Studies on Two-Phase Electrorheological Fluid

By

Tam Kwan Leung, B.Sc

A Thesis Presented to
The Hong Kong University of Science and Technology
In Partial Fulfillment
Of the Requirement for
The Degree of Master of Philosophy
In Physics

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Abstract

Electrorheological (ER) Fluids, consisting of dielectric particles dispersed in insulating fluids, are a class of materials whose rheological properties are controllable by the application of an electric field. This unique property has great potential applications in various fields. In this thesis, I report measurements of shear modulus and static yield stress of two-phase ER-fluids obtained by mixing nano-sized Lead Zirconate Titanate (PZT) particles with micron-sized (~55μm) glass spheres. It is found that the shear modulus of the two-phase ER-fluids, overall, decreases with increasing frequency of the applied electric field. More importantly, soft-mode-like dips as predicted by first-principle calculations are observed for some particle ratios and volume fractions. In contrast to the mono-dispersed glass ER-fluids the static yield stress of the two-phase ER-fluid is found to increase with increasing frequency of the applied electric field. Furthermore, the structures of the ER-fluids observed by optical microscope are found to be frequency dependent.
CHAPTER 1

1.1 Introduction

Electrorheological Fluids (ER – Fluids), often called “Smart Fluids” or “Intelligent Fluids”, have been a hot topic because of their potential applications in various fields. They are formed by dispersing micron-sized dielectric particles in insulating fluids. The unique properties of ER-fluid is that the rheological properties are controllable such that the fluid change in milliseconds from a free-flowing liquid to a ‘semi-solid’ when exposed to an external electric field and instantly back to a liquid when the field is removed. In the liquid state, the ER-fluid exhibits an apparent viscosity which can be increased by orders of magnitude by the application of an electric field. In the solid state, it is visco-elastic with complex moduli that has strong dependence on the electric field.

Electro-rheological phenomenon was first observed by Duff [1] in the late 1800’s. However, the effect was not recognized until one and half decade later. In 1947, Willis M.Winslow obtained the first patent reporting the phenomenon of electrorheology whereby a suspension of fine polarizable particles in an insulating liquid undergoes orders of magnitude increase in the viscosity upon the application of an external electric field. Such effect is now called the “Winslow effect”. [2, 3]

Recently, ER-fluids are studied in different directions. Some works are on
technical applications [4], some concentrate in explaining the structure formation of the fluids in order to find out the mechanism behind the phenomenon [5]. Some try to find new ER materials to increase the strength of the fluids for scientific studies or application purposes [6].

Most researchers focus their studies on semi-mono-dispersed ER-fluids, since they are simple and can be compared with theories. In order to understand more about the properties of ER-fluid, our research group has been studying bi-dispersed (two-phase) ER-fluids (ER-fluids that contain particles of two different materials and sizes). In their researches, the yield stresses of two-phase ER-fluids with different particle ratios and volume fractions have been studied and enhancements of yield stresses are observed at certain particle ratios for fixed volume fractions and frequency of the applied electric field. In this project, I study the electric field frequency dependence of two-phase ER-fluids. In addition, static yield stress, shear modulus and the structures of the two-phase ER-fluids are studied.

1.2 Background

In the following, I firstly explain some basic ideas of mono-dispersed ER-fluids (contain only one size of same material particles) in order to understand our project.

When E-field is applied to ER-fluid, fibrous structures are formed in the direction of the field. The development of columnar structures can be divided into three steps: [7,8]
Figure 1.1a  Random Dispersion

Figure 1.1b  Single Chaining

Figure 1.1c  Columnar Structure
1) Random Dispersion: (Figure 1.1a)
   When no electric field is applied, ER-fluid behaves as Newtonian flow. Particles move freely and are randomly distributed inside the fluid.

2) Single Chaining: (Figure 1.1b)
   When low electric field is applied, particles are aligned in the short chains [9].

3) Columnar structure: (Figure 1.1c)
   When high electric field is applied, single chains will combine with the other chains nearby and start to form thick columns. ER fluid is changed to Bingham behavior [9], i.e. the fluid behaves as a solid until certain threshold of stress is exceeded.

The formation of chain can be explained by dipole-dipole interaction [10]. When an ER particle is under an electric field, the particle is polarized as shown in figure 1.3: [11]

![Figure 1.3 Polarized particle](image-url)
Considering the case of interaction between charged particles, see figure 1.4 [10], the particles attract if a line connecting the two particles is within 55 degrees of the vertical, otherwise, they repel.

![Diagram of charged particle interaction](image)

Figure 1.4 Interaction between charged particles

Once E-field is applied, their positive and negative poles are all align towards the electrodes and in the same direction. Thus, particles line up end to end successively and the chains are formed.

From above explanation, we may expect that individual chains would repel one another. However, the fact is that parallel chains tend to combine as the system equilibrates to form thicker chains or columns. It is because a particle is attracted to
or repelled from a neighboring chain not only by the force from the few nearby chained particles but also by the force from many distant particles and their image charges in the chain [figure 1.5].

![Diagram showing attractive and repulsive forces between charged particles](image)

**Figure 1.5** Process of forming column

Columns stay together because the dipolar force is long-range, and particles respond to the sum of forces from all other dipoles in fluid. Then, thick column is formed. (figure 1.6)

![Image of a column formed by particles](image)

**Figure 1.6** The column formed by particles
To lower the interaction energy would mean the re-arrangement of the solid particles into a periodic structure, i.e., a solid. Based on the dipole-dipole interaction model and later by a first-principle approach, the lowest energy periodic structure to be that of body-centered tetragonal (BCT) [12]. The columns seen during the application of the electric field represent the superstructure built up from the locally BCT-ordered particles.

However, dipole-dipole approximation has some limitations. For examples, the dipole-dipole give good approximation only when two particles are far apart and higher order multi-pole interactions also need to be considered when particles are in the position within a distance of \( r_d \) of another one [13]. Moreover, no ER- properties can be observed when the polarization of the particles is the same as the fluid [14] and the dipole-dipole approximation cannot be used for bi-dispersed particles.

As dipole-dipole approximation cannot be applied in bi-dispersed ER-Fluid. We will use first-principle calculation to model the two-phased ER-fluid by reducing it into, effectively, a mono-phased ER-fluid model.
CHAPTER 2

Studies on Electrorheological Fluids in the Past

ER-fluids have been studied in different directions in the past, for both scientific studies and application purposes. In general, the studies can be classified into four categories:

1) Material Technology:

Controllable of fluids, temperature dependent of yield point, polarization, structuring, rheology and different dielectric constant particulate materials on ER – Fluids. For example, Dr. G. P. Quist and Dr. F. E. Filisko studied the ER suspensions with ER active matrix liquids. Dr. R. Tao studied the electrorheological effect at cryogenic temperature [5].

2) Physical Mechanism:

E-field induced phase separation and structure in ER-fluids, conduction model of ER-effect, simulation of solid structure formation, light scattering studies of different model of ER-fluids. For example, Dr. H. Conrad studied the conductivity in electrorheology. The interaction between two spheres in silicone oil under an electric field was investigated by Dr. Y.R. Wang [5].
3) Properties

Viscoelasticity, fluid flow, yield stresses of ER-fluids, dynamic of structure deformation, pressure responses, static rheological properties of ER-fluids, influence of particle size and the solid concentration on ER-fluids, electrostatic interactions for particle in ER-fluids.

For examples, two experimental methods, a dielectric spectroscopic technique and a channel flow technique, have been found to provide reasonable estimates of an ER fluids response time by K. D. Weiss and J. D. Carlson [6].

4) Application

Application of ER-fluid in shock absorbers and clutches, Bingham plastic analysis of ER valve flow, on-off excitation switch for ER devices, selection of commercial ER devices, simulation and experimental studies of semi-active suspensions.

For examples, Zheng Lou applied the technique to provide high speed ER Clutch [6].
CHAPTER 3

Motivation

In previous chapters, we have already revised the different fields of studies on ER-fluid. We have no difficulty finding it most researches focused on studying mono-dispersed ER phenomenon, as it is simple and can be explained easily by theory. However, in practice, ER- fluids may contain particles with different sizes. Therefore, practical ER-fluids cannot be classified as mono-dispersed, but bi-dispersed or even multi-dispersed.

Our research group members have been investigating bi-dispersed ER-fluid for several years. They studied different kinds of particles in different solid / liquid volume fractions. They discovered the enhancement peaks at certain nanoparticle / microparticle ratios for fixed solid / liquid volume fractions. Moreover, they used a unified framework of first-principles calculation to explain the results instead of using dipole-dipole approximation which has many limitations. By the first-principles calculations, soft modes were found at some specified frequencies when static shear moduli of the ER-Fluids were calculated [15].

