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Structure of electrorheological fluids: A dielectric study of chain formation

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A dielectric measurement method has been proposed to apply to the study of the microstructure of electrorheological (ER) fluids. To test our measurement method the dielectric permittivity increment caused by pair and chain formation was measured in dilute Brownian ER fluids composed of silicone oil and nanosized silica particles. The critical values of the electric field required to induce structure formation were experimentally determined from the electric field dependence of the measured permittivity increment. From the electric field induced time evolution of the relative permittivity of ER fluids, the characteristic times of the pair and chain formation were calculated. Our experimental results for the time constants are in good agreement with the corresponding theoretical data obtained from the Eyring theory.

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I. INTRODUCTION

The apparent viscosity of an electrorheological (ER) fluid (composed of solid particles with dielectric permittivity ϵ_p dispersed in a fluid with dielectric permittivity $\epsilon_\mathrm{f} < \epsilon_\mathrm{p}$) increases abruptly when an external electric field is applied to the fluid. The increase of the apparent viscosity is caused by the chain formation of the particles carrying dipole moments induced by the field. Numerous direct and indirect methods are available to study the structural transition of an ER fluid. If the particles are big enough, the structure is directly observable with optical- and laser-microscopic methods [1–3]. Light scattering and diffraction methods have also been used to investigate the chain and column formation [4,5]. Transmission electron microscopy and scanning electron microscopy are also useful tools for the structural examination of ER fluids [6]. Because the structural change affects the dielectric properties of the fluid [7], the chain formation can be studied with dielectric permittivity measurements. The permittivity of the anisotropic fluid measured parallel with the chains is larger than the permittivity of the isotropic ER fluid (randomly dispersed particles) [7].

The conventional impedance spectroscopy is a useful method to measure the dielectric permittivity of fluids, but this method has limitations in the case of ER fluids. To measure the structure induced permittivity increment of an ER fluid, the impedance measurement has to be carried out in the presence of a high voltage (HV) electric pulse with the impedance analyzer separated from the HV pulse. This technical difficulty can be overcome by measuring the dielectric permittivity before and after the pulse [8], but this is applicable only if the structure is stable enough. Furthermore, this measurement procedure does not give any information about the dynamics of the structure formation. Adolf and Garino [9] investigated the time evolution of the dielectric permittivity of ER fluids based on ceramic particles after an electric field was applied. They used a sinusoidal ac voltage signal and calculated the dielectric permittivity from the measured voltage drop across the sample. In the case of special ER fluids—where the particles are glass microspheres containing an inner ferromagnetic layer—the chain formation can be induced with an external magnetic field. Wen *et al.* [10] measured the structure induced dielectric permittivity increment of this unique type of ER fluid.

II. EXPERIMENT

A. Experimental setup

In this work, we propose the application of a dielectric measurement method for the study of ER fluids. This method makes the continuous measurement of the permittivity of an ER fluid in the presence of an external electric field possible. The characteristic times of the structure formation in ER fluids can be determined experimentally with this technique. An important advantage of this method is that even very small permittivity changes ($\Delta\epsilon_\mathrm{r} \approx 10^{-6}$) can be measured, enabling the study of dilute ER fluids composed of particles with low dielectric permittivity ($\epsilon_\mathrm{p} < 4$). The basic idea behind our measurement setup was previously employed by various authors [11] to investigate the nonlinear dielectric effect in molecular and complex liquids. Furthermore, using a special dielectric cell (where the electrodes of the measuring capacitor are surrounded by an ER fluid reservoir), this method is suitable to measure the electrostriction of an ER fluid. This is a purely nonlinear effect that is beyond the scope of this paper. Because this effect has been mainly studied by theoretical methods [12–14], experimental data are desirable.

