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Concentration dependence of droplet deformation in a phase separation process under an electric field

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We show how deformation of droplets, arising in a phase separation process of a two-phase dielectric or conducting liquid composite material under a low frequency electric field, depends on their volume fraction. The electric interactions between distorted particles is taken into account in a self-consistent way based on the effective medium approach. It follows from our model that the main physical mechanism responsible for the dependence of droplets' deformation on the volume fraction is the formation of an effective anisotropic medium. A two-parameter condition of the droplet instability was derived as a function of the dielectric permittivity or conductivity mismatch between the two phases and the volume fraction of the inclusions.

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I. INTRODUCTION

Anisotropy introduction in originally isotropic materials is widely considered as an effective way to obtain desirable mechanical [1], ferroelectric [2,3], and nonlinear optical material properties [4–6]. During the last decade much attention has been paid to the use of external electric fields to achieve this goal. The desired modification of a material is possible if (i) material demonstrates a high susceptibility with respect to an external field and (ii) induced changes are sufficiently stable. Two different approaches are usually applied. One possibility is to introduce an anisotropy at the molecular level [7,8]. Application of a strong constant electric field to a homogeneous glass or polymer sample, heated to an elevated temperature, results in breakdown of the macroscopic inversion symmetry due to ion displacements and/or reorientation of molecular dipoles [7,9]. The asymmetry is "frozen in," when the sample is cooled down. Such a treatment is termed "the thermal poling." Recently, experimental investigations [10,11] have shown that thermal poling of homogeneous silicate glass probably stimulates preferentially oriented crystallization, which enhances the third-order nonlinearity in addition to the breakdown of the inversion symmetry.

Another approach is based on the use of composite material, whose properties strongly depend on its structural microgeometry. To satisfy the conditions (i) and (ii) for a composite material an electric field should be applied during phase separation process and removed after quenching. Indicative experiments carried out for a number of nonpolar polymer systems subject to a low-frequency electric field $E=1-10$ kV/cm [12,13] demonstrated formation of stable strongly elongated particles with a volume $V\approx 10^{-7}-10^{-8}$ cm^3. In general, the degree of elongation depends in a complicated way on relations between the polarization energy U_{el} of the particle, the interface energy U_s, and the elastic ones [14]. The influence of elastic strains upon the shape of inclusions can be neglected if phase separation process occurs in a liquid-liquid system. Such an approximation is also acceptable for glass melts with a forming micro-crystal phase and polymer melt/solvent systems, where inclusions grow like liquid drops and are crystallized by aftercooling [12,15].

Effect of an external electric field on the shape of a droplet surrounded by a liquid dielectric matrix has been thoroughly investigated by Garton and Krasucki [16], who considered the balance between the electric and surface forces. It was shown that (1) the droplet is approximately an ellipsoid elongated along the electric field and (2) at a certain electric field the droplet becomes unstable and breaks up on condition that the ratio of the dielectric constants of two components is bigger than a critical value $p_{cr}\approx 20$. The contribution of the electrostriction effect, which gives rise to a change of the density ρ under an electric field, was neglected in Ref. [16]. In such a case the expression for the surface electric forces is reduced to the much simpler Maxwell stress tensor. The approach is exact for incompressible liquids, but already for weakly compressible media the approximation is satisfactory only for low-frequency electric fields, when the contribution of the electrostriction effect $-\rho(\partial\epsilon/\partial\rho)(E^2/8\pi)$ is compensated by a change of the hydrostatic pressure P and the relation $P-\rho(\partial\epsilon/\partial\rho)(E^2/8\pi)=\text{const}$ remains valid [14,17].

For magnetic suspensions under magnetic field [18] and electrorheological fluids in electric fields [19], a slightly different formalism, based on the consideration of the competi-

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tion between the magnetic/electric polarization energy and the surface energy, was used. The equilibrium shape of a droplet corresponds to the minimum of the free energy

$$F=U_{el}+U_s \tag{1}$$

with respect to the particle shape at given V and $T=\text{const}$. This method gives results which are similar to those obtained from the balance equation for forces [16,18].

