

Final Report

**Two Studies of Colloidal Interactions:
Electric Polarizability
and
Protein Crystallization**

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Final Report

- **Interaction energies of confined colloids.** Measurements of the pair-potential performed by our group [1] and later extended by others [2] have cast doubts that the DLVO potential [3] correctly describes the pair interaction between like-charged colloids in aqueous suspension where the colloids are confined by like-charged planes. Long-range attractive potentials of order $1 k_B T$ in strength have been observed [1, 2]. Additionally, there is interest in whether pair-interactions between like-charged parallel cylinders in monovalent electrolyte can become attractive [4, 5, 6, 7]. We examined the problem of long-range interactions between parallel, like-charged cylinders confined between like-charged plates by numerically solving the two-dimensional, non-linear Poisson-Boltzmann equation. **The repulsive pair-potential between like-charged cylinders is substantially reduced by confinement of like-charged plates, but no attraction is observed.** The effective cylinder surface charge is increased by confinement, acting to enhance repulsion, but the effective interaction screening length is reduced, this latter effect being dominant, so that the repulsive cylinder-cylinder interaction is reduced due to confinement. This work has been published: M. Ospeck and S. Fraden, *Solving the Poisson-Boltzmann equation to Obtain Interaction Energies Between Confined, Like-charged Cylinders.*, J. Chem. Phys. 109, 9166-71 (1998).

- **Statistics of chain growth and determination of the interparticle potential.** Neutral spherical colloids become polarized in external electric fields and develop field-induced dipole moments. The spheres are attracted to each other in a direction parallel to the applied field and repel each other in the perpendicular direction. When the suspension is sufficiently dilute and the field sufficiently weak, the colloids associate into individual chains. In thermal equilibrium, there is a steady-state distribution of chain lengths in dynamic equilibrium, with some chains breaking into shorter ones, balanced by smaller ones combining into longer ones. A statistical mechanical model involving few approximations relates the chain length distribution to the particle concentration and interparticle potential [8].

There have been a number of studies of chain formation in ER fluids. The first studies, done before computers made image processing routine, measured the onset of chaining, which is an exponential function of the interaction energy [9, 10]. More recently, a measurement of the equilibrium distribution of monomers and dimers (chains of one and two particles, respectively) by Adriani and Gast [11] was used to determine the pair-potential between poly(methyl methacrylate) (PMMA) spheres suspended in hexane, but convection in their cell prevented formation of larger chains. We studied colloidal suspensions of charge-stabilized polystyrene spheres (PS) of $1 \mu m$ diameter in water. The equilibrium distribution of chain lengths as a function of applied alternating current (AC) field strength and frequency was measured using digital video microscopy and compared with theory. In order to perform optical microscopy, we employed thin, essentially two-dimensional samples, which also suppressed convection and allowed formation of large chains. The AC frequency range (100 - 500 kHz) was high enough that the polarization of the mobile charges on the surface of the PS spheres was negligible. As a result, the polarization of the spheres was entirely due to the dielectric contrast between the water ($\epsilon_w = 80$) and polystyrene ($\epsilon_p = 2.5$), and the PS spheres acted as dielectric holes. We found the measured chain-length distributions compared well with a simple analytic model based on chemical equilibrium between chains of different lengths [8]. Our analysis included precise numerical calculations of the electric field in our experimental cell and incorporated the effect of mutual polarization of the PS spheres. These

