Nonlinear ac response of anisotropic composites

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When a suspension consisting of dielectric particles having nonlinear characteristics is subjected to a sinusoidal (ac) field, the electrical response will in general consist of ac fields at frequencies of the higher-order harmonics. These ac responses will also be anisotropic. In this work, a self-consistent formalism has been employed to compute the induced dipole moment for suspensions in which the suspended particles have nonlinear characteristics, in an attempt to investigate the anisotropy in the ac response. The results showed that the harmonics of the induced dipole moment and the local electric field are both increased as the anisotropy increases for the longitudinal field case, while the harmonics are decreased as the anisotropy increases for the transverse field case. These results are qualitatively understood with the spectral representation. Thus, by measuring the ac responses both parallel and perpendicular to the uniaxial anisotropic axis of the field-induced structures, it is possible to perform real-time monitoring of the field-induced aggregation process.

I. INTRODUCTION

When a suspension of highly polarizable dielectric particles is subjected to an intense electric field, the induced dipole moments cause the particles to form chains along the field direction, resulting in complex anisotropic structures. These chain structures alter the apparent viscosity of the suspension by several orders of magnitude, and are the basis of the electrorheological (ER) effect. Under the action of the ER effect, the arrangement of particles or the shape of the lattice changes, and the local electric field deviates from the Lorentz cavity field [1]. As a result, these structures have anisotropic physical properties, such as in the effective conductivity and permittivity [2], and in the optical nonlinearity enhancement [3]. The rapid field-induced aggregation and the large anistropy in their properties render this field-induced structured material potentially important for technological applications [4].

Moreover, the applied electric field used in most ER experiments is quite high, and important data on nonlinear ER effects induced by a strong electric field have been reported recently [5]. A convenient method of probing the nonlinear characteristics of the field-induced structures is to measure the harmonics of the nonlinear polarization under the application of a sinusoidal (ac) electric field. Thus by measuring the ac responses both parallel and perpendicular to the uniaxial anisotropic axis of the structures, it is possible to perform a real-time monitoring of the field-induced aggregation process.

Recently, the effect of nonlinear characteristics on the interparticle force has been analyzed in an ER suspension of nonlinear particles [6] and further extended to a nonlinear host medium [7]. The nonlinear characteristics are due to the field dependence of the dielectric constants of the materials used in ER fluids, which have a constitutive relation $\mathbf{D} = \epsilon\mathbf{E} + \chi\mathbf{E}^3$. When a nonlinear composite with nonlinear dielectric particles embedded in a host medium, or with a nonlinear host medium, is subjected to a sinusoidal field, the electrical response in the composite will, in general, be a superposition of many sinusoidal functions [8,9]. It is natural to investigate the effects of nonlinear characteristics on the ac response in an ER fluid, which can be regarded as a nonlinear composite medium [10]. The strength of the nonlinear polarization should be reflected in the magnitude of the harmonics.

In this work, we will develop a perturbation expansion [11] method and a self-consistent theory [12] to calculate the ac response of a nonlinear composite. The paper is organized as follows. In the following section, we calculate the dipole moment of the polarized spherical particles in an anisotropic composite and extract the harmonic response. In Sec. III, we perform a series expansion of the local field inside the particles from the self-consistent solution, in an attempt to obtain analytic expressions of the higher harmonics of the dipole moment. Numerical results are performed in Sec. IV to validate the analytic results. Discussions on the results will be given.

II. NONLINEAR POLARIZATION AND ITS HIGHER HARMONICS

We first examine the effect of nonlinear characteristics on the induced dipole moment. We concentrate on the case where the suspended particles have a nonlinear dielectric constant, while the host medium has a linear dielectric constant ϵ_2. The nonlinear characteristics give rise to a field-dependent dielectric coefficient [13]. In which case, the electric-displacement–electric-field relation inside the spheres is given by

$$\mathbf{D}_1 = \epsilon_1\mathbf{E}_1 + \chi\langle E_1^2\rangle\mathbf{E}_1 = \tilde{\epsilon}_1\mathbf{E}_1, \qquad (1)$$

where ϵ_1 and χ are the linear coefficient and the nonlinear coefficient of the suspended particles, respectively.

