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Structure formation in a colloidal suspension film subjected to an external alternating electrical field

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Structure formation in a polystyrene particle suspension film, under the action of an external alternating electrical field perpendicular to the film, is systematically studied in experiments; the interaction force between particles, induced by the electrical field, is analyzed. Based on the experimental results, a phenomenological theoretical interpretation is suggested. A preliminary quantitative comparison between the theory and experiments shows agreement.

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I. INTRODUCTION

There is currently increased interest in structured dispersions, which may be defined as all states of dispersed systems which are more ordered than a random distribution of single free-moving particles [1]. A considerably studied prototype is colloidal suspensions, which can exhibit many kinds of self-organization and phase transition like liquid-solid, order-disorder phase transitions [2,3].

Colloidal dispersions are generally stable, either charge stabilized or sterically stabilized. The colloidal particles, undergoing Brownian motion, are usually in a liquid state. The presence of electrolyte or external fields, like gravity, shear flow, electrical or magnetic fields, and so on, may not only lead to modification of interparticle forces, but also result in structure formation in colloidal systems.

The aggregation of colloidal particles induced by the addition of an electrolyte is a common phenomenon, and has been studied extensively and been well understood since the introduction of the concept of fractal and scaling theory [4]. The effect of gravity may result in phase separation and a crystallization of colloidal particles forming colloidal crystals [4,5]. The presence of shear flow may induce the melting of colloidal crystals due to the weakness of colloidal crystals [6,7], and the aligning order in colloidal suspensions [8].

The effect of applied electrical fields on colloidal dispersions, known as electrorheology, is a long established problem, and there has been a resurgence of interest in it recently due to fundamental and practical interest [9,10].

In previous papers [11,12], the aggregation of colloidal particles confined between two glass slides, subjected to an external alternating electrical field, has been studied. In the present paper, instead, we present our experimental and theoretical studies of the effect of an electrical field on this system at different frequencies. Experimental results show that the external field may modify the mutual-particle interaction, and induce the structure formation. For $f < 100$ Hz, the interaction force is repulsive, and particles form two-dimensional disordered lattices. For $f \sim 1$ kHz, the interaction force is attractive over the short range; particles aggregate forming clusters. For $f > 10$ kHz, the interaction force is repulsive, and no structures are formed. By a theoretical analysis, we suggest that the physical origin of the interaction forces between particles induced by the external electrical field must be the electrical interaction, which is related to the low frequency dielectric dispersion, and qualitatively explains the experimental observations.

II. EXPERIMENTS

We have synthesized the monodisperse colloidal polystyrene aqueous suspension by emulsion polymerization, and the two-step swelling method according to Ref. [13]. The diameter of the particles is about 1.4 μm, and the polydispersity is less than 4%. Particles of this size are large enough to be observed easily by the optical microscope, and small enough to be subject to rigorous Brownian motion, and thus good for experimental study.

The experimental cell is composed of a quasi-two-dimensional colloidal suspension film confined between two parallel glass slides separated by a Mylar film placed between them. The glasses are coated with conductive material, by which an alternating electrical field is applied. The behavior of the particles is observed *in situ* through an optical microscope which is matched with a video system and recorded on tape for later processing.

In our experiments, the thickness of the cell is kept at 50 μm, while the voltage (or field strength) and frequency of the field can be changed. Experiments under electrical fields with the frequency varying from several tens of Hz to several tens of kHz were performed. The results are presented in Sec. III.

III. EXPERIMENTAL RESULTS

The experimental results show that the effects of the alternating electrical field on the colloidal suspension film depend on the frequency of the field. Typical photos are shown in Fig. 1. In Fig. 1(a), without the electrical field, the particles, stable due to their double charge layers, distribute in space randomly and undertake Brownian motion. In Fig. 1(b), with an alternating electrical field of $f \sim$ several ten Hz, the strength beyond some threshold (about 1 V/50 μm), the particles form a two-dimensional disorder lattice, and the distance between them depends on the particle concentration. In Fig. 1(c), with $f \sim 1$ kHz, the field strength beyond a threshold strength, the spheres are attracted to the surface of the cell swiftly after turning on the field, and aggregate there. In Fig. 1(d), with $f > 10$ kHz, the particles are not restricted on the cell surface, and no lattice or aggregates are formed.

