I. Scientific Research Goals

The goals of this research are

• to understand and clarify the physical mechanism underlying the electrorheological (ER) response of fluids and establish an *ab initio* theory for the phenomenon;

• to study the structure of ER fluids and their properties, to investigate the change of viscosity of ER fluids with an applied electric field;

• to apply the ER phenomenon to liquid fuel flows, to control their viscosity and hence their velocity;

• to examine the necessary theoretical and technique problems associated to the design of a new class of liquid fuel control devices which are based on the ER phenomenon.

II. Significant Results in the Past Year

Our research in this period has made significant progress toward the above goals.
1. Structure of ER Fluids (by Tao). What is the structure of ER fluids in an electric field? This is important to understand ER fluids. It was found quite a while ago that in an electric field, ER fluids form thick columns spreading between two electrodes. The structure of these thick columns puzzled many authors in this field until our recent work which clarifies this issue.

We assume that the dielectric particles are balls with radius of \( a \). Inside an electric field \( \vec{E} \), each particle obtains a dipole moment \( \vec{p} = \alpha \vec{E} \) where \( \alpha \) is a constant. We take the direction of electric field as the \( z \)-direction, and define infinite chains with their dipoles at \( z_j = 2ja \) \( (j = 0, \pm 1, \pm 2, \cdots) \) as chains of class A and infinite chains with \( z_j = (2j + 1)a \) as chains of class B. The columns are found to be formed by chains A and B only.

![Three-dimensional body centered tetragonal (bct) structure, the ground state of the induced ER solid (the particles have radius \( a \) and are not shown to the scale).](image)

Fig. 1. Three-dimensional body centered tetragonal (bct) structure, the ground state of the induced ER solid (the particles have radius \( a \) and are not shown to the scale).

The interaction between two infinite chains are short-ranged. Two chains of the same class are repulsive, while two chains of different classes are attractive. Their interaction energies can be represented as

\[
U_{AA}(\rho) = U_{BB}(\rho) = -U_{AB}(\rho) = \nu \pi^2 \sqrt{\frac{2}{a^2 \rho}} \exp(-\rho/a)
\]

where \( \nu = \vec{p}^2/\epsilon_f \). The distance between two chains of different classes is \( \rho \geq \sqrt{3}a \).
but the distance between two chains of the same class is $\rho \geq 2a$. The ground state is the configuration which minimizes the total potential energy. Therefore, the structure of ER fluids is equivalent to finding a ground state for a two-dimensional system which has two classes of particles A and B in $x-y$ plane via the above interactions. Fig.1 shows our finding about the structure of ER solid in three-dimensional space. It is a body-centered tetragonal lattice.

Fig.2 is the projection of the three-dimensional structure to the $x$-$y$ plane. The theoretical prediction has been compared with all other suggested structures in the literature and found to have the lowest energy. Experimental verification of the theoretical result is under way.

![Fig.2. The projection of the three-dimensional structure to the x-y plane where o for A chains and * for B chains.](image)

2. Monte Carlo simulation of ER fluids (by Tao). We have used Monte Carlo simulated annealing process to find the ideal structure of ER fluids in an electric field. The structure of ER fluids is the configuration which minimizes the potential energy. In our simulation, we first give a random distribution of dielectric particles in the space and calculate their interaction energy $U_0$. Meanwhile, we introduce a temperature $T$. Then we try to move the particles randomly in space. After one trial move, we calculate the new interaction energy $U_t$ and find the difference $\delta U = U_t - U_0$. If $\delta U \leq 0$, the move is allowed, the new state replaces the initial state. If $\delta U > 0$, we do not reject the new state immediately. The probability to move to the new state is $\exp(-\delta U/T)$. This slow process
will avoid the possibility to lead our Monte Carlo process to a local minimum. We repeat the above process again and again. Meanwhile, the temperature $T$ is gradually cooling down to 0. Our Monte Carlo simulation verifies the ground state of ER fluids in figures 1 and 2.

3. Experimental determination of the structure of ER fluids (by Chen, Zitter and Tao). To verify the above theoretical prediction, we begin to perform experiments to investigate the structures formed by the particles in the fluid under an applied electric field in static fluid condition.