In our research, we focus on studying the frequency dependence of the bi-dispersed ER-fluid. We add ferroelectric nanoparticles of Lead zincate titanate (PZT) of size ~0.1μm to ER-fluids consisting of 55μm glass spheres. We apply ac
electric field at fixed voltage. The frequency of electric field ranges from 60hz to 4000hz. Static yield stress and shear moduli of ER-fluids are measured at different nanoparticle / microparticle ratios with different solid / liquid volume fractions. On the other hand, we try to study whether the soft mode exist or not in the experimental results.
CHAPTER 4

Theoretical model of Dielectric Electrorheology

In this chapter, we present a general framework for the first-principles of the frequency dependent shear moduli, static yield stress, and the structures of dielectric electrorheological systems [15].

4.1 Mono–dispersed DER Theory

Consider a mono-dispersed Dielectric Electrorheological (DER) system consists of 2 parallel plates where the separation of the plates is $L$, dielectric constant $\varepsilon_p$ particles and dielectric constant $\varepsilon_f$ fluid. As the electric field is applied perpendicular to the parallel plates $\varepsilon_{zz}$ is the effective dielectric tensor along the field (Z) direction.

Since the operating frequencies of ER-Fluids are generally $<10^4$ Hz and the typical particle size and the separation of the ER- fluids are $< 10^{-2}$cm, we can consider the system which are in the “electrostatic limit” or “long-wavelength limit”, by a comfortable margin [16]. Thus, the electrostatic free energy density of the system is $-\left(\varepsilon_{zz} E^2 \right) / 8\pi$, where $\varepsilon_{zz}$ is the effective dielectric tensor along the field and $E$ is the applied electric field that can be written as $E = \Delta \phi / L$ (V/mm), where $\Delta \phi$ is the voltage difference and $L$ is the separation between plates.
An integral equation for the electric potential $\phi$ is defined as

$$
\phi = \frac{-Z}{1 - \Gamma / s}
$$

Eqn : 4.1

where parameter $s = \epsilon_f / (\epsilon_f - \epsilon_p)$ and the linear integral operator $\Gamma$ is defined as :

$$
\Gamma \phi = \int dV' \theta(\vec{r}') \nabla' \Gamma(\vec{r}, \vec{r}') \cdot \nabla' \phi(\vec{r}')
$$

Eqn : 4.2

where $\Gamma(\vec{r}, \vec{r}')$ is the Green’s functions of Laplace operator

By defining the inner product operation,

$$
\langle \phi / \Psi \rangle = \int dV \theta(\vec{r}') \nabla \phi^* \cdot \nabla \Psi
$$

Eqn : 4.3

The effective dielectric constant can be obtained after some calculation,

$$
\frac{\epsilon_{\text{eff}}}{\epsilon_f} = 1 - \frac{1}{V} \sum_{m,n} \frac{\langle z | \phi_n \rangle^2}{s - s_n}
$$

Eqn : 4.4a

or

$$
\frac{\epsilon_{\text{eff}}}{\epsilon_f} = 1 - \frac{1}{V} \sum_{m,n} \langle z | \Psi_n \rangle \langle \Psi_n | \frac{1}{s - \Gamma} | \Psi_m \rangle \langle \Psi_m | z \rangle
$$

Eqn : 4.4b

or

$$
\frac{\epsilon_{\text{eff}}}{\epsilon_f} = 1 - \sum_{n} \frac{f_n z}{s - s_n}
$$

Eqn : 4.4c
where \( f_n^z = \frac{|\langle \phi_n | z \rangle|^2}{V} \)  

Eqn : 4.5

Details of calculation are shown in Appendix B.

The remarkable feature about equation 4.4 is that the geometric information \( f_n \) is completely separated from the material information \( s_n \). The function \( f_n^z \) in equation 4.5 provides the micro-structural information and the eigenvalue \( s_n \) in equation 4.4 provides the location of the poles. Both of them are real and \( s_n \) must lie in the interval [0,1] [17]. Moreover, equation 4.4 includes all multipole interactions and local field effects.

The feature makes us easier to calculate the effective dielectric constants \( \varepsilon_{zz} \) once the eigenfunctions and eigenvalues of \( \Gamma \) in the equation are known.

BCT (body-centered tetragonal) is found to be the favored structure which is in agreement with prior calculations based on dipole interactions [18] and some rigorous approach [19, 20]. The shear stress and shear modulus can be calculated by perturbing the system away from its ground state by applying a shear deformation to the system. For the BCT structure under the shearing in a direction perpendicular to the z-axis, the c axis is tilted by an angle \( \theta \) with respect to the applied field direction. Then, the stress strain relation is \( \frac{\partial f}{\partial \theta} \) versus \( \theta \), where \( \frac{\partial f}{\partial \theta} = \frac{\partial \varepsilon_{zz} (\theta)}{\varepsilon} \frac{\partial \theta}{\partial \theta} \). The maximum stress value is defined as static yield stress and the stress decreases with increasing strain beyond the yield point.
For the small $\theta$, $\varepsilon_{\infty}(\theta)$ may be expanded about its optimal value as:

$$\text{Re} \left[ \frac{\varepsilon_{\infty}(\theta)}{\varepsilon_f} \right] = \text{Re} \left[ \frac{\varepsilon_{\infty}(0)}{\varepsilon_f} \right] - \frac{1}{2} \mu \theta^2 + \ldots$$

Eqn : 4.6

where $\mu$ is the shear modulus in units of $\frac{|\varepsilon_f|E^2}{8\pi}$

Then, the shear modulus $\mu$ can be expressed as:

$$\mu = \text{Re} \left\{ \frac{2\rho e_f}{|\varepsilon_f|\rho_0(0)} \left[ F_1(s) - F_2(s) + \frac{\partial F(s)}{\partial(\theta)} \right]_{\theta=0} \right. $$

$$ \left. + \frac{\rho}{3\rho_0(0)} \left[ \frac{\varepsilon_{BCT}(0) - \varepsilon_f}{\varepsilon_f} \right] \right\}$$

Eqn : 4.7
where \( \varepsilon_{BCT}(\theta) \) represent the dielectric constant of the BCT structure when \( \theta = 0 \)

\[
F_i(s) = \frac{\langle x | \frac{1}{s - \Gamma} | x \rangle}{V}
\]

\[
F_z(s) = \frac{\langle z | \frac{1}{s - \Gamma} | z \rangle}{V}
\]

Once the spectral function is obtained, it is simple to evaluate the effective
dielectric constants, static yield stress, shear modulus and their frequency dependencies.

Figure 4.2 and 4.3 show the comparison between measured and calculated
frequency dependent static yield stress and shear modulus for specify volume fraction
ER-fluid.

![Graph showing comparison between measured and calculated static yield stress](image)

Fig 4.2: Comparison between measured (solid symbols) and calculated (solid lines) frequency dependent
static yield stresses for 22% by volume of 1.5\( \mu \)m glass spheres dispersed in silicon oil on 1.32kV/mm.
A and B denotes the system after and before water removal.
4.2 Assumptions of Two-phased ER-Fluid.

Since the structures of the particles in two-phased ER-Fluids are still not known thoroughly, it is impossible to perform exact calculations. Thus, we use an empirical approach and assume the nano-particles as passive components which modify the dielectric constants of the liquid and the glass spheres [21, 22, 23], attached to the glass particles.

To simplify the two-phased problem to one-phased problem which can be solved by the mono-dispersed DER model, we assume some of the nano-particles attached to the glass particles and the rest are dispersed in the fluid. Therefore, we firstly...
calculate the amount of nano-particles sticking on the glass sphere, and then use
equation 4.4 to model the problem. We assume that the nano-particles change the
dielectric constant of the oil, use first principle to calculate, the effective dielectric
constant by modeling new fluid and new glass sphere are calculated [24].

The fraction of nano-particles $\psi$ attached on the glass spheres is assumed to be a
function of the solid ratio $\theta$ and the solid/liquid volume fraction $\phi$ given as:

$$
\psi = A \chi^b \exp \left[ \frac{b(1-\chi)}{B} \right] \quad \text{Eqn : 4.8}
$$

where

$$
\chi = \frac{1-\theta}{2} \quad \text{Eqn : 4.9}
$$

and

$$
b = \frac{1}{(2\phi)^2} \quad \text{Eqn : 4.10}
$$

A and B are fitting parameters in this model. Figure 4.4 shows the results of the
function for the PZT nano-particles and glass sphere [21]. The value of function $\psi$
increases from zero to a maximum value of 0.84 as $\chi$ changes from 0 to 1. The
maximum value 0.84 is actually the fitting value of A. The physical meaning of the
parameter is that nearly 84% of nano-particles attached on the glass sphere while nearly
all particles in the fluid are nano-particles.