It is possible to understand qualitatively that the structure formation of the particles is found only when the electrical field strength is above some threshold depending on the frequency. The colloidal particles, undergoing Brownian motion, possess thermal energy $\sim kT$. Hence the interaction energy induced by the applied field is necessarily of (or higher than) the order of the thermal energy kT, so that the effect of the field is sufficient to be observed.

From the formation of a disorder lattice under a low frequency electrical field, and a lattice constant which is larger than the particle diameter, one can conclude that there exists a repulsive force between particles; the aggregation of particles under the electrical field of kHz indicates that the interaction forces have attractive terms; the fact that no lattice and clusters are formed for a frequency higher than several ten kHz (typically, 10 kHz) indicates that the interaction between particles is repulsive or much less than the thermal energy, or that the system is not two dimensional.

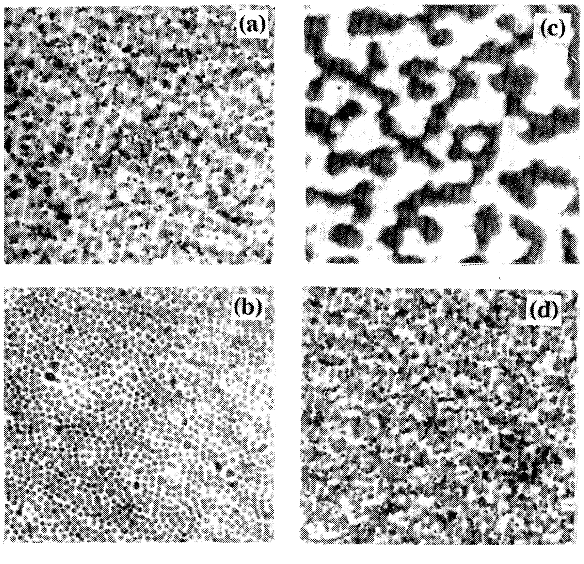

FIG. 1. Microscopic view of structures formed at (a) $V=0$ V; (b) $V=1.3$ V, $f=20$ Hz; (c) $V=1.5$ V, $f=1.5$ kHz; and (d) $V=1.5$ V, $f=15$ kHz.

The aggregation process of the system has been carefully studied previously by Richetti, Prost, and Clark [14] and by us [11,12], including aspects of the geometry of aggregates and the aggregation kinetics. Richetti, Prost, and Clark have also studied the structure formation of particles under an electrical field. Our results are in agreement with theirs. However, the disordered lattice formed under a low frequency field is observed for the first time, to our knowledge.

IV. THE INTERACTION FORCES

Although the behavior of particles under an alternating electrical field has been studied, the interaction force induced by the electrical field is still not completely understood. In this section we present a physical interpretation for the interaction forces between particles induced by an external electrical field.

The colloidal particles used in our experiments are charged, and have a double charge layer. Without the electrical field the interparticle interactions should include (1) electrostatic repulsion resulting from the overlapping of their electrical double layers, and (2) van der Waals attraction. The net superposition of all these interactions determines the energy associated with aggregation and hence the stability. The colloidal suspension is generally stable due to the electrical repulsion barrier.

A candidate for the interaction induced by the electrical field is the hydrodynamic interactions. To obtain the order of its strength, we use the result of Thomson and Tait [15]. Considering two spheres moving in fluid with the same velocity v along a direction perpendicular to the line through their centers, hydrodynamics will result in an attraction between two particles, which reads

$$F = -\tfrac{1}{16}\pi\rho a^6 \frac{v^2}{r^4} , \tag{1}$$

where ρ is the density of the fluid, and a the radius of the particles. Then the attraction potential is $V(r) = -\pi\rho a^6 v^2/16r^3$. In fact, this is equivalent to the case of two static spheres in a flowing fluid of velocity v. In our system, the applied electrical field may result in the flow of the solute due to its action on the ions. The induced flowing velocity can be estimated as $\sim 2\pi a\omega$, where ω is the frequency of the field. By taking $a \sim 10^{-4}$ cm, $\rho \sim 1$ g/cm^3, $\omega \sim 10^3$ Hz, and $r \sim 10a$, we can obtain the order of the hydrodynamical interaction energy, $V \sim 10^{-17}$ erg, which is much less than the thermal energy and thus negligible.