In the experiments, we are using a laser diffraction technique that is an analogue of a standard x-ray diffraction technique used to observe atomic arrangements in crystals. Here, our "atoms" are glass spheres 20 micrometers in diameter floating in low-viscosity oil. If the beads form an ordered structure when an electric field is applied, the diffracted laser beam will show a characteristic spot-pattern which is the spatial Fourier transform of the bead structure. The beads and oil are contained in a cavity measuring $2 \times 2 \times 0.1$mm between glass microscope slides, with electrodes supplying the electric field. The first discernable patterns were achieved in May 1991, and currently we are attempting to (a) improve the patterns, (b) obtain polaroid photographs of the patterns for analysis, and (c) observe the effects of changing the bead concentration. Our preliminary experimental result seems to be consistent with the theoretical prediction about body-centered-tetragonal lattice.

4. Phase transition in ER fluids (by Tao). What is the nature of ER fluids? Why the viscosity of ER fluids increases dramatically upon application of an electric field? This is an important issue to understand the physical mechanism of ER fluids. We are the first to propose a theory for ER fluids, claiming that the nature of ER fluids lies in the electric field induced solidification. When an electric field applies to ER fluids, dielectric particles obtain an induced dipole moment which forces them to align in the field direction to form a solid structure. This structure causes a dramatic increase of viscosity. We find that the phase transition occurs when the osmotic pressure vanishes. Hence, we find the critical electric field $E_c$. When the applied field exceeds $E_c$, ER fluids become a solid. The experiments match the theoretical result of $E_c$ very well.
We have further developed our theory and clarified that the induced phase transition is the first-order phase transition. But the latent heat is found to be very small. We have also calculated the effect of external pressure on the phase transition. Experimental verification of these theoretical results is under preparation.

5. Organizing an International Conference on ER fluids (by Tao)
With the support from ONR and Southern Illinois University at Carbondale (SIUC), Dr. Tao is organizing an International Conference on ER Fluids, to be held on October 15-16, 1991 at SIUC. The conference will cover four topics in the field of ER fluids: (1) physical mechanism, (2) materials technology, (3) measurement and properties, and (4) applications. The international response to the conference is overwhelming. All major research groups in USA, Canada, England, Japan, France, Germany, Soviet Union, and China have submitted their papers to the conference. Before the deadline of June 30, 1991, we have received about 40 papers.

The conference participants will not only have research groups at universities and national labs, but include researchers in industries as well. Especially, Ford Motor, General Motor, and Nissan Motor Companies pay special attention to the conference. US federal government, such as Department of Energy and National Science Foundation, has also expressed interest to attend the conference.

This major international conference will certainly make an important contribution to the field of ER fluids. It provides the opportunity for researchers to discuss and exchange their results and jointly explore the exiting problems.

6. Molecular dynamic simulation of ER fluids (by Jaggi). We have written two computer codes, one simulating the two-dimensional Hamiltonian dynamics and the other simulating the fully dissipative dynamics of an appropriate two-dimensional classical model of dielectric spheres in a suspension. Here the key contribution is summarized. Starting from the proposed dense dipolar gas model, the simulations reproduce the experimentally observed structures. It consists of fibrils (thick columns) that percolate along the field direction, but are not homogeneous in thickness. There is clearly a microscopic phase separation into low density and high density regions: the interfaces between these two re-
regions are rough on a microscopic scale but are nevertheless predominantly along the electric field direction.

7. Viscoelastic response of ER fluids (by Jaggi and Woestman). The rheological response of ER fluids varies from that of a Newtonian fluid at zero and small electric fields to something approaching a Bingham solid at higher electric fields. We have designed an experiment to study the viscoelastic response of ER fluids in the full range from a Newtonian fluid to that of the Bingham solid. We are currently able to study the steady shear stress $\tau$ -shear strain $\gamma$ relationship of the ER fluids as a function of electric field. The additional instrumentation needed to study the stress-strain rate ($\tau$-$\dot{\gamma}$) relationship in the liquid regime, will be put together soon.

