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Evolution of Structure During Phase Transitions

J. E. Martin, J. P. Wilcoxon, R. A. Anderson

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Evolution of Structure During Phase Transitions

J. E. Martin, J.P. Wilcoxon
Nanostructures and Advanced Materials Chemistry Department
R. A. Anderson
Properties of Organic Materials Department
Sandia National Laboratories
Albuquerque, NM 87185

Abstract

Nanostructured materials can be synthesized by utilizing the domain growth that accompanies first-order phase separation. Structural control can be achieved by appropriately selecting the quench depth and the quench time, but in order to do this in a mindful fashion one must understand the kinetics of domain growth. We have completed detailed light scattering studies of the evolution of structure in both temperature- and field-quenched phase transitions in two and three dimensional systems. We have studied these systems in the quiescent state and in shear and have developed theoretical models that account for our experimental results.

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Executive Summary

There is currently much interest in building multiphase composite materials with submicron domain sizes. One natural approach is to take advantage of the evolution of structure that occurs when a two component system is made to phase separate by quenching into a two phase region. This can create various types of structures, depending on the quench conditions. We have investigated a variety of such systems, and have determined both the structures that evolve and the kinetics of their growth.

A shallow quench off the critical isochore will cross the binodal line and will result in a metastable state with a finite lifetime. The lifetime is finite because small concentration fluctuations increase the free energy while large fluctuations decrease the free energy. Thus you have to wait around for a large fluctuation to occur. Far from the critical point interfacial energies are large and the system generally phase separates by the nucleation of spherical domains.

A deeper quench near or along the critical isochore will cross the spinodal line. Beneath the spinodal fluctuations of all amplitudes and wavelengths decrease the free energy and the system phase separates by the spontaneous formation of bicontinuous microdomains, the so-called *spinodal decomposition*. These microdomains are small at first and then slowly grow with time. By "freezing" the system in some fashion these microdomain structures can be pinned to create a nanostructured composite material. Pinning can be achieved by solidifying, vitrifying, or polymerizing one or both phases.

The morphology of such nanocomposites can be tailored to some degree by controlling the quench depth and coarsening time. To do this in a predictable fashion requires an understanding of the kinetics of domain growth. We have studied this growth kinetics by time-resolved, two-dimensional light scattering on a variety of systems that generate morphologies of different dimensionalities.

We chose a micelle forming surfactant system as a model for three dimensional spinodal decomposition. This system was temperature quenched along the critical isochore and both the domain structure and growth kinetics were investigated for a variety of quench paths. We found that the standard theories of spinodal decomposition did not work well and that the domains intrinsically pinned at a size of about 25 microns. Beyond this size growth simply stopped. This effect was quite surprising and is now the subject of theoretical investigation.

We chose an index-matched colloidal suspension as a model for two-dimensional growth. This system couples strongly to an electric field- a vector field- and because of this the dimensionality of the system is essentially two, consisting of interacting colloidal chains that form along linear field lines. Our light scattering studies focused on the structure orthogonal to the field and we generally found behavior somewhat different from that expected for spinodal decomposition. The details are complex, but in the end we were able to develop a new theory of structural evolution in field quenched systems.

We studied the competition between domain growth and mixing in phase separating systems subjected to hydrodynamic shear flow. In this case the system cannot continue to coarsen, but instead reaches a stationary or periodic state with highly nonlinear behavior. These states are actually as dissipative as possible for the stress levels they achieve. We developed rather detailed and complete descriptions of the structural and rheological properties of these suspensions, and this has direct applications to electrorheology.

Finally, we discovered and studied a new effect, the formation of particle sheet structures in a fluid exposed to a rotating electric field. The sheets form in the plane of the field and can rotate either widdershins or deasil, depending on the sign of the dielectric constant contrast in the system. We determined the field frequency dependence of the angular velocity of particles immersed in liquids of different dielectric constants and found a Lorentzian behavior which we were able to understand theoretically. This effect has possible applications to valveless hydraulic systems, although we have not yet demonstrated this experimentally.