Figure 1 shows the schematic block diagram of our apparatus. The concept of the measurement setup is based on the determination of the frequency change of an LC oscillator [15–17]. The sample under investigation is contained in a dielectric cell, which acts as a parallel plate capacitor (C_c). The dielectric cell together with the inductance L are the resonant elements of the LC oscillator, which has a resonance frequency f. Any change in the dielectric permittivity of the fluid causes a change in the capacitance of the dielectric cell. Because the value of C_c is the dominant capacitive element of the LC oscillator, the change in the dielectric permittivity manifests as a change in frequency (Δf). After calibration with two samples of different kinds of material with accurately measured dielectric permittivities, the permittivity change can be calculated from the measured frequency change. Because a

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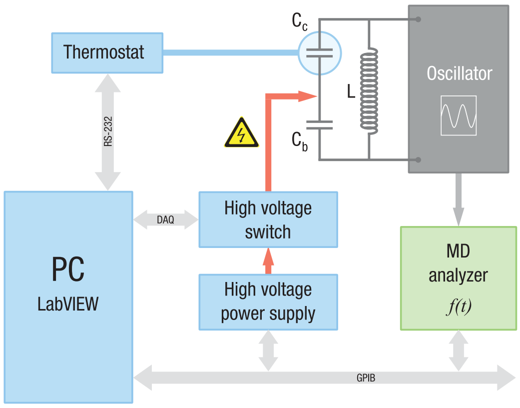

FIG. 1. (Color online) Block diagram of the dielectric equipment.

high stability oscillator is required, a double triode oscillator of type ECC88 valve, used previously by Bradley and Jones [16], was chosen. An advantage of the valve oscillator is its ability to oscillate even when the cell is filled with moderately conducting liquid. When the dielectric cell is empty, the resonant frequency of the oscillator is around $f = 3.48$ MHz. A Hewlett-Packard 53310A modulation domain (MD) analyzer is responsible for the accurate measurement of the frequency over time. The dielectric cell has disklike electrodes made of stainless steel. The electrode gap is set to 0.13 mm with a quartz ring spacer. The temperature of the sample between the electrodes is regulated by a thermostat, which is circulating water in the outer mantle of the dielectric cell. With a high voltage pulse generator, rectangular pulses can be imposed to the cell. The pulse generator is composed of a power supply and a custom built HV switch. The voltage source varied according to the required electric field strength. In the low field region ($0 < E < 0.2$ MV m^{-1}), we used a Hameg HM8040-2 power supply, while above 0.2 MV m^{-1} the voltage source was a Stanford Research PS350 dc high voltage power supply. The HV switch is controlled by a PCI-6052E multifunction data acquisition (DAQ) card made by National Instruments. A high voltage decoupling capacitor (C_b) connected in series with the dielectric cell blocks the pulse from the active elements of the oscillator. The electric field strength between the plates of the cell is on the order of 10^6 V m^{-1}.

B. Materials and sample preparation

In our experiments, we used dilute ER fluids containing nanosized particles. In the case of our ER fluids, $\lambda \simeq 0.01$, which means that the thermal motion plays an important role in the structure formation (Brownian ER fluids). There is a limited number of experimental data in this small λ regime. We used ER fluids composed of nanosized silica (SiO_2) particles dispersed in silicone oils (polydimethylsiloxane) with different dynamic viscosities (0.34 and 0.97 Pa s at 25 °C). The diameter of the silica particles is between 10 and 20 nm. The relative permittivity of the carrier liquid is $\epsilon_f = 2.7$, while the particles have a permittivity of $\epsilon_p = 4.0$. All materials were supplied by Sigma-Aldrich. The silicone oil and the silica were vacuum dried for 2 h at a pressure of 300 Pa and a temperature of 50 °C to remove any absorbed water. After mixing and homogenizing the two components, the suspensions were vacuum dried again for 30 min to remove the air bubbles. The volume fraction of silica particles in the ER fluids was $\phi = 0.02$ and 0.04.

