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Electrorheological properties and microstructure of silica suspensions

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We present experimental and theoretical results on the electrorheological response and microstructure of colloidal suspensions composed of silica nanoparticles dispersed in a silicon oil, as a function of electric field strength and silica water content. Using small-angle neutrons scattering experiments, we determined the evolution of the static structure factor of the suspensions when an electric field is applied. Experimental data were fitted with model calculations using the Percus-Yevick solution for Baxter's hard-sphere adhesive potential. The obtained stickiness parameter is directly related to the polarization interactions that depend on the water content of silica particles. The influence of the polarization interparticle potential on the rheology of the silica dispersions was investigated in a second time. A microscopic theory for the shear viscosity of adhesive hard-sphere suspensions was successfully used which describes the steady shear viscosity of suspension in terms of the fractal concept.

Keywords: Electrorheological fluids; Silica; Rheology; SANS; Dielectric constant

1. Introduction

Electrorheological (ER) fluids, which consist of polarizable particles suspended in an insulating liquid, have recently stimulated considerable interest within the scientific and engineering communities. They are materials that find potential application in a wide variety of systems especially in the realm of smart structures and intelligent systems. Winslow first reported the phenomenon of electrorheology in 1947 [1]. Since, extensive review articles have been published [2].

When an external electric field is applied, the flow behavior of the ER fluids changes from low-viscosity Newtonian fluids to high-viscosity non-Newtonian fluids, which are often empirically described as Bingham plastics [3]. In the presence of an electrical field, the particles are polarized and become small electrical dipoles. If the field exceeds a certain threshold, these dipoles attract each other and assemble into chains that are aligned along the field direction. These chains extend across the whole fluid and block its flow, thus giving rise to the electrorheological effect [4]. A number of stud-

ies have been made related to the field of structure formation in ER fluids [5,6]. A critical feature in the performance of such fluids is the control of interparticle interactions. The electrostatic forces between the particles, which are induced by the electric field, depend on the electrical polarizability of the particles [7] and are very sensitive to all species that may affect the dielectric constant of the particles. In the case of silica particles dispersed in silicon oil, Otsubo et al. [8] found that water molecules adsorbed on the silica surface, because of their high value of dielectric constant, are an essential factor in ER performance. However under some conditions, water in the contact region between two particles can form bridges that connect the particles through surface tension forces [9].

In this paper, our aim is to investigate the role of the interaction forces on the ER response of an electrorheological fluid, in terms of microstructure and flow behavior. We present ER results on a model system that consists of adhesive hard spheres dispersed in a dielectric medium. The system consists of nanometric spherical silicas dispersed in silicone oil. In order to control the polarization forces, the dielectric constants of the silica particles are modified by enclosing different water amounts in the porosity of the silica. We examine the rheology of the fluid in the presence

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of an applied electrical field and we report its influence on the structure of the fluid by small-angle neutron scattering (SANS).

In Section 1 we present a short review of the theories pertinent to electrorheological fluids, SANS technique, and interaction forces relevant to such systems. In Section 2 we discuss the influence of key experimental variables including the applied electric field and the dielectric constant on the rheological behavior and the microstructure of the ER fluids and we present a discussion of how the interparticle forces, through structural changes, affect the ER response.

2. Material and methods

2.1. Silica suspensions preparation

Monodisperse silica particles were synthesized through the sol-gel method proposed by Stöber et al. [10] and Matsoukas and Gulari [11]. Tetraethylorthosilicate (TEOS) (Prolabo, Rectapur) was hydrolyzed in a mixture of ultrapure water and ethanol (99 wt% Carlo Erba) in the presence of ammonium hydroxide (28 wt% Prolabo). In order to minimize the level of insoluble impurities, the ethanol and water were ultrafiltered through 0.22- μ m pore-size Millipore filters. The other chemical reactants were used as received.

For a given synthesis experiment, ethanol, water, and ammonium hydroxide were mixed together into a stirred stainless-steel reactor, giving a solution with concentrations in the range 7 M water and 1.13 M ammonia. TEOS was then regularly added into the reaction mixture with a constant flow rate of 1 ml/s giving a clear and homogeneous mixture with TEOS concentration 0.22 M. The stirring rate was 250 revolutions per minute. The mixture was then left standing for 24 h at 25 °C for 24 h to give an ethanolic suspension of colloidal silica. The silica was then washed with ethanol by repeated centrifugation (5000g) and ultrasonic (probe) dispersion cycles, replacing the supernatant with ethanol prior to each dispersion step; two cycles were performed. The sil-

ica powder (SP32) was recovered by vacuum drying at 60 °C for 6 h. Finally the silica powder was dispersed in the silicone oil by milling for hours, using a centrifugal ball mills giving a silica suspension (SL32) with silica volume fraction of 0.0547.

