Effects of conductivity in electric-field-induced aggregation in electrorheological fluids

Boris Khusid and Andreas Acrivos

The Levich Institute, City College of the City University of New York, T-1M, 140th Street and Convent Avenue,
New York, New York 10031

We examine how the interfacial polarization of the particles affects the electric-field-induced aggregation in electrorheological (ER) fluids. We derive a microstructure-based equation for the free energy of a conducting suspension for the case of a random arrangement of the particles, and show that the thermodynamic properties of a suspension are strongly influenced by the dielectric relaxation. According to our theory, in dc electric fields the particles aggregate only provided that a certain relation between the ratio of the particle-to-suspending liquid dielectric constants and that of the conductances is satisfied. Moreover, we predict that the slow aggregation, which takes place when the conductivity effects determine the interparticle forces, will occur in relatively low dc electric fields, whereas the rapid aggregation, when conductivity effects do not contribute to the interparticle forces, will occur in relatively high dc electric fields. The theory also provides insight into why the electric-field-induced strength of the fully developed microstructure in ER fluids depends on the particle-to-suspending liquid ratio of the conductances and why there exists a correlation between the ER activity of a suspension and its dielectric spectrum. The predictions of the theory are consistent with the currently available experimental data on ER fluids.

PACS number(s): 47.55.Kf, 47.65.+a, 64.75.+g

I. INTRODUCTION

An electrorheological (ER) fluid consists of a suspension of micrometer-size particles in a low-conductivity liquid (usually a dielectric oil). Typical volume fractions are in the range 0.01–0.3. Following the application of an electric field of strength of 0.1–10 kV/mm, an ER fluid undergoes a fluid-viscoelastic solid transition exhibiting a yield stress at low shear rates. Upon removal of the electric field, the ER fluid returns to its original state. In the absence of an electric field, ER fluids have rheological properties typical of colloid suspensions. Research in the area of ER fluids has seen a great deal of activity within the last few years because devices based on their remarkable rheological properties may soon allow the commercialization of interesting electromechanical technologies. Numerous recently published papers, for example [1–14], summarize the state of the art in this field.

It has been found that a large number of materials can be used as the disperse phase to produce ER-active fluids. In the ER fluids which were first developed, the particles (various forms of silica, cellulose, starch, flour, etc.) had to have a small amount of water (or some other polar liquid) adsorbed onto them in order to render the suspension ER active [1,4]. Recently, however, ER-active suspensions have been developed which are water free [2,5]. The disperse phase of these ER fluids can be classified in the following groups: ionic conductors (aluminosilicates or zeolites), semiconductors [poly(acenequinone) radicals], polyelectrolytes, and composite particles (conducting particles coated with a thin nonconducting outer layer). The fact that so many diverse types of materials can be used as the disperse phase is a clear indication that some general physical features of a suspension underlie its ER activity.

It is now generally believed that dramatic changes in the ER fluid rheology result from the field-induced alignment of the suspended particles into chains and columns parallel to the electric field lines. Most of the theories of electric-field-induced structure formation and aggregation in ER fluids use the mechanical model of a suspension which describes the particle motion due to the action of the viscous, interparticle, and Brownian forces. The interparticle force includes the electric-field-induced long-range anisotropic interaction and a short-range isotropic repulsion. The leading term of the former originates from the equation for the energy of the dipole-dipole interaction between two particles. The magnitude of this energy is proportional to $1/R^3$ (where R is the interparticle distance) times the square of the strength of an electric field and the parameter β^2. Here β is the polarizability of a suspended particle in an electric field due to a mismatch between the dielectric constants of the liquid and the particles. This model treats an ER fluid as a suspension of nonconducting hard spherical particles in a viscous nonconducting solvent. Computer simulations based on this mechanical model are able to predict the electric-field-induced particle rearrangement leading to chain and column formation.

Unfortunately, conclusions based on combining the qualitatively correct computer simulation results, which are expressed in terms containing β^2, with the electrostatic model prediction regarding the dependence of β on the properties of the particles and of the fluid are often in contradiction with experimental data. For example, according to the computer simulations, the ER behavior should become more pronounced the higher the value of β. But, according to the electrostatic model, the highest

value of β is attained when $\varepsilon_p/\varepsilon_f \to \infty$, where ε_p is the permittivity of the particles suspended in a fluid of permittivity of ε_f. Therefore, it is impossible to explain on this basis why (i) the ER phenomenon is absent in a suspension of ferroelectric particles (barium titanate where $\varepsilon_p = 1600$, for instance) if the particles are dry, but (ii) this suspension becomes ER active if the particles adsorb a small amount of water [9]. Also, it is impossible to explain why the ER activity passes through a maximum as the bulk conductance of the disperse phase is increased, and that both good conductors and rather poor conductors, when dispersed, do not induce any measurable ER effect [2].

The influence of the conductivity of the two phases on the ER phenomenon has also been examined theoretically and experimentally but only for the situation where the suspension microstructure has been fully formed [15–24]. In this case, the particles form chains and columns that span the electrode gap, and the theoretical models developed to date have dealt with calculation of the resulting yield stress and of the elastic shear modulus of the ER fluids. It has been shown that, under dc conditions, the yield stress is mainly determined by the ratio of the conductance of the particles to that of the fluid and by the distance between the particles in a chain [18–24]. The same factors influence the value of the elastic shear modulus. The latter increases with an increase in the ratio of the particle-to-fluid conductance and a decrease in the distance between the particles [15–17].

The purpose of this paper is to examine the effects of the conductivity on the initial stages of the electric-field-induced aggregation in ER fluids. To solve this problem, we derive an equation for the free energy of conducting particles dispersed in a conducting liquid for the case of a random arrangement of the particles. We shall only deal with the case when the particles and the suspending fluid have no intrinsic dielectric dispersion and their properties are described by the model of a leaky dielectric; i.e., we suppose that the conductances and dielectric constants are frequency independent. Under these conditions, the induced polarization of the particles arises from the buildup of charge at the interface between the particle and the surrounding fluid. The osmotic pressure of the suspension is then evaluated from the free energy as a function of the temperature and particle concentration, and as a functional of the history of the time variations of the applied electric field. The dependence of the thermodynamic properties of a suspension on the value of an electric field at earlier times is caused by dielectric relaxation due to the redistribution of the free charge carriers. Recall that the osmotic pressure refers to the pressure acting across a membrane permeable to the liquid but not the particles. Hence, as long as the derivative of the osmotic pressure with respect to the particle concentration is positive, the random arrangement of the particles is stable. But at sufficiently strong electric fields, when the ratio of the electric-to-thermal energy exceeds a critical value, the derivative of the osmotic pressure becomes negative. In this case the particles tend to aggregate, and their random distribution in a suspension becomes unstable. The initial stage of the electric-field-induced aggre-

gation is therefore determined by the extremum of the osmotic pressure. This model then describes the phase separation of the suspension into low- and high-concentration phases at high electric fields.

The equation for the free energy of an ER fluid contains the expression for the electric energy. In the case of nonconducting particles and liquids, the macroscopic theory shows that the electrostatic energy of a suspension is determined completely by its dielectric constant $\varepsilon(c)$ as a function of the particle concentration c [25]. On the other hand, the general expression of the same type for the electric energy of a conducting system in a time-varying electric field (Brillouin's formula) can be derived only when the variations of the electric field are very slow (as compared to the rate of polarization) and the dielectric loss is negligibly small [25].

We shall develop two microstructure-based techniques for calculating the electric energy of a conducting suspension in a time-varying electric field. To begin with, in order to describe the polarization of a suspension, we use quasisteady electrodynamic equations [25] because the wavelength of even a high-frequency electromagnetic field applied to an ER fluid is much larger than the characteristic interparticle distance in a suspension, $a/c^{1/3}$, where a is the particle radius. These equations contain the complex permittivity of the dispersed and continuous phases, where the permittivity in its complex form, involving the dielectric permittivity (real part) and the dielectric loss (imaginary part), reflects the conductivity of a substance. But to find the average value of the interparticle interaction in a suspension it is necessary to calculate at least the $O(c^2)$ term in the expansion of the electric energy in powers of the particle concentration c.

The first approach is based on a mean-field approximation (a cell model). For the complex permittivity of a suspension, it leads to the Maxwell-Wagner expression which correlates well with experimental data unless the particles start aggregating [26,27]. A mean-field approximation makes it possible to estimate not only the $O(c^2)$ term but the higher order terms as well in the expression for the electric energy.

The second approach makes use of statistical methods for calculating the average properties of a suspension. To begin with, we derive the microscopic-based equation for the electric energy of N conducting spherical particles in a conducting fluid for a time-varying electric field. Then we present the solution of the two-sphere problem for the quasisteady electrodynamic equations which is based on the method of twin spherical expansions [28], and calculate the electric energy of two particles in an unbounded medium. The leading term, proportional to $1/R^3$, refers to the dipole-dipole interaction between two conducting particles in a conducting liquid. But, as is well known, due to the long-range and anisotropic nature of the interparticle interactions, straightforward calculations of the $O(c^2)$ term in the expansion of the electric energy lead to a two-particle integral which is only conditionally convergent. To overcome this difficulty, we use the group expansion method of Ref. [29] and also described in Ref. [30]. This method takes into account the $O(c)$ change in the average electric field when one particle is removed

from the suspension. We then show that the main contribution to the average energy to $O(c^2)$ arises from a term which is equal to the coefficient of $4\pi a^3 (a/R)^3 (1-3\cos^2\vartheta)$ in the formula for the energy of the dipole-dipole interaction between two conducting particles. Comparison of the results for the average values of the interparticle interaction in a suspension, as obtained by both approaches, illustrates the limitations of the mean-field approximation.

Besides examining the case when the behavior of the particles and the suspending fluid is described by a simple model of a leaky dielectric, the theory to be developed offers a clearer insight into the effects of conductivity on the electric-field-induced aggregation in suspensions. In particular, the theory shows that, in dc electric fields, the particles aggregate only if the ratio of the particle-to-suspending fluid dielectric constants and the corresponding ratio of the conductances satisfy a certain relation given by Eq. (35). Furthermore, the theory provides some insight into the kinetics of the aggregation process. Specifically, the slow aggregation which results when the conductivity effects determine the interparticle interaction will occur in relatively low dc electric fields [Eq. (38)], while the rapid aggregation which takes place when the conductivity effects do not contribute to the interparticle interaction will occur in relatively high dc electric field [Eq. (39)]. Although our theory does not treat the rheology of ER fluids, it provides a qualitative indication regarding the dependence of the electric-field-induced strength of the fully developed microstructure in ER fluids on the particle-to-suspending fluid ratio of conductances, as well as on the reasons why there exists a correlation between the ER activity of a suspension and its dielectric spectrum. The predictions of the theory are consistent with the currently available experimental data on ER fluids.

II. THERMODYNAMIC RELATIONS

In this section we shall develop a simple thermodynamic model of aggregation phenomena in a disordered suspension induced by an electric field. The model is based on a rather general expression for the dependence of the electric energy on the particle concentration and makes use of a formula for the entropic factor taken from the existing theories of a suspension of hard spheres. The relationship between the macroscopic parameters, which appear in the concentration dependence of the electric energy, and the strength of the electric field plus the properties of the particles and of the fluid will be derived in the following sections using both a cell model as well as a more rigorous statistical technique.

The free energy of a suspension containing N particles is defined as a function of the volume V, the temperature T, the volume concentration of the particles, c, and as a functional of the history of time variations of an electric field, $\mathbf{E}(t)$, by means of the expression

$$\mathcal{F} = \mathcal{F}_0(V,T,c) - \mathcal{W}\{c;\langle \mathbf{E}\rangle_e\}V , \qquad (1)$$

where $\mathcal{W}$ is the density of the electric energy, and $\langle \mathbf{E}\rangle_e$ denotes the ensemble average value of the strength of the electric field in the suspension. The first term in Eq. (1) refers to the free energy of a suspension in the absence of the electric field, while the dependence of the electric energy on the history of the time variations of the electric field reflects the influence of the dielectric relaxation phenomena.

The osmotic pressure of a suspension can be evaluated from the equation of the free energy,

$$\Pi = - \left[\frac{\partial \mathcal{F}}{\partial V} \right]_{N,T;\langle \mathbf{E}\rangle_e} = \frac{k_B T}{v_p} c Z(c) + \mathcal{W} - c \frac{\partial \mathcal{W}}{\partial c} ,$$

where k_B is Boltzmann's constant, and v_p is the particle volume. In deriving this expression, we took into account that $(\partial c/\partial V)_N = -c/V$, and also replaced the osmotic pressure $\Pi_0 = -(\partial \mathcal{F}_0/\partial V)_{N,T}$ of a suspension in the absence of an electric field by the compressibility factor $Z(c)$.

For $Z(c)$, we use the Carnahan-Starling equation [27]

$$Z(c) = \frac{1+c+c^2-c^3}{(1-c)^3} ,$$

which applies for a suspension of hard spheres in the disordered state when $c \leq 0.4$. We also recall that the compressibility factor of a suspension of hard spheres diverges at random close packing, $c \sim 0.63 - 0.64$ [27].

The disordered state of the spatial configuration of the particles in a suspension is stable if $(\partial \Pi/\partial c) > 0$. As is well known, in the absence of an electric field a suspension of hard spheres is stable for $c < 0.50$ [27]. Theories for such a suspension [27] predict a transition from a disordered state to an ordered face-centered-cubic solid for $0.55 < c < 0.74$.

In the presence of an electric field, we have that

$$\frac{\partial}{\partial c} \left[\frac{\Pi v_p}{k_B T} \right] = Z + c \frac{\partial Z}{\partial c} - c \frac{\partial^2}{\partial c^2} \left[\frac{\mathcal{W} v_p}{k_B T} \right] , \qquad (2)$$

where the third term on the right-hand side accounts for the contribution of the interparticle interactions in an electric field. Specifically, if the particles are attracted to one another, an increase in the strength of the elastic field decreases the value of $(\partial \Pi/\partial c)$ and leads to a phase transition when $(\partial \Pi/\partial c) = 0$. Under this condition, the random distribution of the particles becomes unstable, and aggregation is induced. According to this model then, at sufficiently high electric fields, the suspension separates into two disordered phases with the coexistence region lying between the particle concentrations given by the two roots of the equation

$$\frac{\partial}{\partial c} \left[\frac{\Pi v_p}{k_B T} \right] = 0 . \qquad (3)$$

Since, at the critical point, the particle concentration of the coexisting phases coincide, this critical point corresponds to the inflection point of Π as a function of c, i.e.,

$$\frac{\partial}{\partial c} \left[\frac{\Pi v_p}{k_B T} \right] = \frac{\partial^2}{\partial c^2} \left[\frac{\Pi v_p}{k_B T} \right] = 0, \quad \frac{\partial^3}{\partial c^3} \left[\frac{\Pi v_p}{k_B T} \right] > 0 . \qquad (4)$$

It is easy to show that Eqs. (3) and (4), respectively, are

equivalent to the relations defining the conditions for the existence of a phase transition and for the location a critical point for a binary system [31]

$$\frac{\partial\mu}{\partial c}=0 \quad \text{and} \quad \frac{\partial\mu}{\partial c}=\frac{\partial^2\mu}{\partial c^2}=0, \quad \frac{\partial^3\mu}{\partial c^3}>0 \ .$$

Here $\mu=\delta G/\delta N$ is the chemical potential of the particles, and $G=\mathcal{F}+\Pi v$ is the Gibbs free energy of the suspension.

When the two phases are in equilibrium, the values of the osmotic pressure and the chemical potential of the particles in the coexisting phases are equal, i.e., $\Pi(c_1)=\Pi(c_2)$ and $\mu(c_1)=\mu(c_2)$. The latter leads, as shown in [31], to the following relation between the particle concentrations in both phases:

$$\int_{c_1}^{c_2}\frac{1}{c}d\Pi=0 \ .$$

The microstructure-based theories for the electric energy of a conducting suspension in a time-varying electric field, to be developed in the following sections, allow us to calculate the first terms in the expansion of the electric energy in powers of the particle concentration,

$$\frac{\partial^2}{\partial c^2}\left[\frac{\mathcal{W}v_p}{k_BT}\right]=\Lambda+\gamma c+\cdots \ , \tag{5}$$

where $\Lambda=v_p A\{\langle\mathbf{E}\rangle_e\}/k_BT$ and $\gamma=v_pB\{\langle\mathbf{E}\rangle_e\}/k_BT$. The parameters Λ and γ define the ratio of the average value of energy of the electric interaction between two, $A\{\langle\mathbf{E}\rangle_e\}$, and three, $B\{\langle\mathbf{E}\rangle_e\}$, particles and the thermal energy k_BT. They depend on the dielectric constants and conductances of the particles and of the liquid, as well as on the history of the time variations of the electric field. The statistical theory to be developed leads to a definite expression for Λ, while the mean-field or cell model makes it possible to estimate γ as well. The expansion of the electric energy in powers of c as given by Eq. (5) applies only provided that $|\gamma c/\Lambda|\ll 1$.

On substituting Eq. (5) into Eq. (3) we find that, along the critical line,

$$Z+c\frac{\partial Z}{\partial c}=\Lambda c+\gamma c^2 \ . \tag{6}$$

On the other hand, the parameters of the critical point, namely the particle concentration and the strength of an electric field, are determined from the following equations which follow from Eq. (4):

$$Z-c\frac{\partial Z}{\partial c}-c^2\frac{\partial^2 Z}{\partial c^2}+\frac{\gamma c}{\Lambda}\left[2Z-c^2\frac{\partial^2 Z}{\partial c^2}\right]=0 \ ,$$
$$2Z-c^2\frac{\partial^2 Z}{\partial c^2}=c\Lambda \ . \tag{7}$$

Moreover, when the coexisting phases are at equilibrium, their concentrations c_1 and c_2 are evaluated from the equations

$$\left[cZ-\frac{\Lambda c^2}{2}-\frac{\gamma c^3}{3}\right]_{c_1}^{c_2}=0 \ ,$$

$$\int_{c_1}^{c_2}\frac{Z}{c}dc+\left[Z-\Lambda c-\frac{\gamma c^2}{2}\right]_{c_1}^{c_2}=0 \ ,$$

which follow from the above expressions for the osmotic pressure and the conditions of equilibrium.

If three-particle interactions are neglected ($\gamma=0$), Eq. (7) yields $\Lambda_{cr}=21.202$ and $c_{cr}=0.13$. Figure 1 shows the dependence of Λ_{cr} and c_{cr} on the relative value of the three-particle interaction parameter γ/Λ. It is seen that an increase in γ/Λ leads to a decrease in Λ_{cr} and to an increase in c_{cr}. At a rather high value of $|\gamma/\Lambda|$, Eq. (7) has two roots; for one of them $|\gamma c/\Lambda|<1$, while for the other $|\gamma c/\Lambda|>1$. Since the value of c for which $|\gamma c/\Lambda|>1$ is inconsistent with the fact that the validity of Eq. (5) is restricted to $|\gamma c/\Lambda|\ll 1$, only the smaller root of Eq. (7) has been retained in plotting the curves in Fig. 1.

For $\Lambda>\Lambda_{cr}$, Eq. (6) has two roots which give the respective particle concentrations in the two coexisting phases. Figure 2 illustrates, for a few values of γ/Λ, their dependence on Λ/Λ_{cr} in the low- (the lower part of the curve) and high-concentration (the upper part of the curve) disordered phases. As can be seen, the particle content in the low-concentration phase becomes very small with increasing Λ/Λ_{cr}, and since $Z\approx 1$ for $c\ll 1$, Eq. (6) yields that $c\approx 1/\Lambda$ for this part of the curve. In contrast, the particle content of the high-concentration phase increases dramatically with Λ/Λ_{cr} in that $c\sim 0.5$ at $\Lambda/\Lambda_{cr}\sim 2$ as seen in Fig. 2. This value almost corresponds to that of an ordered face-centered-cubic solid state of hard spheres in the absence of an electric field. This means that the high-concentration phase should actually experience a disorder-order transition at these values of Λ/Λ_{cr}. Describing this transition in the high-concentration phase is beyond the scope of our analysis, however, because it requires knowledge of the free energy of an ordered conducting system.