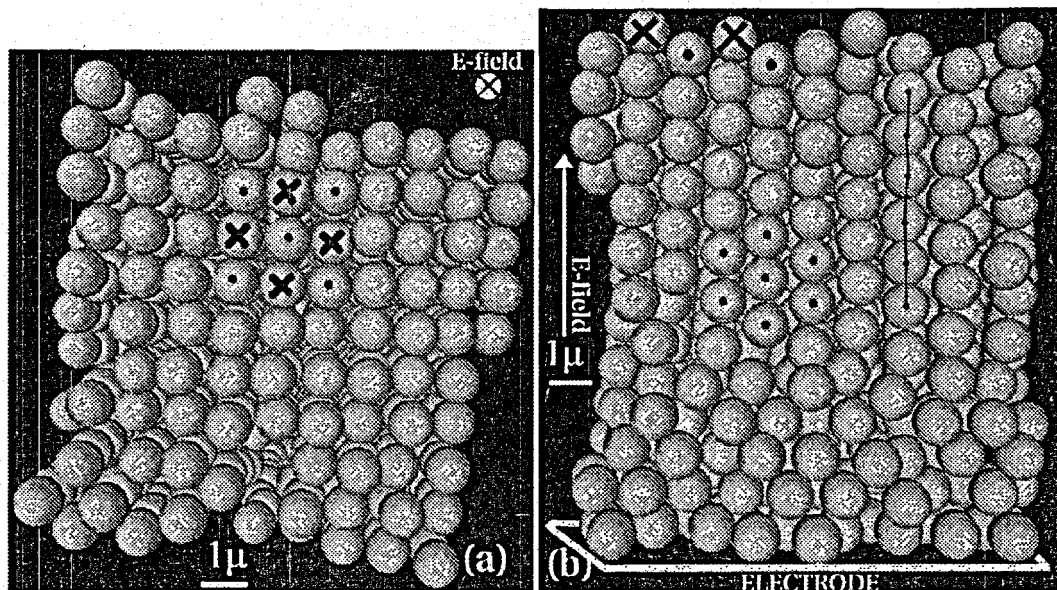


Figure 1: Digitally reconstructed image obtained from laser scanning confocal microscopy of colloids in an electric field. The structure is body-centered tetragonal (BCT) [14]. Chains of spheres parallel to the field are arranged on a square lattice. Adjacent chains, indicated by a \times or \bullet , are offset parallel to the field by half a sphere diameter. (a) The electric field is perpendicular to the image plane. (b) The field is parallel to the image. The structure is BCT in the upper portion of the image. The dots indicate a hexagonal-packed plane, and lines connect the centers of particles in a representative chain. Due to image charges induced in the electrodes, the first four layers of spheres have closed-packed planes parallel to the electrode, and in these layers spheres do not form chains parallel to the field. 3D images of these data sets are available as VRML files on our web page: <http://www.elsie.brandeis.edu>.

results are currently being prepared for submission to the Journal of Chemical Physics.

- **Confocal microscopy: Evolution of ER structures.** We studied the electric field induced temporal evolution of structure in concentrated colloidal samples at volume fractions up to 50%. Our goal was to visualize the position of each particle in a sample as a function of time, particle concentration, and field strength. Although light scattering techniques are fast and can probe large samples, it is difficult to invert the scattering data to obtain particle coordinates in samples that are heavily defected. To accomplish our goal, we chose laser scanning confocal microscopy (LSCM) [12]. In our studies, we employed a novel colloid, synthesized by Dr. A. van Blaaderen. This consisted of a fluorescent dye, Fluorescein Isothiocyanate (FITC), located in a core of $0.2 \mu\text{m}$ diameter embedded in a silica sphere of $1 \mu\text{m}$ diameter [13]. By approximately index-matching the silica shell to the solvent, a glycerol/water mixture, we rendered the particles invisible except for the core. This meant that even when particles were touching each other, the centers of the particles were clearly resolvable with LSCM. High AC frequency (200 kHz) electric fields were used, so dielectric polarization dominated the interparticle interaction. This work has been published: U. Dassanayake, S. Fraden, and A. van Blaaderen. *Structure of Electrorheological Fluids*, J. Chem. Phys. **112**, 385-388 (2000).

A variety of structures were observed, depending on colloid density, field strength, initial conditions,