III. THEORETICAL TIME SCALES OF STRUCTURE FORMATION IN ER FLUIDS

After the technical details we summarize the basic theoretical aspects, which are important to interpret the experimental results. The most important effects controlling the structure of the static, nonsheared ER fluids are the electrostatic force between the polarized particles and the diffusion arising from thermal motion. We calculate the time scale of the pair formation of ER particles according to a theoretical model proposed by Baxter-Drayton and Brady [18]. Let us consider a sphere with a radius a and a dielectric permittivity ϵ_p dispersed in a fluid with a permittivity ϵ_f, where $\epsilon_p > \epsilon_f$. In the presence of an external **E** electric field, the induced dipole moment of the sphere is

$$\mathbf{m} = 4\pi\beta\epsilon_f\epsilon_0 a^3\mathbf{E}, \tag{1}$$

where $\beta = (\epsilon_p - \epsilon_f)/(\epsilon_p + 2\epsilon_f)$ and ϵ_0 is the permittivity of vacuum. We can define a dimensionless parameter (λ) as the ratio of the depth of the dipole-dipole interaction energy at its minimum and the $k_B T$ thermal energy (where k_B is the Boltzmann constant and T is the temperature), which gives the relative importance of the polarization and thermal interactions. If the dipoles are not pointlike [18], the λ parameter can be expressed as

$$\lambda = \frac{12\pi\epsilon_f\epsilon_0 a^3\beta^2 E^2}{k_B T}. \tag{2}$$

At large λ, the electrostatic force between the particles becomes dominant and the particles form chainlike structures. In the case of smaller λ, the chain formation is detained by Brownian motion. The characteristic time τ_p of pair formation is given as the time scale of the particle diffusion out of their potential well in a fluid with a viscosity of η. In the spirit of the Eyring theory [18], this characteristic time can be given as

$$\tau_p = \frac{a^2}{D\lambda}e^{\lambda} \approx \frac{\eta}{2\epsilon_f\epsilon_0\beta^2 E^2}. \tag{3}$$

Because $\lambda < 1$ in our case, the exponential function is approximated with the first term of its Taylor series. The diffusion coefficient according to the Stokes-Einstein equation is $D = k_B T/6\pi\eta a$. The characteristic time of the diffusion of an isolated Brownian particle is

$$\tau_d = \frac{6\pi\eta a^3}{k_B T}. \tag{4}$$

As time progresses, the particle pairs combine to form chains and columns parallel to the applied field. The change of the dielectric permittivity during the time period t during which an external field is applied is

$$\Delta\epsilon_r(t) = \epsilon_r(t) - \epsilon_r(0), \tag{5}$$

where $\epsilon_r(0)$ is the permittivity of the ER fluid at $t = 0$ (before turning on the external field). Since the time evolution of permittivity is caused by both pair and chain (column)

TABLE I. The experimental and theoretical time scales of ER fluids based on silicone oils of different viscosities at different electric field strengths ($\phi = 0.02$, $T = 25\,^\circ$C).

	$\eta = 0.34$ Pa s silicone oil $\tau_d = 0.0015$ s			$\eta = 0.97$ Pa s silicone oil $\tau_d = 0.0044$ s		
E (MV m^{-1})	τ_p (s) Eq. (3)	τ_1 (s) Eq. (6)	τ_2 (s) Eq. (6)	τ_p (s) Eq. (3)	τ_1 (s) Eq. (6)	τ_2 (s) Eq. (6)
1.54	0.159	0.142 ± 0.001	1.233 ± 0.032	0.454	0.303 ± 0.004	1.237 ± 0.056
2.31	0.071	0.073 ± 0.001	0.916 ± 0.012	0.201	0.154 ± 0.001	0.824 ± 0.014
3.08	0.040	0.051 ± 0.001	0.808 ± 0.010	0.113	0.102 ± 0.001	0.677 ± 0.009
3.85	0.025	0.041 ± 0.001	0.764 ± 0.010	0.072	0.073 ± 0.001	0.581 ± 0.008