Another candidate for the interaction is the electrical interaction. When an external field $\mathbf{E} = \mathbf{E}_0 e^{-i\omega t}$ is applied, the colloidal particle should be polarized, and possesses a dipole moment. The mutual interaction is a complicated, many-body problem. As a first step, we consider only two particles in a plane perpendicular to the electrical field, separated by a distance r as shown in Fig. 2. The polarizability of a colloidal particle (actually the particle with its screening layer as a whole) is generally a complex number $\alpha(\omega) = a^3[\epsilon'(\omega) - i\epsilon''(\omega)]$ (a is the radius of particles). Assuming that the electrical field acting on each particle is $\mathbf{E}'$, then

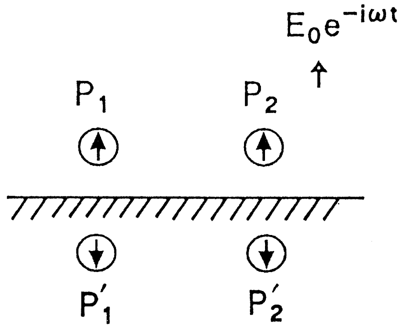

FIG. 2. Two colloidal particles near the conductive surface under an external alternative electrical field. $\mathbf{P}_1$ and $\mathbf{P}_2$ are induced dipole moments of two particles. $\mathbf{P}'_1$ and $\mathbf{P}'_2$ are electrical images.

$$\mathbf{P}=\alpha\mathbf{E}', \quad \mathbf{E}'=\mathbf{E}-\frac{\mathbf{P}}{r^3} , \tag{2}$$

where $\mathbf{P}$ is the dipole moment of two particles $\mathbf{P}=\mathbf{P}_1=\mathbf{P}_2$. Solving for $\mathbf{P}$ and $\mathbf{E}'$ yields

$$\begin{aligned}\mathbf{P}&=\frac{\alpha\mathbf{E}_0e^{-i\omega t}}{1+\alpha/r^3} ,\\ \mathbf{E}'&=\frac{\mathbf{E}_0e^{-i\omega t}}{1+\alpha/r^3} .\end{aligned} \tag{3}$$

The time-averaged electrical interaction energy is

$$W=-\tfrac{1}{2}\mathrm{Re}(\mathbf{P}\cdot\mathbf{E}'^*)=-\tfrac{1}{2}\mathrm{Re}\left[\frac{\alpha E_0^2}{|1+\alpha/r^3|^2}\right] , \tag{4}$$

and the interaction force is

$$F=-\frac{\partial W}{\partial r}=\frac{3E_0^2}{|1+\alpha/r^3|^4r^4}\Delta , \tag{5}$$

with

$$\Delta=\mathrm{Re}(\alpha)\left[\mathrm{Re}(\alpha)+\frac{|\alpha|^2}{r^3}\right] ,$$

where Re means the real part of a complex number, and the asterisk denotes the complex conjugate of a complex number. Thus the interaction force between two particles, induced by the external electrical field, is dependent on the sign of Δ, repulsive for $\Delta>0$ and attractive for $\Delta<0$.

The polarizability of a particle is a function of the frequency of the electrical field. Irrespective of the details of the dielectric relaxation mechanism, as an approximation we can assume that the polarization of a colloidal particle has a Debye form, i.e., $\epsilon'=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)/(1+\omega^2\tau^2)$, $\epsilon''=\omega\tau(\epsilon_0-\epsilon_\infty)/(1+\omega^2\tau^2)$, just as in Ref. [18]. As pointed out by Richetti, Prost, and Clark [14], when ω approaches ∞, the counterion clouds around the particles cannot follow the electrical field, and $\mathbf{P}=a^3\mathbf{E}'/2$, so we can substitute ϵ_∞ with $-\frac{1}{2}$. Then with some algebra one can obtain

$$\begin{aligned}\Delta(\omega)\simeq&\frac{a^6}{4(1+\omega^2/\tau^2)^2}[\omega^2\tau^2-2\epsilon_0] ,\\ &\times[\omega^2\tau^2-2(\epsilon_0+\epsilon_0^2a^3/r^3)] ,\end{aligned} \tag{6}$$

where the condition $r>2a$ has been used.