Silica suspensions having less water content were prepared under the same conditions except that for the silica suspension SL30, the silica powder (SP30) was heat-treated at 120 °C for 1 h and for the silica suspension SL26, the silica powder (SP26) was heat-treated at 600 °C for 1 h before the dispersion in silicone oil. For the three suspensions the silica volume fractions were adjusted to 0.0547.

Physical properties were determined for all silicas. Powder densities were measured using a helium gas pycnometer and specific surface areas were measured by multipoint BET. The water contents of the different silica samples were determined from thermogravimetric analysis. Assessments of the shapes, mean sizes, and size distributions of the silica particles were obtained from scanning electronic microscopy (SEM).

The observation of the different silica powders used showed that the silicas are spherical monodisperse particles. The typical physical properties of the silica powder are listed in Table 1 and the corresponding ERF systems properties are summarized in Table 2.

2.2. Rheological measurements

The rheological behavior of the suspensions was investigated using a Rheometric Scientific rheometer (RM 265-Rheomat) equipped with a rotational concentric cylinder. The gap between the inner and the outer cylinder is 1 mm. The high voltage was applied transverse to the direction of the shear between the concentric cylinders producing an electric field in the gap. Each cylinder is insulated from the rest of the rheometer. The instrument applied a time-varying deformation on the sample and measured the transmitted torque. The accessible shear rate range was 0.001–100 s⁻¹. In practice we found a good ER response in the range of

Table 1
Typical physical properties of the different spherical silica used as electrorheological material

Silica	Heat treatment (°C)	Radius, a (nm)	Water content (% weight)	Surface area, S (m ² /g)	Silica density, d_{SiO_2} (g/cm ³)
SP26	600	162	0.6	16.12	1.789
SP30	120	166	11	330.04	1.628
SP32	60	165	15	471.24	1.575

Table 2
Main physical properties of the different ERF fluids obtained by high-speed dispersion of the silica spherical particles in PDMS oil

Slurry	Water volume fraction, ϕ_w in silica	Dielectric constant		β	λ (for $E = 10$ kV/cm)	Dipolar force F_d (N)	Hamaker constant, A_{121} (J)
		ϵ_m	ϵ_p				
SL26	0.013	2.68	4.789	0.208	3.63	6.66×10^{-14}	2.46×10^{-22}
SL30	0.214	2.68	19.771	0.680	41.82	7.68×10^{-13}	1.79×10^{-21}
SL32	0.280	2.68	24.686	0.732	47.63	8.75×10^{-13}	2.00×10^{-21}

1–20 kV/cm at a frequency of 1000 Hz, so all measurements reported herein were made at the intermediate electric field of 10 kV/cm and a frequency of 1000 Hz. All the dispersions used in this study have an electrical conductivity of the order of 10^{-9} Siemens/m, so that the electrical current was lower than 1 μ A.

2.3. Small-angle neutron scattering measurements

Small-angle neutron scattering was used to monitor the structural modifications of the suspensions under electric field. SANS experiments were carried out with the D11 diffractometer [12] at the high flux reactor of the Institut Laue-Langevin (ILL) at Grenoble (France). The measurements were performed at room temperature using a neutron wavelength $\lambda = 16$ nm and a detector distance of 36.7 m selected to cover proper scattering vector, Q range: the scattering vector domain observed was $5 \times 10^{-3} \text{ nm}^{-1} < Q < 10 \text{ nm}^{-1}$, which defined the explored length scale in real space as $6 \times 10^3 \text{ nm} > r > 0.6 \text{ nm}$.

In order to observe the ER comportment of the suspension transversally to the direction of the electric field, we used a quartz cell of 1 mm thickness containing two electrodes in platinum spaced at 5 mm.

3. Theoretical models

3.1. Interactions in colloidal dispersions

The microstructure of colloidal dispersions results from a balance between the direct interactions of the particles and their Brownian motion.