The schematic figure (Fig.3) illustrates the experiment. The ER liquid is contained in the cell whose bottom is a conducting Copper plate onto which the high voltage connector is mounted as indicated. The ground electrode is in the form of an annular washer to which a fine flexible wire is soldered and returned to the high voltage power supply. In the presence of the applied electric field above the critical field $E_c$, an annular cylindrical ER solid is formed under the annular ground electrode. A strong Alnico permanent magnet is epoxied across the top of the washer and is suspended such that the plane of the washer is horizontal using a string with negligible torsional compliance.

The whole cell is placed at the center of two sets of Helmholtz coils that produce a sufficiently homogeneous magnetic field over the size of the magnet; one of them mounted on a rotatable stage. The coils are driven by independent power supplies. The current through one of the coils is adjusted to cancel the earth's magnetic field so that there is no shear torque on the magnet due to the earth's field. The other Helmholtz pair is then used to produce a well controlled and reproducible shear stress on the ER "cylinder" via the pure torque on the magnet that is epoxied to the washer.

A small (1mm) plane mirror is glued with its plane vertical to the side of the Alnico magnet. A 2 milliwatt He-Ne laser is bounced off this mirror onto a graduated scale mounted on the wall across the lab; the deflection of the spot is used to measure the angular position of the fixed diameter thus giving us the
shear strain $\gamma$.

In the next generation of the experiment, the graduated scale will be replaced by a photodetector array, associated electronics and interfaced to a PC enabling us to measure the shear strain continuously in time. The shear strain rate $\dot{\gamma}$ can be computed either in hardware or later in software from the accumulated $\gamma(t)$ profile.

Since these experiments will be refined to measure dynamically $\tau(E, \gamma, \dot{\gamma})$, we view the present experiments as a first step towards understanding the shear elastic response of ER fluids at very low strain rates.

A body of data is systematically being accumulated, but two important conclusions can already be drawn from the data.

1. It is unambiguous that at high enough electric fields, the ER system behaves like a solid: it has a distinctive shear elastic response, it is possible to extract a shear modulus, it fails at a well defined yield stress notwithstanding earlier arguments in the literature about the reality of a yield stress. It is much more appropriate to call them ER solids in this regime, as opposed to ER fluids.

2. These are the first experiments that have probed the shear response at these very small strain rates ($\dot{\gamma} \leq 10^{-5} \text{ s}^{-1}$). Figure 4 shows one data set that is particularly clean and is suited to make the following very important point. Note that when the ER solid fails at $\tau_y$, the system does not relax fully: only part of the strain and the elastic energy is released. The dashed line indicates the nonequilibrium nature of this response: the yield is followed by a very large strain rate for a very short time (estimated at less than $1/20$ sec) and the system gets locked into another solid like regime which in turn yields at about the same $\tau_y$.

Thus a microscopic description of what happens at larger strain rates seems to be emerging. The shear viscosity above the yield stress and the associated elastic energy dissipation may be describable as a rapid sequence of elementary events each one of which consists of a structure that breaks at a certain "shear stress" and heals within a certain "time constant". We are presently developing this two-parameter model of the viscoelastic response of ER fluids.
Fig. 3. The schematic figure of the experiment to determine the viscoelastic response of ER fluids.
Fig. 4 Shear stress $\tau$ vs shear strain $\gamma$. 
8. Imaging video microscopy (by Jaggi). We have set-up a high resolution video microscopy station to be able to study the structure of electrorheological fluids in the presence of an electric field and under varying flow conditions.

The important feature of the video microscope is described below. Traditional microscopes with all optical magnification are capable of 1 micron resolution but suffer from two major disadvantages. First, they are top of the line and cost a lot. Much more importantly, the working space, viz. the distance between the sample and the objective is so little that only planar slides can easily be viewed. Instead, we have put together a well designed parafocal optical system with a relatively small magnification of 50, but therefore allowing a large working range: big enough to easily slip in our present ER cell as well as the new flow cell under construction. The system stays in focus as we span the 6:1 zoom. The 50X image is focussed onto a high sensitivity 2/3 inch frame transfer CCD array having 800 x 490 pixels. We couple the CCD output to a 14" monitor and have been able to easily resolve 1 micron particles suspended in a very dilute solution.

The very high concentration of the ER fluids made it too opaque for the present illumination set up (a fibre optic ring illuminator) and we could not get good images.

We are trying to improve the illumination set up and add a universal mount for the CCD array to be able to look at the ER cell from different directions.

