

Electrorheological effects depending on the dispersity of lyophilic or lyophobic particles

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Abstract

We theoretically investigate the relations among electrorheological (ER) effects of ER fluids, zero-field dispersity of colloidal particles and particle wettability, and find that well dispersed particles resulting from particle wettability have much stronger attraction than those aggregated into different clusters. We reveal that, to achieve ER effects, besides improving dielectric properties of ER particles, it is also helpful to reduce the surface tension of liquids, which leads to higher wettability of suspended particles and thus better zero-field dispersity of the particles due to lyophilic repulsive forces between them. Our theoretical results are applied to explain qualitatively the experiments by others.

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1. Introduction

Colloidal electrorheological (ER) fluids are a suspension made of nanometer-sized dielectric particles in an insulating carrier liquid. If an external electric field is higher than a certain critical value, the liquid–solid transition happens in several milliseconds, and the transition is reversible as the electric field is turned off [1,2]. The rapid field-induced aggregation and the large anisotropy of ER fluids render these materials potentially important for applications. Various industry applications of such smart materials are suggested and designed [2–7].

The mechanism of ER fluids and the search for better ER fluid materials are focus topics of theoretical and experimental research. In recent years, many authors have investigated the giant electrorheological (GER) effect [5–14]. The yield stress of GER fluids can reach 100 kPa or higher in the applied electric field of 3 kV/mm. It is reported that reducing particle size can significantly enhance the yield stress of GER fluids. Wen et al. [5] proposed that the sat-

uration surface polarization in the contact region between the neighbouring particles is responsible for the GER effect. Their simulation based on a saturation surface polarization model agrees with the experimental yield stress of the GER fluid consisting of core/shell nanoparticles suspended in silicone oil. Lu et al. [6] proposed a polar molecule-ER model to explain the GER effect. In their model, the interaction between charges and polar molecules on particle surfaces were believed to be the key to the GER effect.

As far as the dielectric property of the core/shell structured particles and the polar molecules are concerned, the wetting property of particle surface is important to the GER effect. Zhao and Wang [9] found that the wettability of particles and base oil has an important impact on the ER effect. Cai et al. demonstrated that the particle wetting surface in a liquid could induce ER effects [14]. In their experiment a wetting-induced GER effect was proved. They found that the nanoparticles of barium titanate coated with urea suspended in a hydrocarbon oil gives no measurable ER effect. Interestingly, by adding a small amount of oleic acid to the hydrocarbon oil, they attained a yield stress of 260 kPa in the electric field of 3 kV/mm. The addition of the surfactant changes the non-wetting

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particles into wetting ones which induce the GER effect. In this work, we shall discuss lyophilic repulsive or lyophobic attractive forces between particles arising from their wettability, which modulate the dispersity of the particles in the system, and hence affect ER effects. Our results indicate that the surface tension between particles and oil can be greatly reduced due to the mediating effect of the surfactant molecules, thus allowing particles to disperse very well in a zero-field and then form better particle structure upon application of an electric field.

2. Theory

In this work, our focus is on the particle-liquid wetting effect on the colloidal ER property. The lyophilic repulsive force due to the wettability of particles with respect to the base liquid is our interest, which is compared with the van der Waals force between two colloidal ER particles.

Let us first discuss the van der Waals force and the lyophilic repulsive force, which are both dependent on and sensitive to the distance between particles.

When the external electric field is zero, assuming the particles to be wet with the liquid, we suppose the particles are dispersed in the liquid homogeneously. We use m_{solid} , ρ and n to denote the mass, mass density and number of solid particles, respectively. V_{liquid} and $V_{\text{particle}} = (4/3)\pi R^3$ represent the volumes of liquid and single particle of radius R , respectively. Then, we have the center-to-center distance d between two particles

$$d = V^{1/3} = \left(\frac{V_{\text{solid}} + V_{\text{liquid}}}{n} \right)^{1/3}. \quad (1)$$

The surface-to-surface gap g between the two particles is given by $g = d - 2R$. Take $\rho = 6.017 \times 10^3 \text{ kg/m}^3$, n being the number of the particles with $m_{\text{solid}} = 1 \text{ g}$, $V_{\text{liquid}} = 0.3 \text{ mm}^3$, and the average radius of the particles $R = 30 \text{ nm}$, and then obtain $g = 6.8 \text{ nm}$. The zero-field dispersity of colloidal particles are characterized by the average distance between the particles. The best dispersity means that there exists a largest average distance (or gap) between two adjacent particles.