The equilibrium microstructure is governed by the pair distribution function $g(r)$, which describes the probability of finding another particle located at a distance r from a reference particle chosen at random. This function satisfies the Ornstein-Zernike equation [13],

$$h(r_{12}) = g(r_{12}) - 1 = c(r_{12}) + n \int c(r_{13})h(r_{23}) dr_3, \quad (1)$$

where $c(r_{ij})$ is the direct correlation function and r_{ij} is the distance between particle i and particle j . This function is weighted by the particle number density n . To solve this equation for a particular system, it is necessary to have an additional relation between $h(r)$ and $c(r)$ containing also the pair potential $U(r_{ij})$. We shall consider the Percus-Yevick (PY) closure relation [14]:

$$c(r) = g(r)[1 - e^{U(r)/kT}]. \quad (2)$$

In nonaqueous suspensions two colloidal systems are very often used: the sterically stabilized suspensions of silica spheres and the aggregated suspensions of silica spheres. The first system can be modeled with the hard-sphere interaction potential [15],

$$\frac{U(r)}{kT} = \begin{cases} +\infty & \text{if } r < \sigma, \\ 0 & \text{if } r \geq \sigma, \end{cases} \quad (3)$$

where σ is the contact distance between two particles or the hard-sphere diameter of the particles. A system of hard spheres without any attraction between them cannot be achieved at rest, since van der Waals interactions are always present.

A more realistic system, which is aggregated particle suspensions, corresponds to an adhesive hard-spheres model. The particles interact via a narrow attractive region next to a repulsive core. In the case of a very short-ranged attraction, frequent use is made of the Baxter potential [16], which can be described by

$$U(r)/kT = \begin{cases} \infty & r < \sigma, \\ \ln[12\chi\Delta/(\sigma + \Delta)] & \sigma \leq r \leq \sigma + \Delta, \\ 0 & \sigma + \Delta < r. \end{cases}$$

Here σ is the hard-core diameter and Δ is the range of the attractive well. The attraction is described with the stickiness parameter, χ , which is called the Baxter parameter.

Baxter described such interaction in his sticky hard-sphere model, within which the Percus-Yevick approximation is used to solve the Ornstein-Zernike equation analytically, to first order for an adhesive hard-sphere potential [17].

Colloidal systems consisting of nonmodified silica particles dispersed in silicone oil are stabilized by a protective layer of adsorbed water molecules. At very small distances strong repulsive forces arise due to the structure of the water molecules [18]. The range of such forces is not known precisely, but one expects that it corresponds to the thickness of three layers of adsorbed water molecules [19], and is close to $\delta = 0.76$ nm. These forces can be described as a hard-sphere repulsion and the hard-sphere diameter becomes $\sigma = 2a + 2\delta$, where a is the radius of the particles.

A macroscopic property of the dispersion may be used in order to evaluate the Baxter parameter. The interaction behavior of the silica particle dispersion is given by the second osmotic virial coefficient, which is related to the pair potential as

$$B_2 = 2\pi \int_0^\infty (1 - \exp[-U(r)/kT]) r^2 dr. \quad (4)$$

For a Baxter potential, the Baxter parameter is related to the second virial coefficient by [20]

$$\chi = \frac{1}{4 - B_2/V_{\text{HS}}}, \quad (5)$$

where V_{HS} is the hard-sphere volume given by $V_{\text{HS}} = (4/3)\pi(a + \delta)^3$.

We shall estimate this parameter here, assuming that the particle interactions correspond to a van der Waals interaction,

$$U(h) = -A_{121} \frac{a}{12h} \quad (a \gg h > 2\delta), \quad (6)$$

where A_{121} is the Hamaker constant of the silica particles in a silicone oil, and h is the thickness of the gap between the spheres.

We also assume that a very strong repulsion occurs at small h :

$$U(h) = +\infty \quad (h < 2\delta). \quad (7)$$

In the system consisting of silica in silicon oil, we expect $A_{121} = 9.36 \times 10^{-23}$ J according to the Lifshitz equation in the so-called “symmetric case” of two identical phases 1 of silicon oil interacting across medium 2 of silica [21] and $2\delta = 1.52$ nm. Taking $a = 165$ nm, we have $\chi = 0.25$ by numeric calculation. a is the radius of the particles measured by SEM.

3.2. Electrorheology principle

An induced polarization results at the interface between two materials that differ in their dielectric constants. The current understanding of the origin of electrorheology was reviewed by Gast and Zukoski [22]. The electrorheological effect of a fluid is the result of the electric polarization forces. In our system the electrorheological fluids (ERF) are composed of spherical dielectric particles (silica) of radius a and dielectric constant ε_p suspended in a nonconducting dielectric fluid (silicone oil) of dielectric constant ε_m . Typical physical properties of the ERF system used are summarized in Table 3.

In a simple theory for the solution structure of dielectric spheres in the presence of an electric field, we consider the interaction between the dipoles that results from the polarization of the particles by an external electric field E [23]. The dipole moment p_0 , of an isolated sphere induced by an electric field $E(t)$ is given in the simple form as [24]

$$p_0(t) = 4\pi\varepsilon_0\varepsilon_m\beta a^3 E(t), \quad (8)$$

where ε_0 is the permittivity of free space and β the particle dipole coefficient defined by

$$\beta = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m}. \quad (9)$$

In the presence of an electric field the spheres align in the form of a “chain” where the distance between particles is nearly small [25]. In this case, the dipole moment is modified by the interaction between a dipole and the electrical field produced by a nearby second dipole [26]. For two spheres at contact, the dipole strength may be approximated by $p = p_0[1 + \beta/4 + O(\beta^2)]$.

