Effects of interparticle electric interactions on dielectrophoresis in colloidal suspensions

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Using our recently published statistical theory concerning the phase diagram of a low-conducting colloidal suspension subject to uniform electric fields [Phys. Rev. E **52**, 1669 (1995)], we examine how the long-range electric-field-induced interparticle interactions affect the spatial arrangement of particles in such a suspension under the action of a *nonuniform* ac electric field. We find the conditions under which the resulting dielectrophoresis in *nonuniform* electric fields is accompanied by an electric-field-induced phase transition in the suspension. Moreover we predict that, in the case of positive dielectrophoresis, the particles will form chainlike aggregates aligned parallel to the electric field lines and attracted towards the higher electric-field region; whereas, for negative dielectrophoresis, the particles will form disklike aggregates aligned perpendicularly to the electric-field lines and repelled from the higher electric-field region. The theory also provides some insight regarding the dependence of the particle aggregation on the frequency of the applied nonuniform ac electric field. The predictions of the theory are consistent with the characteristic patterns of cell aggregation observed previously in high-gradient electric fields generated in microelectrode systems. [S1063-651X(96)09611-0]

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I. INTRODUCTION

The past decade has seen a spectacular increase in the use of dielectrophoretic phenomena in colloidal suspensions. The term *dielectrophoresis* is used to describe the electric-field-induced motion of polarized but electrically uncharged particles in *nonuniform* electric fields [1]. The essential feature that distinguishes dielectrophoretic from electrophoretic effects lies in the fact that the former are also observed in ac electric fields where the polarization of the electrodes and the electrolysis of the suspending fluid are eliminated. Also, the charge properties of the particle surface, which, although vital in electrophoresis, are almost impossible to control, are not as significant in dielectrophoretic separations since, in the latter case, the dielectrophoretic force depends primarily on the differences between the values of the dielectric constant and of the conductivity of the particles and those of the suspending fluid.

The dielectrophoretic force experienced by a nonconducting spherical particle immersed in a nonconducting liquid under the application of a nonuniform electric field $\mathbf{E}(\mathbf{r},t)$ can be expressed as [1,2]

$$\mathbf{F}_p = \frac{3}{2} v_p \varepsilon_f \beta \nabla \mathbf{E}^2(\mathbf{r},t). \qquad (1)$$

Here $\beta = (\varepsilon_p - \varepsilon_f)/(\varepsilon_p + 2\varepsilon_f)$ is the polarizability of a particle, v_p is the particle volume, and ε_p and ε_f are, respectively, the dielectric constants of the particle and of the suspending fluid where, for brevity, we have included the permittivity of the vacuum ε_0, as a multiplier in the definition of the dielectric constant. For a conducting particle immersed in a conducting liquid, Eq. (1) still applies provided that the polarizability parameter β for the dielectrophoretic force is taken to depend on the frequency of the applied ac electric field, i.e., $\beta = \beta(\omega)$ [1]. In any event, the particle is attracted towards or repelled from the high electric-field re-

gions depending, respectively, on whether $\beta > 0$ (positive dielectrophoresis) or $\beta < 0$ (negative dielectrophoresis).

The use of dielectrophoretic phenomena in techniques for manipulating and separating colloidal suspensions, cells, bioparticles, and micro-organisms as well as for investigating the biophysical properties of biological materials constitutes currently an active area of research [3–16]. Also, dielectrophoretic separation can be useful in mineral processing, petroleum refining, the recovery of insulating materials, and for removing catalyst fines and corrosion products from industrial streams (see, for example, [17,18]).

To date, however, the interpretation of the experimental data concerning the spatial particle arrangement in colloidal suspensions under the application of nonuniform ac electric fields [3–18] has been based on Eq. (1). But, since this equation refers to the force acting on a single particle in a nonuniform electric field, it can be used to interpret the experimental data on dielectrophoretic phenomena only when the application of a nonuniform electric field to a suspension does not induce aggregation of the particles, i.e., when the electric field is relatively weak and the interparticle electric interactions are negligible. Thus, it is impossible to (i) explain why the particles start aggregating in nonuniform strong electric fields and (ii) evaluate the effects of the aggregation on the spatial particle arrangement in dielectrophoresis. This is a serious drawback because it appears that, without the existence of electric-field-induced aggregation, it is not possible to achieve a high selectivity of the particle separation in nonuniform electric fields [14–16].

In this paper we shall examine the effects of the long-range electric-field-induced interparticle electric interactions on the spatial arrangement and aggregation of particles in a colloidal suspension under the action of *nonuniform* electric fields by adapting, to this case, our recent results pertaining to the statistical theory of the phase diagram of a low-conducting colloidal suspension subject to *uniform* electric fields [19]. Specifically, as shown in Ref. [19], Sec. V, when

the ratio of the average energy of the electric-field-induced interparticle interactions and the thermal energy exceeds a critical value, an increase in the particle concentration leads to a decrease in the osmotic pressure of the particles. This destabilizes the initially random spatial arrangement of the particles in the suspension and leads, in turn, to a phase separation of the suspension into low- and high-concentration phases.

Here, we shall analyze the appearance of this phase transition in a *nonuniform* ac electric field and shall examine its influence on the spatial arrangement of the particles for two limiting cases which arise in a wide variety of recently developed techniques for the manipulation and separation of cells, bioparticles, and micro-organisms [6–16]. One of them, referred to as an open particle system, is relevant to a situation in which an electric field acts only over a small portion of the colloidal suspension with the result that the particles far from this region do not redistribute, whereas in the other, referred to as a closed particle system, the electric field acts over the whole of the suspension.

In Sec. II A, we shall derive the equations for the quasiequilibrium spatial arrangement of the particles in a colloidal suspension subject to a nonuniform ac electric field, while in Sec. II B we shall examine the conditions under which the resulting dielectrophoresis is accompanied by an electric-field-induced phase transition. Finally, in Sec. III, we shall compare the predictions of the theory with the characteristic patterns of cell aggregation observed previously in high-gradient electric fields generated in microelectrode systems.