From figure 4.4, we can observe another feature that the fraction of particles
coating on the glass is proportional to the numbers of micron-particle, i.e. when the
concentration of the nano-particles in the fluid decreases, the percentage of the
nano-particles attached to the glass become lower.

![Image](image-url)

Figure 4.4 $\chi$ vs $\Psi$ for PZT-glass ER system with $A=0.84$ and $B=1.5$ in Eqn. 4.8 for different solid/liquid volume fractions.

On the other hand, we find that the curves change from nearly linear to concave upward as the volume fraction of the fluid shift to become lower, i.e. fewer nano-particles can be coated in our modeling.

For the fitting process, value of $\theta$ and $\phi$ are put into equation 4.4 and equation 4.10 to calculate the values of $\chi$ and $b$, then put the results into equation 4.8 with different fitting parameters $A$ and $B$. As we need to find the effective static yield stress and static shear modulus of the bi-dispersed, we used the mono-dispersed DER theory twice
using equation 4.4. Firstly, we consider that only nano-particles are added to the oil. We assume that the nano-particles change the dielectric constant of the oil. We use first principle one more time to calculate the effective dielectric constant by modeling new fluid and new glass sphere. Finally, we can use the effective dielectric constants to calculate the static shear stress and static shear modulus.
CHAPTER 5

Experimental Outline

5.1 Setup

The experimental setup is shown as figure 5.1, 5.2 and 5.3. The setup consists of four main components: RT-20 Rheometer by Haake, electricity power supply, refrigerated bath circulator and computer to control the rheometer.

RT-20 rheometer, equipped with plate-plate sensor system, is used to measure the shear stress of the fluid where the upper plate rotates and the lower plate is stationary. The computer system controls the applications of the rheometer. The electricity power supply, consisting signal generator and voltage amplifier, applies different voltages with different frequency. The refrigerated bath circulator keeps the temperature constant during the experiment.

Figure 5.1 Rheometer
Figure 5.2-5.3 Experimental Setup

Power Supply: Consisting amplifier, Signal generator.

Computer to control rheometer

Refrigerated Bath Circulator

Conducting Upper plate

ER-Fluid

Stationary Lower plate

Shift up/down switch

rheometer

Signal Generator

Computer to control rheometer

amplifier

Power box
5.2 Device Structure

Shear induced flow in ER-Fluids can occur in 2 model cases: [25]

I ) Flow in the annular gap between two concentric cylinders

- When one of the two is assumed to be stationary while the other can rotate. This flow can be understood as the displacement of concentric layers situated inside of each other. A flow of this type is realized for example in sleeve bearings and in rotational rheometers with coaxial cylinder sensor systems.

II ) Flow between two parallel-plates or between cone-and-plate sensor systems of rotational rheometers

- When one of the two is stationary and the other rotates. This model resembles twisting a roll of coins causing coins to be displaced by a small angle with respect to adjacent coins. This type of flow is caused in rotational rheometers with the samples placed within the gap of parallel-plate or cone- and - plate sensor systems.

In our experiment, we used parallel plate-plate sensor systems.

Figure 5.4 Parallel plate geometry
Figure 5.5  The rotational disks and ER-fluid container

As we use both 50μm glass particles and nano-particles in the experiment, the particles are easily sink to the bottom if concentric-cylinders sensor system is used and the reading of the measurement will drop dramatically. The parallel plate-plate sensor is used because the particles can still maintain within the effective capacity even if the particles sink. We can also consume less samples compared with using concentric- cylinders sensor system. Moreover, we can enlarge or reduce shear stress reading by changing the diameter of the plates. In our experiments, a PP60ER disk ( 60mm length in diameter ) is used. The only disadvantage is that the measuring uncertainty us a little bit larger compared with concentric – cylinder sensor. The Plate – Plate measuring error is shown in section 5.5.
5.2.1. **Plate – Plate Sensor System**

The plate–plate sensor system is determined by the plate radius and the variable distance between the stationary and the movable plate. This distance should not be smaller than 0.5mm and not larger than 3mm as other measurement errors, depending on the substance, could be experienced.

\[ R = \text{Plate Radius} \]
\[ h = \text{Distance} \]

![Diagram showing Plate Plate Sensor System](image)

Figure 5.6   Geometry of Plate-plate Sensor Systems

The distance of the plate should be at least three times larger than the largest particle contained in the substance. The plate-plate sensor system must be very carefully filled in order to minimize measurement errors. Both, too low a filling and too high a filling will cause measurement errors.
\[ R = \text{Plate Radius} \]
\[ h = \text{Distance} \]
\[ R_{\text{eff}} = \text{effective Radius} \]

![Diagram](Figure 5.7 Effective radius of plate-plate sensor)

**Calculation Equations**

**Shear Stress** \( \tau \)

The shear stress \( \tau \) is proportional to the torque \( 'M_d' \) and to the stress factor \( 'A' \).

\[ \tau = A M_d \quad \text{(Pa)} \quad \text{Eqn 5.1} \]

The factor \( 'A' \) is calculated as described in the following equation. It has the unit of an inverse volume:

\[ A = \frac{2}{\pi R^3} \quad \text{with} \quad R = \text{Plate Radius} \quad \text{Eqn 5.2} \]

**Shear Rate** \( \dot{\gamma} \)

The shear rate \( \dot{\gamma} \) is proportionally linked to the angular velocity or speed and the shear factor \( F \).

\[ \dot{\gamma} = F \Omega \quad \text{Eqn 5.3} \]
The angular velocity \( \Omega \) is calculated according to \[
\frac{2\pi n}{60}
\] where \( n \) is revolution/min.

The factor ‘\( F \)’ is calculated as follows:

\[
F = \frac{R}{h}
\]

with \( R=\) Plate Radius \hspace{1cm} \text{Eqn 5.4}

\( h = \) set distance

**Deformation \( \gamma \)**

The deformation \( \gamma \) is linearly linked to the angular deflection and the shear factor \( F \).

\[
\gamma = F \varphi
\]

with \( \varphi = \) Torsion Angle rad \hspace{1cm} \text{Eqn 5.5}

The following conversion equation should be applied:

\( 1 \text{ rad} = 57.296 \text{ deg.} \) \hspace{1cm} or \hspace{1cm} \( 1 \text{ deg.} = 0.0174 \text{ rad} \)

The parallel-plate model helps to define shear stress:

![Diagram of flow between two parallel plates](image)

**Figure 5.8 Flow between two parallel plates**
5.3 Preparation of Samples

In our experiment, “bare” ER-fluid were made by using glass particles (size range from 53 - 58μm in diameter) dispersed in silicon oil (Purchased from Edwards, model 705). Then, the nano-particles Lead Zirconate Titanate EC63-PZT (around 0.1 – 0.2μm in diameter) were added on the fluid and mixed to form two-phased ER-fluid. Both two kinds of particles were placed inside oven and heated to 140 °C for several hours in order to remove the trace water inside particles.

Volume fraction \( \phi \) of the glass and PZT particles in oil is calculated by their corresponding density, where the specific density of glass is 2.5g/cc, the specific density of PZT is 6.83g/cc and the density of silicon oil is 1.09g/cc.

\[
\text{Volume Fraction: } \phi_v = \frac{V_s}{V_i} = \frac{V_{PZT} + V_g}{V_i} \quad \text{Eqn 5.6}
\]

where \( V_s \) is volume of solid (volume of PZT particles \( V_{PZT} \) plus volume of glass particles \( V_g \)) and \( V_i \) is the volume of the oil.

When we considered the mass fraction, the equation is shown as:

\[
\text{Mass Fraction: } \phi_M = \frac{M_s}{M_i} = \frac{\rho_s V_s}{\rho_i V_i} = \rho_s \frac{\phi_v}{\rho_i} \quad \text{Eqn 5.7}
\]

where \( M_s \) is the mass of the solid (mass of glass plus PZT particle), and \( M_i \) is the mass of the silicon oil.
Another parameter which we will use is defined as particle ratio $\theta$:

\[
\theta = \frac{V_g - V_{PZT}}{V_g + V_{PZT}} \quad \text{Eqn 5.8}
\]

From equation 5.6 and equation 5.7, for a given $\phi$ and $\theta$, the mass of glass and mass of PZT particles used can be deduced as:

\[
M_g = \frac{\rho_s \phi (1 + \theta) M_l}{2\rho_l} \quad \text{Eqn 5.9a}
\]

and

\[
M_p = \frac{\rho_p \phi (1 + \theta) M_l}{2\rho_l} \quad \text{Eqn 5.9b}
\]

The deduction of the equation 5.9 is shown in Appendix C.