Table 3
Typical physical characteristics of the different constituents of an ERF fluid

	Water	Pure silica	PDMS
d (g/cm ³)	0.997	2.218	0.963
η^0 (Pa s)	8.90×10^{-4}	–	9.60×10^{-3}
ε_p (25 °C)	78.36	3.81	2.68
A (J)	3.85×10^{-20}	4.14×10^{-20}	4.40×10^{-20}

The time-average potential energy of interaction between two dipoles [27] is given in a mean field approximation as

$$\begin{aligned} \frac{U(r, \theta)}{kT} &= -\lambda \left(\frac{2a}{r} \right)^3 P_2[\cos \theta] \\ &= -\lambda \left(\frac{2a}{r} \right)^3 \left[\frac{3 \cos^2 \theta - 1}{2} \right], \end{aligned} \quad (10)$$

where r is the distance between two particles, θ is the angle between the dipole moment vector and the center to center vector r , and $P_2[\cos \theta]$ is the second Legendre polynomial. Here λ is a dimensionless parameter characterizing the relative importance of the polarization interaction energy to thermal energy, defined by

$$\lambda = \pi\varepsilon_0\varepsilon_m(\beta E)^2 a^3 / kT. \quad (11)$$

The dipolar energy scales as β^2 . Thus the ERF behavior strongly depends on the difference between the dielectric constant of the particles and that of the dispersion medium.

At a given $r = r_0$, $\partial U(\theta)/\partial \theta = 12\lambda(a/r_0)^3 kT \cos \theta \sin \theta$ is equal to 0 at 2 angles: $\theta = 0$ and $\theta = \pi/2$ where the particles are in equilibrium positions. There is a critical angle θ_c below which the dipolar energy of interaction becomes attractive. Thus, the interaction aligns both particles in the direction of the electric field. Beyond θ_c , the energy of interaction will be repulsive. In this case, the two particles are aligned perpendicularly to the electric field. Then, the presence of many particles involves the formation of chains of particles parallel to the direction of the electric field, regularly spaced, and the intensity of the potential interaction energy is proportional to the difference $\varepsilon_p - \varepsilon_m$ [28]. One way to improve the ER effect is to increase the difference of the dielectric constants [29]. In our system, the dielectric constant of silica particles is modified by incorporation of water in the microporosity of the silica particles. This technique permits us to avoid the formation of a permanent water bridge at the contact between two particles [30]. Thus the particles are composite particles constituted by a volume fraction ϕ_{SiO_2} of silica of dielectric constant $\varepsilon_{\text{SiO}_2}$ and a volume fraction ϕ_w of water of dielectric constant ε_w . In a first approximation, we can consider that the dielectric constant of the particle is $\varepsilon_p = \varepsilon_{\text{SiO}_2}\phi_{\text{SiO}_2} + \varepsilon_w\phi_w$, where $\phi_{\text{SiO}_2} = 1 - \phi_w$ [31].

The degradation of these structures by shear stress gives rise to the observed enhancement of suspension shear rate. At equilibrium positions, these dipoles will result in electrostatic forces between particles [32]. At the lowest level of approximation (the point dipole model), the magnitude of the attractive force, F_d , between two particles aligned with the electric field ($\theta = 0$) and with a center-center separation of r is

$$F_d = \left. \frac{\partial U(r)}{\partial r} \right|_{\theta=0} = 12\lambda a^3 kT \frac{1}{r^4}. \quad (12)$$

3.3. Small-angle neutron scattering

Structural information may be extracted from small-angle neutron scattering experiments. Exhaustive review of the theory of small-angle neutron scattering can be found in the literature [33,34].