II. ELECTRIC-FIELD-INDUCED PHASE TRANSITIONS IN NONUNIFORM ELECTRIC FIELDS

A. Quasiequilibrium spatial arrangement of the particles

Due to the Brownian motion of the particles, their concentration and therefore their osmotic pressure are spatially uniform in the absence of an electric field. But, when a nonuniform ac electric field is applied, the particles will be attracted towards or repelled from the high electric-field regions depending, respectively, on the sign of β [see Eq. (1)]. Also, as shown later, this particle spatial redistribution can, under certain conditions (see Fig. 3), be accompanied by an electric-field-induced particle aggregation. The accumulation of the particles in one area, which leads to a corresponding increase in the particle osmotic pressure, will cease after a transit time t_{tr} when the induced osmotic pressure gradient counterbalances the dielectrophoretic force. Let the electric field vary over a characteristic length L. Then, as a rough approximation, t_{tr} equals the time taken for a particle to move over a distance L under the action of the dielectrophoretic force, Eq. (1), and the Stokes drag force, hence, $t_{tr} \sim (L/a)^2 (3\eta_f / \varepsilon_f \beta E^2)$, where η_f is the viscosity of the suspending liquid. For the typical set of parameters $E = 5 \times 10^5$ V/m, $\varepsilon_f / \varepsilon_0 = 3$, $\eta_f = 2 \times 10^{-3}$ Pa s, $\beta(\omega) = 0.6$, $L = 1$ mm, and $a = 1$ μm, we estimate that $t_{tr} \sim 1$ h, and we conclude, therefore, that equilibrium can be reached in a reasonable period of time.

Now, for ac electric fields $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0(\mathbf{r}) \sin \omega t$, the mode of the periodic time variations of the spatial particle arrangement which is eventually established depends on the relative

magnitude of the three time scales t_a, t_e, and t_d, where $t_e = 2\pi / \omega$ is the electric-field time cycle, t_a is the characteristic time for the electric-field-induced aggregation, and $t_d \sim 1_p^2 / D_{Br}$ is the time needed for a particle to drift over distances equal to a characteristic interparticle distance 1_p under the action of the Brownian forces. Here $D_{Br} = k_B T / 6\pi \eta_f a$ is the Brownian diffusion coefficient of a single particle of radius a, with k_B being Boltzmann's constant and T is the temperature. To evaluate the value of t_a, we can use the relation obtained in Ref. [19], Sec. V, for a colloidal suspension subject to a sufficiently strong uniform electric field, $t_a \sim [\eta_f \xi(c) / \Psi(\omega) \varepsilon_f \mathbf{E}^2]$, where $\xi(c)$ is a concentration dependent coefficient and $\Psi(\omega)$ is a frequency dependent coefficient which enters into the expression for the averaged energy of the electric-field-induced interparticle interactions. The quasiequilibrium state of the spatial arrangement of the particles, which is established following the transient period as a result of the applied nonuniform ac electric field, corresponds therefore to the limiting case when t_d is much larger than both t_e and t_a. Under these conditions, the time-averaged dielectrophoretic force is counterbalanced everywhere by the time-averaged thermodynamic force responsible for the osmotic pressure gradient. For the representative set of parameters given above and $T = 300$ K, $c = 0.2$ [giving $\xi(c) \approx 16$], and $\Psi(\omega) = 0.5$, we find that $t_a \sim 10$ ms and that $t_d \sim 10$ s for $1_p = a$. Thus, the particles will retain their quasiequilibrium spatial arrangement provided that the frequency of the ac field exceeds 0.1 Hz.

We next turn to the task of obtaining the equation for a quasiequilibrium spatial arrangement of the particles in a slightly nonuniform ac electric field. This will be achieved by using the results of the statistical theory of the free energy of a disordered colloidal suspension in uniform dc and ac electric fields developed in Ref. [19], Sec. IV.

We recall that, according to Ref. [19], Sec. II, the free energy F, of N particles in a colloidal suspension, is defined as a function of the volume V, the temperature T, the volume concentration of the particles $c = v_p N / V$, and the strength of an electric field $\mathbf{E}(\mathbf{r}, t)$, by means of

$$F = \frac{k_B T}{v_p} f_0(c) V - W(c, \mathbf{E}) V, \tag{2}$$

where the first term in Eq. (2) refers to the free energy of the particles in the absence of the electric field and $W(c, \mathbf{E})$ denotes the increase in the electric energy per unit volume of a colloidal suspension due to the interaction of the particles with the applied electric field as well the long-range electric-field-induced interparticle interactions. For example, as was shown in Ref. [19], Sec. IV, the expression for the ensemble average of the electric energy $W(c, \mathbf{E})$, for a nonconducting suspension reduces to the well-known equation derived from macroscopic electrodynamics [2]

$$W = \frac{1}{2} [\varepsilon_s(c) - \varepsilon_f] \mathbf{E}^2, \tag{3}$$

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

Now, the osmotic pressure of the particles can be evaluated from the equation of the free energy by means of

$$\Pi = -\left[\frac{\partial F}{\partial V}\right]_{N,T,E} = \frac{k_B T}{v_p} cZ(c) + W - c\frac{\partial W}{\partial c}, \quad (4)$$

where $\Pi_0 = -(k_B T/v_p)(f_0 - cf_0')$, the osmotic pressure of the particles in the absence of an electric field, has been replaced by an equivalent expression containing the compressibility factor $Z(c)$, with $Z(c) \to 1$ at infinite dilution. Using the limiting value of $f_0(c)$ for a dilute colloidal suspension, $f_0(c) \to c\ln(c/e)$ at $c \to 0$, we obtain

$$f_0(c) = c\ln\frac{c}{e} + c\int_0^c \frac{Z(c)-1}{c}\,dc. \quad (5)$$

The ratio between the electric and the entropic terms in Eq. (4) reflects the relative contribution of the electric field to the osmotic pressure. For example, for a nonconducting colloidal suspension, the physical meaning of this ratio becomes apparent as $c \to 0$ where, on account of Eqs. (3) and (4), it equals Λc, where $\Lambda = [v_p \mathbf{E}^2 \varepsilon_s''(0)/2k_B T]$, with $\varepsilon_s''(0)$ denoting the second derivation of $\varepsilon_s(c)$ at infinite dilution, which is the same as the ratio of the energy of the interparticle interactions per unit volume [the energy of the electric interaction between two particles $(1/2)v_p \mathbf{E}^2 \varepsilon_s''(0)$, times the particle concentration c], and the thermal energy $k_B T$.