An IBM-compatible PC has just been acquired to hook up to the video microscopy station. We are evaluating an appropriate image grabber to be able to digitize these images to enable postprocessing and analysis.

9. Hunt for ER fuels (by Jaggi and Woestman). In the upcoming second year of the grant, we intend to apply the understanding that we have developed to explore the actual design of ER fuels more thoroughly. During the first year, we have tried two routes to the possibility of fuels with an ER response. Instead of spending a lot of time on precision measurements on unpromising systems, we have decided to screen the systems for a response that is large enough to be easily measured at moderate fields of the order of 4 - 8 kV/cm.

A. Metal-Liquid Oxygen Based Fuels:
We have shown that partially oxidized fine aluminum (Al) powder suspended in mineral oil shows a very strong ER response. We therefore believe that the solid metal - dielectric oxidant liquid route is promising.

We have also shown that using an insulating teflon barrier between the suspension and the electrodes, a reasonable strong ER response exists. There seems to be an ill-understood time dependence (\(g\) - dual decay) of the response when no current is flowing through the suspension. This will be explored carefully.

We have used a make-shift cryogenic cell to test a suspension of the same batch of oxidized fine aluminum powder in liquid nitrogen. Because of the very low viscosity of liquid nitrogen and also the very large density mismatch between Aluminum and liquid nitrogen, settling was a major problem: it was essentially impossible to keep the Al-powder in suspension for longer than a few seconds which was insufficient to do the experiments.

We oxidized a second batch of finer aluminum particles to varying degrees and are in the middle of experiments with these. These finer particles stay in suspension a bit longer and we will also use continuous stirring to keep them suspended.

The non-sealed nature of our present ER cell may be responsible for inclusion of moisture which might have a deleterious effect. We will soon design a safe ER fuel cell to do experiments with unoxidized and partially oxidized Al in liquid N\(_2\) and liquid O\(_2\). We plan to do this in the beginning of our second year of the grant period. The results mentioned in this section have not been made public yet.

B. Alcohol Based Fuels:

Commercial grade methanol and dried ethanol did not show useful ER response in the preliminary experiments. Ethanol is strongly (to some extent methanol also) plagued by the fact that it quickly picks up moisture from the ambient and its conductivity increases so much that it started overloading the high voltage power supply. To do experiments for any extended period of time and at higher fields, we will have to make another air-tight ER flow cell. Experiments on gasoline-alcohol mixtures will also be done in the coming period using the air-tight cell.
10. Laser-Doppler experiments (by Chen and Zitter). The experimental portion of this study of ER fluids is also concerned with how an applied electric field affects fluid flow through various volumes or orifices.

Laser-interferometric diagnostics are being employed. In the 1990-91 year, a helium laser (red light) and an argon-ion laser (violet, blue or green light) were purchased, together with associated optics for interferometric experiments. Additional purchases included fluid pumps, tubing, and tubing, and a simple flow-meter. Other components, including a photomultiplier tube, oscilloscope, microscope, and power supplies, were supplied by the Physics Department at SIUC. Optical mounts, platforms, and flow cells were designed here and constructed in our machine shop.

In the fluid flow experiments, we have been successful in achieving laser-Doppler data for fluids with low particle content. For high particle concentrations, which have the main interest in ER effects, the large amount of random light scattering has so far precluded meaningful data. We are continuing to experiment with different methods of signal analysis, with different optical geometries, and with alternate flow cell designs.

III. Work Planned for Next Year

As stated above, our research in last year has clarified several key issues in this field. However, more important questions remain to be solved.

1. The mechanism of viscosity change of ER fluids. It is very important to understand why the viscosity of ER fluids changes with the applied electric field. Our present state of understanding is incomplete and only qualitative.

In an electric field, dielectric particles have induced dipole moments and tend to align in the field direction. As the liquid suspension is forced to flow, these induced structures of the dielectric particles are continuously being broken and reformed as the system flows. This produces a strain-rate dependent increase viscosity. The excess stress is associated with the need to rupture the electric field induced structure of the dielectric particles, when one has to force a flow. Therefore, ER fluids have a close relationship to the problem of flow in porous media. We need to clarify this relationship.
The transport of polarized particles or polarized liquid molecules in an electric field also has a direct contribution to the increase of viscosity. This contribution has been neglected by most people. On a microscopic scale, viscosity is related to the rate of momentum transport, resulting from thermal rearrangement of particles on a local scale, hopping into vacant neighboring positions, interchange of two neighbor particles etc. Therefore, the transport of polarized particles or polarized molecules certainly has a direct contribution to the viscosity of the whole ER fluids. From the studies of amorphous materials, under a certain condition, this second contribution may play an important role.