A thermodynamic description of the electric-field-induced transition in ER fluids for the case of nonconducting spherical particles in a nonconducting liquid has been presented in Ref. [32]. But since the compressibility factor $Z(c)$ was not included in the equation for the osmotic pressure of a suspension, the model developed in Ref. [32] has led to the conclusion that the phase transition should occur when the osmotic pressure of a suspension changes sign.

It should be noted that the analysis developed above provides a rather general description of aggregation phenomena when a suspension of attracting particles separates into two coexisting low- and high-concentration phases if the attraction becomes high enough, and that
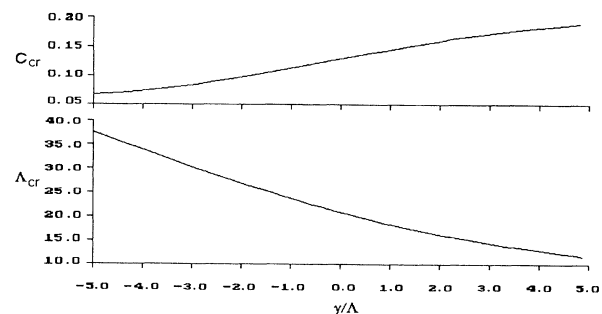

FIG. 1. The dependence of c_{cr} and Λ_{cr} on the relative value of the three-particle interaction parameter γ/Λ.
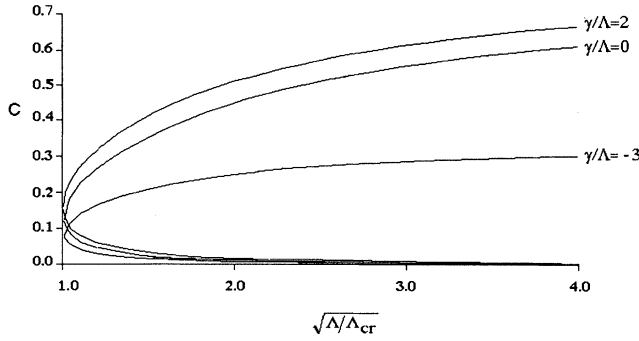
FIG. 2. The dependence of the particle concentration c in the low- (the lower part of the curve) and high-concentration (the upper part of the curve) phases on $\sqrt{\Lambda/\Lambda_{cr}}$ for indicated values of γ/Λ.

the nature of this attraction is reflected by the values of only two macroscopic parameters, i.e., Λ and γ in Eq. (5).

III. CONDUCTING PARTICLES AND FLUID IN A TIME-VARYING ELECTRIC FIELD

A. The effects of conductivity on the electric energy

We begin by briefly recalling (Sec. III A 1) the mathematical relation between the quasisteady electromagnetic equations and the electrostatic equations, and by illustrating (Sec. III A 2) the effects of the interfacial polarization on the electric energy of a two-layered composite. Next we calculate the electric energy of one (Sec. III B) and two (Sec. III C) conducting particles in a time-varying electric field. Also, we derive expressions for the force and the rotational torque exerted on a conducting particle in a slightly nonuniform electric field (Sec. III B). The calculations to be presented also show clearly that the long-range character of the dipole electric field induced by the particles is responsible for the difference between the probe electric field acting on a particle and the actual electric field in the system. The results to be obtained in Sec. III are then used in Sec. IV to develop the microstructure-based theory of the electric energy of a conducting suspension.

1. Quasisteady electromagnetic equations

For a quasisteady electric field, the system of Maxwell's equations reduces to the well-known relations [25]

$$\nabla\times\mathbf{E}=0, \quad \nabla\cdot\mathbf{P}=-\rho^{(p)}, \quad \mathbf{j}^{(p)}=\frac{\partial\mathbf{P}}{\partial t} ,$$

$$\varepsilon_0\nabla\cdot\mathbf{E}=\rho^{(e)}, \quad \frac{\partial\rho^{(e)}}{\partial t}+\nabla\cdot(\mathbf{j}^{(f)}+\mathbf{j}^{(p)})=0 .$$

Here $\mathbf{P}$ is the polarization density, $\rho^{(e)}$ is the density of the charges, and $\mathbf{j}^{(f)}$ and $\mathbf{j}^{(p)}$ are the current densities,

$$\mathbf{j}^{(f)}=\int_0^t\sigma(t-t')\mathbf{E}(t')dt' ,$$

$$\mathbf{P}=\varepsilon_0\int_0^t\kappa(t-t')\mathbf{E}(t')dt' ,$$

where σ is the conductivity and κ the permittivity. The general expressions for these parameters are

$$\sigma=\sigma_0\delta(t)+\sum_i\frac{\sigma_i}{\lambda_i}\exp(-t/\lambda_i) ,$$

$$\kappa=\kappa_0\delta(t)+\sum_i\frac{\kappa_i}{\lambda_i}\exp(-t/\lambda_i) .$$

The Laplace transform of Maxwell's equations yields

$$\nabla\times\hat{\mathbf{E}}=0, \quad \nabla\cdot\hat{\mathbf{P}}=-\hat{\rho}^{(p)}, \quad \hat{\mathbf{j}}^{(p)}=p\hat{\mathbf{P}} ,$$

$$\varepsilon_0\nabla\cdot\hat{\mathbf{E}}=\hat{\rho}^{(e)}, \quad \hat{\rho}^{(e)}=-\nabla\cdot\left[\frac{\hat{\sigma}}{p}\hat{\mathbf{E}}+\varepsilon_0\hat{\kappa}\hat{\mathbf{E}}\right] ,$$

where

$$\hat{f}(p)=\mathcal{L}\{f(t)\}=\int_0^\infty f(t)\exp(-pt)dt .$$

The above system of equations, when rearranged, is equivalent to the electrostatic equations [25]

$$\nabla\times\hat{\mathbf{E}}=0, \quad \nabla\cdot\hat{\mathbf{D}}=0, \quad \hat{\mathbf{D}}=\hat{\varepsilon}(p)\hat{\mathbf{E}} ,$$

where

$$\hat{\varepsilon}(p)=\varepsilon_0\left[1+\hat{\kappa}(p)+\frac{\hat{\sigma}(p)}{p\varepsilon_0}\right] .$$

For brevity, we included the value of ε_0 as a multiplier in the definition of the complex permittivity $\hat{\varepsilon}$ and of its real part ε.

The boundary conditions for the quasisteady electromagnetic equations

$$[\mathbf{E}]_\tau=0, \quad \varepsilon_0[\mathbf{E}]_n=\rho_s^{(e)} ,$$

$$\frac{\partial\rho_s^{(e)}}{\partial t}+[\mathbf{j}^{(f)}]_n+\frac{\partial[\mathbf{P}_n]}{\partial t}=0$$

also reduce to the boundary conditions of the steady-state electrostatic equations

$$[\hat{\mathbf{E}}]_\tau=0, \quad [\hat{\mathbf{D}}]_n=0 ,$$

where the brackets denote the change in the respective variable along the tangential (τ) and normal (n) directions to the particle surface from the particle to the fluid.

We shall only examine the case when the behavior of the particles and the suspending fluid is described by the model of a leaky dielectric, i.e., a material with no relaxation on its own [$\sigma=\sigma_0\,\delta(t)$, $\kappa=\kappa_0\delta(t)$], and shall set $\varepsilon=\varepsilon_0(1+\kappa_0)$ and $\sigma=\sigma_0$. Under these conditions, a suspension exhibits only dielectric relaxation due to the redistribution of the charge at the interface between the particle and the surrounding fluid.

2. Electric energy of a conducting two-layered composite

To illustrate the effect of the conductivity on the electric energy of a system, we consider a simple example of a parallel-plate capacitor filled with two layers (h_1 and h_2 in width) of materials with different dielectric constants (ε_1 and ε_2) and conductances (σ_1 and σ_2). This example reflects the effects of conductivity on the electric field and on the interparticle forces for the situation where the chainlike microstructure of ER fluids has been fully formed [16].

Next we suppose that a time-varying voltage $u(t)$ is impressed on one of the plates while the other is grounded. This system corresponds to two nonideal capacitors placed in series. From the equivalent electrostatic equations, we obtain that the Laplace transforms of the volt-

age on the layers are

$$\hat{u}_1 = \frac{(\varepsilon_2 + \sigma_2/p)/h_2}{(\varepsilon_1 + \sigma_1/p)/h_1 + (\varepsilon_2 + \sigma_2/p)/h_2}\hat{u} ,$$

$$\hat{u}_2 = \frac{(\varepsilon_1 + \sigma_1/p)/h_1}{(\varepsilon_1 + \sigma_1/p)/h_1 + (\varepsilon_2 + \sigma_2/p)/h_2}\hat{u} .$$

Hence we have that

$$u_1(t) = \frac{\varepsilon_2/h_2}{\varepsilon_1/h_1 + \varepsilon_2/h_2}u(t)$$

$$+ \frac{(\varepsilon_1\sigma_2 - \varepsilon_2\sigma_1)}{(\varepsilon_1/h_1 + \varepsilon_2/h_2)^2 h_1 h_2}j(t) ,$$

$$u_2(t) = \frac{\varepsilon_1/h_1}{\varepsilon_1/h_1 + \varepsilon_2/h_2}u(t)$$

$$- \frac{(\varepsilon_1\sigma_2 - \varepsilon_2\sigma_1)}{(\varepsilon_1/h_1 + \varepsilon_2/h_2)^2 h_1 h_2}j(t) ,$$

where the dielectric relaxation time of the composite is

$$t_s = \frac{\varepsilon_1/h_1 + \varepsilon_2/h_2}{\sigma_1/h_1 + \sigma_2/h_2} ,$$

and

$$j(t) = \int_0^t \exp\left[-\frac{t-t'}{t_s}\right]u(t')dt' .$$

A charge at the interface between the layers,

$$Q_s(t) = \frac{\varepsilon_1}{h_1}u_1(t) - \frac{\varepsilon_2}{h_2}u_2(t) = \frac{(\varepsilon_1\sigma_2 - \varepsilon_2\sigma_1)}{(\varepsilon_1 h_2 + \varepsilon_2 h_1)}j(t) ,$$

builds up only if the time constants of the layers are different, i.e., if $\varepsilon_1/\sigma_1 \neq \varepsilon_2/\sigma_2$.

According to the model of a leaky dielectric, we assume that the electric energy is stored only by its dielectric constituent. In this case, the total electric energy per unit square, W, of the two-layered composite is

$$W(t) = \tfrac{1}{2}[\varepsilon_1\mathscr{E}_1^2(t)h_1 + \varepsilon_2\mathscr{E}_2^2(t)h_2] ,$$

where $\mathscr{E}_i(t) = [u_i(t)/h_i]$, $i = 1$ and 2. On substituting the expressions for $u_1(t)$ and $u_2(t)$ into this equation, we obtain

$$W(t) = \frac{1}{2}\frac{\varepsilon_1\varepsilon_2/h_1 h_2}{\varepsilon_1/h_1 + \varepsilon_2/h_2}u^2(t)$$

$$+ \frac{1}{2}\frac{(\varepsilon_1\sigma_2 - \varepsilon_2\sigma_1)^2}{(\varepsilon_1/h_1 + \varepsilon_2/h_2)^3 h_1^2 h_2^2}j^2(t) .$$

Here the first term equals the energy of two ideal capacitors placed in series, while the second term corresponds to the energy required to build the charge at the interface between the layers and to redistribute the electric field inside the layers.

Consider the case of a suddenly applied voltage, $u(t) = uH(t)$, where the Heaviside function $H(t) = 0$ for $t < 0$ and $H(t) = 1$ for $t > 0$. For short times, when $t \ll t_s$ and $j(t) \approx 0$, the electric energy of the composite is the

same as that of two capacitors connected in series and, thus, is determined solely by the dielectric constants of the layers. On the other hand, at long times, when $t \gg t_s$ and $j(t) \approx ut_s$, an interfacial charge

$$Q_s \approx \frac{\varepsilon_1\sigma_2 - \varepsilon_2\sigma_1}{\sigma_1 h_2 + \sigma_2 h_1}u ,$$

that has developed due to the conductivity of the layers, renders the voltages on the layers the same as those of two resistors connected in series and thus depends solely on the conductances

$$u_1 \approx \frac{\sigma_2/h_2}{\sigma_1/h_1 + \sigma_2/h_2}u, \quad u_2 \approx \frac{\sigma_1/h_1}{\sigma_1/h_1 + \sigma_2/h_2}u .$$

Therefore, for $t \gg t_s$, the electric energy of the composite becomes the same as that of two ideal capacitors placed in parallel with these resistors connected in series, i.e.,

$$W \approx \frac{1}{2}\left[\frac{\varepsilon_1}{h_1}\left[\frac{\sigma_2/h_2}{\sigma_1/h_1 + \sigma_2/h_2}\right]^2 + \frac{\varepsilon_2}{h_2}\left[\frac{\sigma_1/h_1}{\sigma_1/h_1 + \sigma_2/h_2}\right]^2\right]u^2 .$$

The main goal of the theory to be developed in the following sections is to examine how the interfacial polarization of the particles affects the electric-field-induced aggregation in a suspension.

B. Single spherical particle in an unbounded fluid

1. Equation for the electric energy

Let $\mathscr{E}(t)$ be the probe electric field acting on a spherical particle. The change in the electric field induced by this particle is given by the well-known expressions [25,26]

$$\varphi_f = -\mathscr{E}(t)\cdot\mathbf{r} + \frac{a^3\mathbf{A}(t)\cdot\mathbf{r}}{r^3} ,$$

$$\nabla\varphi_f = -\mathscr{E} + \frac{a^3}{r^3}\left[\mathbf{A} - \frac{3\mathbf{A}\cdot\mathbf{r}}{r^2}\mathbf{r}\right], \quad r \geq a ,$$

$$\varphi_p = [\mathbf{A}(t) - \mathscr{E}(t)]\cdot\mathbf{r}, \quad \nabla\varphi_p = \mathbf{A} - \mathscr{E}, \quad r \leq a .$$

The Laplace transform of the relative dipole strength of the particle is equal to $\hat{\mathbf{A}} = \hat{\beta}(p)\mathscr{E}$, with

$$\hat{\beta} = \frac{\hat{\varepsilon}_p - \hat{\varepsilon}_f}{\hat{\varepsilon}_p + 2\hat{\varepsilon}_f} = \frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} + \frac{3(\sigma_p\varepsilon_f - \sigma_f\varepsilon_p)}{(\varepsilon_p + 2\varepsilon_f)^2}\frac{1}{p + 1/t_p} ,$$

where $t_p = (\varepsilon_p + 2\varepsilon_f)/(\sigma_p + 2\sigma_f)$ is the relaxation time for the charge redistribution caused by the particle and fluid conductivity. Henceforth the subscripts p and f will refer to the particle and the fluid, respectively. Hence, we have that

$$\mathbf{A}(t) = \frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}\mathscr{E}(t) + \frac{3(\sigma_p\varepsilon_f - \sigma_f\varepsilon_p)}{(\varepsilon_p + 2\varepsilon_f)^2}$$

$$\times \int_0^t \exp\left[-\frac{t - t'}{t_p}\right]\mathscr{E}(t')dt' \ .$$

On account of the model of a leaky dielectric described in Sec. III A 2, the total electric energy W of the particle and the fluid in a volume V containing the particle is

$$2W = \int_{V/v_p}\varepsilon_f(\nabla\varphi_f)^2 d\mathbf{r} + \int_{v_p}\varepsilon_p(\nabla\varphi_p)^2 d\mathbf{r} \equiv I_1 + I_2 \ , \quad (8)$$

where

$$I_1 = \int_{S_f}\varepsilon_f\varphi_f\nabla\varphi_f\cdot\mathbf{n}\,dS \ ,$$

$$I_2 = \int_{S_p}(\varepsilon_p\varphi_p\nabla\varphi_p - \varepsilon_f\varphi_f\nabla\varphi_f)\cdot\mathbf{n}\,dS \ ,$$

with v_p and S_p being the volume and surface of the particle, and S_f denoting the surface enclosing the volume V.

Let us analyze the first integral in Eq. (8) for the case $R_f \to \infty$, where R_f refers to the distance from the particle to the surface S_f. For $R_f \to \infty$, we have that

$$\varphi_f\nabla\varphi_f = \mathscr{E}(\mathscr{E}\cdot\mathbf{r}) - \frac{a^3}{r^3}\left[\mathbf{A} - \frac{3\mathbf{A}\cdot\mathbf{r}}{r^2}\mathbf{r}\right](\mathscr{E}\cdot\mathbf{r})$$

$$-\mathscr{E}\frac{a^3}{r^3}(\mathbf{A}\cdot\mathbf{r}) + O\left[\frac{1}{R_f^3}\right] \ ,$$

and therefore

$$I_1 = \varepsilon_f\int_{S_f}(\mathscr{E}\cdot\mathbf{n})(\mathscr{E}\cdot\mathbf{r})dS$$

$$-\varepsilon_f\int_{S_f}\left[\frac{a^3}{r^3}\left[\mathbf{A} - \frac{3\mathbf{A}\cdot\mathbf{r}}{r^2}\mathbf{r}\right]\cdot\mathbf{n}\right](\mathscr{E}\cdot\mathbf{r})dS$$

$$-\varepsilon_f\int_{S_f}(\mathscr{E}\cdot\mathbf{n})\frac{a^3}{r^3}(\mathbf{A}\cdot\mathbf{r})dS + O\left[\frac{1}{R_f}\right] \ . \quad (9)$$

The first integral in Eq. (9) is equal to $\varepsilon_f\mathscr{E}^2 V$, where $V \sim R_f^3$, while the second and the third integrals in Eq. (9) are $O(1/R_f^0)$.

To link the probe electric field $\mathscr{E}(t)$ to the actual electric field $\mathbf{E}$ in the system, we use the expressions

$$-\mathbf{E} = (1/V)\left[\int_{V_f}\nabla\varphi_f d\mathbf{r} + \int_{v_p}\nabla\varphi_p d\mathbf{r}\right]$$

$$= (1/V)\int_{S_f}\varphi_f\mathbf{n}\,dS$$

$$= (1/V)\int_{S_f}\left[-\mathscr{E}\cdot\mathbf{r} + \frac{a^3(\mathbf{A}\cdot\mathbf{r})}{r^3}\right]\mathbf{n}\,dS$$

$$= -\mathscr{E} + (1/V)\int_{S_f}\frac{a^3(\mathbf{A}\cdot\mathbf{r})}{r^3}\mathbf{n}\,dS \ .$$

The above illustrates the physical meaning of the probe field in that the value of $\mathscr{E}$ takes into account the change in the potential distribution over the fluid surface caused by the presence of a particle within a fluid sample. Thus this value depends on the shape of the fluid sample.