formation, a biexponential fitting function is applied in the processing of the experimental data:

$$\Delta\epsilon_r(t) = A\left(1 - e^{-\frac{t}{\tau_1}}\right) + B\left(1 - e^{-\frac{t}{\tau_2}}\right), \qquad (6)$$

where the constants τ_1 and τ_2 are interpreted as the characteristic time scales for pair and chain formation, respectively. We note that a similar correlation equation was used by Ly *et al.* [19] (who investigated the microstructure formation of magnetorheological fluids) to describe the magnetic permeability response to the switched-on external magnetic fields. Equation (6) is further supported by the fact that the electric field induced time evolution of pattern formation in colloid suspension can be characterized by a similar biexponential fitting curve. Park and Saintillan [20], on the basis of the work of Kumar *et al.* [1], characterized their numerical simulations by a "gray level" function, which exhibited biexponential time dependence with the corresponding characteristic times. These functional forms are based on the exponential function approximation of the solutions of kinetic equations of particle aggregation.

IV. RESULTS AND DISCUSSION

Our dielectric measurement results are summarized in the following figures and in Table I. Figure 2 illustrates the dielectric permittivity change of the ER fluid caused by a rectangular electric pulse train. The duration of the pulses and the time between them is 0.1 s. The amplitudes of three consecutive pulses are the same. During the first pulse, the permittivity is increasing exponentially, indicating the formation of chains. After the first pulse, the electric field strength drops to zero ($\lambda = 0$) and the permittivity of the fluid is decreasing very slowly. In the absence of the external field, the structural change in the fluid is governed by diffusion alone, meaning that the chains are being destroyed by the Brownian motion of the particles. Because the characteristic time of diffusion $\tau_d \simeq 0.0044$ s [see Eq. (4) and Table I] is much smaller than the characteristic time of pair formation $\tau_p \simeq 0.2$ s [see Eq. (3) and Table I], the disruption of the structure (the drop of the dielectric permittivity) is negligible during the 0.1 s time gap. The dielectric permittivity change during the second and third pulses is consistently smaller than during the first pulse. This is because the particles are not randomly distributed and the chain-like structures remain intact before the second and third pulses.

The measured permittivity increment during one long HV pulse with different electric field strengths is shown in Fig. 3. The length of a single rectangular pulse was 140 s. Approximately 90 s after the start of the pulse, the permittivity

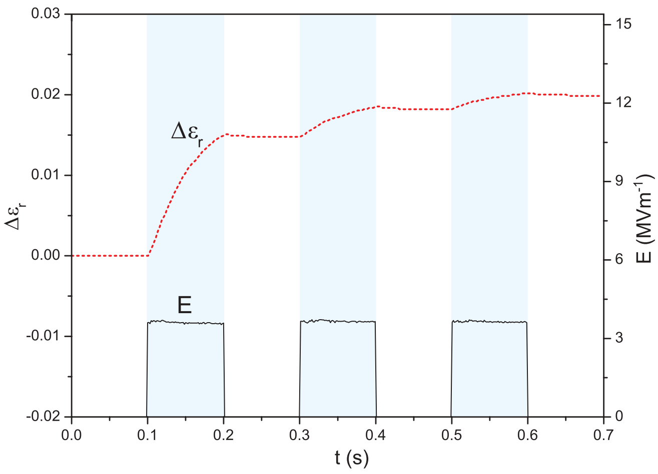

FIG. 2. (Color online) The change in dielectric permittivity of the ER fluid (dashed line) over time during the HV pulse train (full line) ($E = 3.85$ MV m^{-1}, $\eta = 0.97$ Pa s silicone oil, $\phi = 0.02$, $T = 25\,^\circ$C).