For a dispersion of identical spherosymmetrical particles, each of radius a , containing n particles per unit volume, the normalized scattering intensity can be written as

$$I(\mathbf{Q}) = K(\rho_p - \rho_s)^2 \left(\frac{4}{3} \pi a^3 \right)^2 n P(\mathbf{Q}) S(\mathbf{Q}). \quad (13)$$

Here ρ_p and ρ_s are the average neutron scattering length density of silica and PDMS. $\mathbf{Q}$ is the scattering vector or momentum transfer where the magnitude is related to the scattering angle, α , and the neutron wavelength, λ_n , by

$$Q = |\vec{Q}| = \frac{4\pi}{\lambda_n} \sin(\alpha/2). \quad (14)$$

K is an instrumental constant that depends on the intensity of the incident beam and the distance between the scattering sample and the detector. $P(Q)$ is the form factor, reflecting the distribution of scattering material inside the particles. For a homogeneous sphere it is defined as

$$P(Q) = \left(\frac{3(\sin Qa - Qa \cos Qa)}{(Qa)^3} \right)^2. \quad (15)$$

The function $S(Q)$ is called the structure factor and describes interference effects of correlations between particle positions. This function is directly related to the radial distribution function, $g(r)$, via a Fourier transformation

$$S(Q) = 1 + 4\pi n \int_0^\infty [g(r) - 1] r^2 \frac{\sin(Qr)}{Qr} dr, \quad (16)$$

where n is the particle number density. $S(Q)$ contains the effects of the particle interactions and is experimentally accessible. When fitting experimental data, theoretical values of $S(Q)$ may be calculated by using approximate integral equations. For hard spheres and for the Baxter potential, an analytical expression for $S(Q)$ can be obtained by applying the Percus-Yevick approximation to the Ornstein-Zernike relation [35].

3.4. Flow behavior of electrorheological fluids

Our system consists of silica particles dispersed in silicon oil, which can be assimilated either to a hard-spheres colloidal dispersion [36] or to an adhesive hard-spheres colloidal dispersion [37]. This hard-sphere model may serve as a basis for obtaining an understanding of mechanisms in electrorheology.

In the absence of an external electrical field, the steady-state shear viscosity of a stable dispersion of Brownian hard spheres depends on two dimensionless groups. The relative

viscosity is determined by the volume fraction of the particles which is defined as $\phi = (4/3)n\pi a^3$, where n is the number density of the particles and a is the particle radius. The second determining group is the Peclet number defined by

$$\text{Pe} = \frac{a^2 \dot{\gamma}}{D_0} = \frac{6\pi \eta_m a^3 \dot{\gamma}}{kT}, \quad (17)$$

where D_0 is the Stokes-Einstein self-diffusion coefficient of an isolated particle given by $D_0 = kT/(6\pi a \eta_m)$, η_m is the solvent viscosity, $\dot{\gamma}$ is the shear rate, and kT is the thermal energy. This number expresses the ratio between the time scale on which the structure of the dispersion is deformed by the shear and the time scale of Brownian motion that restores the structure.

For adhesive particle dispersions in which attractive interparticle forces play a prominent role, a new dimensionless group must be considered. The characteristic parameter describing the interplay between attractive forces and flow is the ratio of the viscous forces tending to disrupt the structure and the attractive forces responsible for the aggregation of particles. Such dimensionless group can be defined by [38]

$$G = \frac{\tau_0}{\tau_m} = \frac{\pi a^2 \eta_m \dot{\gamma}}{F_a}, \quad (18)$$

where $\tau_0 = \eta_m \dot{\gamma}$ is the shear stress of the dispersion medium, F_a represents attractive interparticle forces and $\tau_m = F_a/(\pi a^2)$ is related to the yield strength of the closely packed system of particles.

In the simplest case where these interactions can be attributed to van der Waals forces, the interaction parameter F_a , between two spherical particles, close to contact, can be approximated by the relation $F_a = F_{\text{vdw}}$, with

$$F_{\text{vdw}} = A_{121} \frac{a}{12h_a^2}, \quad (19)$$

where A_{121} is the Hamaker constant of particles 1 in medium 2 and h_a is scale length range of the van der Waals forces.

When an external electrical field is applied, polarization forces must be taken into account and the interactions parameter F_a is equal to $F_a = F_{\text{vdw}} + F_d$, where F_d is defined by Eq. (12).

In the presence of an external electrical field, E , the characteristic parameter describing the interplay between dipole forces and flow is the Mason number given by [39]

$$\text{Mn} = \frac{\text{Pe}}{\lambda} = \frac{6\eta_m \dot{\gamma}}{\epsilon_0 \epsilon_m (\beta E)^2}. \quad (20)$$

This number is the ratio of the viscous forces tending to disrupt the structure and the polarization forces responsible for the structure. Here λ is the dimensionless dipole interaction strength. The viscosity of such dispersion depends on ϕ , Pe , G , and Mn .