Future work is focused on using this knowledge to create novel anisotropic field-structured materials. This work is proceeding quite well and we have made structured materials in both electric and magnetic fields. These materials show promise for certain weapons applications.

I. Background and Motivation

The purpose of this proposal is to investigate fundamental issues concerning the evolution of order in materials that undergo phase separation. Scattering techniques are optimal *in* situ probes of structures on these length scales and we have recently developed a new Time-Resolved, Two-Dimensional Light Scattering (TRLS) apparatus that enables us to investigate structural anisotropy, as well as a high resolution Very Small Angle (.001°) Bonse-Hart X-ray scattering instrument at the Brookhaven National Synchrotron Light Source.

There is currently much interest in multiphase materials with structures in the nanometer length scale regime, since such materials have many useful properties. For example, because it is difficult to propagate a Griffith's failure in a composite structure, substantial fracture toughness is often observed. An ordinary seashell, though formed mostly of calcium carbonate, a friable material, exhibits a fracture toughness that far exceeds any reasonable expectation. It happens that the shell is composed of neatly stacked 2 micron hexagonal tiles that are bound by a polymeric glue. Such elegant, fracture resistant structures have been crudely, but effectively, mimicked by man by simply mixing various fillers with polymeric resins. However, a finer degree of mixing can be achieved by taking advantage of phase separation processes such as nucleation, spinodal decomposition, and gelation, or by exploiting the spherical, cylindrical and lamellar phases that occur in microemulsions and block copolymers.

Commercial examples of nanostructured materials abound. For example, in the manufacture of Vycor glass a hot melt is quenched into the two-phase region where phase separation occurs via spinodal decomposition. The predominate length scale is largely determined by the quench depth and the anneal time. After spinodal growth develops into the nonlinear regime where coarsening takes place, the two-phase glass is cooled beneath the glassy transition temperature, and the metastable, bicountinuous solid thus produced is exposed to an acid that dissolves one phase. The result is a low-density glass with a continuous pore structure. Polymeric foams and sub-micron filters are commercially produced by similar spinodal decomposition processes. Alternatively, gelling in a solvent produces a structure whose pore size depends on the initial monomer concentration. When this wet gel is critical-point dried a very low density porous glass is produced that is both a good insulator and a useful Cerenkov detector.

There are a number of fundamental issues related to the kinetics of phase separation and the structures that evolve. Some of these concern the kinetics of phase separation in systems that are described by mean field theories. W. Klein, a theorist from Boston University, has pointed out that systems with long range order are described by a mean-field theory, and the binodal curve coalesces with the spinodal, a line of critical points. Nucleation thus occurs near a critical point, where the surface energy is zero and droplet theories of nucleation consequently break down. Nucleating no longer occurs around a spherical droplet, but at the core of a ramified percolation cluster. Novel nucleation behavior is therefore expected, the main result being that there is no stationary length scale about which structure evolves, rather as phase separation occurs the dominant fluctuation length scale continuously grows. A good physical example is the first order phase transition that occurs when an electric field is applied to a colloidal solution. In this case the induced dipole interaction is long ranged, and the system should be described by a mean field theory. Our TRLS apparatus is ideally suited to following the kinetics of this phase separation process, as well as being able to determine the structural anisotropy that evolves.

In micellar systems the structural units can be very large and it is possible that the phase behavior can be described by a mean field theory. We have done some preliminary experiments that show a very strong 'spinodal ring' when laser light illuminates the sample, indicating the presence of domains of a nearly uniform size. This three dimensional system is ideal for testing current theories of phase separation, including the existence of an initial linear regime.

We have also investigated phase separating colloidal systems subjected to steady and oscillatory shear flow. In this case the phase separation is induced by the application of an external electric field. This is a very interesting case as there is a competition between the external field, which drives phase separation, and the shear flow, which induces mixing. The competition between these forces leads to complex non linear behavior which we have explored using light scattering.

The results of this work have been thoroughly documented in the publications cited at the end of this report. In the following we give a summary of these studies.