The one-particle approximation for the polarization energy [16–19] is only valid in the limit of a small volume fraction f of embedded particles, when the electric interaction between droplets can be neglected. Consequently, this approach results in an expression for the droplet deformation, which is independent of the inclusion concentration [16–19].

To modify properties of a macroscopic system to a degree suitable for a practical application a remarkable value of f is usually required. On increase of the second phase concentration, characteristics of medium surrounding a precipitating particle during phase separation are modified. Such a modification can result in different magnitudes of a droplet deformation at different stages of phase separation process, as it was recently observed [13].

In our work we extend the model of Refs. [16,18] to the case of finite-f composite materials by considering the electric interparticle interaction, which becomes significant on increase of f. Deformation of an individual inclusion is treated in a self-consistent way, taking into account the local electric field, which is formed by the system of distorted inclusions. We derive the dependence of a droplet deformation on the inclusion volume fraction and the droplet instability criterion for a given value of f.

II. MODEL

We consider a two-component system built from identical dielectric liquid droplets immersed into a liquid dielectric matrix. The dielectric permittivities of these components are $\epsilon^{(in)}$ and $\epsilon^{(m)}<\epsilon^{(in)}$ for the inclusion and the host, respectively. Such a two-component "inclusion-host" system is nonsymmetric with respect to the two phases; the property demonstrated by typical composite system investigated in Refs. [12,13,18], for which separation of a matrix and a phase that forms inclusions was immediately observed.

The free energy of an ellipsoidal particle elongated along the direction of a low-frequency (the field is assumed uniform over the particle size) electric field E, which corresponds to the z axis, is given by

$$F_1=-\tfrac{1}{2}P_z(\gamma)E+\alpha s(\gamma)V^{2/3}, \tag{2}$$

where $\gamma=a/b$ is the ratio of the ellipsoid semiaxes (a and b), α is the interface tension coefficient, $P_z(\gamma)$ is the dipole moment of the particle, and

$$V^{2/3}s(\gamma)=\left(\frac{9\pi}{2\gamma^2}\right)^{1/3}\left(1+\frac{\gamma}{ec(\gamma)}\sin^{-1}[ec(\gamma)]\right)V^{2/3} \tag{3}$$

is the ellipsoid surface, with $ec(\gamma)=(1-\gamma^{-2})^{1/2}$ being the eccentricity.

Within the effective medium approach the analyzed system is considered as a set of identical noninteracting ellipsoidal particles with a dielectric permittivity $\epsilon^{(in)}$ in a confocal coat with $\epsilon^{(m)}$, immersed in effective anisotropic medium. The components of the effective dielectric permittivity tensor $\epsilon^{(eff)}$ satisfy the following condition:

$$\epsilon^{(m)}<\epsilon_x^{(eff)}=\epsilon_y^{(eff)}<\epsilon_z^{(eff)}<\epsilon^{(in)}. \tag{4}$$

In this case the equation for the electrostatic potential distribution is

$$\epsilon_x^{(eff)}\frac{\partial^2\varphi}{\partial x^2}+\epsilon_y^{(eff)}\frac{\partial^2\varphi}{\partial y^2}+\epsilon_z^{(eff)}\frac{\partial^2\varphi}{\partial z^2}=0. \tag{5}$$

By means of the coordinate transformation $x'=x/\sqrt{\epsilon_x^{(eff)}}$, $y'=y/\sqrt{\epsilon_y^{(eff)}}, z'=z/\sqrt{\epsilon_z^{(eff)}}$ Eq. (5) is reduced to the Laplace equation for isotropic medium, $\Delta\varphi=0$ [14]. In this way the electrostatic problem for an ellipsoid characterized by a γ, embedded in an anisotropic medium, is transformed into the problem for an ellipsoid with a renormalized $\gamma_r=\gamma(\epsilon_x^{(eff)}/\epsilon_z^{(eff)})^{1/2}$ in an isotropic medium [20].