Flow behavior of Brownian dispersions and aggregated dispersions are investigated using theoretical models re-

viewed by Batchelor [40]. For Brownian dispersions, hydrodynamic and thermodynamic interactions are considered in terms of the self-consistent approach [41]. According to the analysis of Batchelor [42], for dilute dispersion of hard spheres, in the limit domain where three-body and higher order interactions can be neglected, the macroscopic stress may be deduced from the hydrodynamic and potential interactions between the particles and the resulting microstructure. In the weak flow limit, the viscosity of hard-sphere dispersions assumes the form [43]

$$\eta_r \equiv \frac{\eta}{\eta_m} = 1 + 2.5\phi + 6.2\phi^2. \quad (21)$$

For aggregated dispersions, the flow behavior may be defined from the self-consistent analysis by an equation [44] which determines η_r as a function of G , as

$$\zeta^\sigma + 2K\zeta - 1 = 0, \quad (22)$$

where $K \equiv (\phi/2\phi_m)(2/5G)^{1/\nu}$, $\sigma \equiv \nu/(2.5\phi_m)$, and $\zeta \equiv \eta_r^{-1/\nu}$. ϕ_m is the dense packing volume fraction and $\phi_m = 0.64$ for random dense packing.

According to a fractal concept [45], the parameter ν is described in terms of the fractal dimension as

$$\nu = \frac{6 - 2d_f + 2d_f/3}{3 - d_f}, \quad (23)$$

where d_f is the fractal dimension of the aggregates developed in the dispersion. Equation (22) may be solved numerically in terms of ζ . The relationship between shear stress, τ , and shear rate $\dot{\gamma}$ is given by

$$\tau = \zeta^{-\nu} \eta_m \dot{\gamma}. \quad (24)$$

4. Experimental results

4.1. Rheological measurements

The rheological behavior of the composite is described as a Bingham plastic where the shear stress plotted against the shear rate beyond a critical shear rate is described by $\tau = \tau_B + \eta_{pl}\dot{\gamma}$.

The plastic viscosity, η_{pl} , corresponds to the zero field strength viscosity of the composite and is approximated by the slope of the linear part of the shear stress vs shear rate plot.

The Bingham plastic nature of the fluids motivates analysis of their response based on the Bingham yield stress rather than the apparent viscosity.

4.2. Steady-state flow behavior of silica-PDMS suspensions

The experiments were performed in two regimes of flow for the dispersions: structured regime ($Pe < 1$) and destructured regime ($Pe \gg 1$).

Fig. 1. Shear stress versus shear rate (Peclet number = shear rate $\times$ 5.35 s) for a set of silica suspensions at constant volume fractions ($\phi = 0.055$), as a function of water content. Dashed line represents the Newtonian curve.

In the first stage, the dispersions were submitted to continuous deformations and the rate of deformation was kept fast compared to internal relaxation modes of the dispersion. At this rate, disturbances caused by the flow are not relaxed and dominate the flow.

In the second regime, the rates of continuous deformations could be faster than the rates of motion of individual particles. The structure of the suspension would break up and the suspension flows as a Newtonian liquid.

The rheological experiments were carried out at a steady-shear rate by stepping up the shear rate in order to measure the equilibrium stress. Fig. 1 shows the measured stress as a function of shear rate, for a set of silica suspensions at constant volume fractions ($\phi = 0.055$) and constant temperature ($T = 298$ K), but containing silica particles with widely different water contents. The horizontal scale is labeled as shear rates or according to the values of the Peclet number, which compares the rates of forced motions to those of spontaneous motions in dilute suspensions.

Despite the fact that the particle concentrations are low, $\phi = 0.01547$, shear thinning is observed at a low shear rate: typically at $Pe \leq 1$. For each one of these suspensions, the stress remains on a plateau, independent of shear rate and a yield stress can be determined by extrapolating to the stress axis.

At a higher shear rate, above a critical Peclet number $Pe > 1$, the flow rates of these suspensions are extremely high and a Newtonian regime will be recovered.

It is interesting to note that the effect of the water content of silica particles is quite negligible. According Table 1, the silica water contents are well correlated with the silica surface areas and it can be expected that most of the water molecules are included in the microporosity of silica particles.

In a hard-sphere suspension, the yield stress is due to dense packing of particles and flow occurs when the structure is distorted enough to allow particles to move. Moreover, at low silica volume fraction, van der Waals attractions must be incorporated and we suppose an aggregated suspension. According to the experimental data of Sonntag and Russel [46] the aggregates are fractal and their fractal dimen-

Fig. 2. Shear stress versus dimensionless shear rate for a set of silica suspensions at constant volume fractions ($\phi = 0.055$) for different values of the particle dipole coefficient β . Straight line represents the theoretical curve obtained from numerical solution of Eq. (22).

sion ($d_f < 3$) may be determined from SANS experiments. In order to calculate the rheological curve, a microrheological model of aggregation may be used, which describe the steady shear viscosity of suspension in terms of the fractal concept. In Fig. 2 it is shown that the shear thinning behavior scales with the dimensionless shear rate G [Eq. (19)], which incorporates the van der Waals interactions. In our system we expect $A_{121} = 9.36 \times 10^{-23}$ J and we assume that the particles are in contact through their adsorbed water layers and $h = 1.52$ nm. Taking $a = 165$ nm, we have $F_a = 5.66 \times 10^{-13}$ N.