We intend to undertake this task by combining experiments, analytical work, and computer simulations together.

2. Define order parameters for ER fluids. From the theory of critical phenomenon, it is well known that the order parameters are the key quantities to specify the many-body system in the study of phase transition. Since we have clarified the structure of induced ER solid, we have a clear way to define the order parameters. We will first use the defined order parameters to do Monte Carlo simulation. Meanwhile, we will perform necessary experiments to examine the phase transition and compare the results with theoretical predictions.

3. The Fluid Dynamics of ER Fluids. Fluid dynamics of ER fluids are important. It is immediately apparent that the fluid dynamics of these ER fluids are not simply that of a viscous Newtonian fluid. In the presence of a field, they behave like a Bingham plastic with a field dependent excess shear stress over that of the fluid with no field. In addition to the liquid, there are particles of micrometers size. Under an electric field, there are also interactions between the dielectric particles which can be approximated as dipole-dipole interactions.

We will use the set-up of laser-Doppler experiments to study fluid dynamics of ER fluids and apply classical many particle dynamics to do computer simulations, then compare the experimental results with the theoretical ones.

4. Use our set-up of video microscopy to perform experiments on ER fluids. We will complete assembly of the system (with improved illumination and a universal CCD mount); make a new ER cell where the "thickness" of the liquid is about 0.5 mm for better transparency; and start studying the structures
formed in ER fluids. We will investigate

- the effects of particle size
- the effects of quid dielectric constant
- the effects of liquid viscosity
- evolution of structure under flow
- structures under a stress below the yield stress

5. The ER response in applied ac fields. The ER effect in an ac field is an important but unclear problem now. We will first extend our theory by replacing the d.c. dielectric constant by the a.c. dielectric constant. Meanwhile, we will perform experiments to study this problem. Since the ER phenomenon is related to polarization and aggregation induced by this polarization, it takes a small but finite amount of time. Obviously, therefore, the ER effect cannot exist for all frequencies of the applied fields. For example, if the frequency of field $\omega >> 1/\tau$ where $\tau$ is the relaxation time of the polarization, the ER effect may vanish. But it is unclear whether this change is smooth or rapid. Since the ac ER effect will have many important applications, we will carefully investigate this issue next year.

6. Dependence of $E_c$ and yield stress on particle-size. This issue will be addressed in the very near future for a number of reasons. Our theory predicts that $E_c$ is inversely proportional to the square root of the particle volume, if everything else remains constant. Thus as technology forces us to go to smaller particles, $E_c$ which is now in the comfortably small range of about 2 kV/cm, will increase and appear in the typical working window of most ER devices. An effect that has always been ignored will dominate the scene. Indeed, some experiments have confirmed this “difficulty of seeing the ER effect in smaller particles”. This increase of freezing field for smaller particles that comes out quantitatively in our picture, can be qualitatively explained to the engineering community in terms of the increasing role of Brownian motion for smaller particles, in disrupting the structure induced by the electric field.

We will study and quantify the dependence of $E_c$ and the yield stress as a function of $E$, for specially engineered ER formulations that have a tightly
controlled and characterized particle size distribution. An equally important byproduct of these experiments with particles having a narrow size-distribution, will be the ability to address issues of phase-transition more reliably. A wide distribution of particle volume $v$ may result in an accompanying distribution of $E_c$. In particular the variation of dynamic quantities like low frequency elastic loss moduli or flow-dependent dielectric losses can get washed out. A number of commercial vendors have started supplying particles with controlled size distribution.