For a coated inclusion solution of the Laplace equation with the boundary conditions corresponding to the continuity of the potential and the normal component of the electric induction on the "inclusion-coat" and "coat–effective medium" interfaces [21] results in the following expression for the dipole moment of an inclusion with a volume V:

$$P_z(\gamma)=(\epsilon^{(in)}-\epsilon^{(m)})\frac{\epsilon^{(m)}+n_z(\gamma_r)(\epsilon_z^{(eff)}-\epsilon^{(m)})}{\epsilon^{(m)}+n_z(\gamma_r)(\epsilon^{(in)}-\epsilon^{(m)})}\frac{EV}{4\pi}, \tag{6}$$

where

$$n_z(\gamma_r)=\frac{1-ec(\gamma_r)^2}{ec(\gamma_r)^3}\{\tanh^{-1}[ec(\gamma_r)]-ec(\gamma_r)\} \tag{7}$$

is the depolarization coefficient along the z axis [14] and the renormalized semiaxis ratio $\gamma_r<\gamma$ takes into account the effect of macroscopic dielectric anisotropy.

In order to determine $\epsilon^{(eff)}$ we use the Maxwell-Garnett approximation (MGA), which takes into account the dipolar interparticle interaction by means of the Lorenz local field [22]. Strictly speaking, the MGA is not applicable to systems with a high density of embedded particles, where a strong correlation between particles' position requires account of both the pair or higher-order particle correlation and higher multipole moments contribution into the interparticle interaction. However, this approximation gives very good results for the description of properties of random composite systems even with remarkable magnitudes of $f<0.4$, when the component identification as "inclusion-host" mentioned above is possible [23]. For the simple-cubic arrangement of particles the MGA is exact (within the dipole approximation) and for other ordered systems principal features related to the dependence of the dielectric permittivity on f can also be analyzed within the MGA [19,24].

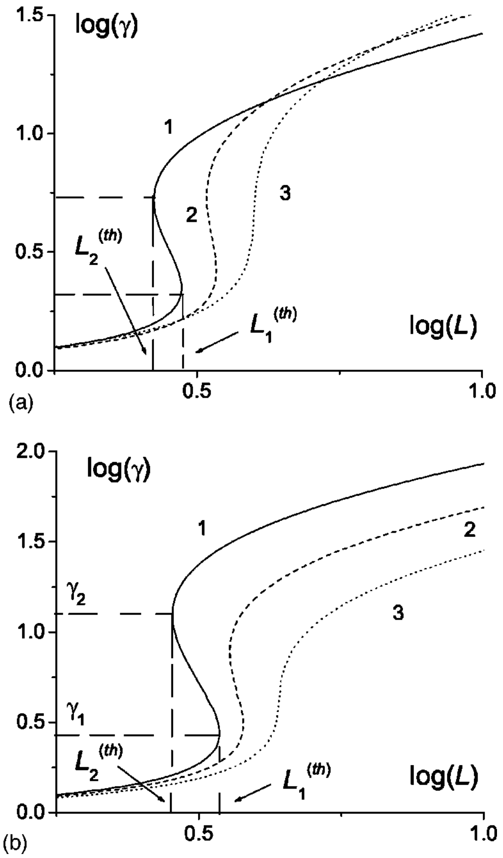

FIG. 1. Dependence of the ellipsoid semiaxis ratio $\gamma(L)$ on the dimensionless parameter L for (a) different volume fractions of inclusions and $p=30$; 1, small volume fraction limit $f\to 0$; 2, $f=0.05$; 4, $f=0.4$ and (b) different ratios of the dielectric constants and $f=0.2$; 1, $p=50$; 2, $p=35$; 3, $p=25$. In this paper function $\log(x)$ designates the decimal logarithm of x.