On substituting this expression for $\mathscr{E}$ in Eq. (9), we obtain (for $R_f \to \infty$) that

$$I_1 = \varepsilon_f\mathbf{E}^2 V + \varepsilon_f\int_{S_f}\left\{(\mathscr{E}\cdot\mathbf{n})\frac{a^3}{r^3}(\mathbf{A}\cdot\mathbf{r})\right.$$

$$\left. -\left[\frac{a^3}{r^3}\left[\mathbf{A} - \frac{3\mathbf{A}\cdot\mathbf{r}}{r^3}\right]\cdot\mathbf{n}\right](\mathscr{E}\cdot\mathbf{r})\right\}dS \ .$$

(10)

The integral in Eq. (10) can be written as

$$\int_{S_f}\left[\frac{a^3}{r^3}(\mathbf{A}\cdot\mathbf{r})\nabla(\mathscr{E}\cdot\mathbf{r})\cdot\mathbf{n} - (\mathscr{E}\cdot\mathbf{r})\nabla\left[\frac{a^3}{r^3}\mathbf{A}\cdot\mathbf{r}\right]\cdot\mathbf{n}\right]dS \ ,$$

but since both $\mathscr{E}\cdot\mathbf{r}$ and $(a^3/r^3)\mathbf{A}\cdot\mathbf{r}$ satisfy Laplace's equation for $|\mathbf{r}| > 0$, this integral is independent of the size and shape of the surface S_f, as long as the latter encloses the point $\mathbf{r} = 0$. Hence, letting S_f be a sphere, we obtain that

$$I_1 = \varepsilon_f\mathscr{E}^2 V + \frac{4\pi a^3}{3}\varepsilon_f 3\,\mathbf{A}\cdot\mathscr{E} \ .$$

On the other hand, in view of the expressions for φ_f and φ_p, the second integral in Eq. (8) becomes

$$I_2 = \frac{4\pi a^3}{3}[\varepsilon_p(\mathbf{A} - \mathscr{E})^2 + \varepsilon_f(\mathbf{A} - \mathscr{E})(2\mathbf{A} + \mathscr{E})] \ ,$$

which, when substituted together with the expression for I_1 into Eq. (8) and using the integral relation between $\mathbf{A}(t)$ and $\mathscr{E}(t)$, leads to

$$W = \frac{\varepsilon_f\mathbf{E}^2}{2}\mathbf{V} + v_p\left[\frac{3\varepsilon_f}{2}\frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}\mathbf{E}^2\right.$$

$$\left. + \frac{9(\sigma_p\varepsilon_f - \sigma_f\varepsilon_p)^2}{2(\varepsilon_p + 2\varepsilon_f)^3}\mathbf{J}^2\right] \ , \quad (11)$$

where $v_p = 4\pi a^3/3$ is the particle volume and

$$\mathbf{J}(t) = \int_0^t \exp\left[-\frac{t - t'}{t_p}\right]\mathbf{E}(t')dt' \ .$$

In the second term of Eq. (11), we have replaced $\mathscr{E}$ by $\mathbf{E}$ because $\mathbf{E} = \mathscr{E} + O(1/V)\mathscr{E}$.

The second term of Eq. (11) equals the energy of a particle at the fixed value of the external charge generating the electric field. But to obtain the energy of a particle at the fixed value of the external potential generating the electric field (i.e., the fixed value of the strength of the electric field), we require the negative of this term [25].

2. Force and torque exerted on a particle in nonuniform electric fields

The ponderomotive behavior of electrically uncharged particles in nonuniform electric fields has been analyzed in many papers (see [33,34]). Since the force and the torque have been calculated only for some particular cases (oscillating and rotating fields, transient regimes, etc.), we briefly outline how general expressions can be derived for the force and torque acting on a conducting particle in slightly nonuniform electric fields.

In a slightly nonuniform electric field, the disturbance

field due to the presence of a particle contains a quadru-pole moment in addition to the dipole. Hence the electric field can be written as [25]

$$\varphi_f = -\mathscr{E}(t)\cdot\mathbf{r} - \tfrac{1}{2}\nabla\mathscr{E}(t):\mathbf{rr} + \frac{a^3\mathbf{A}(t)\cdot\mathbf{r}}{r^3} + \frac{a^5\mathbf{B}(t):\mathbf{rr}}{r^5} \ ,$$

$$r \geq a \ ,$$

$$\varphi_p = \left[\mathbf{A}(t)-\mathscr{E}(t)\right]\cdot\mathbf{r} + \mathbf{d}:\mathbf{rr}, \quad r \leq a \ .$$

On substituting the Laplace transform of these expressions in the boundary conditions on the particle surface, we find that the relative quadrupole strength of the particle equals $\hat{\mathbf{B}} = \tfrac{1}{2}\hat{\beta}_2(p)\nabla\mathscr{E}(t)$ with

$$\hat{\beta}_2 = \frac{\hat{\varepsilon}_p - \hat{\varepsilon}_f}{\hat{\varepsilon}_p + \tfrac{3}{2}\hat{\varepsilon}_f} = \frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + \tfrac{3}{2}\varepsilon_f} + \frac{3(\sigma_p\varepsilon_f - \sigma_f\varepsilon_p)}{2(\varepsilon_p + \tfrac{3}{2}\varepsilon_f)^2}\frac{1}{p + 1/t_{p2}} \ ,$$

where $t_{p2} = (\varepsilon_p + \tfrac{3}{2}\varepsilon_f)/(\sigma_p + \tfrac{3}{2}\sigma_f)$ is the relaxation time for the quadrupole strength. Hence we have that

$$\mathbf{B}(t) = \frac{1}{2}\left[\frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + \tfrac{3}{2}\varepsilon_f}\nabla\mathscr{E}(t) + \frac{3(\sigma_p\varepsilon_f - \sigma_f\varepsilon_p)}{2(\varepsilon_p + \tfrac{3}{2}\varepsilon_f)^2}\right.$$
$$\left.\times\int_0^t \exp\left[-\frac{t-t'}{t_{p2}}\right]\nabla\mathscr{E}(t')dt'\right] \ .$$

The components of the net force $\mathbf{F}$ and of the torque $\mathbf{L}$ on the particle are [25]

$$F_i = \varepsilon_f\int_{S_p}(E_iE_l - \tfrac{1}{2}E_sE_s\delta_{ll})n_l dS \ ,$$

$$L_i = e_{ijk}\int_{S_p}E_kE_lx_jn_l dS \ ,$$

where $E_i(t) = [u_i(t)/h_i]$, $i = 1$ and 2. On substituting the

known relations

$$\int_{4\pi}n_in_k d\Omega = \frac{4\pi}{3}\delta_{ik} \ ,$$

$$\int_{4\pi}n_in_jn_kn_l d\Omega = \frac{4\pi}{15}(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \ ,$$

we obtain

$$F_i(t) = 4\pi\varepsilon_f a^3\left[\int_0^t\beta(t-t')\mathscr{E}_k(t')dt'\right]\frac{\partial\mathscr{E}_k(t)}{\partial x_i} \ ,$$

$$L_i(t) = L_i^{(1)}(t) + L_i^{(2)}(t) \ ,$$

where

$$L_i^{(1)}(t) = 4\pi\varepsilon_f a^3 e_{ijk}\left[\int_0^t\beta(t-t')\mathscr{E}_j(t')dt'\right]\mathscr{E}_k(t) \ ,$$

$$L_i^{(2)}(t) = \frac{4\pi}{3}\varepsilon_f a^5 e_{ijk}\left[\int_0^t\beta_2(t-t')\frac{\partial\mathscr{E}_j(t')}{\partial x_n}dt'\right]\frac{\partial\mathscr{E}_k(t)}{\partial x_n} \ .$$

In the above, $\mathbf{L}^{(1)}$ is induced by the dipole moment of the particle and corresponds to the torque acting on the particle in an uniform field, while $\mathbf{L}^{(2)}$ is induced by the quadrupole moment of the particle and is due to the nonuniformity of the electric field. For oscillating fields and in a transient regime, the expressions for $\mathbf{F}$ and $\mathbf{L}^{(1)}$ reduce to those derived in Refs. [33,34], whereas the formula for the correction $\mathbf{L}^{(2)}$ appears to be new.

C. Solution for the two-particle problem

The solution of the two-sphere problem for the Laplace transform of the quasisteady electromagnetic equations is based on the twin spherical expansion method used in Ref. [28] for the solution of the corresponding two-sphere electrostatic problem

$$\hat{\varphi}_p^{(1)} = -\hat{\mathscr{E}}\cdot\mathbf{r} + \sum_{m=0}^{1}\sum_{n=m}^{\infty}\hat{a}_{mn}^{(1)}\left[\frac{r_1}{a}\right]^n P_n^m(\cos\theta_1)\cos m\phi, \quad r_1 \leq a \ ,$$

$$\hat{\varphi}_f = -\hat{\mathscr{E}}\cdot\mathbf{r} + \sum_{m=0}^{1}\sum_{n=m}^{\infty}\left[\hat{b}_{mn}^{(1)}\left[\frac{a}{r_1}\right]^{n+1}P_n^m(\cos\theta_1) + \hat{b}_{mn}^{(2)}\left[\frac{a}{r_2}\right]^{n+1}P_n^m(\cos\theta_2)\right]\cos m\phi, \quad r_1,r_2 \geq a \ ,$$

where the subscripts 1 and 2 identify the appropriate particle; $\mathbf{r}_i$ ($i = 1$ and 2) is a vector from the center of a particle i to an arbitrary point $\mathbf{r}$; $\mathbf{R}$ is the vector from the center of particle 1 to that of particle 2; θ_1 and θ_2 are the angles between the vectors $\mathbf{r}_1$ and $\mathbf{R}$ and between $\mathbf{r}_2$ and $-\mathbf{R}$, respectively; and the angle ϕ is common to both coordinate systems.

On using the identity [28]

$$\left[\frac{a}{r_2}\right]^{n+1}P_n^m(\cos\theta_2) = \left[\frac{a}{R}\right]^{n+1}\sum_{s=m}^{\infty}\left[\begin{array}{c}n+s\\n+m\end{array}\right]\left[\frac{r_1}{R}\right]^s P_s^m(\cos\theta_1)$$

and substituting the expressions for $\hat{\varphi}_p^{(1)}$ and $\hat{\varphi}_f$ in the boundary conditions on the surface of the first sphere, we obtain

$$\hat{a}_{mn}^{(1)} = \hat{b}_{mn}^{(1)} + \sum_{s=m}^{\infty}\left[\begin{array}{c}n+s\\n+m\end{array}\right]\hat{b}_{ms}^{(2)}\left[\frac{a}{R}\right]^{n+s+1} \ ,$$

$$n\hat{\varepsilon}_p\frac{\hat{a}_{mn}^{(1)}}{a} + \hat{\varepsilon}_f\left[\frac{(n+1)\hat{b}_{mn}^{(1)}}{a} - \sum_{s=m}^{\infty}\frac{n\hat{b}_{ms}^{(2)}}{a}\left[\begin{array}{c}s+n\\n+m\end{array}\right]\left[\frac{a}{R}\right]^{n+s+1}\right] = (-1)^m(\hat{\varepsilon}_p - \hat{\varepsilon}_f)\hat{\mathscr{E}}_m\delta_{1n} \ .$$

$$(12)$$

Here we used the expression

$$\hat{\mathscr{E}}\cdot\mathbf{e}_r^{(1)}=\hat{\mathscr{E}}_0\cos\theta_1+\hat{\mathscr{E}}_1\sin\theta_1\cos\phi$$

$$=\sum_{m=0}^{1}\sum_{n=m}^{\infty}(-1)^m\hat{\mathscr{E}}_m\delta_{1n}\left[\frac{r_1}{a}\right]^n$$

$$\times P_n^m(\cos\theta_1)\cos m\phi\ .$$

Taking into account that $\hat{b}_{ms}^{(2)}=(-1)^{m-1}\hat{b}_{ms}^{(1)}$, from Eq. (12) we derive the relation

$$(-1)^m\frac{\hat{\varepsilon}_p n+\hat{\varepsilon}_f(n+1)}{\hat{\varepsilon}_p-\hat{\varepsilon}_f}\frac{\hat{b}_{mn}^{(1)}}{a}$$

$$-n\sum_{s=m}^{\infty}\frac{\hat{b}_{ms}^{(2)}}{a}\begin{bmatrix}s+n\\n+m\end{bmatrix}\left[\frac{a}{R}\right]^{n+s+1}=\hat{\mathscr{E}}_m\delta_{1n}\ .\quad (13)$$

Letting $n=0$ in the above, we conclude that $\hat{b}_{m0}^{(1)}=0$.

To solve Eq. (13), we expand $\hat{b}_{ms}^{(1)}$, $s\geq 1$ in powers of (a/R):

$$\frac{\hat{b}_{mn}^{(1)}}{a}=(-1)^m\hat{\beta}_1\hat{\mathscr{E}}_m\delta_{1n}+\sum_{p=1}^{\infty}\hat{A}_{mn,p}\left[\frac{a}{R}\right]^{n+p+1}\ ,\quad (14)$$

where $\hat{\beta}_n=(\hat{\varepsilon}_p-\hat{\varepsilon}_f)/[\hat{\varepsilon}_p+(n+1/n)\hat{\varepsilon}_f]$. We remark that $\hat{\beta}_1$ equals the parameter $\hat{\beta}$, defined earlier at the start of Sec. III B, which determines the dipole strength of one particle. Substituting this series in Eq. (13), we find the relationship

$$\frac{(-1)^m}{\hat{\beta}_n}\hat{A}_{mn,k}=(-1)^m\hat{\beta}_1\hat{\mathscr{E}}_m\begin{bmatrix}n+1\\n+m\end{bmatrix}\delta_{1k}$$

$$+\sum_{s=1}^{1\leq k-2s-1}\begin{bmatrix}s+n\\n+m\end{bmatrix}\hat{A}_{ms,k-2s-1}\ .$$

$$(15)$$

Equation (15) yields

$$\hat{A}_{mn,1}=\hat{\beta}_n\hat{\beta}_1\hat{\mathscr{E}}_m\begin{bmatrix}n+1\\n+m\end{bmatrix},\quad \hat{A}_{mn,2}=\hat{A}_{mn,3}=0\ ,$$

$$\hat{A}_{mn,4}=\begin{bmatrix}n+1\\n+m\end{bmatrix}(-1)^m\hat{\beta}_n\hat{A}_{m1,1},\quad \hat{A}_{mn,5}=0\ ,$$

$$\hat{A}_{mn,6}=\begin{bmatrix}n+2\\n+m\end{bmatrix}(-1)^m\hat{\beta}_n\hat{A}_{m2,1},$$

$$\hat{A}_{mn,7}=\begin{bmatrix}n+1\\n+m\end{bmatrix}(-1)^m\hat{\beta}_n\hat{A}_{m1,4}\ .$$

Clearly, $\hat{A}_{mn,k}$ can be represented as a polynomial expression in powers of $\hat{\beta}_1$. In this expression the term with

the lowest power of $\hat{\beta}_1$ is determined by the highest number of s in the sum of Eq. (15). For $k=2l+1,l\geq 3$, we get $s_{\max}=l-2$, and this term is

$$\begin{bmatrix}l+n-2\\n+m\end{bmatrix}\begin{bmatrix}l-1\\l+m-2\end{bmatrix}\begin{bmatrix}2\\1+m\end{bmatrix}\hat{\beta}_1^2\hat{\beta}_{l-2}\hat{\beta}_n\hat{\mathscr{E}}_m\ .$$

For $k=2l,l\geq 2$, we get $s_{\max}=l-1$, and this term is

$$(-1)^m\begin{bmatrix}l+n-1\\n+m\end{bmatrix}\begin{bmatrix}l\\l+m-1\end{bmatrix}\hat{\beta}_2\hat{\beta}_{l-1}\hat{\beta}_n\hat{\mathscr{E}}_m\ .$$

Since

$$\begin{bmatrix}s+n\\n+m\end{bmatrix}\sim\frac{s^{n+m}}{(n+m)!}\quad\text{for }s\gg 1\ ,$$

the main contribution to the sum of Eq. (15) is given by the term having the highest number for s. Thus expressions corresponding to the term with the lowest power of $\hat{\beta}_i$ also determine the asymptotic behavior of $\hat{A}_{mn,k}$ for $k\gg 1$.

Using the first and second expressions in Eq. (12), we obtain the following relation:

$$n(\hat{\varepsilon}_p-\hat{\varepsilon}_f)\frac{\hat{a}_{mn}^{(1)}}{a}+\hat{\varepsilon}_f(2n+1)\frac{\hat{b}_{mn}^{(1)}}{a}$$

$$=(-1)^m(\hat{\varepsilon}_p-\hat{\varepsilon}_f)\hat{\mathscr{E}}_m\delta_{1n}\ .$$

Letting $n=1$ in the above, we conclude that $\hat{a}_{m0}^{(1)}=0$.

The substitution of Eq. (14) into this relation yields

$$\frac{\hat{a}_{mn}^{(1)}}{a}=(-1)^m\hat{\beta}_1\hat{\mathscr{E}}_m\delta_{1n}$$

$$-\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p-\hat{\varepsilon}_f}\frac{2n+1}{n}\sum_{p=1}^{\infty}\hat{A}_{mn,p}\left[\frac{a}{R}\right]^{n+p+1}\ .\quad (16)$$

To calculate the integrals over the particle surface, let us present a more compact form for the following expressions:

$$\frac{\hat{\varphi}_p^{(1)}}{a}\bigg|_{r_1=a}=-\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p-\hat{\varepsilon}_f}\sum_{m=0}^{1}\sum_{n=m}^{\infty}\frac{2n+1}{n}\frac{\hat{b}_{mn}^{(1)}}{a}$$

$$\times P_n^m(\cos\theta_1)\cos m\phi\ ,$$

$$(\varepsilon_p\nabla\hat{\varphi}_p^{(1)}-\varepsilon_f\nabla\hat{\varphi}_f)_{r_1=a}\cdot\mathbf{n}$$

$$=-\frac{\varepsilon_p\hat{\varepsilon}_f-\varepsilon_f\hat{\varepsilon}_p}{\hat{\varepsilon}_p-\hat{\varepsilon}_f}\sum_{m=0}^{1}\sum_{n=m}^{\infty}(2n+1)\frac{\hat{b}_{mn}^{(1)}}{a}$$

$$\times P_n^m(\cos\theta_1)\cos m\phi\ ,$$

which on account of Eq. (14) become, respectively,

$$\frac{\hat{\varphi}_p^{(1)}}{a}\bigg|_{r_1=a}=\sum_{m=0}^{1}\sum_{n=m}^{\infty}\left[(\hat{\beta}_1-1)(-1)^m\hat{\mathscr{E}}_m\delta_{1n}-\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p-\hat{\varepsilon}_f}\frac{2n+1}{n}\sum_{p=1}^{\infty}\hat{A}_{mn,p}\left[\frac{a}{R}\right]^{n+p+1}\right]P_n^m(\cos\theta_1)\cos m\phi$$

and

$$(\varepsilon_p \nabla \hat{\varphi}_p^{(1)} - \varepsilon_f \nabla \hat{\varphi}_f)_{r_1=a} \cdot \mathbf{n} = \sum_{m=0}^{1} \sum_{n=m}^{\infty} \left\{ [(\varepsilon_p + 2\varepsilon_f)\hat{\beta}_1 - (\varepsilon_p - \varepsilon_f)](-1)^m \hat{\mathscr{E}}_m \delta_{1n} \right.$$

$$\left. - \frac{\varepsilon_p \hat{\mathscr{E}}_f - \varepsilon_f \hat{\mathscr{E}}_p}{\hat{\mathscr{E}}_p - \hat{\mathscr{E}}_f}(2n+1) \sum_{p=1}^{\infty} \hat{A}_{mn,p} \left[\frac{a}{R} \right]^{n+p+1} \right\} P_n^m(\cos\theta_1)\cos m\phi \ ,$$

D. Electric energy of two particles in an unbounded medium

The calculation of the electric energy of two particles closely follows that of one particle. The total electric energy W of the two particles and of the surrounding fluid in a rather large volume V is given, as before [cf. Eq. (8)], by

$$2W = \int_{V/v_p} \varepsilon_f (\nabla\varphi_f)^2 d\mathbf{r} + \int_{v_p} \varepsilon_p (\nabla\varphi_p)^2 d\mathbf{r} \equiv I_1 + I_2 \ , \tag{17}$$

where

$$I_1 = \int_{S_f} \varepsilon_f \varphi_f \nabla\varphi_f \cdot \mathbf{n}\, dS, \quad I_2 = \sum_{i=1}^{2} \int_{S_p} (\varepsilon_p \varphi_p \nabla\varphi_p - \varepsilon_f \varphi_f \nabla\varphi_f)\mathbf{n}\, dS \ .$$

To calculate these integrals, we take the solution of a two-particle problem for the probe electric field $\mathscr{E}(t)$.