II. Phase Separation in Micellar Solutions

We conducted a time-resolved, two-dimensional light scattering study (Fig. 1) of the evolution of structure in a two component nonionic micelle system during phase separation via spinodal decomposition. [1,2] Spinodal decomposition is a first-order phase separation process characterized by the formation of random, bicontinuous microdomains of the majority and minority phases and occurs when the interfacial energy of the system is too small to favor nucleation. Spinodal decomposition is of great interest to metallurgists, because many high strength alloys are thermodynamically unstable and coarsen via this process.

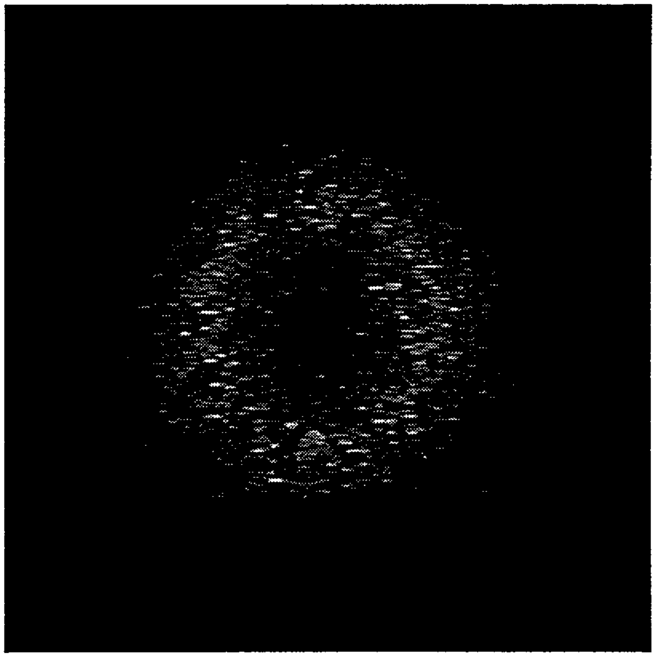

Figure 1. The scattered light from a spinodally decomposing micelle solution forms a slowly collapsing ring centered on the beam stop. By analyzing this ring we obtain information about the domain structure and growth kinetics.

Our principal finding was that domain growth proceeds much slower than the cube root of time prediction for simple binary fluids. In fact, the growth kinetics can be empirically described as a stretched exponential approach to a pinned domain size. Although the kinetics are not yet understood, this anomalous behavior may be due to the ability of the spherical micelles to reorganize into more complex structures. The domain structure also shows some anomalies. At short times the expected structure factor for a critical quench is observed, but at long times the structure factor crosses over to the off-critical form. However, in all cases the average scattered intensity is proportional to the cube of the domain size. In our published articles these findings are discussed in comparison to standard theories of and experimental work on binary fluids.

The slow kinetics observed in our experiments is not accounted for by any theory of which we are aware, possibly because of the ability of micelles to reorganize into more complex structures. Lifshitz-Slyozov growth was observed for the shallowest quench, but the best *empirical* description of our system appears to be a stretched exponential approach to an asymptote with a fixed exponent of b=0.5 and fixed pinning value of ~ 25 microns. This description is satisfying since only one variable parameter describes virtually all of our data. The anomalous kinetics appears to be related to the large structures observed in previous light and neutron scattering measurements of a phase separated sample in the two-phase region near the critical point. Thus it may be that this anomalous kinetics is not a universal feature of spinodal decomposition but is unique to surfactant systems.

III. Phase Separation in a Field-Quenched Line Liquid

Phase separation is normally induced by changing temperature or pressure, however, some systems are strongly coupled to external fields and phase separation can be induced by applying these fields. Most of our work was conducted on colloidal suspensions because they undergo a phase transition to a bct solid in the presence of an applied electric field. This phase transition is the basis of the well known electrorheological effect, so choosing this as a model system has the added benefit of forthcoming practical applications. This system is also of interest because it is nearly a two dimensional fluid, being composed of particle chains that form along field lines. In fact, it is technically an example of a line liquid- a fluid of continuous, interacting, more-or-less parallel lines.