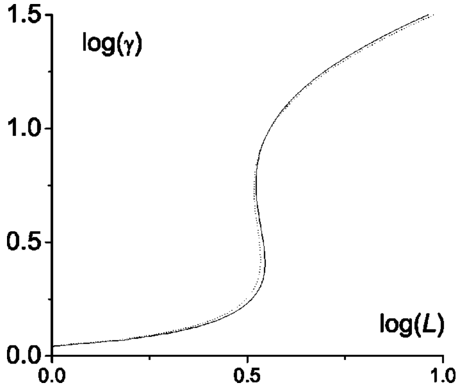

FIG. 2. Dependence of the ellipsoid semiaxis ratio γ on the dimensionless parameter L. Solid curve, Eqs. (6)–(9) and dashed curve, Eqs. (14)–(16); $f=0.05$, $p=30$.

Taking into account the macroscopic anisotropy of the medium, the components of $\epsilon^{(eff)}$ are determined by the system of nonlinear equations [20]

$$\frac{\epsilon_z^{(eff)}}{\epsilon^{(m)}}=\frac{1+[n_z(\gamma_r)(1-f)+f](p-1)}{1+n_z(\gamma_r)(1-f)(p-1)}, \tag{8}$$

$$\frac{\epsilon_x^{(eff)}}{\epsilon^{(m)}}=\frac{1+[n_x(\gamma_r)(1-f)+f](p-1)}{1+n_x(\gamma_r)(1-f)(p-1)}, \tag{9}$$

where $n_x(\gamma_r)=[1-n_z(\gamma_r)]/2$, and $p=\epsilon^{(in)}/\epsilon^{(m)}$ is the ratio of the dielectric permittivities. Within the effective medium approach the free energy F of a unit volume of a composite material can be written as

$$F=-\frac{1}{8\pi}\varepsilon_z^{(eff)}E^2+\frac{f}{V^{1/3}}\alpha s(\gamma). \tag{10}$$

Taking into account that the MGA is exact for the model of identical coated particles filling the entire space [23], Eqs. (8) and (10) can be rewritten as

$$\frac{\epsilon_z^{(eff)}}{\epsilon^{(m)}}=1+4\pi f q_z(\gamma), \tag{11}$$

$$F=F_1\frac{f}{V}-\epsilon^{(m)}\frac{E^2}{8\pi}, \tag{12}$$

where $q_z=P_z(\gamma)/(VE\epsilon^{(m)})$ is the effective polarizability of a volume unit of the model system. Therefore, minimum search of F or F_1 with respect to γ gives an identical result. The equation determining the position of the free energy F_1 extremum can be written as

$$\left(\frac{ds(\gamma)}{d\gamma}\right)\left(\frac{dq_z(\gamma)}{d\gamma}\right)^{-1}=L. \tag{13}$$

The right-hand side of Eq. (13) is a dimensionless parameter $L=(\epsilon^{(m)}E^2V^{1/3})/(2\alpha)$, which characterizes the relative strength of the electric and surface forces.

Figure 1 shows the dependence of the droplet deformation $\gamma(L)$, Eq. (13), for different values of p and f. This dependence is either a monotonic or an S-shaped curve, just as it was obtained within the one-particle approximation for the free energy [16,18]. However, one can see, (Fig. 1) that in addition to the dependence on the dielectric permittivity ratio p, the deformation depends on the volume fraction and is very sensitive to a change of f at large p. Even an increase of f up only to 5% significantly displaces $\gamma(L)$ and makes the S shape less curved, as compared to the limit $f\to 0$ analyzed in Ref. [16]. [cf. curve 1 and curve 2, Fig. 1(a)]. For a small but finite volume fraction the deformation is described well by Eq. (13) with the following approximations for Eqs. (6), (8), and(9) (Fig. 2):

$$P_z(\gamma)\approx\frac{\epsilon^{(m)}(\epsilon^{(in)}-\epsilon^{(m)})}{\epsilon^{(m)}+n_z(\gamma_r)(\epsilon^{(in)}-\epsilon^{(m)})}\frac{EV}{4\pi}, \tag{14}$$

$$\frac{\epsilon_z^{(eff)}}{\epsilon^{(m)}}\approx 1+\frac{f(p-1)}{1+n_z(\gamma_r)(p-1)}, \tag{15}$$

$$\frac{\epsilon_x^{(eff)}}{\epsilon^{(m)}}\approx 1+\frac{f(p-1)}{1+n_x(\gamma_r)(p-1)}. \tag{16}$$

As compared to the case of noninteracting particles [16,18], γ was replaced by γ_r in Eq. (14). This replacement takes into account anisotropic properties of the effective medium. Therefore, when $f \ll 1$ the differences between the results of the one-particle approximation and the MGA are mainly due to the macroscopic anisotropy of the composite system.