For $R_f \to \infty$, where R_f is the distance from the particles to the surface S_f ($R_f \gg R$, R being the distance between the particle centers), we have

$$\varphi_f = -\mathscr{E} \cdot \mathbf{r} + \sum_{i=1}^{2} \frac{a^2}{r_i^3} \mathbf{b}_1^{(i)} \cdot \mathbf{r}_i + O(1/R_f^3) \ ,$$

where $\mathbf{b}_1^{(i)} = b_{01}^{(i)} \mathbf{e}_0 - b_{11}^{(i)} \mathbf{e}_1$, $b_{01}^{(1)} = -b_{01}^{(2)}$, and $b_{11}^{(1)} = b_{11}^{(2)}$, with $\mathbf{e}_0$ and $\mathbf{e}_1$ being unit vectors, respectively, parallel and perpendicular to the line of centers of the particles.

Thus the integral I_1 in Eq. (17) can be written as

$$I_1 = \varepsilon_f \mathscr{E}^2 V - \varepsilon_f \sum_{i=1}^{2} \int_{S_f} \left\{ (\mathscr{E}\cdot\mathbf{n})\frac{a^2}{r_i^3}(\mathbf{b}_1^{(i)}\cdot\mathbf{r}_i) + \frac{a^2}{r_i^3}\left[b_1^{(i)} - \frac{3}{r_i^2}(\mathbf{b}_1^{(i)}\cdot\mathbf{r}_i)\mathbf{r}_i \right] \cdot \mathbf{n}(\mathscr{E}\cdot\mathbf{r}) \right\} dS + O\left[\frac{1}{R_f} \right] \ .$$

Once again, to link the probe electric field $\mathscr{E}(t)$ to the actual electric field $\mathbf{E}(t)$, we use the expression

$$-\mathbf{E} = \frac{1}{V}\left[\int_{V_f} \nabla\varphi_f d\mathbf{r} + \int_{v_p} \nabla\varphi_p d\mathbf{r} \right] = \frac{1}{V}\int_{S_f} \varphi_f \mathbf{n}\, dS = -\mathscr{E} + \frac{1}{V}\sum_{i=1}^{2}\int_{S_f} \frac{a^3}{r_i^3}(\mathbf{b}_1^{(i)}\cdot\mathbf{r}_i)\mathbf{n}\, dS + O\left[\frac{1}{R_f^4} \right] \ ,$$

which, when substituted into the expression for I_1, yields

$$I_1 = \varepsilon_f \mathbf{E}^2 V + \varepsilon_f \sum_{i=1}^{2} q_i + O\left[\frac{1}{R_f} \right] \ ,$$

where

$$q_i = \int_{S_f} \left\{ (\mathscr{E}\cdot\mathbf{n})\frac{a^2}{r_i^3}(\mathbf{b}_1^{(i)}\cdot\mathbf{r}_i) - (\mathscr{E}\cdot\mathbf{r})\frac{a^2}{r_i^3}\left[\mathbf{b}_1^{(i)} - \frac{3}{r_i^2}(\mathbf{b}_1^{(i)}\cdot\mathbf{r}_i)\mathbf{r}_i \right] \cdot \mathbf{n} \right\} dS \ .$$

Once again, since the functions $\mathscr{E}\cdot\mathbf{r}$ and $(a^2/r_i^3)(\mathbf{b}_1^{(i)}\cdot\mathbf{r}_i)$ satisfy Laplace's equation for $|\mathbf{r}_i| > 0$, the value of q_i does not depend on the size and shape of the surface around the point $\mathbf{r}_i = 0$. Choosing S_f to be a sphere, we find that $q_i = (4\pi/3)a^2 3\mathscr{E}\cdot\mathbf{b}_1^{(i)}$. Therefore, for $R_f \to \infty$ we have

$$I_1 = \varepsilon_f \mathbf{E}^2 V + \varepsilon_f \frac{4\pi}{3}a^3 \left[\sum_{i=1}^{2} 3\mathscr{E}\cdot\frac{\mathbf{b}_1^{(i)}}{a} \right] \ ,$$

where

$$\mathscr{E}\cdot\frac{\mathbf{b}_1^{(1)}}{a} = \sum_{m=0}^{1} \varepsilon_f A_m \mathscr{E}_m + \sum_{s=1}^{\infty} \left[\frac{a}{R} \right]^{s+2} \sum_{m=0}^{1} (-1)^m \varepsilon_f \mathscr{E}_m \mathscr{L}^{-1}\{\hat{A}_{m1,s}\} \ .$$

The terms for $s = 2$, 3, and 5 vanish.

Substituting the expressions for φ_f and $\varphi_p^{(1)}$ in the equation for the integral I_2 yields, for the first particle,

$$\frac{4\pi}{3}a^3\left[\sum_{m=0}^{1}[(\varepsilon_p+2\varepsilon_f)A_m-(\varepsilon_p-\varepsilon_f)\mathscr{E}_m](A_m-\mathscr{E}_m)\right.$$

$$-3\sum_{s=1}^{\infty}\left[\frac{a}{R}\right]^{s+2}\sum_{m=0}^{1}(-1)^m\left[[(\varepsilon_p+2\varepsilon_f)A_m-(\varepsilon_p-\varepsilon_f)\mathscr{E}_m]\right.$$

$$\left.\times\mathcal{L}^{-1}\left\{\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p-\hat{\varepsilon}_f}\hat{A}_{m1,s}\right\}+(A_m-\mathscr{E}_m)\mathcal{L}^{-1}\left\{\frac{\varepsilon_p\hat{\varepsilon}_f-\varepsilon_f\hat{\varepsilon}_p}{\hat{\varepsilon}_p-\hat{\varepsilon}_f}\hat{A}_{m1,s}\right\}\right]$$

$$+\frac{3}{2}\sum_{s=6}^{\infty}\left[\frac{a}{R}\right]^s\sum_{m=0}^{1}\sum_{n,k,k'\geq 1}^{s=2(n+1)+k+k'}\frac{(n+m)!(1+\delta_{m0})(2n+1)}{(n-m)!n}$$

$$\left.\times\mathcal{L}^{-1}\left\{\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p-\hat{\varepsilon}_f}\hat{A}_{mn,k'}\right\}\mathcal{L}^{-1}\left\{\frac{\varepsilon_p\hat{\varepsilon}_f-\varepsilon_f\hat{\varepsilon}_p}{\hat{\varepsilon}_p-\hat{\varepsilon}_f}\hat{A}_{mn,k}\right\}\right],$$

and similarly for the second particle. For the first series, the terms for $s=2$, 3, and 5 vanish; for the second series, the term for $s=7$ vanishes.

Combining the expressions for I_1 and I_2 and subtracting $\varepsilon_f E^2 V$, we arrive at the equation for the energy of two particles at the fixed value of the external charge generating the electric field. The first term in this equation coincides with the expression for the energy of one particle, Eq. (11). The second term, which is proportional to $(a/R)^3$, refers to the energy of the dipole-dipole interaction $W^{d\text{-}d}$ between conducting particles. For a fixed orientation of the electric field, we get

$$W^{d\text{-}d}=-4\pi a^3\left[\frac{a}{R}\right]^3\sum_{m=0}^{1}(-1)^m\left[\begin{array}{c}2\\1+m\end{array}\right]\left[\varepsilon_f E_m\mathcal{L}^{-1}\{\hat{\beta}^2\hat{E}_m\}\right.$$

$$+3\left[\mathcal{L}^{-1}\left\{\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}\hat{E}_m\right\}\mathcal{L}^{-1}\left\{\frac{\varepsilon_p\hat{\varepsilon}_f-\varepsilon_f\hat{\varepsilon}_p}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}\hat{\beta}\hat{E}_m\right\}\right.$$

$$\left.\left.+\mathcal{L}^{-1}\left\{\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}\hat{\beta}\hat{E}_m\right\}\mathcal{L}^{-1}\left\{\frac{\varepsilon_p\hat{\varepsilon}_f-\varepsilon_f\hat{\varepsilon}_p}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}\hat{E}_m\right\}\right]\right].\tag{18}$$

Consider the case of a suddenly applied electric field, $E(t)=EH(t)$. For short times, when $t\ll t_p$ ($p\to\infty$, respectively), we obtain the same expression as that for nonconducting particles in a nonconducting fluid:

$$W^{d\text{-}d}=4\pi a^3\varepsilon_f\Psi_\infty^d E^2\frac{a^3}{R^3}(1-3\cos^2\theta),$$

$$\Psi_\infty^d=\beta^2=\left[\frac{\varepsilon_p-\varepsilon_f}{\varepsilon_p+2\varepsilon_f}\right]^2,\tag{19}$$

while, for $t\gg t_p$ ($p\to 0$, respectively), we have that

$$W^{d\text{-}d}=4\pi a^3\varepsilon_f\Psi_0^d E^2\frac{a^3}{R^3}(1-3\cos^2\theta),$$

$$\Psi_0^d=\frac{\sigma_p-\sigma_f}{\sigma_p+2\sigma_f}\left[\frac{\sigma_p-\sigma_f}{\sigma_p+2\sigma_f}+6\frac{\sigma_f(\varepsilon_p\sigma_f-\varepsilon_f\sigma_p)}{\varepsilon_f(\sigma_p+2\sigma_f)^2}\right].\tag{20}$$

Here θ is the angle between the vectors E and R.

To derive the expression for the oscillating field, $E(t)=E_0\sin\omega t$ and $t\gg t_p$, we use the relation

$$\langle\mathcal{L}^{-1}\{\hat{X}(p)\hat{E}_m(p)\}\mathcal{L}^{-1}\{\hat{Y}(p)\hat{E}_m(p)\}\rangle_T$$

$$=\tfrac{1}{2}E_{m,0}^2\text{Re}[\hat{X}(i\omega)\hat{Y}^*(i\omega)],$$

where $\langle\ \rangle_T$ denotes the time average, and $\hat{X}(p)$ and $\hat{Y}(p)$ are arbitrary functions. As a result, we get

$$\langle W^{d\text{-}d}\rangle_T=2\pi a^3\varepsilon_f\Psi_\omega^d E_0^2\frac{a^3}{R^3}(1-3\cos^2\theta),$$

$$\Psi_\omega^d=\left[\frac{\varepsilon_p-\varepsilon_f}{\varepsilon_p+2\varepsilon_f}\right]^2$$

$$+\frac{3(2\varepsilon_p-5\varepsilon_f)(\sigma_p\varepsilon_f-\sigma_f\varepsilon_p)^2}{\varepsilon_f(\varepsilon_p+2\varepsilon_f)^2(\sigma_p+2\sigma_f)^2}\frac{1}{1+\omega^2 t_p^2}$$

$$+\frac{18(\sigma_p\varepsilon_f-\sigma_f\varepsilon_p)^3}{\varepsilon_f(\varepsilon_p+2\varepsilon_f)^2(\sigma_p+2\sigma_f)^3}\frac{1}{(1+\omega^2 t_p^2)^2},\tag{21}$$

Clearly, $\Psi_\omega^d\to\Psi_\infty^d$ when $\omega\to\infty$, and $\Psi_\omega^d\to\Psi_0^d$ when $\omega\to 0$.

On comparing Eq. (19) with Eqs. (20) and (21), we see that the effect of the interfacial polarization of the particles on the interparticle interaction is reflected by the difference between the coefficient $\Psi_\infty^d=\beta^2$ for nonconducting particles and that of Ψ_0^d and Ψ_ω^d for conducting particles. Moreover, whereas Ψ_∞^d is always non-negative, Ψ_0^d and Ψ_ω^d could become negative if the dielectric constants and conductances of the particles and the fluid do not satisfy certain specific relations which will be presented in Sec. V, Eq. (35).

The currently available theoretical predictions regarding the structure formation in ER fluids have been obtained from computer simulations based on the mechanical model which describes the motion of nonconducting particles in a nonconducting liquid under the action of the viscous, Brownian, and electric-field-induced dipole forces between particles; see for example, [35–41]. Therefore, the fact that Eq. (19) is of the same form as Eqs. (20) and (21) for the case $\Psi_0^d > 0$ and $\Psi_\omega^d > 0$ makes it possible to use the results of the available computer simulations in order to estimate the kinetics of the structure formation in a conducting suspension, by merely replacing β^2 with Ψ_0^d and/or Ψ_ω^d.

IV. ELECTRIC ENERGY OF A CONDUCTING SUSPENSION

In this section, we shall develop the microstructure-based theory of the electric energy of a conducting suspension in a time-varying electric field. First, in Sec. IV A, we shall use the mean-field approximation which is based on the cell model. It leads to a simple compact equation which estimates the concentration dependence of the electric energy and allows us to analyze various forms of the time variation of an electric field. In Sec. IV B, we shall develop the statistical theory of the electric energy in a disordered suspension and use the renormalization technique in order to account for the difference between the average electric field in a suspension and the average electric field acting on a test particle. The statistical approach leads to a relation between the interparticle forces and the macroscopic electric energy of a suspension, and also illustrates the limitations of the cell model.

A. Cell model

A number of methods have been developed, based on the mean-field approximation, which lead to the derivation of the Maxwell-Wagner expression for the complex permittivity $\hat{\varepsilon}_s$ of a suspension [26]

$$\frac{\hat{\varepsilon}_s - \hat{\varepsilon}_f}{\hat{\varepsilon}_s + 2\hat{\varepsilon}_f} = \frac{\hat{\varepsilon}_p - \hat{\varepsilon}_f}{\hat{\varepsilon}_p + 2\hat{\varepsilon}_f} c \ .$$

This expression is actually based on the assumption that the dipole strength of a suspension is equal to the sum of the dipole strengths of all the particles.

According to the Maxwell-Wagner relationship,

$$\hat{\varepsilon}_s(p) = \varepsilon_f \frac{1 + 2c\dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}}{1 - c\dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}} + \frac{\sigma_f}{p}\frac{1 + 2c\dfrac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f}}{1 - c\dfrac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f}}$$

$$+ \frac{9c(1-c)(\varepsilon_f\sigma_p - \varepsilon_p\sigma_f)^2}{(1+pt_s)(\varepsilon_p + 2\varepsilon_f)\left[1 - c\dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}\right](\sigma_p + 2\sigma_f)^2\left[1 - c\dfrac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f}\right]^2} \ ,$$

where

$$t_s = \frac{(\varepsilon_p + 2\varepsilon_f)\left[1 - c\dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}\right]}{(\sigma_p + 2\sigma_f)\left[1 - c\dfrac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f}\right]} \ .$$

The value of t_s determines the relaxation time of the redistribution of charge at the particle surface in a suspension caused by the conductivity of the fluid and the particles [26]. The substitution of $i\omega$ for p into the above expression yields the frequency dependence of the real and imaginary parts of the complex permittivity of a suspension, $\hat{\varepsilon}_s(i\omega) = \varepsilon_s'(\omega) + i\varepsilon_s''(\omega)$.

To derive the equation for the electric energy of a suspension, we use the mean-field approximation based on a cell model. It assumes that the complex permittivity and electric energy of a suspension are equal to the corresponding values of a spherical fluid cell of radius $a/c^{1/3}$ containing one particle at its center. At first, we briefly outline a method for deriving the Maxwell-Wagner relationship. We begin by noting that the average parameters of the electric field in the cell are defined by the following expressions:

$$\langle \hat{\mathbf{D}} \rangle = \hat{\varepsilon}_f(1-c)\langle \hat{\mathbf{E}}_f \rangle + \hat{\varepsilon}_p c\langle \hat{\mathbf{E}}_p \rangle \ ,$$

$$\langle \hat{\mathbf{E}} \rangle = (1-c)\langle \hat{\mathbf{E}}_f \rangle + c\langle \hat{\mathbf{E}}_p \rangle \ ,$$

where the symbol $\langle \ \rangle$ denotes the volume average. Let $\mathscr{E}$ be the probe electric field acting on a particle. Using the expressions for φ_f and φ_p of the electric field induced by a particle in an unbounded medium (Sec. III B), we have, for a cell of volume $V = v_p/c$, that

$$\langle \hat{\mathbf{E}}_f \rangle = -\frac{1}{V - v_p}\int_{V/v_p}\nabla\varphi_f d\mathbf{r} = \hat{\mathscr{E}} \ ,$$

$$\langle \hat{\mathbf{E}}_p \rangle = -\frac{1}{v_p}\int_{v_p}\nabla\varphi_p d\mathbf{r} = \frac{3\hat{\varepsilon}_f}{\hat{\varepsilon}_p + 2\hat{\varepsilon}_f}\hat{\mathscr{E}} \ ,$$

As the result of these expressions, the Maxwell-Wagner relationship stems from the definition of the complex permittivity, $\hat{\varepsilon}_s = \langle \hat{\mathbf{D}} \rangle / \langle \hat{\mathbf{E}} \rangle$. It is important to keep in mind that the relation for $\hat{\varepsilon}_s$ was derived using the formula for the electric field induced by a particle in an unbounded medium with boundary conditions at $r \to \infty$, even though the calculation was made for a cell of radius $a/c^{1/3}$. This means that the boundary condition on the cell surface was not taken into account.

Now, as in Eq. (8), the average energy density w in the cell is defined by (cf. Sec. III B)

$$2wV = \varepsilon_f \int_{V/v_p} (\nabla \varphi_f)^2 d\mathbf{r} + \varepsilon_p \int_{v_p} (\nabla \varphi_p)^2 d\mathbf{r} \equiv I_1 + I_2 \ ,$$

$$I_1 = \int_{S_f} \varphi_f \varepsilon_f \nabla \varphi_f \cdot \mathbf{n} \, dS \ ,$$

$$I_2 = \int_{S_p} (\varepsilon_p \varphi_p \nabla \varphi_p - \varepsilon_f \varphi_f \nabla \varphi_f) \cdot \mathbf{n} \, dS \ ,$$

where I_1 is the energy of the charge distributed over the cell surface, and I_2 is the energy of the charge distributed over the particle surface. Using the expressions for φ_f and φ_p of the electric field induced by a particle in an unbounded medium (Sec. III B), we calculate the integrals for I_1 and I_2 and substitute the average electric field in the cell, $\langle \widehat{\mathbf{E}} \rangle = \widehat{\mathscr{E}}(1 - \widehat{\beta}c)$, for $\widehat{\mathscr{E}}$. As the result of these calculations, we arrive at

$$w(t) = \frac{\varepsilon_f}{2} \frac{1 + 2c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}}{1 - c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}} \langle \mathbf{E}(t) \rangle^2$$

$$+ \frac{9c(1-c)(\varepsilon_f \sigma_p - \varepsilon_p \sigma_f)^2}{2(\varepsilon_p + 2\varepsilon_f)^3 \left[1 - c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} \right]^3} \mathbf{I}^2(t) \ , \qquad (22)$$

where

$$\mathbf{I}(t) = \int_0^t \exp\left[-\frac{t - t'}{t_s} \right] \langle \mathbf{E}(t') \rangle dt' \ .$$

The first term in Eq. (22) is consistent with the macroscopic relationship for the electric energy of a nonconducting system [25]

$$\langle w \rangle = \tfrac{1}{2} \varepsilon_s(c) \langle \mathbf{E} \rangle^2 \ ,$$

where

$$\varepsilon_s(c) = \varepsilon_f \frac{1 + 2c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}}{1 - c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}} \ .$$

For a suddenly applied electric field, $\langle \mathbf{E}(t) \rangle = \langle \mathbf{E} \rangle H(t)$, the second term in Eq. (22) for the steady-state regime, $t \gg t_s$, reduces to

$$\frac{9c(1-c)}{2} \frac{(\varepsilon_f \sigma_p - \varepsilon_p \sigma_f)^2 \langle \mathbf{E} \rangle^2}{(\varepsilon_p + 2\varepsilon_f) \left[1 - c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} \right] (\sigma_p + 2\sigma_f)^2 \left[1 - c \dfrac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f} \right]^2} \ ,$$

while, for the oscillating field, $\langle \mathbf{E} \rangle = \mathbf{E}_0 \cos \omega t$, and $t \gg t_s$, we have that

$$w(t) = \frac{\varepsilon_f}{2} \frac{1 + 2c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}}{1 - c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}} \mathbf{E}_0^2 \cos^2 \omega t + \frac{9c(1-c)(\varepsilon_f \sigma_p - \varepsilon_p \sigma_f)^2 \mathbf{E}_0^2 \cos^2(\omega t + \Psi)}{2(1 + \Omega^2)(\varepsilon_p + 2\varepsilon_f) \left[1 - c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} \right] (\sigma_p + 2\sigma_f)^2 \left[1 - c \dfrac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f} \right]^2} \ , \qquad (23)$$

where $\Omega = \omega t_s, \tan \Psi = \Omega$.