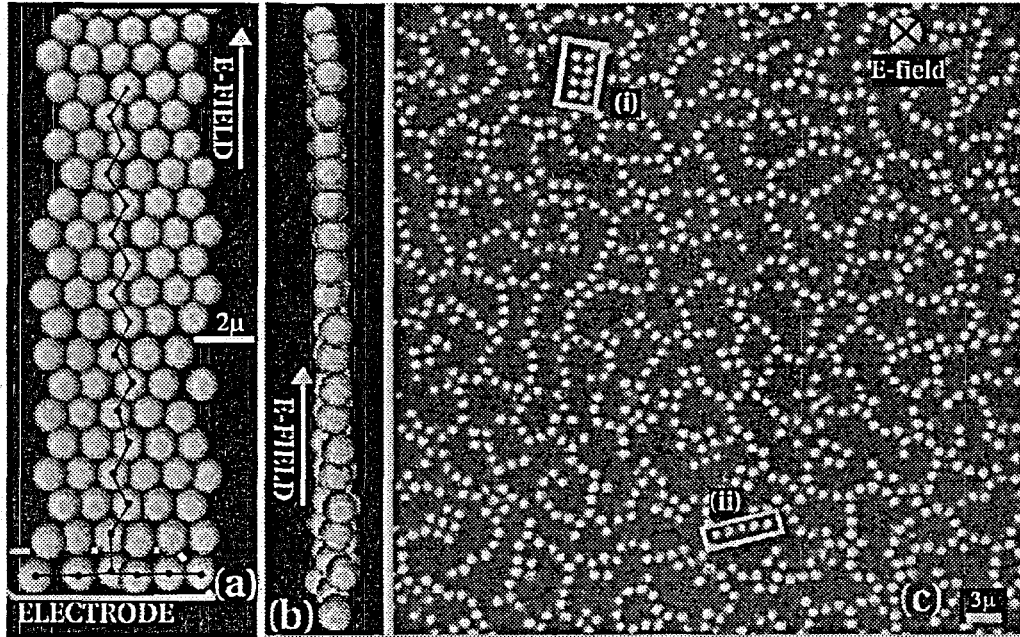


Figure 2: (c) Raw image obtained with a confocal microscope of $1\mu\text{m}$ diameter colloids in an electric field that is perpendicular to the image plane. Before the field was applied, the colloids were uniformly distributed throughout the sample. A field of energy much greater than kT was suddenly applied, and a labyrinth of sheets of spheres rapidly formed. The spheres have a fluorescent core, visible as bright dots in the image, and an invisible shell. Thus, although the spheres were actually in contact with each other, in (c) they appear isolated from one another. Serial sections parallel to (c), but offset perpendicular to the image plane at $0.18\mu\text{m}$ intervals, were used to create a 3-D image of the sample from which the center of each sphere was located in 3-D. In (a) and (b), a sphere of the actual diameter is drawn about the center of each colloid. (a) View of the sheet of spheres enclosed by the white box (ii) in (c). This view is in a plane perpendicular to (c) and parallel to the long axis of the box. The bottom row of spheres is in contact with the electrode. Note that spheres are not arranged in linear chains parallel to the field, in contrast to the chains in the BCT structure shown in Figure 1b. (b) Side view of the same sheet as in (a). Notice in (c) that some of the spheres, such as those in box (i), are organized into a rectangular lattice, illustrating the transition from the metastable planar sheets (a and b) into BCT crystals shown in Figure 1.

and time after application of the field. For dilute samples, we observed chains of spheres spanning the electrodes. In the center of thick, concentrated, and well equilibrated samples, we observed a body-centered tetragonal (BCT) structure [15, 14] (Fig. 1), computed to be the lowest energy structure. However, the first four to five layers in contact with the electrode had a different structure, hexagonal close-packed, arising from image charge interactions. Soon after application of an electric field, we observed two-dimensional sheets of particles, whose planes were oriented perpendicular to the electrodes, spanning the entire distance between the electrodes (Fig. 2). Then, over a period ranging from hours to days, the sheets transformed to the BCT structure. Surprisingly, the particles within a sheet were not arranged as staggered chains, which is what we expected if the sheets were formed as an assembly of individual chains. Instead, again driven by image charges, spheres were centered on lines parallel to the electrode, and then above the electrode, each subsequent layer was horizontally offset by half a sphere diameter (Fig. 2a).

The sheet structure has been observed in computer simulations [16, 17, 18, 19, 20] with and without shear flow perpendicular to the field, and walls of particles have been observed in both electro- and magneto- rheological fluids [21, 22]. Simulations show that in the sheet structure the colloids form chains oriented parallel to the flow direction, which lowers the viscosity compared to a sheet in which the chains are oriented parallel to the field direction. The energy per particle in an infinite sheet is independent of the orientation of the chains because of the symmetry of the dipolar potential and was calculated to be about 10% higher than for the ground state BCT structure [19, 20] and about 10% lower than the energy of isolated chains [19, 20]. Although sheets are not the lowest energy structure, some simulation results indicated that the sheets appeared to be stable, even in the absence of shear flow [16, 18, 19], while other simulations demonstrated coarsening of sheets to the BCT structure [20].