This constitutes an approximation: the local field inside the particles is assumed to be uniform and the assumption is called the decoupling approximation [12]. It has been shown that such an approximation yields a lower bound for the accurate result for the local field [12]. We further assumed that both ϵ and χ are independent of frequency, which is a

valid assumption for low-frequency processes in ER fluids. As a result, the induced dipole moment under an applied field $\mathbf{E}=E(t)\hat{\mathbf{z}}$ is given by

$$\tilde{p}=\tilde{\epsilon}_e a^3 \tilde{b} E(t), \qquad (2)$$

where $\tilde{b}$ is the field-dependent dipolar factor and is given by

$$\tilde{b}=\frac{\tilde{\epsilon}_1-\epsilon_2}{\tilde{\epsilon}_1+2\epsilon_2}=\frac{\epsilon_1+\chi\langle E_1^2\rangle-\epsilon_2}{\epsilon_1+\chi\langle E_1^2\rangle+2\epsilon_2}. \qquad (3)$$

In order to obtain the effective dielectric constant $\tilde{\epsilon}_e$, we invoke the Maxwell-Garnett approximation (MGA) for anisotropic composites [1]. For the longitudinal field case when the ac field is applied along the uniaxial anisotropic axis, the MGA takes on the form

$$\frac{\tilde{\epsilon}_e-\epsilon_2}{\beta_L\tilde{\epsilon}_e+(3-\beta_L)\epsilon_2}=f\frac{\tilde{\epsilon}_1-\epsilon_2}{\tilde{\epsilon}_1+2\epsilon_2}, \qquad (4)$$

whereas for a transverse field case when the ac field is applied perpendicular to the uniaxial anisotropic axis, the MGA reads

$$\frac{\tilde{\epsilon}_e-\epsilon_2}{\beta_T\tilde{\epsilon}_e+(3-\beta_T)\epsilon_2}=f\frac{\tilde{\epsilon}_1-\epsilon_2}{\tilde{\epsilon}_1+2\epsilon_2}, \qquad (5)$$

where β_L and β_T denote the local field factors parallel and perpendicular to the uniaxial anisotropic axis, respectively, and f is the volume fraction of particles. These factors are defined as the ratio of the local field in the particles to the Lorentz cavity field [1]. For isotropic composites, $\beta_L=\beta_T=1$, while both β_L and β_T will deviate from unity for an anisotropic distribution of particles in composites. The β factors have been evaluated in a tetragonal lattice of dipole moments [1] and similar quantities were calculated in various field-induced structured composites [14]; they satisfy the sum rule,

$$\beta_L+2\beta_T=3.$$

In what follows, we denote β_L as β for notational convenience.

On the other hand, the effective nonlinear dielectric constant can be given by [13]

$$\tilde{\epsilon}_e=\frac{1}{E^2(t)V}\int_V \epsilon(\mathbf{r})|\mathbf{E}(\mathbf{r},t)|^2 dV$$

$$=\frac{f\tilde{\epsilon}_1}{E^2(t)}\langle E_1^2\rangle+\frac{(1-f)\epsilon_2}{E^2(t)}\langle E_2^2\rangle, \qquad (6)$$

where V is the volume of the composite and f is the volume fraction. Accordingly, the local electric field inside the spheres can be expressed in terms of the derivative of $\tilde{\epsilon}_e$ with respect to $\tilde{\epsilon}_1$,

$$\langle E_1^2\rangle=\frac{1}{f}E^2(t)\frac{\partial\tilde{\epsilon}_e}{\partial\tilde{\epsilon}_1}. \qquad (7)$$

If we apply a sinusoidal electric field, i.e., $E(t)=E_0\sin(\omega t)$, the induced dipole moment $\tilde{p}$ will depend on time sinusoidally too. By virtue of the inversion symmetry, $\tilde{p}$ is a superposition of odd-order harmonics such that

$$\tilde{p}=p_\omega\sin\omega t+p_{3\omega}\sin 3\omega t+\cdots. \qquad (8)$$

Also, the local electric field contains similar harmonics

$$\sqrt{\langle E_1^2\rangle}=E_\omega\sin\omega t+E_{3\omega}\sin 3\omega t+\cdots. \qquad (9)$$

These harmonic coefficients can be extracted from the time dependence of the solution of $\tilde{p}$ and $E_1(t)$.

III. ANALYTIC SOLUTIONS

In what follows, we will apply two methods to extract the harmonics of the induced dipole moment and the electric field: the perturbation expansion method (PEM) [11,10] and the self-consistent (SC) theory [12]. The self-consistent theory can deal with the case of strong nonlinearity, while the perturbation expansion method is applicable to weak nonlinearity only, i.e., $\chi\langle E_1^2\rangle\ll 1$, limited by the convergence of the series expansion. In the case of weakly nonlinear response, the SC theory should agree with PEM.