For a slowly oscillating electric field, $\omega t_s \ll 1$, Eq. (23) yields the expression for the time average of the electric energy, $\langle w \rangle_T$, of a suspension

$$\langle w \rangle_T = \left[\frac{\varepsilon_f}{4} \frac{1 + 2c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}}{1 - c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}} + \frac{9c(1-c)(\varepsilon_f \sigma_p - \varepsilon_p \sigma_f)^2}{4(\varepsilon_p + 2\varepsilon_f) \left[1 - c \dfrac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} \right] (\sigma_p + 2\sigma_f)^2 \left[1 - c \dfrac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f} \right]^2} \right] \mathbf{E}_0^2 \ ,$$

which is consistent with the expression given by the substitution of the Maxwell-Wagner relation for the frequency dependence of the real part of the complex permittivity of a suspension into Brillouin's formula [25]

$$\langle w \rangle_T = \frac{1}{2} \frac{d}{d\omega} [\omega \varepsilon_s'(\omega)] \langle \mathbf{E}^2(\omega) \rangle_T$$

for the electric energy of a low-conductivity macroscopic system and a slowly varying oscillating electric field, $|\varepsilon_s''(\omega)| \ll \varepsilon_s'(\omega), \omega t_s \ll 1$.

The $O(c)$ term of the expansion of Eq. (22) for the electric energy of a suspension in powers of c is consistent with Eq. (11) for the energy of one particle.

B. Ensemble average equations

1. General equation

The total electric energy W of a suspension is defined by

$$2W = \left\langle \int_{V/\Sigma v_p} \varepsilon_f (\nabla \varphi_f)^2 d\mathbf{r} + \int_{\Sigma v_p} \varepsilon_p (\nabla \varphi_p)^2 d\mathbf{r} \right\rangle_e$$

$$\equiv \langle I_1 \rangle_e + N \langle I_2 \rangle_e \ , \tag{24}$$

where $\langle \ \rangle_e$ denotes the ensemble average, N is the number of particles, and

$$\varphi_f = -\langle \mathbf{E} \rangle_e \cdot \mathbf{r} + \sum_i \frac{a^3 \mathbf{A}_i (\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^3} + O\left[\frac{1}{R_f^3}\right] \ ,$$

$$\nabla \varphi_f = -\langle \mathbf{E} \rangle_e + \sum_i \frac{a^3}{|\mathbf{r} - \mathbf{r}_i|^3}\left[\mathbf{A}_i - 3\frac{\mathbf{A}_i \cdot (\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^2}(\mathbf{r} - \mathbf{r}_i)\right] + O\left[\frac{1}{R_f^4}\right] \ .$$

Hence

$$\langle I_1 \rangle_e = \varepsilon_f \int_{S_f}(\langle \mathbf{E} \rangle_e \cdot \mathbf{r})(\langle \mathbf{E} \rangle_e \cdot \mathbf{n}) dS - \varepsilon_f \int_{S_f}(\langle \mathbf{E} \rangle_e \cdot \mathbf{r})\left\langle \sum_i \frac{a^3}{|\mathbf{r} - \mathbf{r}_i|^3}\left[\mathbf{A}_i - 3\frac{\mathbf{A}_i \cdot (\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^2}(\mathbf{r} - \mathbf{r}_i)\right]\right\rangle_e \cdot \mathbf{n}\, dS$$

$$- \varepsilon_f \int_{S_f}(\langle \mathbf{E} \rangle_e \cdot \mathbf{n})\left\langle \sum_i \frac{a^3 \mathbf{A}_i (\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^3}\right\rangle_e dS + O\left[\frac{1}{R_f}\right] \ .$$

Clearly, the main terms $O(R_f^3)$ and $O(R_f^0)$ of this expression as $R_f \to \infty$ are exactly the same as those given by averaging the expansions listed above for φ_f and $\nabla \varphi_f$ in powers of $1/R_f$ and substituting them into the right-hand side of Eq. (25).

Next, using the identity

$$-\langle \varepsilon_f \nabla \varphi_f \rangle_e = \left\langle \mathcal{L}^{-1}\left\{\frac{\varepsilon_f}{\hat{\varepsilon}_f(p)}\hat{\mathbf{D}}_f\right\}\right\rangle_e$$

$$= \mathcal{L}^{-1}\left\{\frac{\varepsilon_f}{\hat{\varepsilon}_f(p)}\langle \hat{\mathbf{D}}_f \rangle_e\right\} \ ,$$

where $\hat{\mathbf{D}}_f = -\varepsilon_f(p)\nabla\hat{\varphi}_f$, we can write the right-hand side of Eq. (25) as

$$\langle I_1 \rangle_e = -\int_{S_f}\langle \nabla \varphi_f \rangle_e \mathcal{L}^{-1}\left\{\frac{\varepsilon_f}{\hat{\varepsilon}_f(p)}\langle \hat{\mathbf{D}}_f \rangle_e\right\}\mathbf{n}\, dS \ . \tag{26}$$

But, since according to the boundary conditions for the equations for a quasisteady electric field, $\hat{\varphi}$ and $\hat{\mathbf{D}}$ are continuous at the fluid-particle surface, Eq. (26) can be rearranged into

$$I_1 = \int_{S_f} \varepsilon_f \varphi_f \nabla \varphi_f \cdot \mathbf{n}\, dS \ ,$$

$$I_2 = \int_{S_p}(\varepsilon_p \varphi_p \nabla \varphi_p - \varepsilon_f \varphi_f \nabla \varphi_f)\cdot \mathbf{n}\, dS \ .$$

The integral I_2 in Eq. (24) is over the surface of one particle, while S_f is a large surface within the fluid enclosing all the particles.

Let us prove the following equality:

$$\langle I_1 \rangle_e = \int_{S_f} \varepsilon_f \langle \varphi_f \rangle_e \langle \nabla \varphi_f \rangle_e \cdot \mathbf{n}\, dS \ . \tag{25}$$

It is evident that this applies equality for a charged surface (where the value $\varepsilon_f \nabla \varphi_f \cdot \mathbf{n}$ is fixed) and a metallic surface (where φ_f is fixed). For the case of a large fluid volume, $S_f \sim R_f^2$, $R_f \to \infty$, where R_f is a distance from the particles to the surface, we have that

$$\langle I_1 \rangle_e = -\int_V \left[\mathcal{L}^{-1}\left\{\frac{\varepsilon_f}{\hat{\varepsilon}_f(p)}\langle \hat{\mathbf{D}} \rangle_e\right\}\nabla \cdot \langle \varphi \rangle_e\right.$$

$$\left. + \langle \varphi \rangle_e \cdot \mathcal{L}^{-1}\left\{\frac{\varepsilon_f}{\hat{\varepsilon}_f(p)}\nabla \cdot \langle \hat{\mathbf{D}} \rangle_e\right\}\right] d\mathbf{r}$$

$$= V\langle \mathbf{E} \rangle_e \mathcal{L}^{-1}\left\{\frac{\varepsilon_f}{\hat{\varepsilon}_f(p)}\langle \hat{\mathbf{D}} \rangle_e\right\} \ .$$

where account has been taken that $\nabla \cdot \langle \hat{\mathbf{D}} \rangle_e = 0$. But, as

$$\langle \hat{\mathbf{D}} \rangle_e = \hat{\varepsilon}_f \langle \hat{\mathbf{E}} \rangle_e + c(\hat{\varepsilon}_p - \hat{\varepsilon}_f)\langle \hat{\mathbf{E}}_p \rangle_e \ ,$$

we arrive at the following result for the total electric energy:

$$2W = \varepsilon_f \langle \mathbf{E} \rangle_e^2 V + \varepsilon_f N v_p \langle \mathbf{E} \rangle_e \mathcal{L}^{-1}\left\{\frac{\hat{\varepsilon}_p - \hat{\varepsilon}_f}{\hat{\varepsilon}_f}\langle \langle \hat{\mathbf{E}}_p \rangle_e \rangle\right\}$$

$$+ N\langle I_2 \rangle_e \ . \tag{27}$$

Here $\langle \ \rangle$ denotes the volume average, while

$$\langle \langle \hat{\mathbf{E}}_p \rangle_e \rangle = -\frac{1}{v_p}\left\langle \int_{S_p} \hat{\varphi}_p \mathbf{n}\, dS \right\rangle_e \ ,$$

where the integral is calculated over the surface of one particle.

The derivation of Eq. (27) is based on the permutability of spatially integrating over a large surface [Eq. (25)] and ensemble averaging, followed by the transformation of the surface integral into the volume integral, which is typical of the continuum electrodynamics theory [25]. Note that the actual electric field acting on a particle and the dipole strength of a particle, which are the key ingredients of any microstructure-based theory, are not explicitly used in this approach.

Next we briefly outline how Eq. (27) emanates from the microstructural point of view. The calculation of the electric energy for N particles makes use of the probe field $\mathscr{E}$, acting on a particle and repeats the steps of the earlier analysis for one and two particles in an unbounded

medium ($V \rightarrow \infty$). As a result, we obtain the equation

$$2W = \varepsilon_f \langle \mathbf{E} \rangle_e^2 V + 3\varepsilon_f N v_p \langle \mathbf{E} \rangle_e \cdot \langle \mathbf{A} \rangle_e + N \langle I_2 \rangle_e \, , \quad (28)$$

which contains the average dipole strength $\langle \mathbf{A} \rangle_e$ of a particle. To calculate the second and third terms of Eq. (28), we can also substitute $\langle \mathbf{E} \rangle_e$ for the probe field $\mathscr{E}$. To relate $\langle \mathbf{A} \rangle_e$ in Eq. (28) to $\langle \langle \mathscr{E} \rangle_e \rangle$ in Eq. (27), we use the identity

$$\int_{S_f} [(\mathscr{E} \cdot \mathbf{r}) \nabla \varphi_f - \varphi_f \nabla (\mathscr{E} \cdot \mathbf{r})] \cdot \mathbf{n} \, dS$$

$$= \sum_i \int_{S_p} [(\mathscr{E} \cdot \mathbf{r}) \nabla \varphi_f - \varphi_f \nabla (\mathscr{E} \cdot \mathbf{r})] \cdot \mathbf{n} \, dS \, ,$$

which follows from the fact that both φ_f and $\mathscr{E} \cdot \mathbf{r}$ satisfy Laplace's equation in the fluid. For $R_f \rightarrow \infty$, the left-hand integral of this identity is equal to

$$\sum_i \int_{S_f} \left\{ (\mathscr{E} \cdot \mathbf{r}) \nabla \left[\frac{a^3 \mathbf{A}_i \cdot (\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^3} \right] - \frac{a^3 \mathbf{A}_i \cdot (\mathbf{r} - \mathbf{r}_i)}{|\mathbf{r} - \mathbf{r}_i|^3} \nabla (\mathscr{E} \cdot \mathbf{r}) \right\} \cdot \mathbf{n} \, dS = - \sum_i 3 v_p \, \mathbf{A}_i \cdot \mathscr{E}$$

Moreover, on account of the boundary conditions

$$\varphi_f |_{S_p} = \varphi_p |_{S_p}, \quad \nabla \varphi_f \cdot \mathbf{n} |_{S_p} = \mathcal{L}^{-1} \left\{ \frac{\hat{\varepsilon}_p}{\hat{\varepsilon}_f} \nabla \hat{\varphi}_p \cdot \mathbf{n} \Big|_{S_p} \right\}$$

on the particle surface, the right-hand integral of the identity equals

$$- \sum_i \mathscr{E} \cdot \mathcal{L}^{-1} \left\{ \frac{\hat{\varepsilon}_p - \hat{\varepsilon}_f}{\hat{\varepsilon}_f} \int_{v_{p_i}} \hat{\mathbf{E}}_p \, d\mathbf{r} \right\} \, ,$$

which corresponds to the second term of the right-hand side of Eq. (27). Thus we have shown that Eqs. (28) and (27) are identical.

The second and third terms of Eq. (27) represent the energy of the particles at the fixed value of the external charge generating the electric field. For a nonconducting systems we note that $I_2 = 0$, $\hat{\varepsilon}_p = \varepsilon_p$, and $\varepsilon_f = \hat{\varepsilon}_f$, and hence Eq. (27) reduces to the macroscopic relationship for the electric energy of a nonconducting system [25]

$$2w = \langle \mathbf{D} \rangle_e \cdot \langle \mathbf{E} \rangle_e = \varepsilon_s(c) \langle \mathbf{E} \rangle_e^2 \, ,$$

where $\varepsilon_s(c)$ is the permittivity of the suspension.

2. First and second approximations

To derive the expression for the energy of one particle in a suspension, we need to calculate two integrals in Eq. (27), i.e., $\langle \langle \hat{\mathbf{E}}_p \rangle_e \rangle$ and $\langle I_2 \rangle_e$. To obtain the first and second approximations for them, we use the group expansion method developed in Ref. [29] and also described in Ref. [30].

Specifically, for $k + 1$ particles in an electric field $\hat{\mathscr{E}}_{k+1}$, let us write $U\{\mathbf{r}_1, \ldots, \mathbf{r}_k; \hat{\mathscr{E}}_{k+1}\}$ as the general notation for these integrals over the surface of the test particle placed at the origin $\mathbf{r}_1, \ldots, \mathbf{r}_k$ being the set of position vectors of the other particles. To a first approximation, $(k = 0, \hat{\mathscr{E}}_1 = \langle \hat{\mathbf{E}} \rangle_e)$, and hence using the value of $U\{\cdot; \langle \hat{\mathbf{E}} \rangle_e\}$ for a single particle yields the same expres-

sion for the energy as derived from either the cell model when $c \rightarrow 0$ or from the energy equation for a single particle in an unbounded medium

$$N v_p \left[\frac{3\varepsilon_f}{2} \frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} \langle \mathbf{E} \rangle_e^2 + \frac{9(\sigma_p \varepsilon_f - \sigma_f \varepsilon_p)^2}{2(\varepsilon_p + 2\varepsilon_f)^3} \mathbf{J}^2 \right] \, ,$$

where

$$\mathbf{J} = \int_0^t \exp \left[-\frac{t - t'}{t_p} \right] \langle \mathbf{E}(t') \rangle_e \, dt' \, .$$

To construct the second approximation ($k = 1$), we place the test particle at the origin and a second particle at $\mathbf{r}_1$. Note that to order $O(c)$, we can neglect the difference between $\hat{\mathscr{E}}_2$ and $\langle \hat{\mathbf{E}} \rangle_e$, hence the average increment $\langle \Delta U' \rangle$ due to the presence of the second particle is

$$\langle \Delta U' \rangle = \int (U\{\mathbf{r}_1; \langle \hat{\mathbf{E}} \rangle_e\} - U\{\cdot; \langle \hat{\mathbf{E}} \rangle_e\}) P\{\mathbf{r}_1 | 0\} d\mathbf{r}_1 \, ,$$

where $P\{\mathbf{r}_1 | 0\}$ is the conditional probability density for a second particle being at $\mathbf{r}_1$ given that the test particle is at the origin. The expressions for $U\{\mathbf{r}_1; \langle \hat{\mathbf{E}} \rangle_e\}$ are given by the corresponding terms in the solution of the two-particle problem in an unbounded medium.

We also have to take into account that the average electric field acting on the test particle, $\hat{\mathscr{E}}_1$, is different from $\langle \hat{\mathbf{E}} \rangle_e$ because one particle is removed from a suspension. To calculate this field to order $O(c)$, the average field induced by one particle needs to be subtracted from $\langle \hat{\mathbf{E}} \rangle_e$. Hence we get

$$\hat{\mathscr{E}}_1 = \langle \hat{\mathbf{E}} \rangle_e - \int (\hat{\mathscr{E}}_a\{\mathbf{r}_1; \langle \hat{\mathbf{E}} \rangle_e\} - \langle \hat{\mathbf{E}} \rangle_e) P\{\mathbf{r}_1\} d\mathbf{r}_1 \, .$$

Here $\hat{\mathscr{E}}_a\{\mathbf{r}_1; \langle \hat{\mathbf{E}} \rangle_e\}$ is the electric field in an unbounded medium induced by the particle located at $\mathbf{r}_1$, while $P\{\mathbf{r}_1\}$ is the unconditional probability density for a particle being at $\mathbf{r}_1$. The expression for the electric field induced by one particle yields

$$\hat{\mathscr{E}}_a\{\mathbf{r}_1|\langle\hat{\mathbf{E}}\rangle_e\}-\langle\hat{\mathbf{E}}\rangle_e=\begin{cases}-\hat{\beta}\langle\hat{\mathbf{E}}\rangle_e & \text{for } |\mathbf{r}|_1\le a \\ -\dfrac{a^3}{|\mathbf{r}_1|^3}\hat{\beta}\left[\langle\hat{\mathbf{E}}\rangle_e-\dfrac{3\langle\hat{\mathbf{E}}\rangle_e\cdot\mathbf{r}_1}{|\mathbf{r}_1|^2}\mathbf{r}_1\right] & \text{for } |\mathbf{r}|_1>a\ .\end{cases}$$

The average increment $\langle\Delta U''\rangle$ merely corresponds to a change in the expressions for I_1 and I_2 in Eq. (8) for the energy of a single particle due to a change in the electric field acting on it:

$$\langle\Delta U''\rangle=[U\{\cdot;\hat{\mathscr{E}}_1\}-U\{\cdot;\langle\hat{\mathbf{E}}\rangle_e\}]\ .$$

For the first and second integrals in Eq. (27), respectively, we obtain

$$U\{\cdot;\hat{\mathscr{E}}_1\}-U\{\cdot;\langle\hat{\mathbf{E}}\rangle_e\}=3\hat{\beta}(\hat{\mathscr{E}}_1-\langle\hat{\mathbf{E}}\rangle_e)\ ,$$

$$\begin{aligned}U\{\cdot;\hat{\mathscr{E}}_1\}-U\{\cdot;\langle\hat{\mathbf{E}}\rangle_e\}=v_p\Big[&\mathscr{L}^{-1}\{[(\varepsilon_p+2\varepsilon_f)\hat{\beta}-(\varepsilon_p-\varepsilon_f)]\langle\hat{\mathbf{E}}\rangle_e\}\cdot\mathscr{L}^{-1}\{(\hat{\beta}-1)(\hat{\mathscr{E}}_1-\langle\hat{\mathbf{E}}\rangle_e)\}\\ &+\mathscr{L}^{-1}\{(\hat{\beta}-1)\langle\hat{\mathbf{E}}\rangle_e\}\cdot\mathscr{L}^{-1}\{[(\varepsilon_p+2\varepsilon_f)\hat{\beta}-(\varepsilon_p-\varepsilon_f)](\hat{\mathscr{E}}_1-\langle\hat{\mathbf{E}}\rangle_e)\}\Big]\ .\end{aligned} \tag{29}$$

As the result, the $O(c^2)$ term of the group expansion is $\langle\Delta U\rangle=\langle\Delta U'\rangle+\langle\Delta U''\rangle$.