Finally, the Gibbs free energy of the particles $G = F + \Pi V$, and the chemical potential of a particle $\mu = (\delta G/\delta N)$, follow from Eqs. (2) and (4), respectively, hence

$$\mu = k_B T f_0' - v_p \frac{\partial W}{\partial c}. \quad (6)$$

When the particles have reached their quasiequilibrium spatial arrangement in a nonuniform time-variable electric field, the chemical potential becomes independent of position. Therefore, on account of Eq. (6), the quasiequilibrium particle concentration distribution must satisfy

$$f_0'[c(\mathbf{r})] - \frac{v_p}{k_B T}\frac{\partial W}{\partial c}[c(\mathbf{r}), \langle \mathbf{E}^2(\mathbf{r},t)\rangle_{t_e}] = \text{const}, \quad (7)$$

where f_0' and $(\partial W/\partial c)$ are evaluated at $c = c(\mathbf{r})$, and $\langle \mathbf{E}^2(\mathbf{r},t)\rangle_{t_e}$ refers to the time-averaged local value of the square of the strength of the electric field. Therefore, as seen from Eq. (7), the determination of the quasiequilibrium particle concentration distribution is reduced to finding the spatial variation of the time-averaged local value of the square of the strength of the electric field since $c(\mathbf{r}) = c(\langle \mathbf{E}^2(\mathbf{r},t)\rangle_{t_e})$.

To this end, using the expression $\nabla\mu = 0$, which is equivalent to Eq. (7), and the relation $cf_0'' = Z + cZ'$, we obtain that

$$\left[Z + cZ' - c\frac{v_p}{k_B T}\frac{\partial^2 W}{\partial c^2}\right]\frac{dc}{d\langle\mathbf{E}^2\rangle_{t_e}} = c\frac{v_p}{k_B T}\frac{\partial^2 W}{\partial c\,\partial\langle\mathbf{E}^2\rangle_{t_e}}. \quad (8)$$

The term $c(v_p/k_B T)(\partial^2 W/\partial c^2)$ in brackets on the left-hand side of Eq. (8), which originates from the term $(\partial\Pi/\partial c)\nabla c$, reflects the concentration dependence of the osmotic pressure of the particles in an electric field due to their long-ranged electric-field-induced interparticle interactions, while the

term on the right-hand side of Eq. (8), which arises from the term $[\partial\mu/\partial\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e}]\nabla\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e}$, reflects the presence of the dielectrophoretic force exerted on the particles per unit volume of suspension due to their interaction with an applied nonuniform electric field. Actually, the parameter $(\partial^2 W/\partial c\,\partial\langle\mathbf{E}^2\rangle_{t_e})$ represents the effective polarizability of a particle in a suspension.

For a closed particle system, i.e., when the applied electric field acts over the whole colloidal suspension, the particle concentration distribution to be found from Eq. (8) must also satisfy the requirement that the number of particles be conserved, i.e., that

$$\int_{V_s} c(\mathbf{r})d\mathbf{r} = v_p N, \quad (9)$$

where V_s is the volume occupied by the suspension under the action of an electric field.

Now, let $V(\mathbf{E}^2)$ be the volume of the suspension within which the time-averaged square of the local strength of the electric field $\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e}$ is less than or equal to the given value $\mathbf{E}^2$, i.e., $V(\mathbf{E}^2) = \int_{\mathbf{E}^2 \geq \langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e}} d\mathbf{r}$. But, since $c(\mathbf{r}) = c(\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e})$, by using the function $V(\mathbf{E}^2)$ we can convert the integral over the suspension volume on the left-hand side of Eq. (9) into an integral over the time-averaged squared strength of the electric field and thus arrive at

$$\int_{\min_{V_s}(\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e})}^{\max_{V_s}(\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e})} c(\mathbf{E}^2)\frac{dV(\mathbf{E}^2)}{d\mathbf{E}^2}\,d\mathbf{E}^2 = v_p N. \quad (10)$$

It is worth pointing out that the function $V(\mathbf{E}^2)$ is the only characteristic of the spatial distribution of the electric field in the system which influences the spatial arrangement of the particles. Moreover, it makes no difference whether the area of the fixed value of the strength of the electric field is a simply connected region or not.

For an open particle system, i.e., when the electric field acts only over a small portion of the suspension outside of which the particle concentration remains equal to c_0, the integral condition Eq. (9) is replaced by the requirement that Eq. (8) is subject to the boundary condition

$$c \to c_0 \quad \text{as} \quad \langle\mathbf{E}^2\rangle_{t_e} \to 0. \quad (11)$$

In addition, if, for the example of a nonconducting colloidal suspension, $c \ll 1$, in which case $Z \approx 1$, then $\varepsilon_s' \approx 3\varepsilon_f \beta$, and the electric interaction between particles can be neglected in comparison with the thermal energy so that

$$\frac{cv_p}{k_B T}\frac{\partial^2 W}{\partial^2 c}\bigg|_{c=0} = \frac{c\varepsilon_s''(0)v_p\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e}}{2k_e T} \ll 1,$$

hence Eq. (8) is equivalent to the simple expression

$$\frac{c}{v_p}\mathbf{F}_p = \nabla\Pi, \quad (12)$$

where $(c/v_p)\mathbf{F}_p$ with $\mathbf{F}_p$ given by Eq. (1) is the dielectrophoretic force exerted on the particles per unit volume of the

suspension, and the osmotic pressure Π equals $(k_B T/v_p)c$. For this special case then, the solution to Eq. (8) subject to Eq. (11), leads to the Boltzmann distribution of the particles in a nonuniform electric field [1]

$$c = c_0 \exp\left(\frac{3v_p \varepsilon_f \beta \langle \mathbf{E}^2(\mathbf{r},t) \rangle_{t_e}}{2k_B T}\right). \tag{13}$$

In our subsequent numerical calculations we shall use the Carnahan-Starling equation [20]

$$Z(c) = \frac{1 + c + c^2 - c^3}{(1-c)^3}, \tag{14}$$

which applies for a suspension of hard spheres in the disordered state as long as c remains below approximately 0.5. We recall that the compressibility factor for hard spheres diverges at random close packing according to [20]

$$Z(c) \approx \frac{A}{c_m - c} \quad \text{where} \quad A \sim 1.85 \quad \text{and} \quad c_m \sim 0.64. \tag{15}$$

But since we shall not examine in detail the concentration profile when c approaches its value for closest packing, we shall not take into account that the exact expression for $Z(c)$ could depart from that given by Eqs. (14) or (15) due to the occurrence of a possible transition from a disordered state, for $c < 0.50$, to an ordered face-centered-cubic solid for $0.55 < c < 0.74$ [20].