We calculated and compared the energy of isolated chains, BCT crystals, and sheets for samples contained by parallel plate electrodes. Our results indicated that for electrode spacings less than 10 particle diameters the ground state would be sheets, rather than chains or BCT crystals, as was previously assumed [19]. This explains the stability of the sheets in simulations [16, 17, 19], because there the simulated electrodes were separated by about 10 particle diameters. We confirmed this prediction experimentally. In thin samples, sheets were stable indefinitely, but in thick samples, sheets were a metastable structure of relatively low energy, lasting about 24 hours in a high field. They were ubiquitous and formed after sudden application of a high field, before the colloid had had the opportunity to densify into the BCT structure. At high fields, the transformation from the sheets to BCT was a slow process, involving rearrangement of many particles over large distances.

Wall-like structures have been observed by others in ER and MR fluids [21, 22], but without resolution of the structure within the walls. Ours is the first experimental study to determine the structure of the sheets and to calculate their energy for finite electrode gaps. 3D images obtained from the confocal microscope are available in VRML format on our web site: <http://www.elsie.brandeis.edu>.

- **Simulations of surface charge polarization.** We were motivated for several reasons to simulate the electrical polarization of mobile charges confined to the surface of colloids. Firstly, there is the repeated observation in the literature that the electrorheological response is promoted by the presence of water or another conducting substance on the surface of colloids [23, 24].

Secondly, it has been observed that at low frequencies (below 100 KHz) the qualitative behavior of the charge-stabilized colloidal suspensions dramatically changes [25, 26, 27] from the behavior described in the previous two sections. Even in dilute samples, the PS spheres assemble into clusters, rather than chains. An electrohydrodynamical instability occurs in which the spheres within a cluster rotate in a direction determined by the oblique orientation of the cluster with respect to the field. Furthermore, the induced dipole moment changes sign, and at low frequencies the PS spheres act as dielectric inclusions, rather than holes. The mechanism cannot be polarization arising from bulk conductivity, because the colloids are insulating, and thus the dipole moment would have the same sign as dielectric holes. This implies that the mechanism of polarization is due to the surface conductivity of the colloid, and not dielectric polarization, or bulk conductivity. Notably, this low frequency or surface conductivity regime is in the frequency range relevant to ER fluids.

Thirdly, standard theories of the electrokinetics of charged colloidal particles focus primarily on modeling the diffuse double layer [3, 28]. Theoretical predictions about particle motion and di-

electric properties of the suspensions in electric fields depend on particle size, electric potential at the particle surface (ζ -potential), and ionic strength of the suspensions. Careful studies by several laboratories have revealed that there is a large discrepancy between experimental results and predictions of the standard theory, differing by up to an order of magnitude [29, 30]. The discrepancy is especially pronounced for "hairy" particles, like polystyrene spheres, which have significant surface conductivity, and less so for "smooth" particles, such as silica, where surface conductivity is absent [31, 32, 33, 34]. Theories that consider polarization of the inner layer of ions in contact with the surface of the spheres, referred to as either the "inner Helmholtz" or "Stern" layer, have been more successful in modeling the data [33, 34]. However, these theories have strong couplings between the inner and diffuse layers of ions and fail to predict the characteristic relaxation frequency of the colloid [33, 34, 35, 36], which is also a shortcoming of the "standard model" that considers only polarization of the double layer [3, 28, 34].

Our work has made significant progress in understanding this long-standing unresolved problem of polarization of charged colloidal particles in electric fields [37, 38]. We have developed a theoretical model that focuses on the inner Helmholtz layer [37], the tightly bound charged layer at the particle-liquid interface. The charges in this inner layer are mobile along the particle surface, but exchange of charges with the diffuse double layer is absent. However, the diffuse layer does act to screen the field seen by the inner layer. Using this model, we have been able to obtain excellent fits to a set of dielectric constant and electrical conductivity data on latex particles (Figure 3). The data were first published in 1989 by Prof. Saville's group [29], and our work represents the best fit to this set of experimental data. The relaxation frequency in our model is a function of the surface mobility of ions, in contrast to previous models for which the relaxation frequency was independent of the surface transport properties [33]. Our results [37, 38] suggest that **surface conductivity is the dominant contribution to electric-field-induced polarization of colloids**. Publications describing this research are: (1): Y. Hu, *Effects of an inner Helmholtz layer on the dielectric dispersion of colloidal suspensions*, *Langmuir* 14, 271-276 (1998) and (2): Y. Hu and M. W. Chen, *Computer simulation of polarization of mobile charges on the surface of a dielectric sphere in transient electric fields*, *J. Electrostatics* 43, 19-38 (1998).