7. **Pursue our work on ER fuels.** As mentioned early, we will continue to pursue our work on ER fuels. We will focus on two approaches: (1) Investigate the liquid-liquid, bi-phasic systems for possible ER effect. This will be petroleum fuel mixed with ethanol, methanol, or glycerine. Gasoline, kerosine, diesel, all have dielectric constant close to 2. Ethanol, methanol, and glycerine have dielectric constant 25.7, 33.7, and 45.8 respectively. From our theory, we expect that this kind of mixed fuel will show an ER effect. On the other hand, because the ER effect is inverse to the size of dielectric particles in the liquid, these mixed fuels will have a very weak ER effect if the particles of ethanol, methanol, or glycerine in petroleum fuels are of molecular size. We will build an air-tight ER flow cell to do the experiment and see how the viscosity of the mixed fuel increases with an electric field. If the effect is too weak, we will examine any possible way to increase the size of ethanol particles in petroleum fuels. (2). Metallic powders in liquid oxygen. Liquid oxygen and aluminum powders are an important liquid fuel. From our experiment with aluminum powders in oil, we believe that this liquid fuel is an ideal ER system. Liquid oxygen has a very low dielectric constant, 1.465. Aluminum powders, though having oxidized films, still have a very high dielectric constant. We will build an air-tight cryogenic cell to test a suspension of aluminum powders in liquid nitrogen. To reduce the problem of density mismatch, we may make finer aluminum powders to let them suspend in liquid nitrogen longer. The experiment will examine the change of viscosity of the suspensions and see the condition for solidification.

8. **Study the structure of ER fluids in different electric fields.** We have found that the ideal structure of ER fluids in a uniform parallel electric field is a body-centered tetragonal lattice. There are more to be learned about
the relationship between the structure of ER fluids and the structure of applied electric field. If the applied electric field is not parallel, what would the ideal structure of ER fluids? We plan to study this by computer simulation. The computer simulation will take several hundred dielectric particles in an applied electric field. The induced electric dipole moment of each particle will depend on the strength of the electric field and the configuration of particles. There is dipolar interaction between particles.

We will use Monte Carlo simulation to find the structure of ER fluids. The simulation will use the variational method and some other techniques. It will start from one possible configuration to calculate the energy of the system, then move to a "neighboring" state picked randomly and compute the change of the total energy. If the energy gets lower, the trial is successful and the old state is replaced by the new one. Otherwise, the original state is retained in future trials. After each Monte Carlo trial in this way, one has a state having an energy lower or equal to the previous one. This procedure will be iterated until the lowest energy state is reached. After getting the lowest energy state, we plan to calculate the correlation function and study its physical properties, such as shear modulus, elastic properties, and phonon spectrum, which will provide information about the properties of the field induced solid phase.

9. Optimal Structure of Applied Electric Field. After understanding the relationship between the structure of ER fluids and the structure of applied electric field, we will seek the optimal structure of electric field to yield a strong ER system. If the induced ER solid has a similar structure as polymer chains, then the strength is greatly enhanced. This may need a combination of one DC electric field and one low AC field.

This task needs us to solve the "inverse" problem. First, we need to consider a best polymer-like structure which produces a strong yield stress, then we go back and see what is the necessary structure of an applied electric field to produce this structure.

After we find a way to produce polymer-like ER solid, we will study the physical properties of the ER fluid. What is the basic excitation in ER fluids? How is the yield stress? How does the viscosity change with the electric field? What
about elastic modulus and shear modulus? These questions will be investigated.

IV. Invited Papers Presented at Conference


V. Invited Seminars

- “Physics of Electrorheological Fluids”, Univ. of Illinois at Urbana-Champaign, Feb. 15, 1991.

- Purdue University, W. Lafayette, IN: Sept 14, 1990

- Southern Illinois University, Carbondale, IL: Sept 28, 1990

- Clark University, Worcester, MA: Nov 13, 1990

- Wayne State University, Detroit, MI: Dec 10, 1990

- University of Michigan, Ann Arbor, MI: Dec 11, 1990

- Harvard University, Cambridge, MA: Jan 9, 1991

- University of Rhode Island, Kingston, RI: Feb 15, 1991


- NIST, Gaithersburg, MD: Feb 25, 1991

- Illinois Wesleyan University, Bloomington, IL: Mar 7, 1991

VI. Papers at Professional Society

VII. Publications with Acknowledgement to ONR


VIII. Papers Submitted

1. R. Tao, "Phase Transition in Electrorheological Fluids" (submitted).