For the sake of simplicity, we performed numerical calculations on a few examples and only for the simplest case of a nonconducting colloidal suspension where the electric energy is determined by Eq. (3). For $\varepsilon_s(c)$, we made use of two expressions. One of them arises from the microstructural theory developed in Ref. [19], Sec. IV, which allows us to calculate the first terms in the expansion of the electric energy of a suspension in powers of the particle concentration

$$\varepsilon_s(c) = \varepsilon_f [1 + 3\beta c + 3\beta^2 F_1(\beta)c^2 + \cdots],$$

$$\text{where} \quad F_1(\beta) = 1 + \beta f_1(\beta). \tag{16}$$

This theory leads to a definite expression for $f_1(\beta)$ which varies from 0.432 for $\beta = -0.5$ to 0.498 for $\beta = 1$. The expansion of the electric energy in powers of c, as given by Eq. (16), applies only provided that $|\beta c| \ll 1$. The other expression for ε_s is Maxwell's well-known equation for the dielectric constant

$$\varepsilon_s(c) = \varepsilon_f \frac{1 + 2\beta c}{1 - \beta c}, \tag{17}$$

which also follows from the mean-field approximation developed for calculating the electric energy of a suspension [19], Sec. IV. Both Eqs. (16) and (17) yield $\varepsilon_s' \approx 3\varepsilon_f \beta$ for $c \ll 1$.

B. Lines of equal chemical potential in the phase diagram

To examine how the long-range electric-field-induced interparticle interactions affect the quasiequilibrium spatial arrangement of the particles in dielectrophoresis, we use the results of a statistical theory [19] concerning the phase diagram of a colloidal suspension subject to *uniform* electric fields in the region $0 \leq c \leq c_m$ and $\mathbf{E}^2 \geq 0$, where c_m is taken from Eq. (15). The trajectories of Eq. (8) represent the lines of equal chemical potential [see Eq. (7)] in this phase diagram.

As seen from Eq. (8), when the term in the brackets on the left-hand side is positive, the particle concentration is increasing or decreasing with $\mathbf{E}^2$ according to whether the particle effective polarizability is positive or negative. Note that $(\partial^2 W/\partial c\, \partial \mathbf{E}^2)$ equals $(1/2)\varepsilon'(c)$ for the case of a nonconducting suspension [see Eq. (3)]. But, from the mean-field approximation Eq. (17), it follows that $\varepsilon_s' = [3\beta\varepsilon_f/(1 - \beta c)^2]$, hence the sign of ε_s' is everywhere equal to that of β. Similarly, by retaining the first three terms in Eq. (16), we obtain from the microstructural theory, that $\varepsilon_s' = 3\beta\varepsilon_f [1 + 2\beta F_1(\beta)c]$. Although, it might seem from the above, that $\varepsilon_s' = 0$ at $c = -1/2\beta F_1(\beta)$, this would be unacceptable since $-1/2\beta F_1(\beta) > 1$ for $\beta < 0$. Consequently, the sign of ε_s' is also everywhere equal to that of β. In view of the fact that, $\varepsilon_s' \to 3\beta\varepsilon_f$ as $c \to 0$, we see that within the region $0 \leq c \leq c_m$, ε_s' does not change its sign which is determined solely by the sign of β. Moreover, we also shall suppose that, in general, the particle effective polarizability $(\partial^2 W/\partial c\, \partial \mathbf{E}^2)$ does not change its sign in the phase diagram of the suspension for $0 \leq c \leq c_m$ and $\mathbf{E}^2 \geq 0$.

Now, the curve

$$Z + cZ' - c\frac{v_p}{k_B T}\frac{\partial^2 W}{\partial c^2} = 0 \tag{18}$$

determines the isocline of the vertical slope of the trajectories of Eq. (8), whereas the straight lines $c = 0$ and $c = c_m$ determine the isoclines of the horizontal slope of the trajectories of Eq. (8). Thus, Eq. (18), which is actually equivalent to $(\partial \Pi/\partial c) = 0$, represents the critical line in the phase diagram of a colloidal suspension beyond which the random spatial arrangement of the particles becomes unstable, and an electric-field-induced aggregation will occur [19], Sec. II. Then, the suspension will separate into two phases with the coexistence region lying between the particle concentrations given by the two roots of Eq. (18). As seen from Eq. (18), for this to happen, the long-range electric-field-induced interparticle interactions should increase the average energy of the suspension, i.e., $(\partial^2 W/\partial c^2)$ should be positive (see Ref. [19], Sec. V in more detail). But, for sufficiently high frequencies, the electric energy of the particles becomes the same as that for a nonconducting suspension Eq. (3), and, thus, we obtain that $(\partial^2 W/\partial c^2) = (1/2)\varepsilon_s''(c)\mathbf{E}^2 > 0$ for $\omega \to \infty$. Therefore, there always exist threshold values of the strength and of the frequency of an ac electric field, above which the particles having a dielectric constant different from that of the suspending liquid will start aggregating as soon as the electric field has been applied. On the other hand, for low frequencies, $(\partial^2 W/\partial c^2)$ could become negative [19], Sec. V. Thus for a low frequency, the electric-field-induced aggregation of the particles will occur only if the dielectric constants and conductivities of the particles and of the liquid lead to a positive value of $(\partial_2 W/\partial c^2)$ at this frequency. The conditions for this to occur in dc electric fields are given in Ref. [19], Sec. V. For example, the particles having a dielectric

constant larger than that of the suspending liquid do not aggregate in dc electric fields unless their conductivity is larger than that of the suspending liquid, as was observed in electrorheological fluids [19].

In addition, an analysis based on the influence of the ponderomotive forces on the type of aggregation pattern [19], Sec. V, shows that there exists a tendency for chainlike formations aligned parallel to the electric field when the particle polarizability $\beta(\omega)$, in Eq. (1), is positive and disklike formations aligned normal to the electric field when $\beta(\omega)$ is negative.