The straight line represents the theoretical calculated rheological curve using the fractal model [41]. The theoretically predicted values are calculated from Eq. (24) where the parameter ζ is obtained from numerical solution of Eq. (22). All calculations are carried out with the estimated value for $d_f = 1.6$ (see SANS results) and $\phi_m = 0.64$ and $\phi = 0.01547$. As seen from the figure, the theory describes the experimental data very well.

4.3. Rheology of electrorheological fluids

Shear stresses as a function of shear rates were obtained at constant applied electrical field strength and volume fraction, for samples at different silica water content. Table 3 summarizes the main characteristics of these suspensions.

Fig. 3 shows the shear stress of the different suspensions with a volume fraction of 0.0547 as a function of shear rate at zero field strength and at constant field strength, $E = 10$ kV/cm. The curves are scaled as a function of the dimensionless polarization interaction parameter, λ .

The samples are shear thinning, showing greater shear rate dependence when the water content of the silica particles is high. It can be seen again that the effect of the electric field is most pronounced below a critical shear rate, which depends on the polarization interaction parameter λ . Above these critical shear rates, a Newtonian response is observed. This behavior suggests that in a situation of shear flow, if

Fig. 3. Shear stress versus shear rate (Peclet number = shear rate $\times 5.35$ s) for a set of silica suspensions at constant volume fractions ($\phi = 0.055$), at constant temperature ($T = 298$ K) with different values of the dimensionless polarization interaction parameter λ . Straight line represents the Newtonian curve.

Fig. 4. Reduced shear stress versus Mason number under 10 kV/cm, for a set of silica suspensions at constant volume fractions ($\phi = 0.055$), and constant temperature ($T = 298$ K) with different values of the particle dipole coefficient β .

the applied stresses are large, we expect the interactions to become less important.

In the absence of external electric fields we conclude that the ERF suspension is composed of adhesive non-Brownian particles. In order to understand the effect of the silica water content on the ERF behavior when an electric field is applied, an additional force must be considered. This force is the dipolar force that arises from the polarization of the silica particles and depends on the parameter β .

Based on this analysis we expect the rheological behavior of ERF in shear and electric fields, to depend on the dimensionless Mason number Mn . Fig. 4 shows that at a given volume fraction and temperature, the reduced shear stress data as a function of Mn reduces to a single master curve. The reduced shear stress is defined by $(\tau_E - \tau_{E=0})/\tau_E$, where τ_E and $\tau_{E=0}$ are the shear stress measured at a given shear rate, in the presence and in the absence of a applied electric field. This behavior suggests that in the low shear rate domain the shear and electric-field dependence of ERF can be expressed as a single function of Mn . The position of the critical shear rate corresponds to the transition from dipolar-controlled structure to the domination of the viscous forces.

Fig. 5. Shear stress versus dimensionless shear rate under 10 kV/cm, for a set of silica suspensions at constant volume fractions ($\phi = 0.055$), at constant temperature ($T = 298$ K) with different values of the particle dipole coefficient β .

Theoretical calculation of the complete rheological curve may be done using the microrheological model of aggregation, which is based on the fractal concept. Fig. 5 shows that the shear thinning behavior obtained at different water content levels scales with the dimensionless shear rate G , which incorporates both the van der Waals and the dipolar interactions. Calculations were carried out on each ERF using the corresponding A_{121} Hamaker constant presented in Table 2 and an average separation of $h = 1.52$ nm. Taking $a = 165$ nm, we have $F_a = 5.66 \times 10^{-13}$ N and F_d is given in Table 2 as a function of the water content. As seen in the figure, the theory describes the data well, although the shear stress measured at the lower shear rate seems to be slightly above the theoretically predicted values.

4.4. Small-angle neutron scattering study

The small-angle neutron scattering technique is used for studying the microstructure evolution of the silica particle suspension that was submitted to electric fields.

At high electrical fields, a two-dimensional set of diffraction spots is obtained, located in the direction of chain alignment (Fig. 8). The spots are extended in the perpendicular direction because the chains are quite thin in this direction. When the field is switched off, the scattering pattern immediately reverts to the original structure, indicating that the effects are fully reversible. Water layers play the role of protective barriers that are able to prevent irreversible silica bonding.