III. DISCUSSION

The derivative of the polarization energy density with respect to γ can be considered as an effective polarization surface force T on condition that an ellipsoidal shape is kept. This force contributes to an inclusion elongation and its magnitude is

$$T=\frac{E^2}{8\pi}\frac{d\epsilon_z^{(eff)}}{d\gamma}=\frac{E^2\epsilon^{(m)}}{2}\frac{dq_z}{d\gamma}. \tag{17}$$

The droplet deformation dependence on f is determined by the behavior of this force as a function of the volume fraction. In the analysis above we considered f as a parameter. It is convenient now to view f as an independent variable along with γ and introduce the function $r(\gamma,f)=\partial q_z/\partial\gamma$. Let γ be fixed. If $r(\gamma,f)$ is a decreasing function of f, then L increases when f increases [see Eq. (13)], i.e., the curve $\gamma(L)$ is displaced toward larger L. It means that for a given L the deformation decreases if the value of f increases and $\partial r(\gamma,f)/\partial f<0$.

From the practical point of view the most interesting situation corresponds to $p \gg 1$ and stable strongly elongated inclusions. For the case $\gamma \gg 1$ the depolarization coefficient can be estimated as

$$n_z(\gamma)\approx\frac{1}{\gamma^2}Z(\gamma), \quad Z(\gamma)=\ln(2\gamma)-1. \tag{18}$$

Equation (18) is already valid for $\gamma>4$ within a 10% accuracy. $Z(\gamma)$ is a slowly varying function and in a first approximation can be considered as a constant. Taking into account that for $f \ll 1\, \gamma_r \approx \gamma(1+fp)^{-1/2}$ we obtain

$$\frac{\partial}{\partial f}r(\gamma,f)>0 \quad \text{for} \quad \gamma>\gamma_0\approx\sqrt{(1+fp)pZ(\gamma_0)}, \tag{19}$$

$$\frac{\partial}{\partial f}r(\gamma,f)<0 \quad \text{for} \quad \gamma<\gamma_0. \tag{20}$$

Thus, in the region $\gamma \gg 1$ for a finite $f=f_{fin}$ the curve $\gamma(L)$ is shifted towards higher L with respect to the curve for $f\to 0$ if $\gamma<\gamma_0(f_{fin})$ and to lower values of L if $\gamma>\gamma_0(f_{fin})$ [Fig. 1(a)]. In accordance with Eq. (19), a rise of f_{fin} results in an increase of $\gamma_0(f_{fin})$. These results mean that for a given L and the volume fraction increase the deformation decreases if $\gamma<\gamma_0(f_{fin})$ and increases if $\gamma>\gamma_0(f_{fin})$.

Differentiating Eq. (13) with respect to L and taking into account that

$$\frac{d^2F}{d\gamma^2}=\alpha V^{2/3}\frac{d^2s(\gamma)}{d\gamma^2}-\frac{\epsilon^{(m)}E^2V}{2}\frac{d^2q_z(\gamma)}{d\gamma^2}, \tag{21}$$

we obtain

$$\frac{d\gamma}{dL}\frac{d^2F}{d\gamma^2}=\alpha V^{2/3}\frac{dq_z(\gamma)}{d\gamma}. \tag{22}$$

The effective polarizability along z axis, $q_z(\gamma)$, increases if a particle becomes more elongated and consequently $(d\gamma/dL)(d^2F/d\gamma^2)>0$. Thus, a point where $d\gamma(L)/dL<0$ corresponds to a free-energy maximum $(d^2F/d\gamma^2<0)$, i.e., a thermodynamically unstable state.