A study of the evolution of structure in a quiescent electrorheological fluid [3,4] was undertaken to understand 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 $q = 0$, as in Fig. 2. 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 domain size, 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. However, quantitatively the standard theory does not give good agreement with experimental results so we developed a new thermal coarsening model.

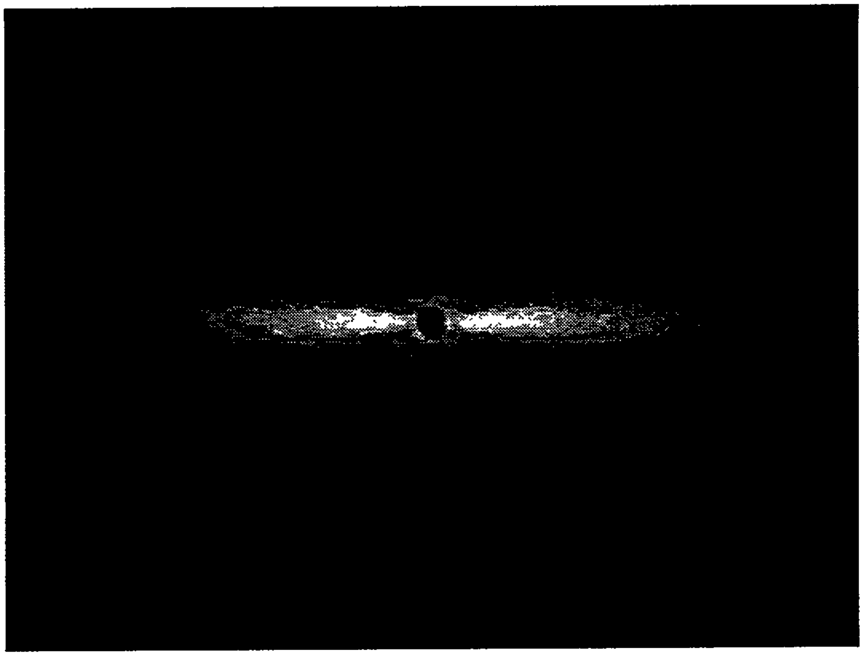

Figure 2. Light scattered from a colloidal suspension in an electric field forms a bow tie pattern, due to the formation of line-like structures. The field is in the vertical direction here, and the scattering pattern is analogous to spinodal decomposition in a two dimensional system.

The thermal coarsening model correctly predicts the observed time and field dependence of the growth kinetics. In this model the longitudinal and transverse fluctuations of the columns creates a fluctuating electrostatic interaction between columns that can be repulsive or attractive at various heights along the columns. These random attractive and repulsive interactions add in a statistical fashion to give the net interaction between columns. When the net interaction is sufficiently attractive that the columns can be deformed from strict field alignment, the columns can coalesce to form a larger column. This process proceeds until the equilibrium solid is produced.

A more complex aspect of this system is the structure of the fluid parallel to the field. [5] By analyzing the anisotropic, bow-tie-shaped scattering pattern in ways suggested by the line liquid theory developed by D. Nelson (see refs. in [5]) we were able to conclude that at least shortly after the field quench the colloidal suspension is an example of a line liquid. A line liquid is best thought of as a two dimensional liquid with a conservation law for a tangent vector associated with each particle. This is a simple consequence of the continuity of lines.

To conclude, we completed a thorough study of the phase separation of a colloidal suspension in an applied electric field. In our current work we have pinned phase separation by polymerizing the continuous phase, thus making a novel class of structured anisotropic materials.

IV. A Phase Separating System in Steady Shear

When a phase separating system is exposed to flow a competition is created between the particle interactions, which lead to the development of domain structures, and the hydrodynamic flow, which tends to fragment and mix these domains. The possibility thus exists that a steady state will emerge where these effects- aggregation and fragmentation- are balanced. This steady state can then be continuously shifted by altering the interactions or the flow. We undertook a study of the steady state structure produced by this competition in a sheared colloidal suspension exposed to an electric field. The phenomenology of this system is striking; the viscosity varies in inverse proportion to the shear rate, creating a dissipation similar to dry friction. We sought to understand the microscopic basis of this and other effects.