The critical point at which the particle concentration of the coexisting phases coincide and Eq. (18) has a multiple root, corresponds to the inflection point of Π as a function of c, i.e., $(\partial\Pi/\partial c)=(\partial^2\Pi/\partial c^2)=0$. The parameters of the critical point, namely, c_{cr} and $\mathbf{E}_{cr}^2$, are determined from

$$Z+cZ'-c\frac{v_p}{k_BT}\frac{\partial^2 W}{\partial c^2}=0,$$

$$2Z'+cZ''-\frac{v_p}{k_BT}\left(\frac{\partial^2 W}{\partial c^2}+c\frac{\partial^3 W}{\partial c^3}\right)=0, \qquad (19)$$

which follows from Eq. (18). For $\mathbf{E}^2\geqslant\mathbf{E}_{cr}^2$, Eq. (18) has two roots. With increasing $\mathbf{E}^2$, the particle content in the low-concentration phase becomes very small, and since $Z\to1$ as $c\to0$, Eq. (18) yields

$$c\frac{v_p}{k_BT}\frac{\partial^2 W}{\partial c^2}\bigg|_{c=0}(\mathbf{E}^2)=1 \qquad (20)$$

for this part of the curve. In contrast, the particle content in the high-concentration phase increases with $\mathbf{E}^2$. Then, on using Eq. (15) we obtain that

$$c_m-c=O\left(\left[A\bigg/\frac{v_p}{k_BT}\frac{\partial^2 W}{\partial c^2}\right]^{-1/2}\right)$$

for this part of the curve. Describing phase transitions in the high-concentration phase is beyond the scope of our analysis, however, because it requires knowledge of the free energy of an ordered polarizable system.

Let us analyze now how the specific type of the concentration dependence of the suspension dielectric constant $\varepsilon_s(c)$ influences the critical line in the phase diagram for the specific case of a nonconducting suspension where the electric energy is given by Eq. (3). As was shown in Ref. [19], Sec. II, Eqs. (19) yields $c_{cr}=0.13$ and $\Lambda_{cr}=21.20$ for the case $\varepsilon_s''(c)=$ const, while the dependence of Λ_{cr} and c_{cr} on β, when $\varepsilon_s(c)$ is given by Eq. (17) is shown in Fig. 1. Note that, as $\beta\to0$, the parameters c_{cr} and Λ_{cr} attain the same values as those given for the case $\varepsilon_s''(c)=$ const, i.e., $\Lambda_{cr}\to21.20$ and $c_{cr}\to0.13$. Moreover, an increase in β from $\beta=-0.5$ to $\beta=1$ leads to a decrease in Λ_{cr} from 25.24 to 11.66 and to an increase in c_{cr} from 0.11 to 0.27.

For $\Lambda>\Lambda_{cr}$, Eq. (18) has two roots which give the respective particle concentrations in the two coexisting phases. Figure 2 shows this dependence for a few values of β, when $\varepsilon_s(c)$ is given by Eq. (17). Clearly, the particle content in the low-concentration phase becomes very small with increasing Λ/Λ_{cr}, and $\Lambda\sim1/c$ for this part of the curve according to Eq.
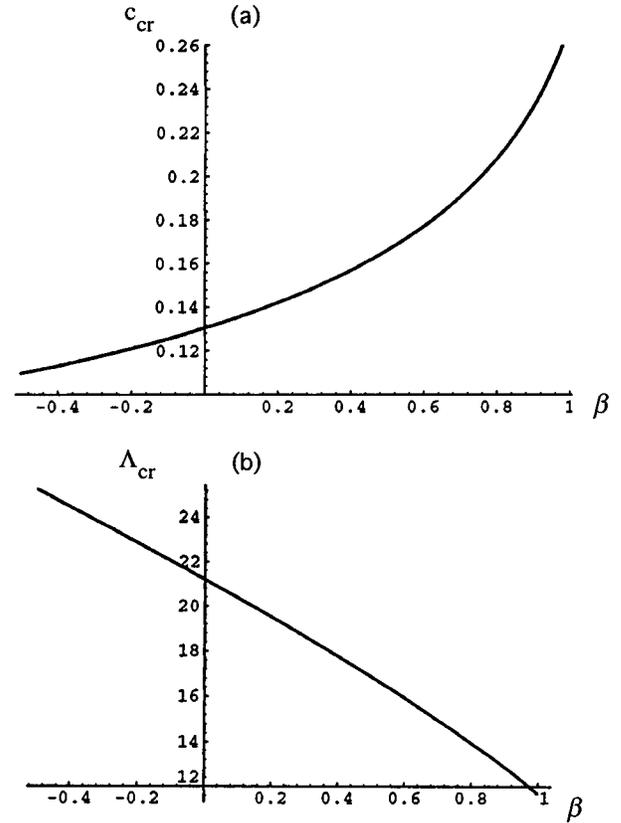
FIG. 1. The dependence of the parameters of the critical point c_{cr} (a) and Λ_{cr} (b) on the particle polarizability β when $\varepsilon_s(c)$ is given by Eq. (17).

(20). In contrast, the particle content in the high-concentration phase increases dramatically with Λ/Λ_{cr} in that at $\Lambda/\Lambda_{cr}\approx2$, $c\approx0.5$, which corresponds to that of an ordered face-centered-cubic solid state of a colloidal suspension of hard spheres in the absence of an electric field. It means that, the high-concentration phase could actually experience a disorder-order transition at these values of Λ/Λ_{cr}.

The results given above demonstrate that the qualitative features of the critical line are rather insensitive to the specific form of the concentration dependence of $\varepsilon_s(c)$. Thus, changes in the function $\varepsilon_s(c)$ predominantly influence the values of c_{cr} and Λ_{cr} but not in a major way.
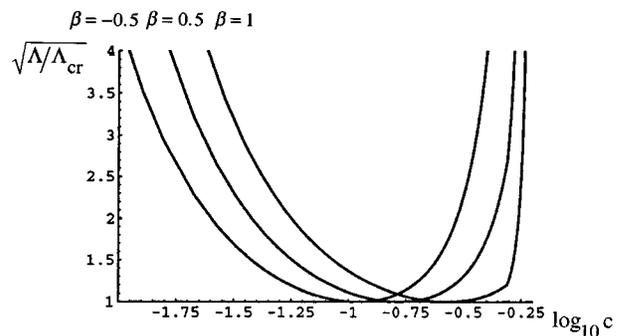
FIG. 2. The dependence of the particle concentration c on $\sqrt{\Lambda/\Lambda_{cr}}$ in the low- (the left part of the curve) and high-concentration (the right part of the curve) phases for indicated values of β when $\varepsilon_s(c)$ is given by Eq. (17).