The presence of the unstable states, corresponding to an interval $\gamma_1<\gamma<\gamma_2$ on the S-shaped curve, means that droplet deformation can be considered as a first-order phase transition [25]. When the inclusion deformation reaches $\gamma_1(L_1^{(th)})$ on increasing the electric field G and/or the volume V a direct transformation occurs from weakly elongated to strongly elongated stable state. The reverse transition happens at $\gamma_2(L_1^{(th)})$ on decreasing E and/or V. Thus, for the S-shaped curve there are two thresholds $L_1^{(th)}>L_2^{(th)}$ bounding the instability area where $d\gamma(L)/dL<0$ (Fig. 1).

The thresholds correspond to extrema of $L(\gamma)$. To estimate $L_2^{(th)}$ and γ_2 we use Eq. (18) and $s(\gamma)\propto\gamma^{1/3}$ for $\gamma \gg 1$. These approximations give

$$\gamma_2\propto\sqrt{p(1+fp)Z(\gamma_2)}, \tag{23}$$

$$L_2^{(th)}\propto p^{-5/6}[(1+fp)Z(\gamma_2)]^{1/6}. \tag{24}$$

An analytical estimation for $L_1^{(th)}$ is not possible because sufficiently accurate approximations of $s(\gamma)$ and $n_z(\gamma)$ are not available for $\gamma\approx 2$–3, the range where γ_1 is located. These thresholds move towards higher L-values if f increases but towards lower L-values if p increases [Fig. 1 and Eq. (24)]. For a given p disappearance of the instability region (transition from the S shape to a monotonic curve) occurs when the volume fraction of inclusions exceeds a critical value $f_{cr}(p)$. Similarly, for a given f the same transition takes place if p becomes smaller than $p_{cr}(f)$. This two-parameter condition of droplet instability can be considered as a dependence of the critical ratio p_{cr} on the volume fraction. We have determined the function $p_{cr}(f)$ numerically. Figure 3 can be considered as a "phase diagram" which shows how the behavior of the system changes with change of parameters. In the area A the deformation increases monotonically with increase of L. The area B located above the curve $p_{cr}(f)$ corresponds to the S-shaped curve of $\gamma(L)$ and, consequently, to the existence of the thermodynamically unstable states. In A one minimum of the free-energy exists for a set of parameters (α,V,G), while in B two equilibrium states are present. Those states correspond to a weak $(\gamma<\gamma_1)$ and a strong $(\gamma>\gamma_2)$ droplet deformation, respectively (Fig. 1). One should note (1) $\lim_{f\to 0}p_{cr}(f)\approx 20$ corresponds to the Garton-Krasuki result; 2) the dependence $p_{cr}(f)$ is relatively strong for $f<0.10$ and weak in the volume fraction interval $0.15<f<0.25$; and (3) for a large ratio

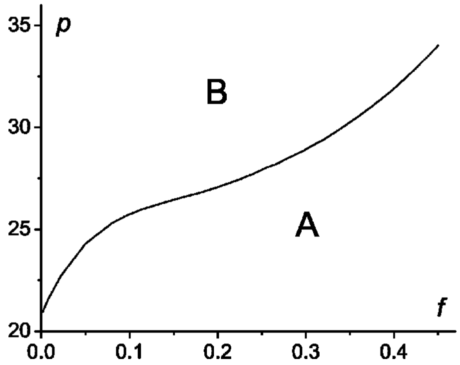

FIG. 3. Graphical representation of the two-parameter condition of droplet stability/instability. The curve represents parameters for which transition occurs between the area where only one (A) or two (B) stable states are possible.

$p > 40$ the instability regime can be observed at any volume fraction, if the MGA is satisfactory.

