of differing volume fractions under various applied fields. Under oscillatory shear flow, the maximum in permittivity coincided with the minimum strain under high fields and low strain amplitudes but coincided with the minimum strain *rate* under low fields and high strain amplitudes.

We have also investigated the attractive forces between colloidal particles leading to anisotropic colloidal aggregation in an electric field. The simplest theories assume that these forces arise from mismatch in the particulate and suspending fluid complex dielectric constants. At low frequencies, polarization mechanisms are clouded by the complexities of ionic conduction. At high frequencies, analytical expressions for the magnitude of the interparticle attractive force include only isolated point dipole interactions. Our experiments indicated that ignoring multi-body and multipole interactions can lead to predictions of particle attraction orders of magnitude less than actually observed [9]. Based on these observations, we synthesized ER fluids from highly polarizable ceramic particulates ($BaTiO_3$). These fluids exhibited performance (yield stress) superior to the best ER fluid reported in the extant literature.

In addition to the particle and solvent phases present in an ER fluid, a dispersant must be present so that in the off-field state the particles are deflocculated, thus producing a low off-field viscosity. We performed several

experiments that involved the effect of the dispersant on the properties of ER fluids. First, we studied the effect of different dispersants on the yield stress of $BaTiO_3$ in dodecane fluids. We found that the yield stress depended strongly on the dispersant used with the dispersant Hypermer LP1 (ICI Americas) giving a higher value than the others tried (Oloa 1200 (Chevron), poly (octadecyl methacrylate), aerosol OT, and dodecyltriethoxysilane). One reason for this result was that the Hypermer LP1 was a more effective dispersant in terms of keeping the particles deflocculated so that they were better able to arrange themselves into chains when the field was on.

We also studied the effect of the concentration of the dispersant on both the yield stress of the fluid and on its thixotropic behavior. We found that the yield stress of barium titanate in dodecane fluids can be a strong function of dispersant concentration in the range of partial surface coverage. For example, the yield stress at 800 V/mm for a 33 volume % solids fluid increased by a factor of three when the OLOA 1200 concentration was change from a value higher than that needed for complete coverage to half that value where the coverage was incomplete. This was most likely due to the closer interparticle approach allowed in the case of partial coverage when the field was on, which leads to stronger interparticle forces.

Finally, the effect of dispersant concentration on the thixotropy of ER fluids was studied. Thixotropy is the time-dependent, isothermal and reversible decrease in viscosity with shear. In some cases it causes a quiescent suspension to form a weak gel which is converted back to the original fluid suspension by shear. We wanted to try to utilize this effect to prevent the settling out of the particles to a dense cake in barium titanate ($\rho$= 5.9 g/cc) in dodecane ($\rho$= 0.75 g/cc) fluids. We found that we could produce thixotropic ER fluids in this system by carefully controlling the dispersant concentration. When the concentration was just enough to give a low viscosity fluid under mild shear, the particles were not completely covered with the dispersant so that at zero shear particles would become weakly bonded to each other when they had a collision at dispersant poor regions. This process would lead up to the formation of a gel structure which prevented settling but was easily broken apart under mild shear [10].

The electrical properties of ER fluids leading to interparticle interactions and aggregation have been theoretically analyzed. Interparticle forces in ER fluids can be described with comparative simplicity if the electric field is applied at an ac frequency well above a crossover frequency, $f_c$, which depends directly on the conductivities of the particles or fluid. Under this condition the field distortion around the particles is governed by the contrast between the dielectric constants, $\pi$ and $\sigma$, of the particles and the surrounding fluid, $\beta=(\pi-\sigma)/(\pi+2\sigma)$. It is a further simplification if the conductivity of the liquid phase is low (less than

roughly $10^{-11}$ S $cm^{-1}$ with a viscosity of 30 cp) so that any field modification from ion-depletion space charge layers is insignificant.