For $r>\epsilon_0^{1/3}a$ $(=r_0)$, $\Delta(\omega)\sim(\omega^2\tau^2-2\epsilon_0)^2/4(1+\omega^2\tau^2)^2>0$, so the long-range interaction force is always repulsive. This is reasonable because for large distance there exists only the field-induced dipole-dipole interaction between particles, which is always repulsive.

For $2a\ll r\ll\epsilon_0^{1/3}a$, there exist three cases: (1) if $\omega^2\tau^2<2\epsilon_0$ or $f<f_1=(2\epsilon_0)^{1/2}/2\pi\tau$ (here $f=\omega/2\pi$), $\Delta(\omega)>0$, and the force is repulsive; (2) if $\omega^2\tau^2>2(\epsilon_0+\epsilon_0^2a^3/r^3)$, $\Delta(\omega)>0$, and the force is repulsive; and (3) if $2\epsilon_0<\omega^2\tau^2<2(\epsilon_0+\epsilon_0^2a^3/r^3)<2(\epsilon_0+\epsilon_0^2/8)$ or $f_1<f<f_2=[2(\epsilon_0+\epsilon_0^2/8)]^{1/2}/2\pi\tau$, $\Delta(\omega)<0$, and the force is attractive.

It can be seen that the qualitative behaviors of the force are in accord with the experimental results. In fact, a long-range repulsive force between particles does exist, which can be seen in the morphology of clusters formed in the intermediate frequency regime. Holes in aggregates [as seen in Fig. 1(c)], which can be seen obviously in a high particle concentration [12], are a sign of the existence of long-range repulsion.

Typical values of ϵ_0 can be estimated from the fact that suspensions of colloidal particles in aqueous electrolyte solutions generally display an unusually high dielectric constant (well above 10^3 for the frequency below 1 kHz for spherical particles about 1 μm in diameter) at low frequencies [16,17]. Considered as a neutral sphere, the electrical displacement of a colloidal particle (equal to $\mathbf{P}+\mathbf{E}$) is of the order of the electrical displacement of the suspension, which is equal to $\epsilon_s\mathbf{E}$, where ϵ_s is the dielectric of the suspension. Thus the typical value of ϵ_0 is about the order (10^3) of the dielectric ϵ_s of the suspension at low frequencies. Taking typical values $\tau\sim10^{-2}$ s [17] and $\epsilon_0\sim10^3$ [16], one obtains $f_1\sim0.7$ kHz and $f_2\sim8.0$ kHz, which agree approximately with the experimental values.

In addition, the predicted attraction range $r_0\sim10a$ is in agreement with the estimation of Richetti [14] (where $r_0\sim100\xi$, and the screening length $\xi\sim a/10$). The interaction length can also be derived from our work at low concentrations to be of the same order [11], where the distance between the particle and the large cluster in late DLA can be considered the maximum of the interaction length. Further, taking $f\sim1$ kHz and $r\sim5a$, some computation shows the electrical interaction $W\sim10^{-13}$–10^{-12} erg, which, being larger than kT, should be effective.

So far, only the dipolar interaction is considered, multipolar interactions may be relevant in the short distance case (i.e., $2a\ll r\ll\epsilon_0^{1/3}a$). However, if the electrical field acting on the sphere is parallel to $\mathbf{E}_0$ (the z axis), the quadrupolar interaction is zero. This can be demonstrated as follows. By considering the axis symmetry along the z axis, only the diagonal elements of the quadrupole tensor can exist. Then the interaction energy of the quadrupole with the electrical field is

$V_Q(r)\sim Q_{zz}\nabla_z E|_{z=0}$, where Q_{zz} is the z component of the quadrupole tensor. Since $\Delta_z r|_{z=0}=0$, $V_Q(r)$ actually is zero. This is true without image interaction. It will be considerably complicated when the image interaction is taken into consideration, but can be considered a perturbation for two reasons: (1) The quadrupolar interaction induced by the image interaction is proportional to the field perpendicular to the z direction, which should be $d/r\sim 0.1$ times the field in the z direction; here d is the distance between particles, and its image $d\sim 2a$ [14]. Additionally, the quadrupolar interaction is $(a/r)^2\sim 10^{-2}$, the order of the dipolar interaction, so the quadrupolar interaction can be considered as a perturbation. (2) Many-body effects should be considered. If the particles are distributed homogeneously in space, the field on each particle should be in the z-axis direction, and thus the quadrupolar interaction should be zero.