For real heterogeneous dielectrics the electric field distribution at low frequencies,

$$\omega \ll \frac{\sigma^{(m)}+(\sigma^{(in)}-\sigma^{(m)})n_z(\gamma)}{\epsilon^{(m)}+(\epsilon^{(in)}-\epsilon^{(m)})n_z(\gamma)}, \qquad (25)$$

is defined by a small but finite components' conductivity $\sigma^{(in)}, \sigma^{(m)}$ [26,27]. In contrast to the case of perfect dielectric systems, charge accumulation at the "droplet-host" interface results in a nonzero tangential component of the Maxwell stress tensor and related liquid motions both inside and outside droplets. This effect must be taken into account to describe droplet deformation [28,29]. In general, combination of the tangential stress and the hydrodynamic motion makes analytical description of the droplet shape very complicated, except for the case of small deformations (close to the spherical shape). In particular, in conductive systems droplet elongation perpendicular to the electric field is also possible. According to the leaky dielectric theory [28] the type of deformation is determined by the sign of the function Φ:

$$\Phi = p^{-1}(R^2+1)-2+3(p^{-1}R-1)\frac{(2M^{-1}+3)}{(5M^{-1}+5)}, \qquad (26)$$

where $M=\eta^{(in)}/\eta^{(m)}, R=\sigma^{(in)}/\sigma^{(m)}$are the viscosity and the conductivity ratios. For $\Phi > 0$ elongation is parallel and for $\Phi < 0$ it is perpendicular to the electric field. Taking into account conductivity such type of droplet deformation can be qualitatively considered within the free-energy minimization method [30]. The approach neglects the hydrodynamic aspects and generally is not suitable for quantitative description of the effect of droplets elongation in the direction perpendicular to the electric field. It is therefore important to know the domain where the hydrodynamic contribution is small and the present model is still applicable for quantitative description of conductive systems.

Numerical simulations showed [31] that if the conductivity ratio $R > 30 \gg p$, the contribution of the tangential component is small and droplet deformation is mainly determined by the normal stresses. In that case the elongated ellipsoid approximation is still valid and the present model can be used. In a real system the conductivity ratio can change in a very wide range, and systems with the ratio as high as > 200 were experimentally investigated (see, for example, [13,34]). Such experiments have shown [12,13,28,29,33,34] that for systems with $R \gg p$ droplet elongation in a direction parallel to the electric field is observed, in agreement with the leaky dielectric theory ($\Phi > 0$).

The free energy of a composite system with weakly conducting components is given by Eq. (10), with $\epsilon^{(eff)}$ determined within, for example, the Maxwell-Wagner approach [26,27]. Taking into account a macroscopic anisotropy this approach results in expressions similar to Eqs. (8) and (9), where all dielectric constants are replaced by the complex conductivities $\sigma^* = \sigma + i\omega\epsilon$. The real and imaginary parts of $\sigma^{(eff)*}$ determine $\sigma^{(eff)}$ and $\epsilon^{(eff)}$, respectively. Those complicated equations are simplified if (i) the electric field satisfies the low-frequency condition, Eq. (25), and the limit $\omega \to 0$ can be assumed; (ii) $R \gg p$; and (iii) $n(\gamma_r)\sigma^{(in)} \gg \sigma^{(m)}$. In this case the equations for $\epsilon^{(eff)}$ are reduced to Eqs. (8) and (9) with the replacement of all the dielectric constants by corresponding real conductivities on the right side. Thus, for conductive systems, which satisfy the conditions (i)–(iii), the main results for the dependence of the droplet deformation and instability thresholds on the volume fraction are still valid with the replacement of p by R. One should note that the conditions above imply that (i) $\epsilon^{(eff)}$ and $\sigma^{(eff)}$ are frequency independent; (ii) charge accumulation is more important than the polarization effect; and (iii) the condition (iii) restricts a droplet elongation to guarantee that the field inside elongated inclusions remains small.