With this information, bi-dispersed ER-fluids for different $\theta$ and $\phi$, can be prepared by simply weighting the corresponding parts by Eq.5.9a and b.

### 5.4 Experiment Procedure

In our experiment, we used plate-plate sensor system. The system was first set to zero gap. Then, the plate was moved up. The ER-fluid was mixed well and then placed uniformly on to the lower stationary plate. The gap spacing between the upper and the lower plates was fixed to 1mm. We needed to estimate the exact volume of gap spacing and fill on right amount of ER-fluid, since too little fluid would reduce the stress of the of the fluid produced and too much fluid would cause "edge effect" which enlarge the reading of the measurement. The correct filling is shown on figure 5.7. Finally, all wires were connected and the signal generator was turned on.
Then measurements were performed for different volume fraction, different particle ratio of ER-fluids using an AC electric source at different amplitudes and frequency. The temperature was kept at 25°C by a bath circulator.

5.5 Plate – plate measuring errors

Significant measuring errors can result when using plate/plate sensor system if:

i) the correct gap between the plates is not observed.

ii) filling is not carried out correctly.

Both errors can be estimated quantitatively:

1. Plate/plate gap error (figure 5.9)

If the desired gap $h$ which is set at the rheometer is not observed, the following measuring uncertainty results:

$$\text{Measuring uncertainty} = \frac{\Delta h}{h} = 0.05\% \quad \text{Eqn 5.10}$$

Such uncertainty is very tiny and can be neglected.
2. **Plate/plate reduced effective radius error** (figure 5.10)

If a plate/plate sensor system is insufficiently filled or the gap empties itself during a measurement, significant measurement errors can result. This condition of insufficient filling can be referred to as a reduced effective radius error and is characterized by a reduction in the effective radius.

\[ R = \text{plate radius} \]
\[ h = \text{gap} \]
\[ R_{\text{eff}} = \text{effective radius} \]

Viscosity measuring

\[
\text{Uncertainty} = 1 - \frac{R^4}{(R - x)^4} = 1.3\% \quad \text{Eqn 5.11}
\]

The details of calculations of uncertainty can be referred to Ref [26].
CHAPTER 6

Measurement of Shear Modulus G and Yield Stress

6.1 Shear Modulus G

6.1.1 Static Shear Modulus G

According to Hook’s law, we can define Shear Modulus G as:

\[ \tau = G \gamma \]  \hspace{1cm} \text{eqt: 6.1}

\[ \Rightarrow G = \frac{\tau}{\gamma} \]  \hspace{1cm} \text{eqt: 6.2}

where \( G \) is the shear modulus
\( \tau \) is the shear stress
\( \gamma \) is the deformation or strain

Shear Modulus G is defined as the resistance of a solid against being deformed.

6.1.2 Dynamic Shear Modulus G*

The dynamic shear modulus \( G^* \), defined as follows, is very useful when we study the visco-elastic behavior of the samples by dynamic tests. [27]
Fluid viscoelasticity is usually described in terms of the response of the fluid to a sinusoidal shearing strain, where the shear strain is given by:

\[ \gamma(t) = \gamma_0 \sin(\omega t) \quad \text{eqn: 6.3} \]

where \( \omega \) is the frequency of the oscillatory strain
\( \gamma_0 \) is the strain amplitude

If the strain amplitude is sufficiently small, the shear stress is also sinusoidal and is given by:

\[ \tau(t) = \tau_0 \sin(\omega t + \delta) \quad \text{eqn: 6.4} \]

where \( \delta \) is the phase angle or mechanical loss angle
\( \tau_0 \) is the stress amplitude

The amplitude ratio is the dynamic modulus:

\[ G^* = \frac{\tau_0}{\gamma_0} \quad \text{eqn: 6.5} \]

where \( G^* \) is the dynamic shear modulus
The dynamic shear modulus $G^*$ can also be described in terms of the storage and loss moduli, where $G'$ is storage modulus and $G''$ is loss modulus.

$$G' = G^* \cos \delta = \frac{\tau_0}{\gamma_0} \cos \delta \quad \text{eqt : 6.6}$$

and

$$G'' = G^* \sin \delta = \frac{\tau_0}{\gamma_0} \sin \delta \quad \text{eqt : 6.7}$$

Combine eqt 6.6 and eqt 6.7, we get:

$$\tau_0 = \gamma_0 \left[ G' \sin (\omega t) + G'' \cos (\omega t) \right] \quad \text{eqt : 6.8}$$

where $G'(\omega)$ is the storage modulus

$G''(\omega)$ is the loss modulus

Finally, the complex modulus $G^*$ is formed. The dynamic modulus $G^*$ can be defined as:

$$G^* = G' + iG'' \quad \text{eqt : 6.9}$$

Note: The term “storage” modulus $G'$ indicates that the stress energy is temporarily stored during the test but that it can be recovered afterwards. The term “loss” modulus $G''$ hints at the fact that the energy which has been used to initiate flow is irreversibly lost having been transformed into shear heat.
6.2 Yield Stress

Isaac Newton expressed the basic law of viscometry describing the flow behavior of an ideal liquid:

\[ \tau = \eta \dot{\gamma} = \eta \frac{d\gamma}{dt} \quad \text{eqt: 6.10} \]

where \( \tau \) is the shear stress

\( \eta \) is the viscosity

\( \dot{\gamma} \) is the shear rate

Fluids in which shear stress \( \tau \) directly proportional to deformation rate are classified as “Newtonian Fluid”.

However, ER-fluids are not this kind of ideal liquid when electric field is applied. They are classified as “Bingham” plastics. The fluid behaves as a solid until certain threshold of stress is exceeded and subsequently exhibits a linear relation between stress and rate of deformation. The threshold point is defined as “Yield Point” and the stress on this point is defined as “Yield Stress”. See figure 6.1 [28].

Experimentally, ER-fluid is often placed between two electrodes with electric field applied. While one of the electrodes is displaced, a shearing force acts on the ER-fluid. Within a range of small shearing force, the columns formed by the particles in the fluid will tilt and stretch, but are not broken. However, the columns will be broken and the E-fluid will start to flow if the force is increased to certain critical value.
Here, we define the "Yield Stress" as the stress at which stationary flow begins.

![Diagram showing shear stress vs deformation rate with Bingham and Newtonian fluids]

Figure 6.1  Comparison of different kinds of Fluids

The appropriate shear stress model is:

$$\tau = \tau_y + \eta \frac{d\gamma}{dt}$$  \hspace{1cm} \text{eqt: 6.11}

where $\tau_y$ is the yield stress

From eqt 6.11, absolute viscosity can be rewrite to:

$$\eta = \frac{\tau - \tau_y}{\dot{\gamma}}$$  \hspace{1cm} \text{eqt: 6.12}
6.3 Method to measure static shear modulus G

In our experiments, control stress mode is selected in order to measure small strain. We set the stress applied in fixed value and measure the deformation $\gamma$ of the ER-fluids. The deformation $\gamma$ will increase slowly and then reach a saturated point as shown in figure 6.2:

![Graph of finding shear strain on constant stress applied](image)

Figure 6.2 Graph of finding shear strain on constant stress applied

From figure 6.2, we can find that the shear strain is 0.0189 in the case. In this example, 4000hz 2000V alternating current was applied. The volume fraction $\phi$ and the particles ratio were 0.25 and −0.75 respectively. The stress $\tau$ applied was kept on 15 Pa.
Then we repeated the experiments with different values and the relative strain values could be obtained. (Note: The stress $\tau$ cannot be set in too large values, otherwise, the chains formed by the particles inside the ER-fluid will be broken and the saturated point cannot be found.)

Recalling the equation 6.2,

$$G = \frac{\tau}{\gamma}$$

From the equation, we find the relationship between the modulus $G$, strain $\gamma$ and the stress $\tau$. In order to measure the Static modulus $G$, we plot a stress $\tau$ against strain $\gamma$ graph and we can get the value of modulus $G$ by measuring the slope of the graph, as shown in figure 6.3.

From figure 6.3, a line passing through origin is drawn. We can find that the slope of the line is 2500, which interprets the value of $G$ in this case is 2500 Pa. In this example, 100hz 2000V alternating current was applied. The volume fraction $\phi$ and the particles ratio were 0.25 and -1 respectively.

Then, the procedures are repeated and we can calculate the values of static moduli $G$ for different conditions.
Figure 6.3  stress $\tau$ against strain $\gamma$
6.4 Method to measure the Yield Stress

To measure the static yield stress, parallel-plates sensor is used. Stress ramps method is used to control stress to ramp up slowly within a range (0 – 500Pa)[29].