The SANS scattering curves of the slurries as a function of silica water content at $\phi = 0.0547$ and without applied field are shown in Fig. 6. The scattering curves show an increase of the intensity at low wave vector Q , reflecting the aggregation of silica particles into large entities. The curves do not show any systematic water content dependence, indicating that the silica particles may be considered as adhesive hard-sphere particles, with quite the same effective diameter. Experimental scattering intensities are compared with model

Fig. 6. SANS scattering curves of slurries as a function of silica water content, at $\phi = 0.055$, sticky hard-sphere (SHS), and Percus-Yevick (PY) presented on this figure ($a = 165$ nm, $\chi = 0.25$, $h = 1.52$ nm).

Fig. 7. SANS scattering curves of the ER fluid SL32 at $\phi = 0.055$, under an electric-field intensity of 10 kV/cm. Two model curves are presented: sticky hard-sphere (SHS) and fractal model ($a = 165$ nm, $\chi = 0.40$, $d_f = 1.6$).

calculations based on the Ornstein-Zernike relation in the Percus-Yevick approximation for a hard-sphere fluid and an adhesive hard-sphere fluid. In the last case, the pair potential was described by Baxter's model. In the model calculations, we used the particle radius obtained from electronic microscopy measurements ($a = 165$ nm). The stickiness parameter, χ , is calculated from Eq. (5) using a van der Waals potential, taking $h = 1.52$ nm. The stickiness parameter thus was to be $\chi = 0.25$. It can be seen from Figs. 6 and 7 that agreement with the sticky hard-sphere (SHS) model is quite satisfactory at low Q . The differences between the experimental data and the results from the theoretical model for monodisperse system are significant at intermediate values of Q where the theoretical curve is below the experimental points. These differences are due to the intrinsic polydispersity of the silica particles, which have up to 10% size polydispersity. All these results suppose an attractive van der Waals potential between the silica particles. We expect the attraction to become less important if a stress is applied. The surfaces are protected from irreversible bonding by the adsorbed water layers.

Fig. 7 shows the scattered intensities of the ER fluid SL32 at $\phi = 0.0547$ as a function of the wave vector when an elec-

Fig. 8. Electric-field effect on silica particles dispersed in silicone oil ($\phi = 0.055$; $\beta = 0.73$): diffraction pattern (D11, $\lambda = 15$ Å; sample detector distance, 36.7 m; asymmetric collimation diaphragm at 40.5 m).

tric field $E = 10$ kV/cm was applied. Comparison of SANS curves at $E = 0$ kV/cm and $E = 10$ kV/cm shows some qualitative differences in shape, indicating that the correlation between the silica particles increases when an electric field is applied.

If the field exceeds a certain threshold, the particles attract each other and assemble into chains that are aligned along the field direction. The structures are formed under the combined effects of applied field and interparticle repulsions. The forces are the attractive force due to the interaction of the electrical dipoles carried by the particles, the repulsive force due to the water layer adsorbed on the particles, and the van der Waals attractive force. When the field is switched off, the scattering pattern immediately reverts to that of a weakly attractive isolated particles system. The particles repel each other at short distances, otherwise the field-induced aggregation is not fully reversible. But under the combined effect of Brownian motion and effective attraction a local liquid-like structure is generated. This may explain why the effect of an electrical field on the local structure remains small.

Theoretical values of $I(Q)$ may be calculated by using the sticky hard-sphere model. An analytical expression for $S(Q)$ was obtained by applying the Percus-Yevick approximation to the Ornstein-Zernike relation for an adhesive hard-sphere system. The Baxter potential was calculated from the stickiness parameter χ , taking into account both the van der Waals and the polarization interactions. In this case, the stickiness parameter is evaluated at $\chi = 0.4$. The straight line represents the theoretical calculated SANS curve (Fig. 7). The fit is quite good, reflecting the effect of the polarization interactions on the microstructure of the phase domains inside the chains formed under an electric field. Fig. 7 shows again that the SANS curve may be fitted with an empirical expression for a mass fractals consisting of spheres with a radius $a = 165$ nm [47] using $d_f = 1.6$.

5. Conclusions

Our main point is that at low shear, dispersions are in an aggregated state with discrete clusters. When an electric field is applied a phase transition is observed with the formation of infinite clusters. The equilibrium structure depends on the balance of four interactions: van der Waals force, electrostatic repulsion, thermal energy, and field-induced dipole attraction.

The analysis of the experimental SANS data and the rheological data shows that there is a strong link between the electrically induced microstructure and the rheological properties of these suspensions. These results may be modeled with good agreement by using the sticky hard-sphere model.

The polarization forces are the main parameters in determining the electric-field-induced aggregation. The silica water content has enormous influence on the ER properties of these suspensions.

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