In performing the evaluation of the integrals which appear in the expressions for $\langle\Delta U\rangle$, we shall consider only the case of a well-mixed suspension for which

$$P\{\mathbf{r}_1\}=n,\quad P\{\mathbf{r}_1|0\}=\begin{cases}0 & \text{for } |\mathbf{r}_1|\le 2a \\ n & \text{for } |\mathbf{r}_1|>2a\ ,\end{cases}$$

where n is the number density of the particles. The region of integration for these integrals consists of three parts: $|\mathbf{r}_1|\le a$, $a<|\mathbf{r}_1|\le 2a$, and $|\mathbf{r}_1|>2a$. The first and second parts do not contribute to the average increment $\langle\Delta U'\rangle$, which is caused by the presence of the second particle. Moreover, since

$$\int_{4\pi}\frac{a^3}{|\mathbf{r}_1|^3}\hat{\beta}\left[\langle\hat{\mathbf{E}}\rangle_e-\frac{3\langle\hat{\mathbf{E}}\rangle_e\cdot\mathbf{r}_1}{|\mathbf{r}_1|^2}\mathbf{r}_1\right]d\mathbf{r}_1=0$$

$$\text{for } a\le|\mathbf{r}_1|\le 2a\ ,$$

the contribution to $\langle\Delta U''\rangle$ from the second part is also nil. On the other hand, the contribution to $\langle\Delta U''\rangle$ from the region $|\mathbf{r}_1|\le a$ can be obtained simply by replacing $\hat{\mathscr{E}}_1-\langle\hat{\mathbf{E}}\rangle_e$ in Eq. (29) with $c\hat{\beta}\langle\hat{\mathbf{E}}\rangle_e$, which is the change

in the average electric field acting on the test particle in the region $|\mathbf{r}_1|\le a$ because one particle has been removed from the suspension.

For the region $|\mathbf{r}_1|\ge 2a$, the contribution to the first and second integrals in Eq. (27) stems from both $\langle\Delta U'\rangle$ and $\langle\Delta U''\rangle$. The expressions for $\langle\Delta U'\rangle$ as expansions in powers of $(a/|\mathbf{r}_1|)$ are given by the corresponding terms in Eq. (17) for the energy of two particles in an unbounded medium. The expressions for $\langle\Delta U''\rangle$ are derived by making the substitution

$$\hat{\mathscr{E}}_1-\langle\hat{\mathbf{E}}\rangle_e=\frac{a^3}{|\mathbf{r}_1|^3}\hat{\beta}\left[\langle\hat{\mathbf{E}}\rangle_e-\frac{3\langle\hat{\mathbf{E}}\rangle_e\cdot\mathbf{r}_1}{|\mathbf{r}_1|^2}\mathbf{r}_1\right]$$

into Eq. (29). For the region $|\mathbf{r}_1|\ge 2a$, it turns out that the integrands for both $\langle\Delta U'\rangle$ and $\langle\Delta U''\rangle$ contain terms proportional to $(a/|\mathbf{r}_1|)^3$, which cancel each other when combined. This procedure has been justified in Ref. [30]. This leads to an absolutely convergent integral for $|\mathbf{r}_1|\ge 2a$.

Finally, on performing the integration, we arrive at the equation for the $O(c^2)$ term of the electric energy of a suspension at the fixed value of the external charge, generating the electric field

$$\begin{aligned}3c^2\Bigg[&\varepsilon_f\langle\mathbf{E}\rangle_e\cdot\mathscr{L}^{-1}\{\hat{\beta}^2\langle\hat{\mathbf{E}}\rangle_e\}+3\bigg[\mathscr{L}^{-1}\left\{\frac{\varepsilon_p\hat{\varepsilon}_f-\varepsilon_f\hat{\varepsilon}_p}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}\langle\hat{\mathbf{E}}\rangle_e\right\}\cdot\mathscr{L}^{-1}\left\{\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}\hat{\beta}\langle\hat{\mathbf{E}}\rangle_e\right\}\\ &+\mathscr{L}^{-1}\left\{\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}\langle\hat{\mathbf{E}}\rangle_e\right\}\cdot\mathscr{L}^{-1}\left\{\frac{\varepsilon_p\hat{\varepsilon}_f-\varepsilon_f\hat{\varepsilon}_p}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}\hat{\beta}\langle\hat{\mathbf{E}}\rangle_e\right\}\bigg]\Bigg]\\ +\sum_{s=t}^{\infty}&\frac{1}{2^{s-1}(s-1)}\Bigg[\varepsilon_f\langle\mathbf{E}\rangle_e\cdot\mathscr{L}^{-1}\{(\hat{\zeta}_{01,s}-2\hat{\zeta}_{11,s})\hat{\beta}\langle\hat{\mathbf{E}}\rangle_e\}\\ &+3\bigg[\mathscr{L}^{-1}\left\{\frac{\varepsilon_p\hat{\varepsilon}_f-\varepsilon_f\hat{\varepsilon}_p}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}\langle\hat{\mathbf{E}}\rangle_e\right\}\cdot\mathscr{L}^{-1}\left\{\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}(\hat{\zeta}_{01,s}-2\hat{\zeta}_{11,s})\langle\hat{\mathbf{E}}\rangle_e\right\}\\ &+\mathscr{L}^{-1}\left\{\frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}\langle\hat{\mathbf{E}}\rangle_e\right\}\cdot\mathscr{L}^{-1}\left\{\frac{\varepsilon_p\hat{\varepsilon}_f-\varepsilon_f\hat{\varepsilon}_p}{\hat{\varepsilon}_p+2\hat{\varepsilon}_f}(\hat{\zeta}_{01,s}-2\hat{\zeta}_{11,s})\langle\hat{\mathbf{E}}\rangle_e\right\}\bigg]\Bigg]\end{aligned}$$

$$+ \sum_{s=6}^{\infty} \frac{1}{2^{s-3}(s-3)} \sum_{\substack{n,k,k' \geq 1}}^{s=2(n+1)+k+k'} \frac{2n+1}{n} \left[\mathcal{L}^{-1} \left\{ \frac{\hat{\varepsilon}_f}{\hat{\varepsilon}_p + 2\hat{\varepsilon}_f} \hat{\zeta}_{0n,k'} \langle \hat{E} \rangle_e \right\} \cdot \mathcal{L}^{-1} \left\{ \frac{\varepsilon_p \hat{\varepsilon}_f - \varepsilon_f \hat{\varepsilon}_p}{\hat{\varepsilon}_p + 2\hat{\varepsilon}_f} \hat{\zeta}_{0n,k} \langle \hat{E} \rangle_e \right\} \right.$$

$$+ (n+1)n \mathcal{L}^{-1} \left\{ \frac{\varepsilon_f}{\hat{\varepsilon}_p + 2\hat{\varepsilon}_f} \hat{\zeta}_{1n,k'} \langle \hat{E} \rangle_e \right\}$$

$$\left. \times \mathcal{L}^{-1} \left\{ \frac{\varepsilon_p \hat{\varepsilon}_f - \varepsilon_f \hat{\varepsilon}_p}{\hat{\varepsilon}_p + 2\hat{\varepsilon}_f} \hat{\zeta}_{1n,k} \langle \hat{E} \rangle_e \right\} \right] . \qquad (30)$$

Here $\hat{\zeta}_{mn,s} = \hat{A}_{mn,s} / \hat{\beta}_1 \hat{\varepsilon}_m$, where the coefficients $\hat{A}_{mn,s}$ are calculated from Eq. (15), which was obtained from the solution of the two-particle problem.

The $O(c^2)$ term represents the average value of the interaction energy between two particles. The sum of the first two terms in Eq. (30) equals the coefficient of $4\pi a^3 (a/R)^3$ in Eq. (18), which gives the energy of the dipole-dipole interaction $W^{d\text{-}d}$ between two particles. Also, this sum coincides with the corresponding $O(c^2)$ term of the expression for the electric energy as derived from the cell model and expanded in powers of $c(\varepsilon_p - \varepsilon_f)/(\varepsilon_p + 2\varepsilon_f)$ and $c(\sigma_p - \sigma_f)/(\sigma_p + 2\sigma_f)$.

For a suddenly applied electric field, $\langle E \rangle_e = E_0 H(t)$, and for $t \ll t_p$ ($p \to \infty$, respectively), we obtain the same relation as that for a nonconducting system when $\hat{\varepsilon}_p = \varepsilon_p$, $\hat{\varepsilon}_f = \varepsilon_f$, and thus $\varepsilon_p \hat{\varepsilon}_f - \varepsilon_f \hat{\varepsilon}_p = 0$:

$$3c^2 \varepsilon_f E_0^2 \left[\frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} \right]^2 F_1 \ ,$$

$$F_1 = 1 + \frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} f_1 \left[\frac{\varepsilon_p}{\varepsilon_f} \right] \ , \qquad (31)$$

where

$$\left[\frac{\alpha-1}{\alpha+2} \right]^2 f_1(\alpha)$$

$$= \sum_{s=4}^{\infty} \frac{1}{2^{s-1}(s-1)} (\zeta_{01,s} - 2\zeta_{11,s}), \quad \alpha = \frac{\varepsilon_p}{\varepsilon_f} \ .$$

Equation (31) gives the $O(c^2)$ term in the expression for the effective dielectric constant of a suspension, and is identical to that derived in Ref. [28].

For $t \gg t_p$ ($p \to 0$, respectively), we have

$$3c^2 \varepsilon_f E_0^2 \frac{(\sigma_p - \sigma_f)\sigma_f^2}{(\sigma_p + 2\sigma_f)^3} F_1 F_2$$

$$\times \left\{ 6 \frac{\varepsilon_p}{\varepsilon_f} - \frac{1}{F_2} \left[2 + (6F_2 - 1) \frac{\sigma_p}{\sigma_f} - \left[\frac{\sigma_p}{\sigma_f} \right]^2 \right] \right\} , \qquad (32)$$

where

$$F_1 = 1 + \frac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f} f_1 \left[\frac{\sigma_p}{\sigma_f} \right], \quad F_2 = 1 + \frac{1}{6} \left[\frac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f} \right] \frac{f_2(\sigma_p/\sigma_f)}{F_1} \ ,$$

$$\left[\frac{\alpha-1}{\alpha+2} \right]^2 f_2(\alpha) = \sum_{s=6}^{\infty} \frac{1}{2^{s-3}(s-3)} \sum_{\substack{n,k,k' \geq 1}}^{s=2(n+1)+k+k'} \frac{2n+1}{n} [\zeta_{0n,k'}\zeta_{0n,k} + n(n+1)\zeta_{1n,k'}\zeta_{1n,k}], \quad \alpha = \frac{\sigma_p}{\sigma_f} \ .$$

The difference between Eqs. (31) and (32), respectively, for $t \ll t_p$ and $t \gg t_p$ as derived from the statistical theory and those given by the cell model for these cases, lies in the fact that, for the latter, $F_1 = F_2 = 1$. The values of the coefficients f_1, f_2, F_1, and F_2 for various α [and the corresponding value of $\beta = (\alpha-1)/(\alpha+2)$] are presented in Table I. The numerical values given in Table I required the summation of over 100 terms in order to achieve an accuracy to three significant figures. The reasoning why all the functions shown in Table I are relatively insensitive to variations in α can be traced to the asymptotic behavior of $\hat{A}_{mn,k}$ for $k \gg 1$, and stems from the fact that the terms of the series for f_1 and f_2 contain the coefficients $\hat{\zeta}_{mn,k}$, which depend only weakly on α when $k \gg 1$. Specifically,

$$\frac{\hat{\zeta}_{mn,k}}{\hat{\beta}_1^2} \sim \frac{(-1)^m \hat{\beta}_n \hat{\beta}_l l^{n+1}}{\hat{\beta}_1^2 (n+m)!(1-m)!} \quad \text{for } k = 2l, \ l \gg 1 \ ,$$

and

$$\frac{\hat{\zeta}_{mn,k}}{\hat{\beta}_1^2} \sim \frac{2\hat{\beta}_n \hat{\beta}_l l^{n+1}}{\hat{\beta}_1 (n+m)![(1-m)!]^2 (1+m)!}$$

$$\text{for } k = 2l+1, \ l \gg 1 \ .$$

TABLE I. Values of f_1, f_2, F_1, and F_2 for various α.

α	β	f_1	f_2	F_1	F_2
0	-0.500	0.432	1.398	0.784	0.851
0.02	-0.485	0.431	1.386	0.791	0.858
0.1	-0.429	0.428	1.348	0.817	0.882
0.5	-0.200	0.421	1.272	0.916	0.954
1.0	0.000	0.421	1.264	1.000	1.000
2.0	0.250	0.427	1.308	1.107	1.049
5.0	0.571	0.445	1.466	1.254	1.111
50.0	0.942	0.488	1.940	1.460	1.209
10^4	1.000	0.498	2.071	1.498	1.230

Moreover, for the transient period $t \sim t_p$, the cell model involves only one relaxation time of t_s, while the statistical theory equation contains a band of relaxation times, $t_{pn} = [\varepsilon_p + ((n+1)/n)\varepsilon_f]/[\sigma_p + ((n+1)/n)\sigma_f]$, $n = 1, 2, \ldots$, of multipoles. However, as seen from Table I, the overall contribution of the multipolar terms is only about 50%, since the values of F_1 and F_2 do not differ that much from unity.

The results obtained thus far indicate that the main contribution to the electric energy of a suspension is given by multiparticle interactions leading to a change in the average electric field acting on a particle. The contribution of the direct two-particle interactions is not so essential. An analogous behavior of interparticle interactions in a suspension has been described in Refs. [42] and [28]. That is the reason why the cell model, which takes into account only multiparticle interactions, can yield an expression for the electric energy of a suspension which is of acceptable accuracy.

The main advantage of the statistical theory which has been developed lies in fact that it reveals the connection between the coefficient of the term $4\pi a^3 (a/R)^3$ in the expression for W^{d-d} given by Eq. (18), which determines the dependence of the dipole-dipole interparticle interactions on the electric field, and the macroscopic electric energy of a suspension. Moreover, the microstructural theory shows the dependence of the macroscopic electric energy of a suspension and therefore of its thermodynamic properties, on the ratio of the particle-to-fluid dielectric permittivity and conductivity. Also, it provides a connection between the real and imaginary parts of the complex permittivity of a suspension and its thermodynamic properties which, for example, determines the conditions for aggregation. In Sec. V, we shall use these relations to assess the degree to which the present theory is consistent with the currently available experimental data on ER fluids.

V. DISCUSSION AND COMPARISON WITH EXPERIMENTAL DATA

The theory developed above predicts that the application of an electric field of sufficient strength induces a separation of a suspension into low- and high-concentration phases when $\Lambda(t) \geq \Lambda_{cr}$ (Fig. 2), where Λ is the ratio of the average energy of the electric interaction between two particles and the thermal energy. The average energy of the interparticle interaction is equal to the $O(c^2)$ term in the expansion of the electric energy of a suspension in powers of the particle concentration, c [Eq. (5)], and its dependence on the time-varying electric field is given by Eq. (30). The main contribution to the value of this energy arises from the dipole-dipole interaction W^{d-d}, between two particles [Eq. (18)]. The expression for the electric energy of a suspension, Eq. (22), as obtained from the cell model, yields the leading dipole-dipole term in Eq. (30), and allows us to estimate the coefficient γ of the $O(c^3)$ term of Eq. (5) which represents the ratio of the average energy of the three-particle interaction to the thermal energy. Figures 1 and 2 show that the contribution of the three-particle interac-

tion is of minor importance when $|\gamma/\Lambda| < 3$.

To analyze the dependence of the aggregation phenomena on the particle-to-fluid ratio of the dielectric constants and of the conductances, we consider first the case when an electric field is suddenly applied, i.e., $E(t) = E_0 H(t)$. Then, on account of the presence of dielectric relaxation phenomena leading to the redistribution of the charge at the interface between the particle and the surrounding fluid, the thermodynamic driving force which causes the aggregation of the particles becomes time dependent. Specifically, when $t \ll t_p$, where $t_p = (\varepsilon_p + 2\varepsilon_f)/(\sigma_p + 2\sigma_f)$ is the characteristic time scale of dielectric relaxation, the interaction between conducting particles [Eq. (19)] is the same as that between nonconducting particles. In this case, the statistical theory yields Eq. (31) for the suspension energy, and the random arrangement of the particles becomes unstable if

$$\Lambda_\infty = \frac{3v_p \varepsilon_f E_0^2}{k_B T} \Psi_\infty \geq \Lambda_{cr}, \quad \Psi_\infty = \left[\frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} \right]^2 F_1, \quad (33)$$

where the superscript ∞ denotes the high-frequency (short time) limit. On the other hand, when $t \gg t_p$, the interaction between conducting particles [Eq. (20)] differs from that between nonconducting particles. In this case, the statistical theory yields Eq. (32) for the suspension energy, and leads to the prediction that aggregation will occur if

$$\Lambda_0 = \frac{2v_p \varepsilon_f E_0^2}{k_B T} \Psi_0 \geq \Lambda_{cr},$$

$$\Psi_0 = \frac{(\sigma_p - \sigma_f)\sigma_f^2}{(\sigma_p + 2\sigma_f)^3} F_1 F_2 \left\{ 6\frac{\varepsilon_p}{\varepsilon_f} - \frac{1}{F_2} \left[2 + (6F_2 - 1)\frac{\sigma_p}{\sigma_f} \right. \right.$$

$$\left. \left. - \left[\frac{\sigma_p}{\sigma_f} \right]^2 \right] \right\}. \quad (34)$$

where the superscript 0 denotes the low-frequency (long time) limit.

The coefficients $F_1(\alpha)$ and $F_2(\alpha)$ where $\alpha = \varepsilon_p/\varepsilon_f$ for
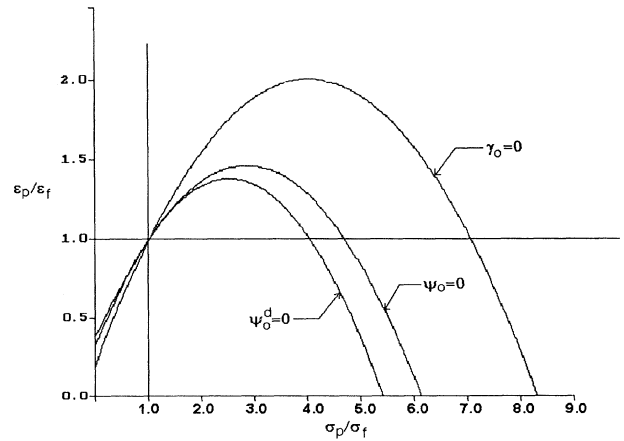

FIG. 3. The lines $\Psi_0^d = 0$, $\Psi_0 = 0$, and $\gamma_0 = 0$ in the $\varepsilon_p/\varepsilon_f$ and σ_p/σ_f plane. The expressions for Ψ_0^d [Eq. (20)] and γ_0 are obtained from the cell model [Eq. (22)], when the expression for Ψ_0 is derived from the statistical theory [Eq. (34)].

Eq. (33) and $\alpha = \sigma_p/\sigma_f$ for Eq. (34) incorporate the influence of all multipolar terms on the interaction between two particles. For the cell model expressions, $F_1 = F_2 = 1$, and, thus, $\Psi_\infty = \Psi_\infty^d$ and $\Psi_0 = \Psi_0^d$ [see Eqs. (33) and (34)]. However, since the deviation of $F_1(\alpha)$ and $F_2(\alpha)$ from unity, the latter being the value for the

dipole-dipole term, is less than 50% (Table I), the difference between the expressions for Ψ_∞ and Ψ_0 as obtained from the cell model and from the statistical theory is not of crucial importance (Fig. 3).

As seen from Eqs. (33) and (34), $\Psi_\infty > 0$ if $\varepsilon_p \neq \varepsilon_f$, whereas $\Psi_0 > 0$ only in two cases:

$$
(1) \quad \frac{\sigma_p}{\sigma_f} > 1 \quad \text{and} \quad 6\frac{\varepsilon_p}{\varepsilon_f} > \frac{1}{F_2}\left[2 + (6F_2 - 1)\frac{\sigma_p}{\sigma_f} - \left[\frac{\sigma_p}{\sigma_f}\right]^2\right],
$$

$$
(2) \quad \frac{\sigma_p}{\sigma_f} < 1 \quad \text{and} \quad 6\frac{\varepsilon_p}{\varepsilon_f} < \frac{1}{F_2}\left[2 + (6F_2 - 1)\frac{\sigma_p}{\sigma_f} - \left[\frac{\sigma_p}{\sigma_f}\right]^2\right].
$$

$$(35)$$

This means that, in the short-time limit, there always exists a threshold value of the strength of the electric field, above which the particles having $\varepsilon_p \neq \varepsilon_f$ will start aggregating as soon as the electric field has been applied. On the other hand, the redistribution of charge over the particle surface gives rise to the dependence of Ψ_0 on the particle-to-fluid ratio of the dielectric constants $\varepsilon_p/\varepsilon_f$, and conductances σ_p/σ_f. Thus, in the long time limit, the electric-field-induced aggregation of the particles will occur only if the dielectric constants and conductances of the particles and of the fluid lead to positive values for Ψ_0. The conditions for this to occur are given in Eq. (35) and Fig. 3.