A. Perturbation expansion method

We expand $\tilde{p}$ and $\sqrt{\chi\langle E_1^2\rangle}$ into a Taylor expansion

$$\tilde{p}=a^3 E(t)\sum_{n=0}^{\infty} a_n(\chi\langle E_1^2\rangle)^n, \qquad (10)$$

$$\sqrt{\chi\langle E_1^2\rangle}=\frac{\sqrt{\chi E^2(t)}}{f^{1/2}}\sum_{m=0}^{\infty} d_m(\chi\langle E_1^2\rangle)^m, \qquad (11)$$

where

$$a_n=\frac{1}{n!}\frac{\partial^n}{\partial\tilde{\epsilon}_1^n}(\tilde{\epsilon}_e\tilde{b})\bigg|_{\tilde{\epsilon}_1=\epsilon_1}, \qquad d_m=\frac{1}{m!}\frac{\partial^m}{\partial\tilde{\epsilon}_1^m}\sqrt{\frac{\partial\epsilon_e}{\partial\tilde{\epsilon}_1}}\bigg|_{\tilde{\epsilon}_1=\epsilon_1}.$$

For weak nonlinearity, we can rewrite Eqs. (10) and (11) keeping the lowest orders of $\chi E^2(t)$ and $\chi\langle E_1^2\rangle$,

$$\sqrt{\chi\langle E_1^2\rangle}=\frac{\sqrt{\chi E^2(t)}}{f^{1/2}}(d_0+d_1\chi\langle E_1^2\rangle), \qquad (12)$$

$$\tilde{p}=a^3 a_0 E(t)+\frac{1}{f}a^3 a_1 d_0^2\chi E^3(t)\equiv h_1 E(t)+h_3\chi E^3(t). \qquad (13)$$

In the case of a sinusoidal field, we can expand $E^3(t)$ in terms of the first and the third harmonics. A comparison with Eq. (8) yields the harmonics of the induced dipole moment,

$$p_\omega = h_1 E_0 + \frac{3}{4} h_3 \chi E_0^3, \quad p_{3\omega} = -\frac{1}{4} h_3 \chi E_0^3.$$

Similarly, we find the harmonics of the local electric field

$$\chi^{1/2} E_\omega = j_1 \chi^{1/2} E_0 + \frac{3}{4} j_3 (\chi^{1/2} E_0)^3,$$

$$\chi^{1/2} E_{3\omega} = -\frac{1}{4} j_3 (\chi^{1/2} E_0)^3,$$

where

$$j_1 = d_0 / f^{1/2}, \quad j_3 = d_0^2 d_1 / f^{3/2}.$$

In the above analysis, we have used the identity $\sin^3 \omega t = \frac{3}{4} \sin \omega t - \frac{1}{4} \sin 3\omega t$ to obtain the first and the third harmonics. Similar analysis can be used to extract higher-order harmonics, by retaining more terms in the series expansion.

B. Self-consistent theory

Equation (7) is actually a self-consistent equation since its right-hand side depends on the local field itself. It must be solved self-consistently, and the local electric field reads

$$\sqrt{\chi \langle E_1^2 \rangle} = \frac{-2(3)^{1/3} R + 2^{1/3} (9Q\sqrt{T} + \sqrt{3}\sqrt{4R^3 + 27Q^2 T})^{2/3}}{6^{2/3} \sqrt{T} (9Q\sqrt{T} + \sqrt{3}\sqrt{4R^3 + 27Q^2 T})^{1/3}}, \tag{14}$$

where

$$Q = 3\epsilon_2 \chi^{1/2} E(t), \quad R = \epsilon_1 T + \epsilon_2 (2 + f\beta), \quad T = 1 - f\beta.$$

For a sinusoidal applied electric field, we determine numerically the harmonics of the induced dipole moment and the local electric field, which is a subject for the following section.

IV. NUMERICAL RESULTS

In this section, we perform numerical calculations to investigate the effects of nonlinear characteristics on the harmonics of the induced dipole moment and the local electric field. As shown in Sec. III, the harmonics of the induced dipole moment and the local electric field are both related to the field-induced anisotropy parameter β. In order to investigate the effect of field-induced anisotropy on the harmonics, we perform numerical calculations. Without loss of generality, we let $f = 0.09$, $a = 1$, $\epsilon_1 = 10$, and $\epsilon_2 = 1$ for model calculations. We let $p_0 = \epsilon_e a^3 b E_0$ to normalize the induced dipole moment.