When the electrodes are sheared with respect to each other, a finite force is needed before the plates decouple. A stress ramp can be performed to determine the yield point of a sample. When very small stress is applied to the sample, the columns of particles in the fluid will tilt and stretch but not break. The deformation rate is tend to zero at the time due to the solid behavior of the material.

However, when the columns are tilted, the attractive force between the ER particles is diminished, because the columns are no longer aligned parallel to the electric field. As the applied stress increases, the particles will slip out of the zone where they mutually attract when the columns tilt too far, resulting in columns breakage and the fluid will start to flow.

The static yield stress is determined as the point when slipping just occurs between the two plates. If one increases the stress above the yield point, the behavior of the sample will be that of a viscous liquid, showing a considerably larger deformation rate with stress as shown in Figure 6.4.
Figure 6.4  Graph of finding Yield Stress

From figure 6.4, we can find that the yield stress is 213Pa in the case. In this example, 60hertz 2000V alternating current was applied. The volume fraction $\phi$ and the particles ratio were 0.4 and $-0.875$ respectively. The stress $\tau$ applied was ranging from 0 to 250Pa.
6.5 Results

We measured static yield stresses, moduli $G$ of the bi-dispersed ER- Fluids ($\phi = 0.25$), their particles ratios $\theta$ were 0, -0.5, -0.75, -0.875 and -1 respectively for the fixed voltage gap 2000V/mm. The electric frequencies ranged from 60hz to 4000hz. The results are presented in this chapter. Then, the microscopic observations of the ER-fluids will be shown on next chapter in order to study structures and the formation of clusters of fluids.

6.5.1 Results of measuring Static Shear Modulus

Figure 6.5 and Figure 6.6 show the graphs of static shear modulus against different electric frequencies.

In figure 6.5, we keep the volume fraction $\phi$ between the solid particles and fluid on 0.25 and the curves of different glass/ PZT particles ratio $\theta$ are shown. From the curves, we observe that that static shear modulus of the bi-dispersed ER-fluid is strong (applied field) frequency dependence. For the cases of five different particles ratio $\theta$ we measured, the static shear moduli are high in low frequency and decrease when the frequency increases. Comparing the curves of different particles ratio, we can find that such phenomenon is more obvious for higher particles ratio of PZT in the fluid and the static shear moduli decrease as the particle ratio change from -1 to 0.

On the other hand, soft mode like dips can be found. The dips of the static shear moduli appear on different electric frequencies for different particles ratio $\theta$. The dips of the different particles ratio $-1, -0.875, -0.75, -0.5$ and 0 are on 400hz, 550hz, 700hz,
700hz and 1000hz respectively as shown in Figure 6.8. There is a trend that the values of electric frequency on soft modes shift to become larger for the particles ratio from −1 to 0.

From Figure 6.6, the particles ratio is fixed on −0.875. We compare the difference of the shear moduli with different volume fraction (0.25 – 0.40) while the electric frequency applied varies from 60hz to 4000hz. Among the curves of different volume fraction $\phi = 0.25, 0.30, 0.35$ and 0.4, the shear moduli decrease with increasing electric frequencies. Such phenomenon is more obvious for higher volume fraction $\phi$ and shear modulus increases as the volume fraction increases. We can also observe that the shear moduli tend to be saturated at high frequencies (1000hz - 4000hz) when the volume fraction is high ( $\phi = 0.35$ and 0.40 ). On the other hand, soft modes exist on the curves of volume fraction $\phi = 0.25$ and 0.35, but no soft mode is on the curves of other volume fractions.

Figure 6.7a-g show the graphs of static shear modulus against particles ratio $\theta$ for different frequencies (60hz – 4000hz). The figures show that the static shear modulus decreases as the particles ratio changing from −1 to 0 at different frequencies (ranged from 60hz to 4000hz), except figure 6.7d (frequency at 400hz). From figure 6.7d, the value of shear modulus is lower on $\phi = -1$ than $\phi = -0.875$. It is because the soft mode is in the 400hz when $\phi = -1$.

6.5.2 Results of measuring Static Yield Stress

Figure 6.9 and figure 6.10 show the graphs of static yield stress against different
electric frequencies.

In figure 6.9, we keep the volume fraction $\phi$ between particles and fluid at 0.25 and the curves of different glass/PZT particles ratio $\theta$ are shown. We observe that the values of static yield stress become larger as the particles ratio changes from 0 to $-1$. For the curves of the particles ratio $\theta = -1, -0.875$ and $-0.75$, yield stresses increase with increasing electric frequencies (from 60hz to 1000hz) and reach a peak on 1000hz. The values of yield stresses decrease with further increasing frequencies beyond that point. For the particles ratio $\theta = -0.5$, the shape of the curve is similar but the peak shifts to around 550hz. For the particles ratio $\theta = 0$, no peak can be observed and the yield stress increases slightly as the electric frequency increases.

Moreover, form the graph, we observe the peak shifts to larger frequency as the particles ratio shifts from 0 to $-1$.

From figure 6.10, the particles ratio is fixed on $-0.875$. We compare the difference of the static yield stress with electric frequency applied varies from 60hz to 4000hz. From the graph, we observe that the yield stress increases as the volume fraction increases. Moreover, the curves show that the yield stresses of different volume fractions increase with increasing electric frequency.

Figure 6.11 shows the frequency dependence of the yield stress of the mono-dispersed ER-fluid containing glass only ($\phi = 0.35, \theta = 1$). The values of yield stresses are very small ($< 10Pa$) and decreases as electric frequency increases.
Figure 6.6 Static Shear Modulus vs Electric Frequency (Particle ratio = 0.875)
Figure 6.7a  Shear Modulus vs Particles Ratio
(60Hz 2000V Volume Fraction = 0.25)

Figure 6.7b  Shear Modulus vs Particles Ratio
(100Hz 2000V Volume Fraction = 0.25)
Figure 6.7e  Shear Modulus vs Particles Ratio
(700hz 2000V Volume Fraction = 0.25)

Figure 6.7f  Shear Modulus vs Particles Ratio
(1000hz 2000V Volume Fraction = 0.25)
Figure 6.7g  Shear Modulus vs Particles Ratio
(4000Hz 2000V Volume Fraction = 0.25)

Figure 6.8  Frequency (position of dip) vs Particles Ratio
(2000V Volume Fraction = 0.25)
Figure 6.9: Static Yield Stress vs Electric Frequency (volume fraction = 0.25)
Figure 6.10 Static Yield Stress vs Electric Frequency (Particle Ratio = 0.875)
Figure 6.11 Static Yield Stress vs Electric Frequency (glass only)

- Volume fraction = 0.35
- Particles ratio = 1

Static Yield Stress [Pa]

Electric Frequency [Hz]
CHAPTER 7

Microscopic Observation of Cluster Formation of Two-phased ER-Fluid on different electric frequencies

Besides yield stresses and the shear moduli of the ER-Fluids, we also studied the structures of the two-phased ER-Fluids when a.c. voltage with different electric frequencies were applied.

In the experiment, the electrodes were 10mm wide copper plates shock simply glued to glass microscope slides. The electrode spacing was 2mm. A known gap width was used to set the image scale [30].

The fluids used could be divided into containing PZT particles only and both two kinds of particles (50μm glass particles and PZT particles where particles ratio θ = 0) were filled in the gap respectively. We fixed the voltage on 2000V and the electric frequencies ranged from 60Hz to 4000Hz were applied. Then we took photos on different scales in order to study the columnar structures formed by the ER-Fluids when different electric frequencies applied. The PZT particles seen in the optical microscope are indeed aggregate, as optical microscopy does not have sufficient resolution to reveal individual PZT particles.

In the followings, figure 7.1a to figure 7.1f show the structures of the fluids
(containing PZT only, $\phi = 0.05$) when different electric frequencies were applied.
(ranged from 60hz to 4000hz). From the figures, wide views of the structures are shown in order to study the overall patterns of the fluids formed.

Figure 7.2a to figure 7.2f produced higher resolution views in order to study the structures of the fluids and how the particles attracted to each other and how the chains formed on different electric frequencies.

In figure 7.2a (no voltage was applied), the PZT particles randomly dispersed in the fluid. In figure 7.2b (4000hz 2000v applied), we found that the particles were tend to form some chains, however the particles could not move fast enough to follow such high frequencies [19], so just some short chains were formed. Figure 7.2b to Figure 7.2d (4000hz-300hz 2000V), show that when the frequency of the field was decreased further, more clusters grew into chains. However, the phenomenon was not obvious. But when the frequency was decreased to the 100hz (figure 7.2e) or 60hz (figure 7.2f), stable columnar structures were formed under the electric field, the clusters tended to attract each others and held together tightly.