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, Fig. 3. 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 our theoretical prediction of the steady state structure of fragmenting particle droplets. This result implies power law shear thinning of the fluid viscosity, as observed in low field experiments. By contrast, a solution of non fragmenting rods would have a rotation angle that increased in direct proportion to the shear rate and a more-or-less fixed viscosity.

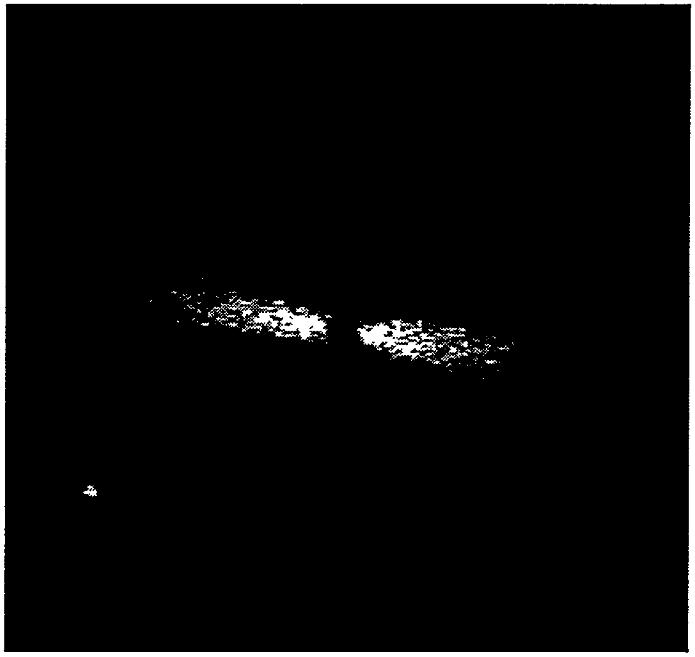

Figure 3. When a colloidal suspension is both ordered by an electric field and subjected to shear, chain-like structures form that are rotated away from field alignment in the direction of fluid vorticity.

V. A Phase Separating System in Oscillatory Shear

In the studies of a phase separating system in steady shear we found that the competing influences of aggregation and fragmentation led to a steady state structure we could characterize through light scattering. The approach to steady state is a separate issue that can be effectively studied by applying an oscillatory shear strain to the sample. In a linear system the response will be sinusoidal, with a phase shift dependent on the strain frequency but independent of the strain amplitude. The colloidal suspension of interest to us has a pronounced nonlinear response and cannot be characterized by this approach.

The light scattering studies we conducted [8,9] show that ER fluids can have strongly nonlinear orientational dynamics in oscillatory shear at strain amplitudes exceeding about 0.5, as in Fig. 4. This nonlinearity is due to the chain fragmentation that occurs as the chains rotate to larger angles. The nonlinearity can best be described as a clipping of the sinusoidal response, although more exotic nonlinearities occur as well. We find there is a maximum chain angle, beyond which chains fragment completely to particles. Chains aggregate as they rotate to smaller orientation angles on the return stroke of the electrodes.

We have derived a simple kinetic chain model that describes qualitatively the observed chain rotational dynamics. Several simplifications were made, including the point dipole approximation, that render the model tractable while eroding the agreement with experiment. Still, this model successfully describes features such as rotational clipping and retrograde motion, with only a single adjustable parameter