When the external electric field is larger than a critical value, solid particles are polarized with an effective moment for each particle. Due to certain attractive interactions between solid particles the two colloidal particles are brought closer to each other. The distance between the particles is no longer a constant value, and the gap of two adjacent particles in a column can be reduced to about 0.2 nm [5,6].

The van der Waals force between two colloidal particles is attractive. It is small either when the distance between the particles is large or when the particle size is large. However, it can not be ignored when the particle has a size as small as nanometer scale and the gap is at sub-nanometer scale. The van der Waals interaction potential U_{vdW} between two colloidal spherical particles can be written as [7,15]

$$U_{\text{vdW}} = -\frac{1}{6}A \left\{ \frac{2R^2}{4Rg + g^2} + \frac{2R^2}{(2R + g)^2} + \ln \left[\frac{4Rg + g^2}{(2R + g)^2} \right] \right\}. \quad (2)$$

A derivative of the above expression with respect to g gives the force F_{vdW} between the two particles

$$F_{\text{vdW}} = -\frac{1}{6}A \left[\frac{64R^6}{(2R + g)^3(4Rg + g^2)^2} \right], \quad (3)$$

where A is the Hamaker constant, which is related to the dielectric constants of the base liquid and the particles.

The lyophilic repulsive force and lyophobic attractive force are dependent on the particle wettability with respect to the liquid. The surface energy [16] of the particles' surfaces and liquid is

$$F(h) = \gamma_{\text{sl}} + P(h), \quad (4)$$

where γ_{sl} is solid-liquid interfacial tensions, h the local thickness of liquid between two particles, and $P(h)$ the disjoining force of the liquid. The spheres are completely immersed in the liquid, so the interface between the solid particles and liquid is unaltered and hence γ_{sl} can be omitted here. When h is larger than the molecular size a_0 , $P(h)$ [16–18] is controlled by a long range van der Waals force

$$P(h) = \frac{A}{12\pi h^2} \quad (a_0 \ll h \ll R). \quad (5)$$

The disjoining pressure Π of the thin wetting films is the derivative of $P(h)$, which is vertical to the film, so it is along the line joining the centers of the two particles

$$\Pi = \frac{A}{6\pi h^3}. \quad (6)$$

If the particle surface is wet with the liquid between two particles, the local distance between the two particles, or alternatively the local thickness of liquid between them, is then given by

$$h = 2(R - R \cos \theta) + g. \quad (7)$$

By integrating the disjoining pressure of the section, one gets the wetting force F_w as

$$\begin{aligned} F_w &= \int \Pi dS = \int \frac{A \cdot 2\pi R \sin \theta}{6\pi[2(R - R \cos \theta) + g]^3} dR \sin \theta \\ &= \int_0^{\frac{\pi}{2}} \frac{A \cdot 2\pi R^2 \cos \theta \sin \theta}{6\pi[2(R - R \cos \theta) + g]^3} d\theta, \end{aligned} \quad (8a)$$

$$F_w = \frac{A(2R - g)}{24g^2} + \frac{A}{24(2R + g)}. \quad (8b)$$

Next, the composition of the two forces is

$$\begin{aligned} F_w &= \frac{A(2R - g)}{24g^2} + \frac{A}{24(2R + g)} \\ &\quad - \frac{1}{6}A \left[\frac{64R^6}{(2R + g)^3(4Rg + g^2)^2} \right]. \end{aligned} \quad (9)$$

When the Hamaker constant is positive, it has a trend to enlarge the thickness of the wetting film thus causing the lyophilic repulsive force and vice versa. Without electric field, wetter particles in an oil leads to better dispersity of

the particles, whereas less wet particles cause themselves to be aggregated into clusters.

The interaction between two adjacent clusters under an electric field is calculated using the finite element approach and the dipole–dipole interaction between the particles is taken into account. We used the finite element approach to solve the Laplace equation for the electrostatic potential everywhere in our model. Electrostatic energy of particles and clusters can be calculated according to the electrostatic potential, then we get the yield stress of two dispersed particles and that of two adjacent clusters. By comparing these two interactions, we can clearly see the effect of the particle aggregation or good dispersity of particles on ER effects. The interaction of the two independent particles is much larger and more details will be reported in the next section.