Figure 7.3a to Figure 7.3g, are the microscopic observation of the clusters formations of the two-phased ER-Fluid ($\phi = 0.05$, $\theta = 0$) under different electric frequencies (ranged from 60hz to 4000hz)

Both glass particle and PZT particles were randomly dispersed when no voltage was applied (Figure 7.3a). Same as the case of the fluids containing PZT only, just
few short chains were formed on high electric frequency (4000hz 2000V, figure 7.3b) and more particles grew into chains when the frequency of the field was decreased further. The response of the glass particles seemed to be much less than the PZT particles as they were much heavier in weight.

When the electric frequency was lowered to 100hz (figure 7.3f), PZT particles and the glass particles began to attach each other to form thicker clusters. From figure 7.3g (60hz 2000V), stable columnar structure was formed, clusters containing both PZT and glass particles became several glass particles width thick and became stable.

Here, we focused on studying the arrangements of the two different sized particles to investigate whether they form individual chains or act together to form chains. The nanoparticles fill the interstitial spaces between the microspheres or act together with microspheres randomly.

We just tested one high frequency (4000hz) and one low (60hz) 2000V on the ER-fluids. We used the same concentration ER-Fluid as the previous experiments measuring yield stress, i.e. $\phi = 0.25$ and $\theta = 0$. The results were shown on figure 7.4a to figure 7.4d. The figures showed that the small PZT particles were mixed with large particles and acted together randomly, but not filled in the gap between two particles. However, the images were not two clear as it is very different difficult to view the structures in such high concentration fluid.

Thus, we used more dilute fluid ($\phi = 0.01$) and tried to focus on just few particles.
The range of the electric frequencies used was 60hz-4000hz. The results are shown on figure 7.5a to figure 7.5f. The PZT particles were dispersed randomly around the glass particles when no voltage was applied (figure 7.5a). The PZT particles formed short chains and attached to the glass particles nearby in high frequency (figure 7.5b). More and longer chains were formed as the frequency decreased (figure 7.5b to figure 7.3d). When low frequencies were applied, (figure 7.5c to figure 7.5f, 60hz to 300hz), single short formed by PZT particles combined to form longer and thicker clusters, and the glass particles nearby were also attracted. Two kinds of particles attached together and form meta-table structures.

By the observations, we found that nano- PZT particles were not filled in the interstitial spaces between the chains or clusters formed by glass particles, but mixed together to construct thick clusters.
Figure 7.1a-g
PZT only,
$\phi = 0.05$
Resolution
$= 1.5 \times 10$

Figure 7.1a:
No voltage applied

Figure 7.1b :
4000hz 2000V

Figure 7.1c :
1000hz 2000V
Figure 7.1d:
700hz 2000V

Figure 7.1e:
300hz 2000V

Figure 7.1f:
100hz 2000V
Figure 7.1g
60hz 2000V

Figure 7.2a-f
PZT only,
$\phi = 0.05$
Resolution
$= 4 \times 10$

Figure 7.2a
4000hz 2000V

Figure 7.2b
1000hz 2000V
Figure 7.2c
700hz 2000V

Figure 7.2d
300hz 2000V

Figure 7.2e
100hz 2000V
Figure 7.2f
60hz 2000V

Figure 7.3a-g
θ = 0
ϕ = 0.05
Resolution
= 1.5 x 10

Figure 7.3a
No voltage

Figure 7.3b
4000hz 2000V
Figure 7.3f
100hz 2000V

Figure 7.3g
60hz 2000V

Figure 7.4a-d
\[ \theta = 0 \]
\[ \phi = 0.25 \]

Figure 7.4a
4000hz 2000V
Resolution
= 40 \times 10
Figure 7.4b
4000Hz 2000V
Resolution
= 10 x 10

Figure 7.4c
60Hz 2000V
Resolution
= 15 x 10

Figure 7.4d
60Hz 2000V
Resolution
= 10 x 10
Figure 7.5a-f
60Hz to 4000Hz
2000V
Resolution
= 10 x 10

Figure 7.5a
No voltage

Figure 7.5b
4000Hz 2000V

Figure 7.5c
1000Hz 2000V
CHAPTER 8

Discussion and Conclusion

8.1 Discussion

To understand the strength of ER-fluids in terms of fundamental physical properties and mechanisms, we must first define what we mean by “strength”. Yield stress is generally taken as being representative of the strength of an ER-fluid. Yield stress is defined as the point of stress where the columns break down or collapse and the fluid start to flow. In this project, we also measured the static yield stress of the fluids. On the other hands, we try to measure static shear modulus G to represent the strength of the ER-fluids studied. Although the measurements of shear modulus are difficult and time-consuming, it is more representative for the strength of the ER-fluid.

It is better to use shear modulus rather than the yield stress to represent the strength of an ER-fluid, because the tilt angle of the columns formed by the ER-particles increases from zero to even more than 20 degrees just before the fluid starts to flow while measuring the yield stress. The tilt angle of columns formed by the ER-particles is very small or even tends to zero during the process of measurement and an equilibrium position can be reached. We can consider measurements of the ER-fluid are taken in static state and that the measurements of static shear modulus are representative of the strength of the ER-fluid in the static state.
Now, we begin to analysis our experimental results. The results of the measurement of yield stress of the fluids are discussed first. Figure 6.11 shows the frequency dependence of the yield stress of the mono-dispersed ER-fluid containing glass only ($\phi = 0.35, \theta = 1$). The yield stress of the fluid decreases as electric frequency increases. The results are consistent with theoretical results [15]. Compare with figure 4.2, the shape of the curve is similar, where figure 4.2 shows the comparison between measured and calculated frequency-dependent static yield stresses of the fluid containing glass only with specify volume fraction.

In Figure 6.9, we keep the volume fraction $\phi$ between particles and fluid at 0.25 and the curves of different glass/PZT particles ratio $\theta$ are shown. We observe that peaks are reached at certain frequencies and the peaks are shifting to larger frequency as the particles ratio varies from 0 to $-1$. The phenomenon can be explained by considering the fluids containing glass only and containing PZT only respectively. As mentioned above, the yield stress of the fluid containing glass particles only decreases as electric frequency increases. However, from Figure 6.9, we find that the yield stress of the fluid containing PZT nano-particles only ($\theta = -1$) increases with the electric frequency until the maximum is reached at 1000hz. The ER effect of the fluid containing PZT particles only is much larger than the fluid containing glass particles only, thus the character of the curves of the two-phased ER-fluids with different glass/PZT particles ratio $\theta$ ($\theta = -0.875, -0.75, -0.5$) are similar to the curve $\theta = -1$. The peaks are shifting to lower frequency as the particles ratio varies from $\theta = -1$ to 0, since the fraction of glass particles in the two-phased fluid and the ER-effect of the glass particles increases as the particles ratio varies from $\theta = -1$. 

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From Figure 6.10, for fixed particles ratio $\theta = -0.875$, the curves of the static yield stress against electric frequency shift up with the solid/liquid volume fractions (from 0.25 to 0.40), i.e. the larger the volume fraction of the fluid, the larger the static yield stress. This is easily to be explained as the solids concentration in the fluid increases, more and thicker columns are formed by the ER-particles and the ER-fluid can resist larger shear stresses before it starts to flow.

After analyzing the experimental results of the electric frequency dependence of yield stress of the bi-dispersed fluid, we will discuss the experimental results for the electric frequency dependence of shear modulus of the bi-dispersed fluid next.

In Figure 6.5, we keep the volume fraction $\phi$ between the particles and the fluid at 0.25 and the curves of different glass/pzt particles ratio $\theta$ are shown. We observe that the curves shift up as the particles ratio varies from 0 to −1. It is because the ER-response of the PZT nano-particles is much higher than that of the glass. Thus, the shear moduli we measured are higher for the curves with higher PZT particles ratio. For all the curves with different particles ratio, the shear moduli of the fluid decrease as electric frequencies increase. Compared with Figure 4.3, the shape of the curves is similar and the shear moduli of the fluids in both graphs decrease with frequency increase, where Figure 4.3 shows the calculated frequency-dependent shear modulus of the fluid with specific volume fraction based on Equation 4.7. Moreover, from Figure 4.3, it shows that soft modes can be seen on some specified frequencies as calculated using Equation 4.7. In Figure 6.5, the soft mode features are clearly seen at different specified frequencies from the curves of the fluids with different particle ratio, which
are similar with the feature of mono-dispersed ER-fluid. Thus, our experimental results are consistent with theoretical results [15].