To examine the behavior of the trajectories of Eq. (8) in the phase diagram of a colloidal suspension, let us consider the conditions under which those trajectories intersect the critical line. As seen from Eq. (8), the slope of such a trajectory becomes infinite at the intersection point, i.e., the trajectory becomes vertical. But since the critical line has an infinite slope only at the critical point, there exists only one limiting trajectory of Eq. (8) tangent to the critical line. This is the trajectory passing through the critical point. To find the asymptotic behavior of the limiting trajectory near the critical point, we expand the terms of Eq. (8) in powers of $(c-c_{cr})$ and $(\langle \mathbf{E}^2 \rangle_{t_e} - \mathbf{E}_{cr}^2)$ and integrate the resultant equation with boundary condition $c = c_{cr}$ at $\langle \mathbf{E}^2 \rangle_{t_e} = \mathbf{E}_{cr}^2$. As a result, we obtain that

$$(c-c_{cr})^{1/3} \approx p_{cr}(\langle \mathbf{E}^2 \rangle_{t_e} - \mathbf{E}_{cr}^2), \qquad (21)$$

where

$$p_{cr} = \frac{6 \left(\dfrac{c v_p}{k_B T} \dfrac{\partial^2 W}{\partial c \, \partial \langle \mathbf{E}^2 \rangle_{t_e}} \right)_{cr}}{\left[3Z'' + cZ''' - \dfrac{v_p}{k_B T} \left(2 \dfrac{\partial^2 W}{\partial c^2} + c \dfrac{\partial^3 W}{\partial c^3} \right) \right]_{cr}}.$$

Moreover, let c_{tr} be the intersection point of the limiting trajectory with the vertical line $\mathbf{E}^2 = 0$. According to Eq. (7), the value of c_{tr} can be evaluated from the equation

$$f_0'(c_{tr}) = f_0'(c_{cr}) - \frac{v_p}{k_B T} \frac{\partial W}{\partial c}(c_{cr}, \mathbf{E}_{cr}^2), \qquad (22)$$

thus, c_{tr} is smaller or larger than c_{cr} according to whether the particle effective polarizability $(\partial^2 W / \partial c \, \partial \mathbf{E}^2)$ is positive or negative. Note that, for a nonconducting suspension, the second term on the right-hand side of Eq. (22) equals $\Lambda_{cr}[\varepsilon_s'(c_{cr})/\varepsilon_s''(0)]$. But since it is proportional to $1/\beta$ and, therefore, tends to $\mp\infty$ when $\beta \to \pm 0$, we can estimate c_{tr} by using the first term in the expression for $f_0'(c_{tr})$ for $c_{tr} \to 0$ at $\beta > 0$ and for $c_{tr} \to c_m$ at $\beta < 0$, which follows from Eqs. (5) and (14) and Eqs. (5) and (15), respectively. Thus we obtain that

$$\ln c_{tr} \approx \left[f_0' - \Lambda_{cr} \frac{\varepsilon_s'}{\varepsilon_s''(0)} \right]_{c_{cr}} \qquad \text{for } \beta > 0,$$

$$\frac{A}{c_m - c_{tr}} \approx \left[f_0' - \Lambda_{cr} \frac{\varepsilon_s'}{\varepsilon_s''(0)} \right]_{c_{cr}} \qquad \text{for } \beta < 0.$$

Figure 3 illustrates the behavior of the trajectories of Eq. (8), which, as was said earlier, are the lines of equal chemical potential, in the phase diagram of a colloidal suspension. It can be seen that the limiting trajectory separates the trajectories into two families. Those of the first, which intersect the axis $\mathbf{E}^2 = 0$ at $c < c_{tr}$ for $(\partial^2 W / \partial c \, \partial \mathbf{E}^2) > 0$ [Fig. 3(a)] and at $c > c_{tr}$ for $(\partial^2 W / \partial c \, \partial \mathbf{E}^2) < 0$ [Fig. 3(b)], will intersect the curve $(\partial \Pi / \partial c) = 0$, but those of the second family, which intersect the axis $\mathbf{E}^2 = 0$ at $c > c_{tr}$ for $(\partial^2 W / \partial c \, \partial \mathbf{E}^2) > 0$ [Fig. 3(a)] and at $c < c_{tr}$ for $(\partial^2 W / \partial c \, \partial \mathbf{E}^2) < 0$ [Fig. 3(b)], will not. It is worth pointing out that, as seen from Fig. 3, $\mathbf{E}^2 / \mathbf{E}_{cr}^2 \to \infty$
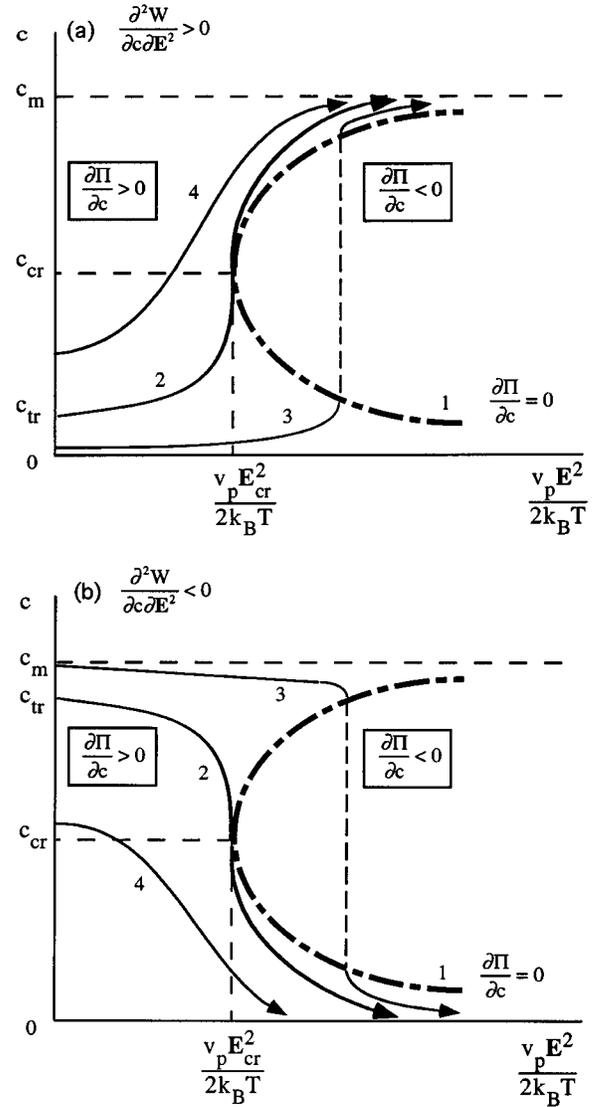
FIG. 3. The lines of equal chemical potential in the phase diagram of a colloidal suspension for $(\partial^2 W / \partial c \, \partial \mathbf{E}^2) > 0$ (a) and for $(\partial^2 W / \partial c \, \partial \mathbf{E}^2) < 0$ (b). 1 is the critical line where aggregation will first occur, 2 is the limiting trajectory of Eq. (8), 3 is the trajectory of Eq. (8) which leads to a phase transition when it intersects 1, whereas 4 is the trajectory of Eq. (8) along which a phase transition does not take place. $(v_p \mathbf{E}^2 / 2 k_B T)$ is the ratio of the electric energy to the thermal energy.