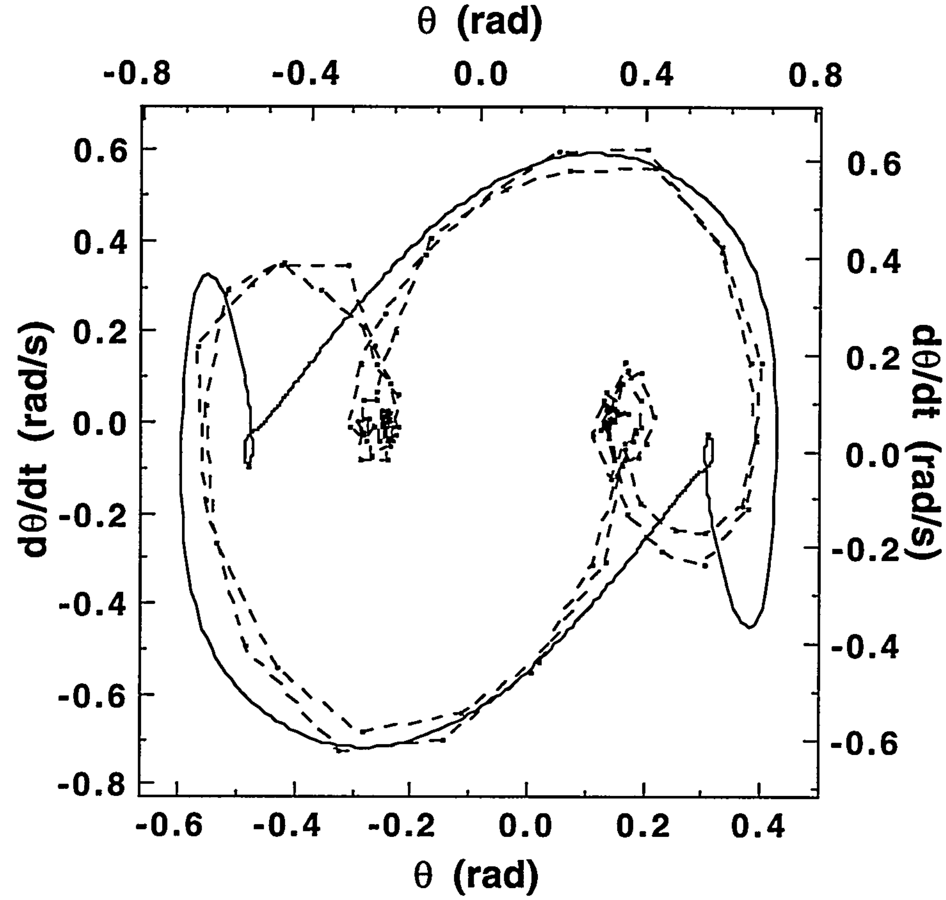

Figure 4. Lissajous plot of the angular velocity versus the angle of a field-quenched colloidal suspension subjected to oscillatory shear. The solid line is theoretical, right ordinal axis. A linear oscillator would give a circular plot.

that describes the rate of aggregation and fragmentation. Much of our experimental data can be described by assuming rapid aggregation and fragmentation, however, at low fields strong nonlinearities suggest that the kinetics is slow.

Finally, the model of the chain dynamics is shown to be a model of electrorheology. Light scattering thus indirectly measures stress. There is good agreement between the plots observed in direct stress-strain measurements and those reported here for light scattering data. Future studies will concentrate on concentrated solutions, where the very notion of chains probably breaks down.

VI. Theory of Field-Quenched Colloidal Suspensions

We have developed a simple model of the structure and dynamics of colloidal suspensions in an electric field that is based on chains of spheres held together by dipolar interactions. [10] The predictions of this model are in reasonable agreement with experimental work in many cases.

We first considered unconfined chains in steady shear. We computed the shape of such chains self consistently and found a universal shape function that is independent of Mason number, the ratio of hydrodynamic to electrostatic forces on a particle pair. We showed that there is a critical Mason-number-independent chain orientation angle, taken relative to the field at the chain center, beyond which chains are unstable to fragmentation. The primary effect of the Mason number is thus to determine the chain size.

We next made a linear approximation to the chain shape, in order to simplify computations. With the linear chain model we were able to compute the orientation of a chain of a given size as a function of Mason number, and showed that there is a fixed critical angle beyond which the chain will fragment. The maximum stable chain size was found to increase as the inverse square root of the Mason number, all of which led to a pseudoplastic rheology, with the viscosity thinning in inverse proportion to the shear rate. The chain angle was found to be independent of Mason number.