The cell model also allows us to estimate the energy of the three-particle interaction. Thus on expanding Eq. (22) in powers of c, we obtain

$$
\gamma_\infty = \frac{9v_p\varepsilon_f E_0^2}{k_B T}\left[\frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f}\right]^3 \quad \text{at } t \ll t_p ,
$$

and

$$
\gamma_0 = \frac{9v_p\varepsilon_f E_0^2}{k_B T}\frac{(\sigma_p - \sigma_f)^2\sigma_f^2}{(\sigma_p + 2\sigma_f)^4}
$$

$$
\times \left[9\frac{\varepsilon_p}{\varepsilon_f} - 2 - 8\frac{\sigma_p}{\sigma_f} + \left[\frac{\sigma_p}{\sigma_f}\right]^2\right] \quad \text{at } t \gg t_p ,
$$

where the superscripts ∞ and 0 once again denote the high-frequency (short time) and low-frequency (long time) limits, respectively. It turns out that the role of the three-particle interaction is different depending on whether $t < t_p$ or $t > t_p$. Specifically, in the former case, since $|\gamma_\infty/\Lambda_\infty| = 3|(\varepsilon_p - \varepsilon_f)/(\varepsilon_p + 2\varepsilon_f)| < 3$, the contribution of the three-particle interaction energy does not radically alter the values of the aggregation process parameters Λ_{cr} and c_{cr} (Figs. 1 and 2). For $t \gg t_p$, however, the lines $\Lambda_0 = 0$ and $\gamma_0 = 0$ in the $\varepsilon_p/\varepsilon_f$ and σ_p/σ_f planes do not coincide (Fig. 3). Therefore, near the line $\Lambda_0 = 0$, the thermodynamic driving force causing the aggregation of the particles is mainly due to the three-particle interaction, a case which is not covered by our theory.

The coefficients Ψ_∞^d and Ψ_0^d determine the relative contribution of the particle properties relative to those of the

fluid, i.e., $\varepsilon_p/\varepsilon_f$ and σ_p/σ_f, to the thermodynamic driving force, leading to the aggregation governed by the dipole-dipole interaction. As seen from Eq. (19), Ψ_∞^d increases monotonically to unity with increasing $\varepsilon_p/\varepsilon_f$. On the other hand, the dependence of Ψ_0^d on $\varepsilon_p/\varepsilon_f$ and σ_p/σ_f is much more complicated. Thus, from Eq. (20), we obtain that

$$
\frac{\partial\Psi_0^d}{\partial(\varepsilon_p/\varepsilon_f)} = \frac{6(\sigma_p/\sigma_f - 1)}{(\sigma_p/\sigma_f + 2)^3} ,
$$

$$
\frac{\partial\Psi_0^d}{\partial(\sigma_p/\sigma_f)} = \frac{6(5 - 2\sigma_p/\sigma_f)}{(\sigma_p/\sigma_f + 2)^4}\left[\frac{\varepsilon_p}{\varepsilon_f} - \frac{\sigma_p}{\sigma_f}\right] .
$$

Therefore, when $\sigma_p/\sigma_f > 1$, Ψ_0^d increases linearly with $\varepsilon_p/\varepsilon_f$. But, with increasing σ_p/σ_f, Ψ_0^d grows only if (1) $\sigma_p/\sigma_f < 5/2$ and $\sigma_p/\sigma_f < \varepsilon_p/\varepsilon_f$, or (2) $5/2 < \sigma_p/\sigma_f$ and $\varepsilon_p/\varepsilon_f < \sigma_p/\sigma_f$. In addition, along the line $\varepsilon_p/\varepsilon_f = \sigma_p/\sigma_f$, we have that $\Psi_0^d = (\sigma_p/\sigma_f - 1)^2/(\sigma_p/\sigma_f + 2)^2$, while, for constant $\varepsilon_p/\varepsilon_f$, $\Psi_0^d \to 1$ for $\sigma_p/\sigma_f \to \infty$. These results show that the optimal way of increasing Ψ_0^d and, thus, the dipole-dipole interaction between the particles and the thermodynamic driving force responsible for the aggregation process, is to increase $\varepsilon_p/\varepsilon_f$ and to maintain σ_p/σ_f equal to 5/2.

We shall next compare the predictions of our theory, which is based on the relation between the energy of the dipole-dipole interaction between two particles [Eqs. (19) and (20)] and the thermodynamic driving force [Eqs. (33) and (34)], with the relevant results available in the literature. We begin by discussing the various simulation models [37,38,43,44]. The threshold value of the electric field above which polarizable nonconducting particles in a nonconducting fluid start aggregating was estimated by means of a simulation model [37,38,43] which involved particles, each having an induced dipole moment along the direction of the applied electric field. The dipole moment was assumed to be the same as that of an isolated particle, i.e., the contribution to the electric field at the center of a given particle due to all the other particles was ignored. The interparticle forces included the point-dipole interaction and a short-range repulsive force, while the influence of the fluid was represented by Brownian and Stokes drag forces. The simulations reported in Refs. [45] and [46], which include a much more complete

treatment of hydrodynamic and electrostatic forces, do not consider thermal fluctuations. The relative strength of dipolar interactions and the thermal energy was characterized by a dimensionless parameter λ which equals $\Lambda/8F_1(\beta)$ in our notation. The simulations described in Ref. [43], which were performed at a particle concentration of $c=0.31$, showed that the electric field required for phase separation was given by $\lambda_c \sim 0.48$. For $\lambda < \lambda_c$, small clusters of four or five particles were found to form and to break up, but they never grew larger. The simulations in Refs. [37] and [38] which were performed at $c=0.1$, 0.3, and 0.5, showed that $\lambda_c \sim 6.5-7$; below λ_c the suspension was found to have an amorphous structure. Another approach to the calculation of λ_c was described in Ref. [44], where the induced dipole moments were treated as internal degrees of freedom and the equilibrium two-particle distribution function, which included the direction of the dipole moments, was also calculated in a self-consistent manner within the mean-spherical approximation. This model considered the enhancement of the mean dipole moment over its value for an isolated particle, but only on account of the nonuniformity in the dipole moment angular distribution. Numerical calculations which were performed at $c=0.25$ for a few values of β showed that λ_c decreased from ~ 5 to ~ 2 with increasing β from 0.5 to 1.0; for $\beta=0.25$, a phase transition was not predicted to occur. Despite some differences in the model of a nonconducting suspension, the range of our values [$\Lambda_{cr}/8F_1(\beta)$ varies between 3.4 for $\beta=-0.5$ and 1.5 for $\beta=1$] correlates well with those reported in the papers referred to above.

Reference [47] reported the results of computer simulations of the phase behavior of soft-sphere dipolar fluids (a sphere has a permanent dipole moment) in applied field. When the applied field was sufficiently high (in comparison with the thermal energy), the dipole moments of the spheres aligned predominantly with the field. In this case, the phase behavior of the dipolar fluid was similar to that of a suspension of the polarizable particles except for the contribution of all other particles to the induced dipole moment of a given particle. The simulations at various field strengths revealed a coexistence curve [47]. The value of λ_{cr} was found to decrease from 8.9 to 5.5 (the infinite field limit) with increasing strength of the applied field, whereas the critical density ($6c_{cr}/\pi$ in our notation) was independent of the field strength and equaled ~ 0.03. Since increasing the field strength in the model of dipolar fluids enhances the alignment of the dipole moments of the spheres, these results correspond to our calculations in the sense that λ_{cr} decreases with increasing β, whereas c_{cr} is independent of β and of the strength of the electric field. However, the value of the critical density (~ 0.25) from our model is different from that of the model of dipolar fluids. This difference might result from the fact that we considered only the case for which the suspension separated into two disordered phases. On the other hand, simulations [47] showed that the coexisting phases contained chains of spheres.

The relation between the energy of the two-particle dipole-dipole interaction and the thermodynamic driving force also provides some insight into the kinetics of the aggregation process. Let t_a be a characteristic time scale for structure formation. The behavior of the suspension depends on the ratio of t_a to t_p, the dielectric relaxation time. The time scale t_a can be estimated by considering the time taken for a particle to move a characteristic distance between the particles, $\sim a(1/c^{1/3}-1)$, under the action of the dipole-dipole attraction and the Stokes drag force. To estimate t_a for the relatively rapid aggregation when $t_a \ll t_p$, in which case there is no contribution of the conductivity effects to the interparticle interaction [Eq. (19)], we can use the expression [48,39] for the time of the structure formation in a suspension of nonconducting particles in a nonconducting fluid, which is applicable for rather high electric fields when Brownian motion can be neglected, $\Lambda \gg \Lambda_{cr}$. In our notation, this is written as

$$t_a^\infty \approx \frac{\eta_f}{\varepsilon_f \Psi_\infty^c \mathbf{E}_0^2}\xi(c), \quad \xi(c) \approx 4\left[\left[\frac{\pi}{6c}\right]^{5/3}-1\right], \quad (36)$$

where t_a^∞ is the time scale of the rapid aggregation, η_f is the viscosity of the base fluid, and $\xi(c)$ is a concentration dependent coefficient. Computer simulations reported in Ref. [39] have shown that the first percolating chain appears at roughly t_a^∞. On the other hand, for relatively slow aggregation $t_a \gg t_p$, the dipole-dipole interaction between conducting particles is described by Eq. (20). Since this leads only to a change in the relative strength of the interparticle forces in the mechanical model which describes the particle motion, the time scale for the slow structure formation can be represented by an expression similar to Eq. (36),

$$t_a^0 \approx \frac{\eta_f}{\varepsilon_f \Psi_0^d \mathbf{E}_0^2}\xi(c) , \quad (37)$$

where t_a^0 is the time scale of the slow aggregation. Equations (36) and (37) show that the mode of the structure formation kinetics depends on the strength of the electric field. Specifically, the slow aggregation will occur at a relatively weak electric field

$$E_0 \ll E_0^s \quad \text{where} \quad E_0^s = \left[\frac{\eta_f \xi(c)}{\varepsilon_f \Psi_0^d t_p}\right]^{1/2} , \quad (38)$$

while rapid aggregation will occur at a relatively strong electric field

$$E_0 \gg E_0^r \quad \text{where} \quad E_0^r = \left[\frac{\eta_f \xi(c)}{\varepsilon_f \Psi_\infty^d t_p}\right]^{1/2} . \quad (39)$$

As seen from Eqs. (38) and (39), there exists an upper bound for the thermodynamic parameter Λ_0 responsible for the slow aggregation

$$\Lambda_0 \ll \Lambda_0^s = \frac{3v_p \eta_f \xi(c)}{k_B T t_p} , \quad (40)$$

as well as a lower bound for the thermodynamic parameter Λ_∞ responsible for the rapid aggregation

$$\Lambda_\infty \gg \Lambda_\infty^r = \frac{3v_p \eta_f \xi(c)}{k_B T t_p} . \quad (41)$$

It should be noted that increasing Ψ_0^d and, hence, the interparticle interaction by raising $\varepsilon_p/\varepsilon_f$, while keeping σ_p and σ_f fixed, is also accompanied by an increase in the dielectric relaxation time. As seen from Eqs. (38) and (40), this lowers the range of electric fields where this mode of structure formation can occur. The interesting case when the random arrangement of the particles becomes unstable in the short time limit and the electric-field-induced aggregation can start [i.e., Eqs. (33), (39), and (41) are satisfied], but where this random arrangement retains its stability in the long time limit [i.e., Eq. (34) is not satisfied] is beyond the scope of this analysis.

Simple reasoning based on the pondermotive behavior of uncharged particles in electric fields provides some insight into how the type of aggregation pattern depends on the properties of the particles. Recall that, for short times, the particle dipole moment is aligned with the applied electric field when $\varepsilon_p > \varepsilon_f$, and is opposed to it when $\varepsilon_p < \varepsilon_f$. Thus an anisotropic cluster formed by a few particles tends to rotate so as to render the longest axis perpendicular to the electric field, when $\varepsilon_p < \varepsilon_f$, and parallel to it, when $\varepsilon_p > \varepsilon_f$. Moreover, for the rapid aggregation, the rotational time for the orientation of a cluster is estimated to be $t_r^\infty \sim \eta_f/\varepsilon_f \Psi_\infty^d E_0^2$ by equating the hydrodynamic torque on an ellipsoid to the electric torque exerted on a nonconducting ellipsoid in a nonconducting fluid [49]. On the other hand, for $t \gg t_p$, the dipole moment of a conducting ellipsoid in a conducting fluid is obtained by substituting σ_p/σ_f for $\varepsilon_p/\varepsilon_f$ in the expression for the nonconducting case [26]. Therefore, an anisotropic cluster formed during the slow aggregation tends to rotate so as to render the longest axis perpendicular to the electric field when $\sigma_p < \sigma_f$, and parallel to it when $\sigma_p > \sigma_f$. Consequently, for slow aggregation, the rotational time for the orientation of a cluster is estimated at

$$t_r^0 \sim \frac{\eta_f(\sigma_p + 2\sigma_f)^2}{\varepsilon_f(\sigma_p - \sigma_f)^2 E_0^2} \ .$$

The nonuniformity of the electric field around an anisotropic cluster also contributes to the aggregation pattern formation due to the force exerted on a polarized particle by a nonuniform electric field. This has been called the dielectrophoretic force [50]. In the short-time limit, this force is the same as that for a nonconducting particle ([25], Sec. III B 2):

$$\mathbf{F} = 4\pi\varepsilon_f a^3 \left| \frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} \right| (\mathbf{E} \cdot \nabla)\mathbf{E} \ .$$

Therefore, the particle is attracted toward the high electric field regions when $\varepsilon_p > \varepsilon_f$, and is repelled from the high electric field regions when $\varepsilon_p < \varepsilon_f$. For a cluster consisting of a few particles, the characteristic scale of the spatial variation of the electric field around it is

$$|\nabla \mathbf{E}| \sim \left| \frac{\varepsilon_p - \varepsilon_f}{\varepsilon_p + 2\varepsilon_f} \right| \frac{E_0}{a} \ .$$

Due to the dielectrophoretic force, a particle, when added to a cluster, moves toward its narrower part if $\varepsilon_p > \varepsilon_f$,

and toward its wider part if $\varepsilon_p < \varepsilon_f$. The particle velocity along the cluster is determined by a balance between the dielectrophoretic force and the Stokes drag force, and hence the time required for a particle to move a characteristic distance $\sim a$ is estimated at $t_d^\infty \sim \eta_f/\varepsilon_f \Psi_\infty^d E_0^2$. In the long-time limit, the dielectrophoretic force is (Sec. III B 2)

$$\mathbf{F} = 4\pi\varepsilon_f a^3 \left| \frac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f} \right| (\mathbf{E} \cdot \nabla)\mathbf{E} \ ,$$

so that the particle is attracted toward the high electric field regions when $\sigma_p > \sigma_f$, and is repelled from the high electric field regions when $\sigma_p < \sigma_f$. Thus a particle added to a cluster moves toward its narrower part if $\sigma_p > \sigma_f$, and toward its wider part if $\sigma_p < \sigma_f$. On equating the dielectrophoretic force to the Stokes drag force, we then estimate that the time required for a particle to move along the cluster over a characteristic distance $\sim a$ is

$$t_f^0 \sim \frac{\eta_f(\sigma_p + 2\sigma_f)^2}{\varepsilon_f(\sigma_p - \sigma_f)^2 E_0^2} \ .$$

In the short- and long-time limits, the time scales of the rotational and dielectrophoretic mechanisms responsible for the orientation and shape of a cluster are of the same magnitude as the time scale of the rapid and slow aggregations, respectively. Therefore, three processes— i.e., aggregation of the particles, rotational alignment of the clusters already created, and the generation of a nonuniformity in the distribution of particles added to a cluster—proceed simultaneously. As a result, for rapid aggregation at $\varepsilon_p > \varepsilon_f$ and slow aggregation at $\sigma_p > \sigma_f$, there is a tendency for these combined effects to lead to chainlike formations which are observed in ER fluids. On the other hand, for rapid aggregation at $\varepsilon_p < \varepsilon_f$ and slow aggregation at $\sigma_p < \sigma_f$, disklike formations are predicted.

For the oscillating field $\mathbf{E}(t) = \mathbf{E}_0 \sin \omega t$, the behavior of the suspension depends on the relative magnitudes of the three time scales, i.e., t_p, t_a, and $2\pi/\omega$. In the limit of high electric fields and high frequencies, when t_p is much larger than both t_a and $2\pi/\omega$, the conductivity effects do not contribute to the rapid aggregation. In this case, the interparticle interactions are determined by the instantaneous value of $\mathbf{E}(t)^2$ for $2\pi/\omega \gg t_a$ [Eq. (19)], and by the time average value $\langle \mathbf{E}(t)^2 \rangle_T$ for $t_a \gg 2\pi/\omega$ [Eq. (21)]. On the other hand, for very low frequencies, when $2\pi/\omega$ is much larger than both t_a and t_p, the dielectric relaxation and the aggregation processes are faster than the variation of the electric field. Hence the interparticle interaction corresponds to that for the long-time limit [Eq. (20)], and the slow aggregation begins (if $\Psi_0^d > 0$) as soon as the electric field reaches the threshold value [i.e., as soon as Eq. (34) is satisfied].

The case of the relatively low electric fields and intermediate frequencies, when t_a is much larger than both t_p and $2\pi/\omega$, shows a greater variety in the aggregation mode. Under these circumstances, the interparticle forces are determined by the time-averaged value of the dipole-dipole interaction, $\langle W^{d\text{-}d} \rangle_T$ [Eq. (21)], where the

coefficient Ψ_ω^d determines the relative contribution of the particle properties relative to those of the base fluid, $\varepsilon_p/\varepsilon_f$ and σ_p/σ_f, to the thermodynamic driving force causing the aggregation. The possible forms of the dependence of Ψ_ω^d on frequency are depicted in Fig. 4. Since $\Psi_\omega^d \rightarrow \Psi_\infty^d > 0$ when $\omega t_p \rightarrow \infty$, there always exists a threshold value of the strength and frequency of the oscillating electric field, above which the particles having $\varepsilon_p \neq \varepsilon_f$ start aggregating regardless of the ratio σ_p/σ_f (see Figs. 3 and 4). In fact Ψ_ω^d decreases monotonically with increasing frequency (Fig. 4) only if

$$\frac{\varepsilon_p}{\varepsilon_f} > \frac{5}{2} \quad \text{and} \quad \frac{\sigma_p}{\sigma_f} > \frac{8\varepsilon_p + 10\varepsilon_f}{2\varepsilon_p + 7\varepsilon_f} \;.$$

In contrast, when

$$\frac{\varepsilon_p}{\varepsilon_f} < \frac{5}{2} \quad \text{and} \quad \frac{\sigma_p}{\sigma_f} > \frac{2\varepsilon_p + 10\varepsilon_f}{2\varepsilon_p + \varepsilon_f} \;,$$

Ψ_ω^d attains a minimum (Fig. 4) at the intermediate frequency

$$\omega^2 t_p^2 = \frac{\sigma_p(2\varepsilon_p + 7\varepsilon_f) - \sigma_f(8\varepsilon_p + 10\varepsilon_f)}{(\sigma_p + 2\sigma_f)(5\varepsilon_f - 2\varepsilon_p)} \;.$$

Note that, for this case, the high-frequency limit Ψ_∞^d is also less than the low-frequency limit Ψ_0^d (Fig. 4).