3. Results and discussion

In the experiment of [14], the two suspensions of the same particles suspended in different oils exhibit completely different appearances. Whereas the silicone oil suspension has the consistency of light cream, in the case of hydrocarbon oil with the same solid concentration the appearance is just like a lumpy paste. That the particles form clusters in the lumpy paste due to the lyophobic attractive forces between particles seems to be a reasonable explanation.

Let us consider a system in which the suspended particles are wet with the base liquid. Then, the wetting force is a repulsive force, which makes the particles disperse homogeneously in the liquid. We take the gap g between two particles to be about 6.8 nm under a zero-field. The wetter the particles are in an oil, the better the particles are dispersed, while the less wet the particles are in an oil, the more the particles are aggregated. When the electric field is applied to an ER system, we take the reduced gap between the particles as small as 0.2 nm. The change of lyophilic repulsive force with particle size is calculated using Eq. (8b) (Fig. 1a). As shown in Fig. 1b, the repulsive force of different particle size decays when the gap increases. Fig. 2 shows the composition of the van der Waals force and the lyophilic repulsive force as a function of the gap between two particles. When the electric field is applied, compared to the electrical force, the composition of the van der Waals force and lyophilic force is small enough to be neglected. It does not reduce the yield stress and shear stress of ER fluids, which are essential to applications of ER fluids. When the electric field is withdrawn, the composition of the van der Waals force and lyophilic repulsive force is repulsive, and it can disperse the particles very well again, destroying the columnar micro-structure of the particles and making the ER fluid a well-proportioned system.

When the particles are not wet with the liquid just like the particles composed of barium titanate coated with urea in hydrocarbon oil without surfactant, the particles aggregate in the liquid becoming a lumpy paste. This is because both lyophobic and the van der Waals forces are attractive. Due to the two attractive forces, the particles

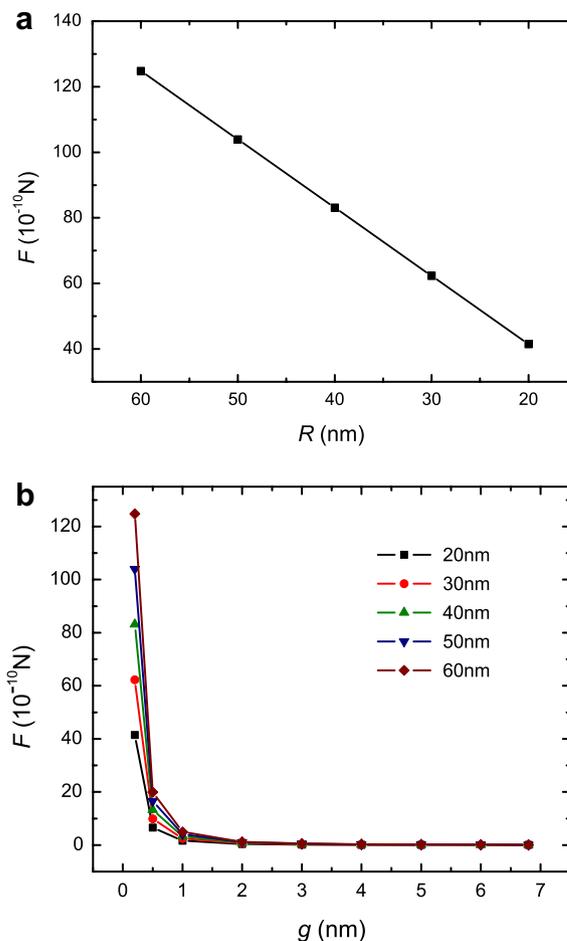


Fig. 1. (a) The lyophilic repulsive force for different particle with radius 20, 30, 40, 50, and 60 nm, at the Hamaker constant $A = 1 \times 10^{-19}$ (a typical numerical value of the Hamaker constant) and gap $g = 0.2$ nm. (b) The lyophilic repulsive force changes with the particle gap g for different particle radius 20, 30, 40, 50, and 60 nm at the same Hamaker constant. The force decays dramatically as the particle gap increases.