By expanding Eq. (4) in powers of a/r for large r, one obtains $W\sim C_0+C_1/r^3+C_2/r^6+\cdots$, where C_0 represents the interaction of the dipole with the external field; C_1/r^3 represents the field-induced dipole-dipole repulsive interactions; and the third term C_2/r^6 is a kind of dispersion force, just as that in the van der Waals force. While for a short distance $r<r_0$, $W\sim r^6$ from Eq. (4), the form of the short distance force is complex, which results mainly from the dipole-induced-dipole interaction. The attraction comes from the low frequency dielectric dispersion of the colloidal particles.

In order to understand why no lattice is formed at high frequencies ($f>10$ kHz), where the mutual interaction is also repulsive as at low frequencies, the interaction of the colloidal particle with the conductive surface, i.e., the dipole image interaction, as shown in Fig. 2, should be involved. Denoting the distance of the particle center to the conductive surface by d, one can write the image interaction energy as

$$W=-\frac{2P^2}{(2d)^2}\ . \tag{7}$$

Here the effects of other particles are not considered. For high frequency ($f>10$ kHz), taking $E_0=0.9$ statvolt/cm, $a=0.7$ μm, $\tau=10^{-2}$s, $P=-a^3E_0/2$, and $T=27\,^{\circ}\mathrm{C}$, a simple computation gives $W\sim 0.2\times 10^{-17}$ erg. It can be seen that the electrical image attraction energy is less than the thermal energy ($\sim 10^{-14}$ erg), and thus that particles cannot be restricted to the surface forming a two-dimensional system. For low frequency, this is not the case. Taking $P\sim 10^2a^3E_0$ gives $W\sim 10^{-13}>kT$. Thus the image interaction at low frequencies can produce a two-dimensional system, and the mutual particle interaction derived above makes the particles form a two-dimensional structure.

Our model is rather phenomenological; however, it can explain the experimental results well. Our observations that the aggregation process can hardly proceed when the ions in the suspension are overfiltered may provide evidence supporting our model. Further experiments are obviously needed to test our model.

V. SUMMARY

We have experimentally studied the structure formation in a two-dimensional colloidal system, which consists of polystyrene particle suspension confined between two conductive glass slides. Under the action of an external alternating electrical field perpendicular to the film, the particles may form different structures depending on the field frequency. This implies that the interaction force between particles induced by the field depends on the frequency of the field.

Based on experimental results, a phenomenological physical explanation is suggested. The interaction forces between particles induced by the electrical field are the electrical interaction forces, which are related to the low frequency dielectric dispersion, while the image interaction is relevant only to the formation of two-dimensional particles. Qualitative results are in agreement with experimental results.

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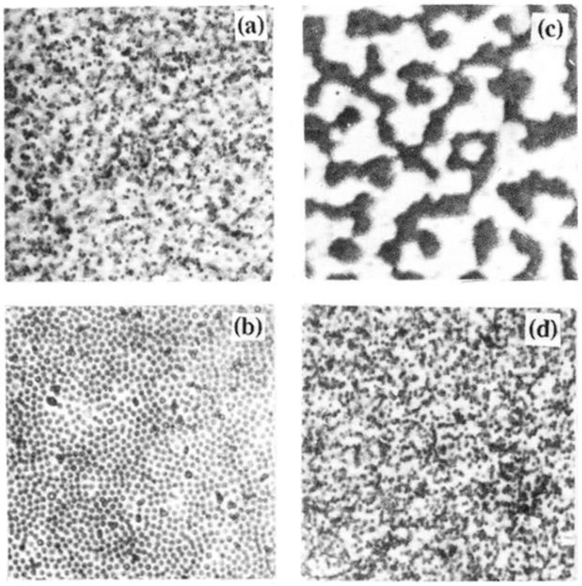

FIG. 1. Microscopic view of structures formed at (a) $V=0$ V; (b) $V=1.3$ V, $f=20$ Hz; (c) $V=1.5$ V, $f=1.5$ kHz; and (d) $V=1.5$ V, $f=15$ kHz.