- **Synthesis of novel colloids.** During 1997 Fraden and two graduate students spent three months each in the Netherlands working with our collaborator, Dr. A. van Blaaderen. During this period we synthesized a new colloid specifically designed for ER studies. The colloid consists of an outer shell of sterically stabilized poly(methyl methacrylate) (PMMA) of 1-2 micron diameter that can be suspended in a variety of low dielectric organic solvents. The surface charge of the PMMA can be varied by adding Calcium Octanoate (CaOct), an organic salt, to the solvent [39, 40]. It was shown that addition of CaOct to the solvent conveyed positive charge to the colloid and was essential for producing an ER effect [39]. The PMMA particles contain a fluorescent FITC core, and as with the silica particles described above, this renders the colloids ideal for confocal microscopy. The index of refraction of PMMA (1.49) is closer to that of the microscope immersion oil (1.51) than that of the silica particles (1.45), thus reducing the effect of spherical aberration for PMMA compared to silica and thereby enabling confocal microscopy deep ($\sim 100\ \mu\text{m}$) inside bulk samples. These colloids are ideal to use in studies of the effect of surface conductivity on electric-field-induced polarization, and for use with confocal microscopy. These new colloids make possible for the first time, the ability to simultaneously index- and density-match colloids and also locate the position of each particle in concentrated, bulk samples. The colloids are also designed

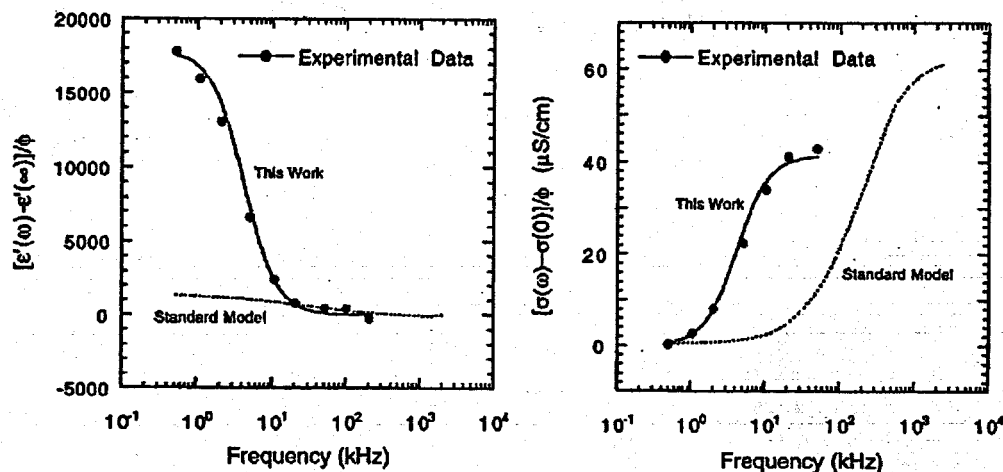


Figure 3: Incremental frequency-dependent dielectric constant $\epsilon'(\omega) - \epsilon'(\infty)$ (a) and electrical conductivity $\sigma(\omega) - \sigma(0)$ (b) both normalized by the volume fraction ϕ of aqueous suspensions of 0.191 μm latex particles in 10⁻⁴ M HCl [29]. The solid dots are experimental data [29]. The dashed lines are also taken from ref. [29] and represent the predictions of the diffuse double layer model [28] (the standard model) with a ζ -potential of 100 mV. The solid lines are the fits provided by our inner Helmholtz layer model [37, 38].

to permit independent variation of the surface conductivity and the dielectric contrast between colloid and solvent. A paper describing the synthesis is in preparation.