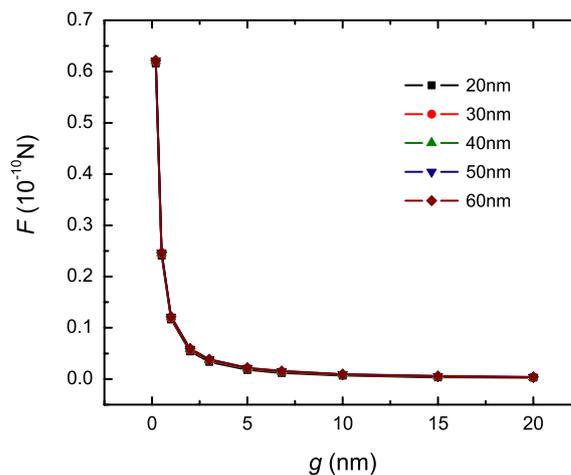


Fig. 2. The composition of the van der Waals force and the lyophilic repulsive force is a repulsive force which does not change apparently with the diameter of particles. In this figure, all the curves are almost overlapped.

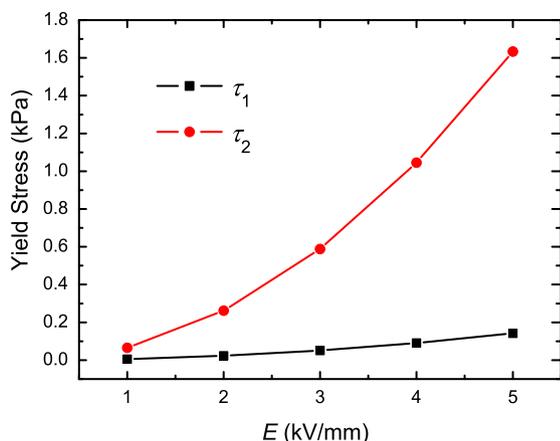


Fig. 3. The yield stress τ_1 of two particles located in two different clusters and the yield stress τ_2 of two well dispersed particles, as a function of electric field E .

are very close to each other, and as the particles get closer, the attraction gets stronger accordingly. So particles assemble to form clusters in the liquid. The mutual position of the particles in one cluster is occasional. When the external electric field is applied to the system, the interaction of two particles located in two different clusters is weaker than that of two well dispersed independent particles. Thus, the particles can not be easily directed by the applied electric field, so the columnar micro-structure may not be easily established along the direction of the external field. In our simulation, there are 14 particles in each cluster of 250 nm in diameter. The gap between two neighboring particles is 1 nm and the gap between two well dispersed particles is the same as that of the nearest particles in clusters. The volume fraction of dielectric particles is about 30% in two situations mentioned before. Under the same electric field, the yield stress τ_1 of two particles in two adjacent clusters is found to be about 12 times smaller than that τ_2 of two independent particles as shown in Fig. 3.

4. Conclusion

The dispersity of particles suspended in a liquid has a direct effect on ER effects. The wettability of the particles with respect to the liquid is the key to the dispersion of the particles in the liquid. Previously, the main interests are in the modification of suspended particles, which causes the improvement of particle interactions. In fact, the modification of base liquids is also of particular importance, since the surface property of the liquid can be modulated by additives [17,19]. The particles should be wet with the base liquid, to achieve better ER fluids. If the particles are not wet with the liquid, some surfactant may be added.

To sum up, the relations among ER effects of ER fluids, zero-field dispersity of colloidal particles and the particle wettability in the liquid have been theoretically investigated. The zero-field dispersity of ER particles is characterized by the average distance between the particles. Wetter particles in a liquid can lead to larger lyophilic repulsive

forces between particles. If the lyophilic repulsive force overcomes the attractive van der Waals force between colloidal particles, it would make particles be well dispersed in a liquid under a zero-field. However, if the particles are not wet with the liquid, the lyophobic attractive force between particles would cause the particles to aggregate into clusters even under the zero-field. To show the effect of the particle dispersity on ER effects, the average particle–particle interaction for two particles in two different clusters is calculated, and it is compared with the interaction between two independent particles. The calculation indicates that well dispersed particles show much stronger interaction than those aggregated into clusters. Thus, to improve colloidal ER effects, besides improving the dielectric property of particles, it is also worth paying attention on reducing the surface tension of base liquids, which leads to higher wettability of particles in the liquid and hence better zero-field dispersity of the colloidal particles due to lyophilic repulsive forces between them.

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