In Fig. 1, we plot the normalized harmonics versus β by using the SC theory for the longitudinal electric field. It is evident that, for increasing β, the harmonics of the induced dipole moment and the local electric field are both increased. Similarly, in Fig. 2 the same quantities are plotted but for the transverse electric field. We find that the harmonics are decreased as β increases.
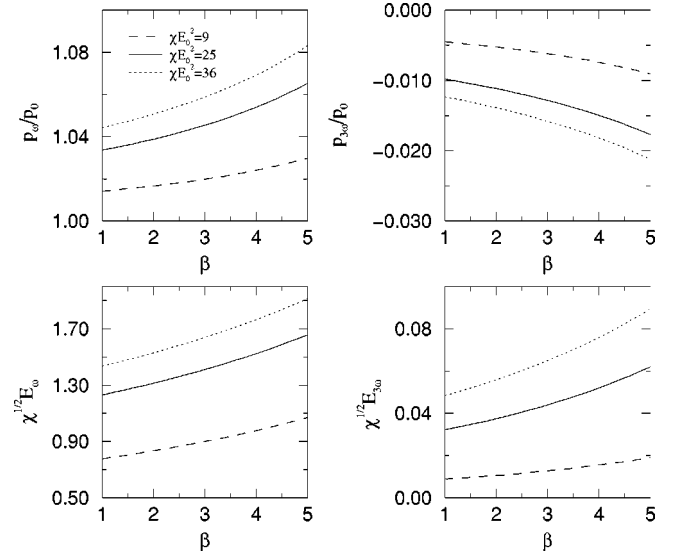
Both Figs. 1 and 2 also show that the harmonics are

FIG. 1. The harmonic responses of the induced dipole moment and the local electric field versus β for the longitudinal field case: $\chi E_0^2 = 9$ (dotted lines), $\chi E_0^2 = 25$ (solid lines), and $\chi E_0^2 = 36$ (dashed lines).

strongly dependent on the nonlinear response of the suspended particles. Moreover, increasing the nonlinear response leads to an increase in the harmonics. This is consistent with the results of our recent work [15], in which a pair of nonlinear particles suspended in a linear host was considered.

In Figs. 3 and 4, we compare the SC theory and PEM. For weak nonlinearity, $\chi E_0^2 = 0.09$, the PEM results coincide with the SC results, while for moderate nonlinearity, $\chi E_0^2 = 0.9$, there are some deviations. In both cases, we find that the PEM results are in good agreement with the SC results for weak nonlinearity. For strong nonlinearity, there are large deviations (not shown here) and the SC theory must be used.

The β dependence of the local field can qualitatively be understood from the spectral representation [16]. From Eq.
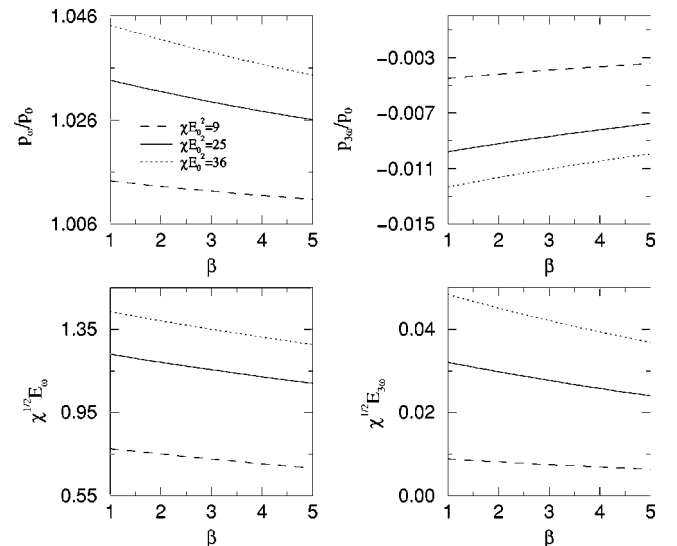