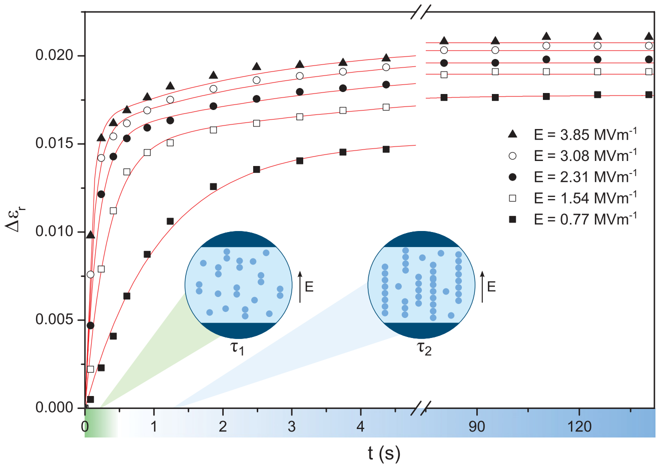

FIG. 3. (Color online) The dielectric permittivity of the ER fluid (symbols) over time during one long HV pulse with different electric field strengths ($\eta = 0.97$ Pa s silicone oil, $\phi = 0.02$, $T = 25\,^\circ$C). The solid lines are the fitted double exponential functions [see Eq. (6)].

of the fluid does not increase further, which indicates that the structure of the fluid is stable. The limiting value of the change in the dielectric permittivity ($t \to \infty$) becomes larger as the electric field strength is increased because more and more particles become part of the chains. Increasing E beyond a certain limit ($E \approx 6\,\mathrm{MV\,m^{-1}}$, $\lambda \approx 0.15$) does not cause further increase in the limiting permittivity change (saturation). This indicates that almost every particle is aggregated into chainlike and columnar structures beyond this field strength limit.

As we have mentioned, the experimental $\Delta\epsilon_r(t)$ data are correlated by Eq. (6). The experimental time scales τ_1 measured in ER fluids using silicone oil of different viscosities are compared to the theoretical τ_p time scales calculated from Eq. (3) in Table I. Despite the approximative nature of Eq. (3), the agreement between the experimental and theoretical values is satisfactory. On the basis of the flocculation theory and computer simulations, Hass [21] predicted that the characteristic time of aggregation of pairs into chains and columns (τ_2) can be approximated as $\tau_2 \simeq 10\,\tau_1$. These findings are in agreement with those of Ly *et al.* [19], who found that in magnetorheological fluids the time constant τ_2 is larger than τ_1 by a factor of 5 to 10. Table I shows that the relation between τ_2 and τ_1 follows these estimations at both viscosities. This means that τ_2 can be identified with the characteristic time of chain and column formation.

The dielectric permittivity increment can be estimated according to a simple theoretical model proposed by Wen *et al.* [7]. The dielectric permittivity of the isotropic ER fluid—containing ϕ volume fraction of dispersed particles—is

$$\epsilon_i = \epsilon_f \frac{\epsilon_p + (\phi - \phi^{1/3})(\epsilon_p - \epsilon_f)}{\epsilon_p - \phi^{1/3}(\epsilon_p - \epsilon_f)}, \qquad (7)$$

and the permittivity of the anisotropic fluid is

$$\epsilon_c = \phi\epsilon_p + (1 - \phi)\epsilon_f. \qquad (8)$$

The model assumes that every particle is part of a chain in the anisotropic fluid. For the ER fluid based on the $\eta = 0.97$ Pa s silicone oil and containing $\phi = 0.02$ silica, the experimental dielectric permittivity change is $\Delta\epsilon_r = 0.021$ at an electric field strength $E = 3.85\,\mathrm{MV\,m^{-1}}$. According to the theoretical model of Wen *et al.* [7]—calculated as the difference between Eqs. (7) and (8)—the permittivity change is $\Delta\epsilon_r = 0.007$. Considering that the theoretical model does not take the interaction of the particles into account, the agreement is reasonable.