If either of the above conditions fails to hold, a variety of complications may arise. At frequencies below $f_c$ the $\beta$ parameter becomes dominated by the contrast between particle and fluid conductivities, rather than dielectric constants. Furthermore, conductive particles may acquire a net charge and fail to participate in chain formation, and a relatively high fluid conductivity may lead to competing processes, including the possibility of a significant distortion of the field distribution in an ER cell if the supply of mobile ions in the liquid phase is fixed. If both particles and fluid are conductive, particle polarization may become sensitive to the high-field electrical properties of the particle-fluid interface. Effects such as these could lead to field, frequency, and time dependent behavior that must be accounted for when experimental results are interpreted [11].

The electrostatics of an ideal ER fluid were constructed from the forces and induced charge associated with an isolated chain of monodisperse spherical particles [12]. Since this study was restricted to nonconductive particles and fluid, the crucial parameter was the dimensionless ratio of particle and liquid phase dielectric constants, a.

Contacting spheres were first analyzed according to the point-dipole approximation. While this model cannot account for the contribution of higher multipoles, it demonstrates that negligible ER effects will be observed in the negative $\beta$ regime ($a<1$), and that with $a>>1$ the repulsive force between particles from an electric field normal to the chain axis is insignificant compared with the attractive force arising from a field parallel to the axis. In most cases, therefore, only the parallel field component needs to be considered.

A chain of nearly contacting spheres was analyzed in the limit of infinite a, where highly accurate analytic approximations of the electric field distribution can be derived. The attractive force in a chain asymptotically approaches a $d^{-1}$ dependence, where d is the gap parameter, and its ratio with the force between an isolated pair of nearly contacting spheres diverges logarithmically as d approaches zero. With d of the order of $10^{-3}$ (which is in the range applicable to ER fluids containing particles that are coated with a lipid layer) models based on pair forces would underestimate the attraction by a factor of five to seven.

Several numerical methods were used to determine the equipotential distributions associated with chains of contacting spheres over the entire range of a. In one of these the potential was synthesized from a distribution of imaginary point charges on the line of symmetry. This novel method yielded empirical formulas, at high a, for the attractive force between particles and the liquid-phase field enhancement near an interparticle contact point. Both quantities are shown to vary precisely with $a^2$ as a approaches infinity. From the other methods, the $a^2$

proportionalities of the attractive force and the field enhancement factor are found to be approximately valid for all a greater than 6. In the case of a chain with small interparticle gaps, one of these methods yielded reasonably accurate equipotential distributions for all a. Results show that the attractive force and the field enhancement both smoothly approach their analytically determined limiting values as a becomes large, and both are nearly saturated at a=1000.

These single-chain results were then applied to regular-lattice arrangements of spheres in order to determine the breaking strength of a dense column of particles at large a. A simple method of accounting for the multiparticle effects was developed which relied on the strong concentration of force density between nearly contacting particles. The increase in strength with particles aggregated into columns, compared on a per-chain basis to isolated chains, is found to be small. It is 33% or less, and is only 25% with the expected body-centered tetragonal (BCT) arrangement.

Although the strength enhancement from columnar aggregations is not large, columns might have a major advantage over isolated chains in a shearing fluid. The columns may be able to deform through particle rearrangement without breaking and become inclined at an angle near 30°, where the contribution of column tension to shear stress is maximal. This new model predicts yield stresses that are significantly above those obtained from conventional models which presume that all the gaps between particles in chains become wider as the ER fluid undergoes a simple shear deformation.

A method analogous to that used in determining the column strength was employed to approximate the effective dielectric constant, in the infinite- a limit, of an ER fluid containing columns of particles. The c-axis aligned BCT arrangement and the close packed lattices, face-centered cubic and hexagonal, are equally effective in producing the highest dielectric constant. Large, easily observable increases in the dielectric constant are indicated as particles subjected to an electric field begin to aggregate into pairs, chains, and then columns. A nearly fourfold increase is predicted for a typical high-a ER fluid. A large dielectric anisotropy also develops in high-a ER fluids. One consequence of this is a restoring torque which opposes the applied shear stress. Within the framework of the shear-stress model we propose, however, this effect is negligible compared to the shear stress arising from tension in the columns of particles. Another consequence is that a small ac mechanical strain applied to an ER fluid causes an easily observable ac fluctuation of the effective dielectric constant at twice the mechanical driving frequency.

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