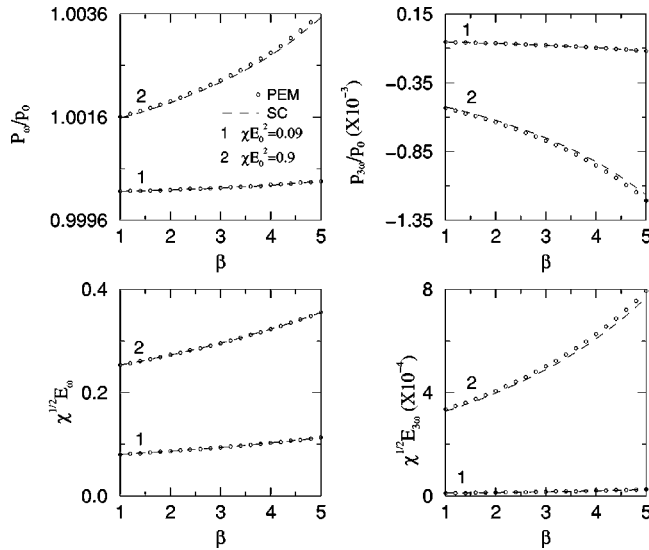FIG. 2. Same as Fig. 1, but for the transverse field case.

FIG. 3. The comparison between the SC theory and PEM with $\chi E_0^2 = 0.09$ and $\chi E_0^2 = 0.9$ for the longitudinal field case.

FIG. 4. Same as Fig. 3, but for the transverse field case.

(7), denoting $s = (1 - \epsilon_1/\epsilon_2)^{-1}$, we find that $E_1 = sE_0/(s - s_1)$, where $s_1 = (1 - \beta f)/3$. Using the numerical values of our model calculations, we find $s = -1/9$ and $E_1 = (1/9)E_0/(1/9 + s_1)$. When β increases, s_1 decreases, leading to an increase in the local electric field E_1.

V. DISCUSSION AND CONCLUSION

Here a few comments on our results are in order. In the present study, we have examined the case of nonlinear particles suspended in a linear host. We may extend our considerations to a nonlinear host medium [7]. In this case, preliminary results show that qualitatively similar yet more complex behaviors in the ac response have been observed.

So far, we have not considered the frequency dependence of the particle dielectric constant. We have assumed that both ϵ and χ are independent of frequency, which is a valid assumption for low-frequency processes in ER fluids. We estimate that $\omega < 10^4$ Hz for these assumptions to be valid. At higher frequencies, the dielectric constant of the particles can decrease with the increase of the frequency. For simplicity, we may adopt the Debye relaxation expression for ϵ_1. Preliminary results show that the ratio of the third to first harmonic decreases with frequency: results that are in accord with recent experimental data of Ref. [5].

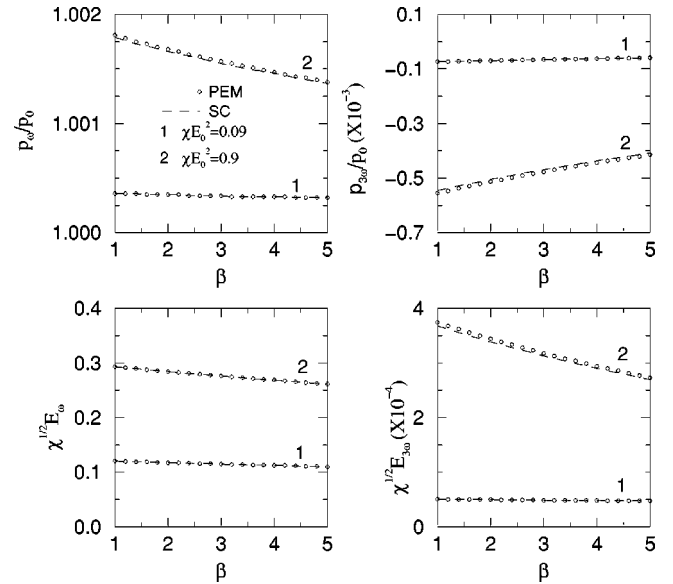Our theory is based on the point-dipole approximation

because the Maxwell-Garnett theory has been used. When the particles approach and finally touch, the mutual polarization effects become important and we expect the Maxwell-Garnett theory to break down. We believe that our theoretical predictions are likely to be valid until the particles form chains along the field direction.

To our knowledge, an accurate evaluation of the local field factor β during field-induced aggregation is lacking. We suggest that the Ewald method [1] can be extended to compute the β factor in the computer simulation of ER fluids. This is a formidable task for the future. Our present theory may be applied to the electrorheology of milk chocolate [17]. By measuring the nonlinear ac response, it may be possible to monitor the food production processes.

In conclusion, a self-consistent formalism has been employed to compute the induced dipole moment for suspensions in which the suspended particles have nonlinear characteristics, in an attempt to investigate the anisotropy in the ac response.

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