In order to study the critical electric field required to induce structural changes in ER fluids, the field dependence of the dielectric permittivity has been measured. Figure 4 shows the dielectric permittivity increment as a function of the electric field strength. The length of a single, rectangular HV pulse was 1 s (this time interval was chosen on the basis of the characteristic times shown in Table I). It is clearly visible that there are two critical values of the field strength. When E is below E_l, the permittivity change is very small, indicating that there is no significant structural change (the particle distribution is close to random). When the field strength becomes larger than E_l, the particle pair and chain formation begins. E_l is the critical electric field required to induce the structure formation. As the field strength is increased over E_h, the permittivity change starts to saturate.

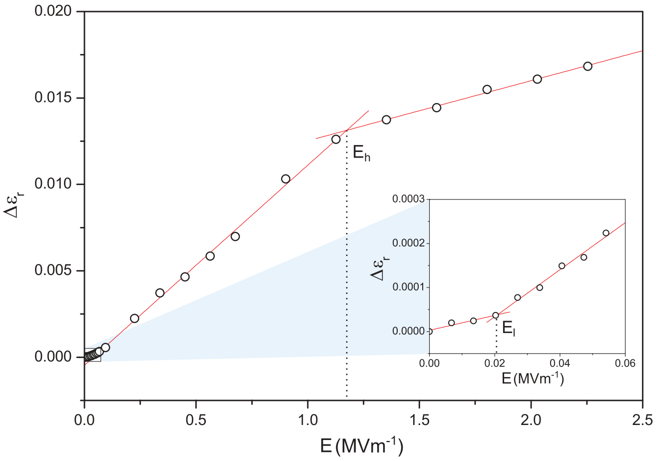

FIG. 4. (Color online) The change in dielectric permittivity of the ER fluid (symbols) as a function of electric field strength. The low field regime is magnified in the inset. ($\eta = 0.97$ Pa s silicone oil, $\phi = 0.02$, $T = 25\,^\circ$C).

It is well known that at high electric field the chains aggregate into columnar structures. According to theoretical and experimental studies, the relative permittivity of an ER fluid has a maximum when the particles are organized into a body-centered-tetragonal structure [22]. E_h can be regarded as the critical electric field where the single chains start to aggregate into columns. Beyond this second critical field strength, the fluid structure is dominated by columns. Between E_l and E_h, the measured $\Delta\epsilon_r$ is increasing linearly as more and more particles become part of the chains. In the case of $\eta = 0.97$ Pa s silicone oil and $\phi = 0.02$ particle concentration, the two critical field strengths are $E_l = 0.02\,\mathrm{MV\,m^{-1}}$ and $E_h = 1.18\,\mathrm{MV\,m^{-1}}$. The experimental error of the permittivity measurement below E_h is 4%, while at higher field strengths it becomes smaller (2.6%).

Increasing the length of the pulse (1 s), results in an increase in the permittivity increment (see Fig. 3), while the values of the critical field strengths, E_l and E_h, remain largely unaffected within a few percent error. Of course, the critical field strength data depend on the quality and concentration of the ER fluids; therefore, it is not easy to make a comparison with the corresponding literature data. Wen *et al.* [7], however, obtained similar results for $\mathrm{KNbO_3}$ silicone oil and $\mathrm{SrTiO_3}$ silicone oil ER systems for critical field strength from ac current measurements.

V. CONCLUSIONS

In conclusion, we constructed a dielectric apparatus to study the electric field induced aggregation in ER fluids. The dielectric permittivity increment caused by pair and chain formation of particles was measured in dilute, Brownian ER fluids composed of silicone oil and nanosized silica particles. From the results of the dielectric measurements we determined the critical electric field necessary to induce structure formation and the characteristic time scales of the particle pair and chain formation. The time scale of pair formation was also calculated on the basis of a theoretical model, and we have found good agreement between the theoretical and experimental values.

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