- **Simulation of stress transfer in ER fluids in a shear flow.** In aqueous systems, it has been a long-standing problem to explain why the polarizability of particles with surface conductivity is significantly larger - by up to an order of magnitude - than particles without surface conductivity [32, 33, 34, 35, 36]. Our theoretical model on the inner Helmholtz layer indicates that the layer of trapped mobile charges could be the main contributor to the large polarizability [37, 38]. In nonaqueous systems, especially ER fluids, the debate over what is responsible for large particle polarization, and hence large ER effects, is far from being settled [41]. As a matter of fact, it is the lack of understanding of the mechanism of particle polarization in ER fluids that hinders the development of practical fluids for industrial applications. Contrary to the original belief that large dielectric contrast between the particles and the fluids is responsible for particle polarization, experimental evidence shows that surface or interfacial charges, either promoted by the presence of water on the particles, or intrinsic to the particles, are a crucial factor in producing large particle polarization [24]. We have extended our previous work on the inner Helmholtz layer in order to elucidate the mechanism responsible for ER effects.

Older theoretical and computer models consider shear stress of ER fluids to be generated by distortion of chains and columns of ordered colloids, or of droplets of colloids [19, 41, 42, 43, 44]. Predictions of the theories are sensitive to the structures of the particles, but experimentally, chain or droplet structures may be destroyed at the high end of practical shear rates, whereas ER effects are still significant [45]. Furthermore, the assumption of independent chains and droplets breaks down for the high volume fractions encountered in ER fluids. In addition, even though many-body

effects and multipole polarization (due to dielectric or conductive mismatch between particles and fluids) have been included in many studies [41], the effects on ER behavior of the modification of the particles' polarization due to rotation brought on by shear flow have been ignored. Measurements on flow-modified permittivity (FMP) have shown that particles rotate basically as free particles, even in the presence of a large applied field [45]. It has been established, both theoretically and experimentally, that the polarization of rotating particles is not collinear with the applied field [46]. In general, rotating particles are elliptically polarized [46], and the electrostatic interactions between particles can be markedly different from linear dipoles (as assumed by most of the existing models).

We have developed a model that takes into account the elliptical polarizability of particles [46] in ER fluids and that uses molecular dynamics (MD) computer simulation methods [18, 19, 41] to investigate stress transfer in ER fluids as a function of shear rate. We have performed simulations modeling the electric polarizability of a single rotating sphere with charges confined to its surface and have found quantitative agreement between our simulation and theory [46]. We used the theoretical expression for the polarization of a rotating sphere [46] in MD simulations to calculate the shear stress. There is experimental evidence [47] showing that the relaxation frequency of particle polarization is a reasonable predictor of ER effects and that there exists an optimal relaxation frequency. Using simulations, we have been able to investigate the influence of relaxation frequency and shear rate on the strength of interparticle interactions and have provided a theoretical basis for the experimental data [47]. This work has been presented at the 8th International ER conference and a manuscript has been submitted.

Publications during grant period

Observation and simulation of electrohydrodynamic instabilities in aqueous colloidal suspensions, Yue Hu, J. L. Glass, A. E. Griffith, and Seth Fraden, *Journal of Chemical Physics* **100**, 4674 (1994).

Simulations of the motion of colloidal particles in alternating electric fields, Yue Hu, *Computers in Physics* **8**, 524 (1994).

Asymmetrical polarization of spherical colloidal particle double layer in electric fields, Yue Hu, Vidya Kumar, and Seth Fraden, *Proceedings of the Electrorheological Materials and Fluids Symposium, 208th National Meeting of the American Chemical Society*, ed. by F. E. Filisko and K. O. Havelka, Plenum Press, New York, p. 349, 1995.

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Effects of an Inner Helmholtz Layer on the Dielectric Dispersion of Colloidal Suspensions, Yue Hu, *Langmuir* **14**, 271 (1998).

Simulation of Polarization of Surface Charges on a Spherical Particle in Alternating Electric Fields and in a Shearing Flow, Yue Hu, Janet Lee, and Ting Bao, the *Proceedings of the 6th International Conference on Electrorheological Fluids, Magnetorheological Suspensions and Their Applications*, p. 123-130, World Scientific 1998.

Structure of Electrorheological Fluids, U. Dassanayake, S. Fraden, and A. van Blaaderen, *J. Chem. Phys.* **112**, 385-388 (2000).

The significance of flow-modified permittivity: A new model and computer simulation of electrorheology, Yue Hu, Ee-Yenn E. Lin, and U. M. Dassanayake, submitted to *Proceedings of the 8th International ER conference*, World Scientific.

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