The fragmentation and polydispersity of chains was briefly considered and it is shown that fragmentation spontaneously occurs when the applied force is such that the pair potential reaches an inflection point. The lifetime of a chain decreases with an increase in the applied force.

We next considered chains confined by shearing electrodes. These can exist in one of three states: they can span the gap, be bound to one electrode, or remain free. Chains in contact with electrodes feel a frictional force, due to the normal force created by their image charge. We showed that confined chains behave very differently than unconfined chains; for example, the orientation of spanning chains, which form at very low Mason numbers, depends on both Mason number and electrode friction. We constructed a phase diagram of spanning, bound, and free chains that shows that there exists a Mason number regime where stationary chain structures cannot exist.

The simple chain model was then extended to oscillatory shear by including a kinetic equation for chain fragmentation and aggregation. The resultant kinetic chain model has a strongly nonlinear dynamics and rheology, as discovered in the light scattering experiments described in the previous section. Historically, the oscillatory shear case was actually treated first, but was absorbed into this much more detailed and complete treatment in order to have a single unified treatment.

Finally, we considered several improvements to the chain model that should improve quantitative agreement with experiment. First, we considered the effect of hydrodynamic interactions along the chain, which render the friction of a rod anisotropic. The primary effect of this is to increase the predicted chain angle. Next, we considered the effect of local field corrections on the bare dipolar interaction and developed a self-consistent pair interaction force. This self-consistent force makes the critical chain angle strongly dependent on the particle-solvent dielectric contrast.

We feel that this model has some utility, especially for oscillatory shear. However, this simple model does not account for chain-chain hydrodynamic interactions, that with the aid of image forces may create a shear slip zone instability. Also, from direct microscopy of solutions in steady shear we know that particle structures are not simple chains, but are typically a couple of particles in diameter; perhaps these structures are better described as elliptical droplets. In any case, a microscopic description of ER fluids should account for at least account for hydrodynamic interactions between chains, so we feel we have presented only the 'hydrogen atom' description of a very complex problem.

VII. Phase Separation in a Rotating Field

We have discussed how colloidal suspensions exposed to a linear AC or DC electric field form one dimensional particle chains along field lines. These chains penetrate a plane orthogonal to the field lines, and the points of penetration are nearly a two-dimensional liquid, albeit with an additional conservation law for the tangent vector of the chains where they intersect the plane. We have discovered that colloidal particles can be organized into two-dimensional sheets by applying a rotating electric field at reasonably high frequencies, of the order of 1 kHz. [11] These sheets intersect a line orthogonal to the plane of the rotating field to create a one-dimensional liquid, albeit one with a conservation law for the tangent plane at the point of intersection. This could be termed a plane liquid.

We completed some basic studies of the formation of particle sheet structures in a rotating electric field. We found that the sheets can rotate either widdershins or deasil, depending on the sign of the dielectric contrast in the system. We determined the field frequency dependence of the angular velocity of particles immersed in liquids of different dielectric constants and found a Lorentzian behavior which we were able to understand theoretically. However, we have not yet developed a theory of plane liquids, nor have we studied the coalescence of sheets into "plates."

This effect has possible applications to valveless hydraulic systems, and we have built a prototype valve, but have not yet demonstrated this experimentally.

VIII. Future Research Directions

In this research program we developed a new understanding of the kinetics of first-order phase separation and how this can be affected by flow. These studies have obvious applications to electrorheological and magnetorheological fluids, but we have taken this in the direction originally stated in the proposal and are now making field-structured, anisotropic magnetic and dielectric materials. This synthesis program is in concert with computer modeling intended to investigate the effects of particle concentration, field strength, lubrication forces, multipolar interactions etc. on the anisotropic structures we make.

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10. *"Chain Model of Electrorheology,"* J. E. Martin, R. A. Anderson, to appear in J. Chem. Phys.

11. *"The Rotary Electrorheological Effect,"* T. C. Halsey, R. A. Anderson, J. E. Martin, Proc. of the 4th International Conference on Electrorheological Fluids, Magnetorheological Suspensions, and Associated Technology.

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