at the intersection point of a trajectory belonging to the first family with the critical line, while the corresponding value of c approaches zero for $(\partial^2 W / \partial c \, \partial \mathbf{E}^2) > 0$ and c_m for $(\partial^2 W / \partial c \, \partial \mathbf{E}^2) < 0$.

The appearance of the two families of trajectories of Eq. (8) implies the existence of two different types of spatial arrangements of the particles under the application of a sufficiently high nonuniform electric field to a colloidal suspension. For one of them, dielectrophoresis will be accompanied by an electric-field-induced phase transition in a suspension whereas, for the other, it will not. In the first case, the spatial arrangement of the particles will change abruptly with an increase in the strength of an electric field when the trajectory of Eq. (8) in the phase diagram intersects the critical line $(\partial \Pi / \partial c) = 0$ (Fig. 3) whereas, in the second case, the corre-
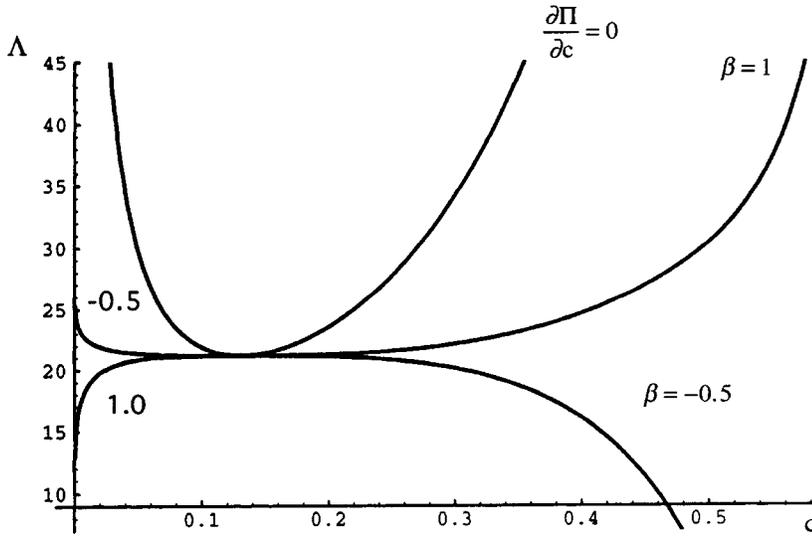
FIG. 4. The limiting trajectories of Eq. (8) at $\beta=-0.5$ and at $\beta=1$ and the critical line $(\partial\Pi/\partial c)=0$ when $\varepsilon_s(c)$ is given by Eq. (16).

sponding change in the spatial particle concentration will be smooth. Figure 4 illustrates the limiting trajectories of Eq. (8) for a nonconducting suspension when $\beta=-0.5$ and $\beta=1$ for the case when $\varepsilon_s(c)$ is given by Eq. (16).

For an open particle system [Eq. (8) subject to Eq. (11)], the condition for the appearance of the phase transition in dielectrophoresis is determined only by the value of c_0, for, as seen from Fig. 3, phase transition will occur when $c_0<c_{\text{tr}}$ for $(\partial^2 W/\partial c\,\partial\mathbf{E}^2)>0$ and when $c_0>c_{\text{tr}}$ for $(\partial^2 W/\partial c\,\partial\mathbf{E}^2)<0$. On the other hand, for a closed particle system [Eq. (8) subject to Eq. (10)], the appearance of a phase transition will depend on the average particle concentration in the suspension. But, since an increase in N in the integral constraint, Eq. (10), corresponds to a vertical shift of the corresponding trajectory describing the particle concentration distribution on the diagram in Fig. 3, there exists a critical value of the number of the particles N_{tr}, such that a phase transition will occur whenever $N<N_{\text{tr}}$ if $(\partial^2 W/\partial c\,\partial\mathbf{E}^2)>0$ and $N>N_{\text{tr}}$ if $(\partial^2 W/\partial c\,\partial\mathbf{E}^2)<0$. This value of N_{tr} is determined by

$$v_p N_{\text{tr}}= \int_{\min_{V_s}(\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e})}^{\max_{V_s}(\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e})} c_{\text{tr}}(\mathbf{E}^2)\,\frac{dV(\mathbf{E}^2)}{d\mathbf{E}^2}\,d\mathbf{E}^2, \quad (23)$$

which follows from Eq. (10), where $c_{\text{tr}}(\mathbf{E}^2)$ is the limiting trajectory on the phase diagram in Fig. 3. Moreover, when the values of the strength of the electric field are close to $\mathbf{E}_{\text{cr}}$, the limiting trajectory Eq. (23) can be approximated by Eq. (21), hence, in this case,

$$N_{\text{tr}}\approx\frac{V_s}{v_p}\left(c_{\text{cr}}+\frac{p_{\text{cr}}^{1/3}}{V_s}\int_{\min_{V_s}(\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e})}^{\max_{V_s}(\langle\mathbf{E}^2(\mathbf{r},t)\rangle_{t_e})}\right.$$
$$\left.\times(\mathbf{E}^2-\mathbf{E}_{\text{cr}}^2)^{1/3}\,\frac{dV(\mathbf{E}^2)}{d\mathbf{E}^2}\,d\mathbf{E}^2\right),$$

where p_{cr} is given by Eq. (21).