As applied to conductive systems the present model describes the competition between the surface energy and the electric energy related with a charge accumulation at the interface, and is valid only for areas where this competition is favorable for existence of stable elongated droplets. In the case of an S-shaped curve, and the parameters corresponding to the instability area ($\gamma_1 < \gamma < \gamma_2$), perturbations connected with the tangential electric stress and hydrodynamic forces can break up deformed droplets, prohibiting their direct transformation into strongly elongated inclusions [13]. That situation is different from magnetic suspensions under magnetic field, which are analogous to perfect dielectrics and where the phase transition described above is immediately observed [18,25].

It is known that composite polymer systems with $R \gg p$ demonstrate on experiment stable columns oriented along the electric field [12,13]. Within the present theory such columns can be considered as a limiting case corresponding to the upper branch of equilibrium states $\gamma > \gamma_2$ (Fig. 1). Their formation is due to fusion of smaller individual droplets [13], which previously formed chains along the field under the influence of interparticle interactions by the same way as dispersed particles in electrorheological fluids [32]. This alignment increases the efficiency of the fusion process, which in the absence of external forces is remarkable only for a high volume fraction of embedded particles [32]. Both the appearance of the strongly elongated states (when E increases) and their destruction (when E decreases) demonstrate a threshold dependence on the magnitude of the electric field [12,13,34]. The existence of the destruction threshold corresponds to the area B (Fig. 3), where both strong and weak deformation states of inclusions are separated by the thermodynamically unstable area. When due to the instability a column breaks down into a set of small droplets the chain arises again as the preferable energetic state. The inverse process of a column formation is not connected to the inclusion instability and is determined by fusion of droplets, when the space between inclusions vanishes as a result of an individual droplet elongation [13].

In general, the deformation magnitude depends on all physical parameters included in the droplet equation of state, Eq. (13). For example, the surface tension can change during phase separation, so that the value of α is not well defined. This effect will give the same tendency in the change of the droplet deformation as the interparticle interaction. Recently, for polystyrene-poly(methyl methacrylate)-toluene mixture ($p \approx 1, R < 10$) an effect of the relatively small droplet deformation in late stages of phase separation in comparison with earlier stages was observed and qualitatively ascribed to an increase of α [13].

However, in systems corresponding to the area B (Fig. 3) the instability thresholds of the deformation (γ_1, γ_2) do not depend on the surface tension. Therefore, for such systems contributions of a surface tension change and the interparticle interaction can be separated by measuring the instability threshold dependence on the volume fraction.

The approach developed here is exact in the case of not very dense random distribution of droplets in a liquid host or their simple-cubic arrangement. Probably, further progress could be obtained on the basis of the microscopic mean-field approach [24], which takes into account anisotropic structure via construction of a pair distribution function of hard spheres with identical rigid dipoles. To apply this approach to the problem of deformation this distribution function should be generalized for identical ellipsoidal particles oriented along the field direction.

A limitation of the present approach is connected with the point-dipole approximation. Although its use for description of electrorheological fluids containing solid ellipsoidal particles gives reasonable results [35], a more rigorous consideration is required for strongly elongated inclusions, because of deviation of the particle from the ellipsoidal shape and a contribution of high multipole moments to the polarization forces.

IV. CONCLUSION

We have considered a two-component system built from identical dielectric or conducting liquid droplets immersed into a liquid dielectric or conducting matrix subject to a low-frequency external electric field. It was shown, for the first time to our best knowledge, how the droplets' deformation depends on their volume fraction, when the electric interaction between droplets in a liquid composite system is taken into account. The expressions describing this dependence were derived in a self-consistent way based on the Maxwell-Garnett approximation. The model predicts a deformation decrease for weakly elongated and an elongation increase for extremely elongated columnlike inclusions on increase of the droplet volume fraction. Within the model, the main physical mechanism responsible for the experimentally observed dependence of droplets' deformation on the volume fraction was found to be the formation of an effective anisotropic medium. The droplet instability condition on the volume fraction was determined numerically. The instability thresholds increase when the inclusion volume fraction increases. Thanks to this effect, it is possible to distinguish the influence of a surface tension change and the electric interaction between droplets on the deformation.

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