As was already mentioned in Sec. I, besides examining the case when the behavior of the particles and the suspending fluid is described by a very simple model of a leaky dielectric, the theory developed above offers a clearer insight into the effects of the conductivity on the electric-field-induced aggregation in suspensions. Specifically the theory shows that, in dc electric fields, the particles aggregate only if the ratio of the particle-to-fluid dielectric constants and conductances satisfy Eq. (35), whereas the electrostatic model predicts that aggregation should occur in all suspensions of polarizable particles having $\varepsilon_p \neq \varepsilon_f$. In particular, the theory explains why dry particles having high dielectric constants $(\varepsilon_p > \varepsilon_f)$ do not aggregate, but that these particles start aggregating if they adsorb a small amount of water [9]. The reason is that the dry particles have a low conductivity $(\sigma_p < \sigma_f)$ and thus $\Psi_0 < 0$, while the addition of water renders the
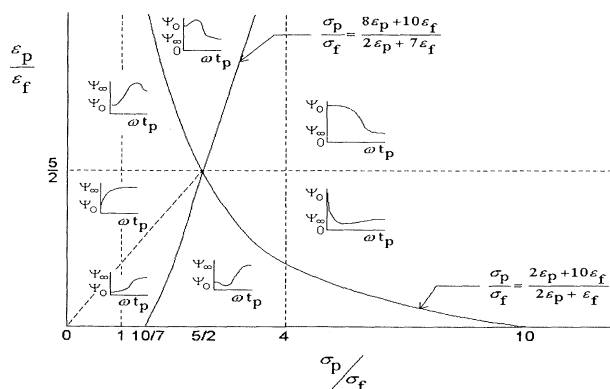
particle conductivity higher than that of the base fluid $(\sigma_p > \sigma_f)$ and, therefore, Ψ_0 becomes positive. Experimental data on corn starch/corn oil suspensions [51] provide support for this view. First of all, the authors of Ref. [51] found that the addition of humidified corn starch did not change the dielectric constant and conductivity of the oil. On the other hand, the increase in the dielectric constant of the suspension with the particle concentration and with their average water content, which was observed in Ref. [51], signifies that the dielectric constant of the dried corn starch particles is higher than that of the oil and that it increases with the addition of water. The dependence of the current density of the suspension on the particle concentration, the average water content of the particles, and the dc electric field strength reported in Ref. [51] shows that, for a water content less than 3% by weight, corn starch particles have a conductivity less than that of the oil, whereas at higher water contents the opposite applies. According to the prediction of our theory then, the corn starch particles should aggregate when the water content exceeds 3 wt %, i.e., when the particle conductivity becomes higher than that of the oil. This result correlates well with observations using optical microscopy that the particles formed chainlike structures under the action of the electric field for water contents higher than 3 wt % but only incomplete chains and partial alignment of the particles at lower water contents [51]. The theory also predicts that the application of ac electric fields of sufficiently high frequency would cause the particles to aggregate, even for cases when these particles do not aggregate in dc electric fields (Fig. 4). This phenomenon was observed in suspensions of anhydrous particles consisting of a conducting core and a nonconducting layer [52]. A more detailed analysis of a suspension with composite particles is beyond the present scope of our theory.

Although our theory does not deal with the rheology of ER fluids, it provides qualitative insight regarding the dependence of the electric-field-induced particle stress on the particle-to-suspending liquid ratio of conductances when the microstructure of the suspension has attained a fully developed state. Specifically, since an increase in the stress of the suspension due to an applied electric field is determined by the interparticle forces, its value in dc electric fields should be proportional to the coefficient Ψ_0^d in Eq. (20) for the energy of the dipole-dipole interaction between conducting particles. As shown above, when $\varepsilon_p/\varepsilon_f > 5/2$, Ψ_0^d increases initially with increasing σ_p/σ_f to a maximum at $\sigma_p/\sigma_f = 5/2$ and then decreases. The effect of the water content on the strength of the corn starch/corn oil suspensions for a particle volume fraction between 0.06 and 0.28 [51] reflects the predicted relationship. Experimental data reported in Ref. [51] cover the broad range (between 10^{-1} and 10^4) of variations of the ratio of the conductivity of the suspension, σ_s, to that of the oil, σ_f, in that the maximum of the strength of the suspensions (the difference between the stress at shear strain equal to 5 with the electric field and that without) in applied electric fields of 0.5–2.5 kV/mm was found to occur within the range of the water content from 6 to 10 wt % when $\sigma_s/\sigma_f \sim 1$–10 and $\sigma_p \sim \sigma_f$. The variation of

FIG. 4. The possible forms of the dependence of Ψ_ω^d on frequency depending on the values of $\varepsilon_p/\varepsilon_f$ and σ_p/σ_f.

the electric-field-induced static yield stresses produced by six semiconducting poly(acenequinones) dispersed in a chlorinated hydrocarbon oil, Cereclor 50LV from ICI, at a volume fraction of 0.35 also shows a peak when plotted vs the bulk conductivity of the particles in their initial state [2]. In experiments reported in Ref. [2] the bulk conductances of the poly(acenequinones) ranged from 10^{-2} to 5×10^{-9} S/m, with the dc electric fields varying from 1.2 to 3 kV/mm. The static yield stresses were found to peak for values of the conductivities between 10^{-4} and 10^{-6} S/m. These values are much higher than the conductivity of Cereclor 50LV, 4.6×10^{-9} S/m, measured in Ref. [53], but are of the same order of magnitude as the conductivity of the suspension, as calculated from the data presented in Ref. [2], of the current density as a function of the static yield stress; the current density of ~ 1–2 Å/m^2 corresponds to the electric field of ~ 2–3 kV/mm. A possible explanation for this discrepancy is that the values of σ_p and σ_f in a suspension could differ by an order of magnitude from those of the pure substances.

The relation between the electric-field-induced particle stress and the coefficient Ψ_ω^d in Eq. (21) for the energy of the dipole-dipole interaction between conducting particles in oscillating electric fields clarifies the reason why there exists a correlation between the ER activity of a suspension and its dielectric spectrum. Such interrelationships were recorded in many papers (see the review provided by Ref. [1]). As seen from Eq. (21), Ψ_ω^d increases when the difference between the time constant of the particles, ε_p/σ_p, and that of the suspending liquid, ε_f/σ_f, increased, i.e., with increasing $(\varepsilon_p/\sigma_p - \varepsilon_f/\sigma_f)^2$. According to the Maxwell-Wagner expression for the complex permittivity of a suspension (see Sec. IV A), this difference also determines the contribution of the interfacial polarization to the dielectric response of the suspension.

Reference [53] presented results of a detailed study of the initial stages of the aggregation of particles suspended in an ER fluid in which the time variation of the electric-field-induced change in the diffuse optical transmittance of a sample was measured. The ER fluid consisted of particles of hydrated lithium salt of poly(methacrylic) acid suspended, at a concentration $c = 0.35$, in a hydrocarbon oil, Cereclor 50LV. The strength of the dc electric fields ranged from 0.05 to 2.4 kV/mm, and a few measurements were made at 300-Hz ac electric fields. Several parameters of the ER fluid were estimated: $a \sim 1.1$ μm, $\eta_f \sim 0.089$ Pa s, $\sigma_f \sim 4.6 \times 10^{-9}$ S/m, and $\varepsilon_f/\varepsilon_0 \sim 8.1$, and therefore $t_f \sim 16$ ms. It was found that the time for structure formation, t_a, varied as E_0^{-2} for ac and low dc electric fields and as E_0^{-1} at high dc electric fields. Utilizing the expression in Ref. [39] for the time of structure formation in a suspension of nonconducting particles in a nonconducting fluid when Brownian motion can be neglected, the relative polarizability β of the particles was estimated in Ref. [53] and yielded $\beta^2 \sim 0.39$ for low dc electric fields, while for ac electric fields $\beta^2 \sim 0.037$. The crossover in the electric field dependence of the time for structure formation was attributed in Ref.

[53] to the presence of monopole forces, i.e., to a nonzero surface charge of the particles.

The experimental data reported in Ref. [53] fit naturally into the scheme of the aggregation processes predicted by our theory. In particular, the relation $t_a \sim E_0^{-2}$ corresponds to the regime of the slow aggregation in dc electric fields where $t_a \gg t_p$, while the relation $t_a \sim E_0^{-1}$ corresponds to the transition region between the regimes of slow and rapid aggregation in dc electric fields where $t_a \sim t_p$. The aggregation in 300-Hz ac electric fields corresponds to the regime where t_a is much larger than both t_p and $2\pi/\omega$, and the interparticle forces are determined by the time-averaged value of the dipole-dipole interaction. For these cases, the parameters estimated in Ref. [53] correspond to the coefficients in Eqs. (37) and (36), i.e., $\Psi_0^d \sim 0.39$ and $\Psi_\infty^d \sim \Psi_\omega^d \sim 0.037$ since, for 300-Hz ac electric fields, $2\pi f t_p \sim 30$. On substituting the parameters of the ER fluid into Eqs. (33) and (34), we estimate the magnitude of the dc electric field which induces aggregation: $E_{cr} \sim 44$ V/mm for $t \ll t_p$ and $E_{cr} \sim 14$ V/mm for $t \gg t_p$. Hence the experiments in dc and ac electric fields were performed under conditions such that $\Lambda \gg \Lambda_{cr}$, which is the case when Eqs. (36) and (37) can be used to evaluate the time scales of rapid and slow aggregations. On the basis of Eqs. (38) and (39) we then obtain that the slow aggregation should occur at $E_0 \ll E_0^s \sim 0.87$ kV/mm, while the rapid aggregation should occur at $E_0 \gg E_0^r \sim 2.83$ kV/mm. Thus the intermediate regime in which $t_a \sim E_0^{-1}$ should lie in the range from 0.87 to 2.83 kV/mm, as revealed by Ref. [53]. For this range, an increase in the strength of the electric field is accompanied by a decrease in the interfacial polarization of the particles, which decreases from its value corresponding to the case of conducting particles in a conducting liquid [Eq. (20)] to that for nonconducting particles in a nonconducting liquid [Eq. (19)].

VI. USEFUL PREDICTIONS AND CONCLUDING REMARKS

In this section we summarize the main results of our theory, which provide some insight into how dipole-dipole interaction between the particles in ER fluids can be optimized. First of all, it should be emphasized that, in dc electric fields, the interparticle forces are determined by the interfacial polarization, which in turn depends on the interparticle forces since the latter govern the ratio of the time scale for the particle motion, t_a, to the time scale for the dielectric relaxation, $t_p = (\varepsilon_p + 2\varepsilon_f)/(\sigma_p + 2\sigma_f)$. We resolved this feedback relation in two limiting cases: relatively weak and strong electric fields.

For weak dc electric fields [Eq. (38)], when $t_a \gg t_p$ and, hence, when the interfacial polarization adjusts itself to changes in the interparticle distances, the energy of the dipole-dipole interaction is described by Eq. (20). The electric-field-induced aggregation of the particles will then occur [Eq. (34)] only if a certain relation between the ratio of the particle-to-suspending liquid dielectric constants, $\varepsilon_p/\varepsilon_f$, and that of the conductances, σ_p/σ_f, is

satisfied [Eq. (35) and Fig. 3]. Therefore, the optimal way of increasing the dipole-dipole interaction between the particles and the thermodynamic driving force responsible for the aggregation process would be to maintain the ratio of the particle-to-suspending liquid conductances, $\sigma_p/\sigma_f \sim 1-10$, and to increase the ratio of the particle-to-suspending liquid dielectric constants. On the other hand, raising $\varepsilon_p/\varepsilon_f$ while keeping both σ_p and σ_f fixed is also accompanied by an increase in the dielectric relaxation time, which in turn narrows the range of electric fields where this mode of interfacial polarization can occur [Eqs. (38) and (40)]. However, as seen from Eqs. (38) and (40), this range can be extended by raising the viscosity of the suspending liquid, η_f.

On the other hand, for strong dc electric fields [Eq. (39)], when $t_a \ll t_p$ and, hence, when the interfacial polarization is the same as that for nonconducting particles in a nonconducting liquid, the energy of the dipole-dipole interaction is described by Eq. (19). In this case, the interparticle forces are determined only by the ratio of the particle-to-suspending liquid dielectric constants and a threshold value of the strength of the electric field always exists [Eq. (33)], above which the particles having $\varepsilon_p \neq \varepsilon_f$ will start aggregating as soon as the electric field has been applied. However, if Eq. (34), which involves the ratio of conductances, is not satisfied—cf. also Fig. 3—the random arrangement of the particles will retain its stability in the long-time limit.

For ac electric fields, however, the interfacial polarization and the energy of the dipole-dipole interaction become frequency dependent, and the behavior of the suspension depends on the relative magnitudes of the three time scales, i.e., t_p, t_a, and $2\pi/\omega$. Specifically, for weak electric fields and intermediate frequencies, when t_a is much larger than both t_p and $2\pi/\omega$, the interparticle forces are determined by the time-averaged value of the dipole-dipole interaction [Eq. (21) and Fig. 4]. In this case, there always exists a threshold value of the strength and frequency of the oscillating electric field, above which the particles having $\varepsilon_p \neq \varepsilon_f$ start aggregating regardless of the ratio σ_p/σ_f. The other cases, treated in detail in Sec. V, have much more in common with those in dc fields.

To understand the nature of the effect of the interfacial polarization on the electric-field-induced aggregation of the particles beyond the model of a leaky dielectric, it would be necessary to consider the general case of particles exhibiting intrinsic dispersion. The theory developed above provides a framework for embarking on such a generalization.

Note added in proof. The prediction of disklike formations is in agreement with recently published [M. Trau, S. Sankaran, D. A. Saville, and I. A. Aksay, Nature **374**, 437 (1995)] experimental data on the electric-field-induced pattern formation in $BaTiO_3$/castor oil dispersions.

ACKNOWLEDGMENT

[1] H. Block and J. P. Kelly, J. Phys. D **21**, 1661 (1988).

[2] H. Block, J. P. Kelly, A. Qin, and T. Watson, Langmuir **6**, 6 (1990).

[3] H. Block, Chemtech **22**, 368 (1992).

[4] A. P. Gast and C. F. Zukoski, Adv. Colloid Interf. Sci. **30**, 153 (1989).

[5] F. E. Filisko, in *Electrorheological Fluids. A Research Needs Assessment–Final Report* (DOE, Washington, 1993), p. 5.9-1.

[6] F. E. Filisko and D. R. Gamota, in *Recent Advances in Non-Newtonian Flows. ASME. Applied Mechanics Division* (ASME, New York, 1992), Vol. 153, p. 75.

[7] T. C. Halsey, Science **258**, 761 (1992).

[8] T. C. Halsey and J. E. Martin, Sci. Am. **269**, 58 (1993).

[9] C. F. Zukoski, Ann. Rev. Mater. Sci. **23**, 45 (1993).

[10] K. D. Weiss, J. D. Carlson, and J. P. Coulter, J. Intelligent Mater. Syst. Structures **4**, 13 (1993).

[11] *Proceedings of the First International Symposium on Electrorheological Fluids,* edited by H. Conrad, A. F. Sprecher, and J. D. Carlson (North Carolina State University, Raleigh, NC, 1989).

[12] *Proceedings of the Second International Conference on Electrorheological Fluids,* edited by J. D. Carlson, A. F. Sprecher, and H. Conrad (Technomic, Lancaster, PA, 1990).

[13] *Proceedings of the International Conference on Electrorheological Fluids: Mechanisms, Properties, Structure, Technology, and Applications,* edited by R. Tao (World Scientific, Singapore, 1992).

[14] *Electrorheological Fluids. A Research Needs Assessment—Final Report* (Ref. [5]).

[15] Y. Chen, A. F. Sprecher, and H. Conrad, J. Appl. Phys. **70**, 6796 (1991).

[16] L. C. Davis, J. Appl. Phys. **72**, 1334 (1992).

[17] L. C. Davis, J. Appl. Phys. **73**, 680 (1993).

[18] J. N. Foulc, P. Atten, and N. Felici, C. R. L'Acad. Sci. Ser. II, **317**, 5 (1993).

[19] Z. P. Shulman, B. M. Khusid, E. V. Korobko, and E. P. Khizhinsky, J. Non-Newtonian Fluid Mech. **25**, 329 (1987).

[20] Z. P. Shulman, B. M. Khusid, E. V. Korobko, and E. P. Khizhinsky, J. Eng. Phys. **52**, 175 (1987).

[21] Z. P. Shulman, A. D. Matsepuro, and B. M. Khusid, Vest-si Akad. Navuk B. SSR Ser. Fiz. Energ. Nauk **3**, 116 (1977).

[22] Z. P. Shulman, B. M. Khusid, and A. D. Matsepuro, Vest-si Akad. Navuk B. SSR Ser. Fiz. Energ. Nauk **3**, 122 (1977).

[23] Z. P. Shulman, A. D. Matsepuro, and B. M. Khusid, Vest-si Akad. Navuk B SSR Ser. Fiz. Energ. Nauk **4**, 62 (1974).

[24] Z. P. Shulman, B. M. Khusid, and A. D. Matsepuro, Vest-si Akad. Navuk B. SSR Ser. Fiz. Energ. Nauk **4**, 70 (1974).

[25] L. D. Landau, L. P. Lifshitz, and L. P. Pitaevski, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1984).

[26] S. S. Dukhin and V. N. Shilov, *Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes*

(Wiley, New York, 1974).

[27] W. B. Russel, D. A. Saville, and W. R. Showalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1989).

[28] D. J. Jeffrey, Proc. R. Soc. London Ser. A **335**, 355 (1973).

[29] D. J. Jeffrey, Proc. R. Soc. London Ser. A **338**, 503 (1974).

[30] A. Acrivos, D. J. Jeffrey, and D. D. Saville, J. Fluid Mech. **212**, 95 (1990).

[31] L. D. Landau and L. P. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1980), Pt. I.

[32] R. Tao, J. T. Woestman, and N. K. Jaggi, Appl. Phys. Lett. **55**, 1814 (1989).

[33] G. Molinari and A. Viviani, J. Electrostat. **5**, 343 (1978).

[34] X.-B. Wang, Y. Huang, R. Holzel, and J. P. H. Burt, and R. Pethig, J. Phys. D **6**, 312 (1993).

[35] D. J. Klingenberg, F. van Swol, and C. F. Zukoski, J. Chem. Phys. **91**, 7888 (1989).

[36] M. Whittle, J. Non-Newtonian Fluid Mech. **37**, 233 (1990).

[37] J. R. Melrose, Phys. Rev. A **44**, R4789 (1991).

[38] J. R. Melrose and D. M. Heyes, J. Chem. Phys. **98**, 5873 (1993).

[39] K. C. Hass, Phys. Rev. E **47**, 3362 (1993).

[40] R. Tao and J. M. Sun, Phys. Rev. Lett. **67**, 398 (1991).

[41] R. Tao and Qi Jiang, Phys. Rev. Lett. **73**, 205 (1994).

[42] G. K. Batchelor and J. T. Green, J. Fluid. Mech. **56**, 461 (1972).

[43] W. R. Toor, J. Colloid Interf. Sci. **156**, 335 (1993).

[44] B. C. Xu and K. C. Hass, J. Chem. Phys. **98**, 2258 (1993).

[45] R. T. Bonnecaze and J. F. Brady, J. Chem. Phys. **96**, 2183 (1992).

[46] R. T. Bonnecaze and J. F. Brady, J. Rheol. **36**, 73 (1992).

[47] M. J. Stevens and G. S. Grest, Phys. Rev. Lett. **72**, 3686 (1994).

[48] M. Shapiro, A. L. Shalom, and I. J. Lin, J. Appl. Phys. **58**, 1028 (1985).

[49] A. Okagawa, R. G. Cox, and S. G. Mason, J. Colloid Interf. Sci. **47**, 568 (1972).

[50] H. A. Pohl, *Dielectrophoresis* (Cambridge University Press, Cambridge, 1978).

[51] Y. Chen and H. Conrad, in *Developments in Non-Newtonian Flows. ASME. Applied Mechanics Division* (ASME, New York, 1993), Vol. 175, p. 199.

[52] A. Inoue, in *Proceedings of the Second International Conference on Electrorheological Fluids* (Ref. [12]), p. 176.

[53] J. M. Ginder, Phys. Rev. E **47**, 3418 (1993).