From Figure 6.6, for the fixed particles ratio $\theta = -0.875$, the curves of the shear moduli against electric frequency shift up with the solid/liquid volume fractions (from 0.25 to 0.40), i.e. the larger the volume fractions of the fluid, the larger the shear moduli. Again, it can be explained as the concentration of the fluid increases, more and thicker columns are formed by the ER-particles for the larger volume fraction and the columns formed inside the fluid can stand for larger shear stress before being tilted far from the vertical. However, soft modes like dips only exist for $\theta = 0.25$ and 0.35, but not all volume fractions. The results show that the existence of soft modes is limited in some conditional cases, such as specify frequency, particles sizes, dielectric constants. However, the shapes and the sizes of PZT are irregular, so the positions of soft modes cannot be calculated.

Figure 6.7a-g show the graphs of static shear modulus against particles ratio $\theta$ for different frequencies (60hz – 4000hz). The figures show that the static shear modulus decreases as the particles ratio changing from −1 to 0 at different frequencies (ranged from 60hz to 4000hz), except figure 6.6d (frequency at 400hz). It is because the ER-response of the PZT nano-particles is much higher than that of the glass. Thus, the shear moduli we measured are higher for the curves with higher PZT particles ratio. From Figure 6.6d, the value of shear modulus is lower at $\phi = -1$ than at $\phi = -0.875$. It is because the soft mode is in the 400hz when $\phi = -1$. 

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After analyzing the measurement results of shear moduli, now we move on to discuss the structures of the bi-dispersed fluids.

Figure 7.1 a-g and Figure 7.2 a-f, show the microscopic observations of the ER-fluids containing PZT only when different electric frequencies were applied. The PZT particles were randomly dispersed in the fluid when no voltage was applied. When high electric frequency was applied, we found that the particles were tend to form some chains, however the particles could not move fast enough to follow such high frequencies [28], so just some short chains were formed. When the frequency of the field was decreased further, more clusters grew into chains. When the frequency was lowered to 60hz, stable columnar structures were formed. From figure 7.3 a-g, we observe that the frequency dependence character of the bi-dispersed ER-fluid containing nano PZT particles and glass particles is the same with mono-dispersed ER-fluid (only PZT). The phenomenon can be explained by considering the response times of the particles on different frequencies. When the particles are under high electric frequency, the particles are not fully polarized and cannot move fast enough. So, the attractive interaction force between particles is just enough to form some short chains. However, the relaxation time is enough for the particles to be fully polarized when low electric frequency is applied [5]. Then, the attractive interaction force along the field between particles increases, more chains are formed and tend to develop longer and thicker columns and finally stable columnar structures are formed in equilibrium.

On the other hand, we found that PZT nano-particles were not filled in the interstitial spaces between the chains or clusters formed by glass particles, but mixed
together to construct thick clusters. We noticed that all the columns observed in Figure 7.3a-g are loose structures and it seems that no ordered structure could be built. However, according to the theoretical prediction, the lowest energy state of ER fluid is a stable state in which all particles should aggregate to form an ordered structure, i.e., in most cases the body centered tetragonal (BCT) structure [20]. We realized that if the rise time of the electric field is short or the field is applied suddenly, the particle's movement is so fast that it cannot reach its lowest energy state, which means that the state presented here might not be an equilibrium state [32].

From Figure 7.5a-f, we observe that the time response of the PZT nano-particles is much faster than that of the glass particles. It is because the time response of the ER-effect changes with particle size. The trend shows that the larger the particle size, the longer the ER effect response time [32].

Now, we can just use the theoretical results for a mono-dispersed ER-fluid calculated by first-principles calculations to compare with our experimental results. However, there is not any theory to predict the theoretical results of bi-dispersed or multi-dispersed ER-Fluids. Moreover, the sizes and the shapes of the PZT nano-particles are irregular which may affect the strength or the structures of the fluid. In future, our research group will try to deduce some well-developed theories for the two-phased or multi-phase ER-Fluids and we will use the double-coated particles in our future experiments, which are stronger in strength and regular in shape and size, in order to make the experimental measurements and the calculations of theoretical results become easier.
8.2 Conclusion

In this research, the shear modulus and the static yield stress of two-phase ER-fluids (containing nano-particles EC63-PZT and 55μm glass particles) are measured under different electric frequencies. The experimental results show that both the shear modulus and yield stress of the two-phase ER-Fluids electric frequency dependence. The yield stress of the fluid reaches a peak under specified frequency and the peak shifts to larger frequency as the particles ratio shifts from 0 to −1. In contract, the shear modulus of the fluid decreases with increasing electric frequency. Moreover, soft-modes-like dips in the shear modulus are observed for some particle ratios and volume fraction. The experimental results are in accord with the theoretical results for mono-dispersed ER-fluid calculated using first – principles approach.

In the previous study, it was assumed that the nano-particles are coated onto the surfaces of the large glass spheres. However, from our microscopic observations of the two-phase ER-Fluids, particles do not arrange as predicted. In fact, the structures are more complicated and have sensitive dependence on particles contraction and applied electric frequency.

ER- fluids are still in the early stages of being applied to our daily lives, as many problems are waiting be solved, such as recovery of the fluid and structural weakness. However, many researchers are putting much efforts on this topic in order to bring us to another level of understanding of the ER-effect and engineers are trying to put their ideas on applications in daily life, such as shock absorbers, clutches and dampers. We
hope that the two-phase or multi-phase technique in ER-fluids can find an application in the nearly future.
Appendix

A. Microscopic Pictures

Figure A1  Microscopic picture for “bare” glass particles.
            (resolution = 10x10)

Figure A2  Microscopic picture for nano-pzt particles
            (resolution = 10x20)
B First-principles Calculation

Consider a DER system consists of dielectric constant $\varepsilon_p$ particles suspended in dielectric constant $\varepsilon_r$ fluid and 2 parallel plates where the separation between the plates is L that eventually extends to infinity. As the electric field is applied perpendicular to the parallel plates, all particles are polarized.

The electrostatic energy in dielectric media is

$$W = -\frac{1}{8\pi} \int E \cdot D d^3x$$  \hspace{1cm} \text{Eqn. B.1}

As $D = \varepsilon E$, the free energy density of the system is

$$W = -\frac{1}{8\pi} \varepsilon_{eff} E^2$$  \hspace{1cm} \text{Eqn. B.2}

Since the operating frequencies of ER-Fluids are generally $< 10^4$ Hz and the typical particle size and the separation of the ER-fluids are $<10^2$ cm, we can consider the system which are in the “long-wavelength limit”. Thus, the $\varepsilon_{zz}$ can be used to represent $\varepsilon_{eff}$, where $\varepsilon_{zz}$ is the effective dielectric tensor along the field and E is the applied electric field that can be written as

$$E = \frac{\Delta \phi}{L} (V/mm)$$  \hspace{1cm} \text{Eqn. B.3}

where $\Delta \phi$ is the voltage difference and L is the separation between plates.
Equation B.2 can be rewritten as

\[ W = -\frac{1}{8\pi} \varepsilon \varepsilon_0 E^2 \]  

Eqn. B.4

It is observed that the free electric energy of the system will be lower for larger electric field.

Set the boundary conditions,

\[ \phi(x, y, z = 0) = 0 \]
\[ \phi(x, y, z = L) = 0 \]  

Eqn. B.5

and the Laplace equation

\[ \nabla \cdot D = 0 \]
\[ \nabla (\bar{r}) \cdot (\varepsilon (\bar{r}) \bar{E}) = 0 \]
\[ \nabla \cdot (\varepsilon_n \nabla \phi) = 0 \]  

Eqn. B.6

To understand the transformation integral operator \( \phi \), we now introduce another indicator function \( \theta(r) \)

\[ \theta(\bar{r}) = 1 \quad \text{when } r \text{ inside sphere} \]
\[ = 0 \quad \text{otherwise} \]  

Eqn. B.7
Thus, we have
\[ \varepsilon_u = \varepsilon_p \theta(\bar{r}') + \varepsilon_f [1 - \theta(\bar{r}')] \]
\[ = \varepsilon_f + \theta(\bar{r}') (\varepsilon_p - \varepsilon_f) \]  
Eqn.B.8

\[ \frac{\varepsilon_{xx}}{\varepsilon_f} = 1 - \left( \frac{\varepsilon_f - \varepsilon_p}{\varepsilon_f} \right) \theta(\bar{r}') = 1 - \mu \theta(\bar{r}') \]  
Eqn.B.9

Here, we define another parameter \( s \) such that
\[ u = \frac{\varepsilon_f - \varepsilon_p}{\varepsilon_f} = \frac{1}{s} \]  
Eqn.B.10