It is worth pointing out again that, if the particle concentration in the suspension approaches zero for $(\partial^2 W/\partial c\,\partial\mathbf{E}^2)>0$ and c_m for $(\partial^2 W/\partial c\,\partial\mathbf{E}^2)<0$, the value of $\mathbf{E}^2/\mathbf{E}_{\text{cr}}^2$, at which the phase transition occurs, approaches infinity (Fig. 3).

III. DISCUSSION AND COMPARISON WITH EXPERIMENTAL DATA

The analysis presented above extends the theory [19] of electric-field-induced phase transitions in colloidal suspensions to the case of dielectrophoretic phenomena. Recall that as shown in Ref. [19], Sec. V, the theoretical predictions given there are consistent with the currently available experimental data on electrorheological fluids. However, it is worth pointing out that this theory is not limited to electrorheological fluids. For example, the predicted dependence on the particle size of the threshold electric field needed to trigger the electric-field-induced aggregation in dilute suspensions, i.e., $\mathbf{E}^2\sim 1/v_p$ [see Eq. (20)], is in accord with the observed dependence in biological materials [3,4].

We also found [see Eq. (12)] that the long-range electric-field-induced interparticle interactions do not influence the spatial arrangement of the particles in a nonuniform electric field only when $c(v_p/k_BT)(\partial^2 W/\partial c^2)|_{c=0}(\mathbf{E}^2)\ll 1$. Under these conditions, the particle concentration distribution in a nonconducting suspension is given by the Boltzmann equation Eq. (13). For typical situations pertaining to dielectrophoretic experiments in colloidal suspensions [5–16], $E=5\times10^5$ V/m, $\varepsilon_f/\varepsilon_0=3$, $T=300$ K, particle radius 1 μm and $\beta=0.6$, we obtain from the above expression that electric-field-induced interparticle interactions are negligibly small only for $c\ll10^{-4}$. But, for higher concentrations, their contribution becomes significant. The electric-field-induced interparticle interactions will then lead to the aggregation of the particles when the line of equal chemical potential for a *nonuniform* electric field in the phase diagram of the colloidal suspension [the trajectory of Eq. (8)] intersects the critical line [Fig. 3(a) for $(\partial^2 W/\partial c\,\partial\mathbf{E}^2)>0$ and Fig. 3(b) for $(\partial^2 W/\partial c\,\partial\mathbf{E}^2)<0$]. In this case, the particles with $\beta>0$ will form chainlike aggregates aligned parallel to the electric-field lines whereas the particles having $\beta<0$ will form disk-like aggregates aligned perpendicularly to the electric-field lines (see [19], Sec. V for details). As seen from Figs. 3(a) and 3(b), for particle aggregation to happen, the particle concentration in a suspension should be sufficiently small for $(\partial^2 W/\partial c\,\partial\mathbf{E}^2)>0$ or sufficiently large for $(\partial^2 W/\partial c\,\partial\mathbf{E}^2)<0$. These predictions of the theory are consistent with the char-

acteristic patterns of cell aggregation observed in high-gradient electric fields in the interdigitated microelectrode systems [6–14], specifically ''pearl-chain'' patterns at $(\partial^2 W/\partial c\,\partial \mathbf{E}^2)>0$ and ''diamond'' patterns at $(\partial^2 W/\partial c\,\partial \mathbf{E}^2)<0$ as they were named in [8].

Although Eq. (3) together with Eqs. (16) or (17) do not account for the frequency dependence of the effective polarizability of a particle in a suspension which is induced by the conductivity of the particles and that of the liquid, they provide some insight on how a particle aggregation pattern is affected by the frequency of the applied electric field as was observed in [6–16]. For example, as was shown in Refs. [8, 9], it is possible to vary the polarizability parameter β by changing the frequency of the applied electric field from a negative to a positive value. Therefore, the main qualitative features of the dependence of the aggregation pattern on the frequency of the applied electric field can be analyzed on the basis of the dependence of the aggregation pattern on the polarizability parameter β. Specifically, at frequencies rather close to those for which $\beta=0$, the particles will not aggregate at all according to our analysis since, under such conditions,

$$\Lambda_{max}\approx\frac{3v_p\varepsilon_f\beta^2 \max_{V_s}(\langle \mathbf{E}^2(\mathbf{r},t)\rangle_{t_e})}{k_B T}<\Lambda_{cr}.$$

Hence, two frequencies will exist, one for a positive and the other for a negative value of β, for which the trajectory of Eq. (8) will touch the critical line [Figs. 3(a) and 3(b)] and, thus, particle aggregation is predicted to occur at higher and at lower frequencies, respectively. Therefore, the local particle concentration in the regions of the higher (for $\beta>0$) and of the lower (for $\beta<0$) strength of the electric field will increase with a further increase in $|\beta|$. Such a change in the spatial particle arrangement was observed in [8–10]. An additional abrupt change in the particle concentration distribution will happen in a closed particle system when Λ_{min} exceeds Λ_{cr}, i.e.,

$$\Lambda_{min}\approx\frac{3v_p\varepsilon_f\beta^2 \min_{V_s}(\langle \mathbf{E}^2(\mathbf{r},t)\rangle_{t_e})}{k_B T}>\Lambda_{cr},$$

since in this case all the particles will be incorporated into aggregates. It is conceivable that such a transition took place in experiments [8] at frequencies below 500 Hz where it was observed that all the particles collected on the electrode surface to form a diamond pattern.

To understand the effects of conductivity on the spatial arrangement of the particles in nonuniform electric fields, it would be necessary to consider the general case of the theory [19]. The results obtained in the present paper provide a framework for embarking on such a generalization.

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