Then, equation B.9 and equation B.6 are combined, we obtain
\[ \nabla \left[ (1 - u \theta(\bar{r}')) \nabla \phi \right] = 0 \]
\[ \nabla^2 \phi = \nabla u \theta(\bar{r}') \cdot \nabla \phi \]  
Eqn.B.11

(As if \( \nabla^2 \phi = 0 \Rightarrow \nabla \phi = \vec{E} \cdot \hat{z} = z \))

Thus, the integral equation for \( \phi \) appeared in equation B.5 as
\[ \phi = z + u \hat{\Gamma} \phi \]  
Eqn.4.1

The linear integral operator \( \hat{\Gamma} \) is defined as
\[ \hat{\Gamma} \phi = \int dV' \theta(\bar{r}') \nabla' \Gamma(r, r') \cdot \nabla' \phi(r') \]  
Eqn.4.2

where \( \Gamma(r, r') \) is the Green’s function of laplace operator.
Properties of $\Gamma(r, r')$ can be written as

$$\nabla^2 \Gamma(r, r') = -\delta(r - r')$$

$\Gamma = 0$ on the boundary \hspace{1cm} Eqt.B.12

Now a scalar product is defined such that operator $\hat{\Gamma}$ is self-adjoint

$$\langle \phi | \psi \rangle = \int dV \theta(\vec{r}') \nabla \phi' \cdot \nabla \psi$$ \hspace{1cm} Eqt.4.3

The effective dielectric constant is then given by

$$\varepsilon_{\text{eff}} \vec{E} = \frac{1}{V} \int \vec{D} dV = \frac{1}{V} \int \varepsilon_{\text{eff}} \vec{E} dV$$ \hspace{1cm} Eqt.B.13

From the relationship in equation B.9 and e-field is in z-direction only, we get,

$$\varepsilon_{zz} = \frac{1}{V} \int dV \varepsilon_j (1 - u \theta(\vec{r}')) \left( \frac{\partial \phi}{\partial z} \right)$$ \hspace{1cm} Eqt.B.14

$$\varepsilon_{zz} = \varepsilon_j \left( 1 - \frac{u}{V} \int dV \theta(\vec{r}') \frac{\partial \phi}{\partial z} \right)$$ \hspace{1cm} Eqt.B.15

From equation 4.3 and as $\nabla \phi = \frac{\partial \phi}{\partial z}$ and $\nabla^* z = 1$, equation B.15 becomes

$$\varepsilon_{zz} = \varepsilon_j \left( 1 - \frac{u}{V} \langle z | \phi \rangle \right)$$ \hspace{1cm} Eqt.B.16

Here, a function F(s) is defined as

$$F(s) = 1 - \frac{\varepsilon_{zz}}{\varepsilon_r} = \frac{u}{V} \langle z | \phi \rangle$$ \hspace{1cm} Eqt.B.17
From equation 4.1, we have

\[ |\phi\rangle = |z\rangle + u\hat{\Gamma}|\phi\rangle \]

\[ (1-u\hat{\Gamma})|\phi\rangle = |z\rangle \quad \text{Eqn. B.18} \]

\[ |\phi\rangle = \left( \frac{1}{1-u\hat{\Gamma}} \right) |z\rangle \quad \text{Eqn. B.20} \]

Combining equation B.17 and equation B.19, we get

\[ F(s) = \frac{u}{Vs} \langle z | \frac{1}{1-\frac{\hat{\Gamma}}{s}} | z \rangle \]

\[ = \frac{1}{V} \langle z | \frac{1}{s-\hat{\Gamma}} | z \rangle \quad \text{Eqn. B.21} \]

For the eigen equation of \( \hat{\Gamma} \):

\[ \hat{\Gamma}|\phi_n\rangle = s_n|\phi_n\rangle \quad \text{Eqn. B.22} \]

where \( s_n \) and \( \phi_n \) are the \( n^{th} \) eigenvalue and eigenfunction of the operator \( \hat{\Gamma} \)

then, consider,

\[ |\phi\rangle = \sum_n |\phi_n\rangle \langle \phi_n | \phi \rangle \quad \text{Eqn. B.23} \]

Inserting equations B.19 and B.10 into equation B.23, we obtain

\[ |\phi\rangle = \sum_n \frac{\langle \phi_n | z \rangle}{1-u\hat{\Gamma}} |\phi_n\rangle \]

\[ = \sum_n \frac{\langle \phi_n | z \rangle}{1-\hat{\Gamma} s^{-1}} |\phi_n\rangle \quad \text{Eqn. B.24} \]
From equation B.22, \( s_n \) is known as the eigenvalue of \( \Gamma \), thus

\[
|\phi\rangle = \frac{s \langle \phi | z \rangle}{s - s_n} |\phi_n\rangle
\]

Eqn. B.25

Insert equation B.25 into equation B.17, we \( F(s) \) can be deduced as

\[
F(s) = \frac{u}{V} \sum_n \frac{s \langle \phi_n | z \rangle}{s - s_n} |\phi_n\rangle
\]

Eqn. B.26

As \( u = 1/s \), then

\[
F(s) = \frac{1}{V} \sum_n \frac{|\langle \phi_n | z \rangle|^2}{s - s_n}
\]

Eqn. B.27

Combining equation B.17 and equation B.27, we conclude

\[
\frac{\epsilon_{\mu\nu}}{\epsilon_f} = 1 - \frac{1}{V} \sum_{m,n} \frac{|\langle z | \phi_n \rangle|^2}{s - s_n}
\]

Eqn. 4.4a

or

\[
\frac{\epsilon_{\mu\nu}}{\epsilon_f} = 1 - \frac{1}{V} \sum_{m,n} \langle z | \Psi_n \rangle \langle \Psi_n | \frac{1}{s - \Gamma} | \Psi_m \rangle \langle \Psi_m | z \rangle
\]

Eqn. 4.4b

or

\[
\frac{\epsilon_{\mu\nu}}{\epsilon_f} = 1 - \sum_{n} \frac{f_n^z}{s - s_n}
\]

Eqn. 4.4c

where

\[
f_n^z = \frac{|\langle \phi_n | z \rangle|^2}{V}
\]

Eqn. 4.5
C. Calculating the amounts of the particles mixed

To calculate the precise amounts of particles mixed, we start with eqn 5.8,

\[ \theta = \frac{V_s - V_p}{V_s + V_p} \]  

Eqn 5.8

then the equation can be converted into

\[ V_p = V_s \left( \frac{1 - \theta}{1 + \theta} \right) \]  

Eqn C.1

Combining equation 5.6 and C1, then

\[ V_s = \frac{\phi(1 + \theta)V_i}{2} \]

\[ V_p = \frac{\phi(1 - \theta)V_i}{2} \]  

Eqn C.2

thus, by equation 5.7 and C.2, we can obtain

\[ M_g = \frac{\rho_s \phi (1 + \theta) M_i}{2 \rho_l} \]  

Eqn 5.9a

and \[ M_p = \frac{\rho_p \phi (1 + \theta) M_i}{2 \rho_l} \]  

Eqn 5.9b
D Calculation of Errors

Error of shear Modulus,

The total errors can be deduced as

\[
\sigma_{\text{total}} = \sigma_1(t) + \sigma_2 \left( \frac{\Delta r}{r}, \frac{\Delta h}{h} \right) + \sigma_3
\]

where \( \sigma_1(t) \) is the error between the strain we measured and the strain when \( t \to \infty \), as \( \sigma_1(t) \approx e^{-t} \) and \( t \) is generally \( >10\tau \), then \( \sigma_1(t) < 0.1\% \) and can be neglected.

\[
\sigma_2 \left( \frac{\Delta r}{r}, \frac{\Delta h}{h} \right) = \left| \frac{\Delta r}{r} \right| + \left| \frac{\Delta h}{h} \right|, \text{ from the previous chapter, } \frac{\Delta r}{r} \text{ is about } 1.35\% \text{ and } \frac{\Delta h}{h} \text{ is less than } 0.05\%.
\]

\( \sigma_3 \) is error calculated by fitting a line in graph stress vs strain.

Errors of static shear stress,

The total errors can be deduced as

\[
\sigma_{\text{total}} = \frac{\Delta r}{r} + \frac{\Delta h}{h} + \frac{\Delta \tau}{\tau}
\]

where \( \Delta \tau = 0.005 \), \( \frac{\Delta r}{r} < 0.01\% \) in general and can be neglected.
Reference:


[26] Instruction Manual of Rotovisco RT20, p97 , HAAKE

[27] Technique in Rheological Measurement, edited by A.A Collyer, Chapman & Hall

[28] Robert W. Fox, Alan T. McDonald, Introduction to fluid mechanics, John Wiley &


