Nonlinear alternating current response of colloidal suspension with an intrinsic dispersion

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When a sinusoidal (ac) field is applied to a suspension containing nonlinear dielectric particles, the electrical response will generally consist of ac fields at frequencies of the higher-order harmonics. The situation is further complicated by an intrinsic dielectric dispersion, which often occurs due to the surface conductivity or inhomogeneous structure of the particles. We develop a perturbation method to investigate the effect of intrinsic dielectric dispersion on the harmonics of local field as well as induced dipole moment. The results showed, for weak intrinsic dispersion strength, the ratio of the third to first harmonics of the induced dipole moment decreases as the frequency increases, which is qualitatively in agreement with experiment. However, for a strong dispersion strength, the harmonics ratio increases as the frequency increases. Moreover, an increase in the intrinsic relaxation time may increase the strength of the harmonics.
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I. INTRODUCTION

When an intense electric field is applied to a suspension containing highly polarized particles embedded in a host fluid, the particles will form chains due to the induced dipole moments inside the particles, and hence complex anisotropic structures occur. Also, the apparent viscosity of the suspension will be enhanced greatly. These structures can have anisotropic physical properties, such as effective conductivity and permittivity.[1,2] In this case, optical nonlinearity enhancement was found as well.[3]

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.[4] Therefore, it is possible to perform a real-time monitoring of the field-induced aggregation process in such a suspension by measuring the optical nonlinear ac responses both parallel and perpendicular to the uniaxial anisotropic axis. Recently, an anisotropic Maxwell–Garnett theory[5] was applied to study the nonlinear polarization of these anisotropic structures.[6] Anisotropic optical nonlinear ac response was indeed found.

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.[7] It is natural to investigate the effects of nonlinear characteristics on the optical nonlinear ac response in a colloidal suspension, which can be regarded as a nonlinear composite medium.[8,9] The strength of the nonlinear polarization should be reflected in the magnitude of the harmonics. For these field-induced anisotropic structures, we found that as more and more chains are formed the harmonics of the local field and induced dipole moment increase (decrease) for the longitudinal (transverse) field case.[6]

On the other hand, the effect of nonlinear characteristics on the interparticle force has been analyzed in a colloidal suspension of nonlinear particles[10] and further extended to a nonlinear host medium.[11]

Actually, the intrinsic dielectric dispersion often occurs due to the surface conductivity or the inhomogeneous structure (e.g., coating effect[12]), which often exists in colloidal suspensions. Hence, it is of particular importance to discuss the effect of an intrinsic dielectric dispersion on the nonlinear polarization. In this regard, we will use a perturbation expansion method to calculate the nonlinear ac response of a nonlinear composite, i.e., harmonics of local field as well as induced dipole moment.

II. NONLINEAR POLARIZATION AND ITS HIGHER HARMONICS

Let us consider the system in which the suspended particles of radius a with a nonlinear dielectric constant are suspended in a host medium of linear dielectric constant ϵ_2. The nonlinear characteristic gives rise to a field-dependent dielectric coefficient.[13] In this case, the electric displacement–electric field relation inside the spheres is given by

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$$\mathbf{D}_1=\epsilon_1\mathbf{E}_1+\chi_1|\mathbf{E}_1|^2\mathbf{E}_1\approx\epsilon_1\mathbf{E}_1+\chi_1\langle|\mathbf{E}_1|^2\rangle\mathbf{E}_1$$
$$=\left(\epsilon_{1H}+\frac{\Delta\epsilon_1}{1+i\omega/\omega_0}\right)\mathbf{E}_1+\chi_1\langle|\mathbf{E}_1|^2\rangle\mathbf{E}_1\equiv\tilde{\epsilon}_1\mathbf{E}_1, \quad (1)$$

with $i=\sqrt{-1}$, where ϵ_1 and χ_1 are the linear coefficient and the weak nonlinear coefficient of the suspended particles, respectively. Here, ϵ_1 is expressed as a Debye expression, ϵ_{1H} is the dielectric constant at high frequency, $\Delta\epsilon_1$ is the intrinsic dispersion of the particle, $\omega_0=2\pi/\tau_0$ is the intrinsic characteristic frequency, with τ_0 being the intrinsic relaxation time, and ω is the angular frequency of the external field. In Eq. (1), we have adopted an approximation: the local field inside the particles is assumed to be uniform. This assumption is called the decoupling approximation.[14] It has been shown that such an approximation yields a lower bound for the accurate result for the local field.[14] We further assumed that χ_1 is independent of frequency, which is a valid assumption for low-frequency processes in colloidal suspensions. As a result, the induced dipole moment under an applied field $\mathbf{E}(t)=E(t)\hat{\mathbf{z}}$ along the z axis, with t being time, is given by[6]

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

where $\tilde{\epsilon}_e$ is the effective dielectric constant of the suspension, and $\tilde{b}$ is the field-dependent dipole factor:

$$\tilde{b}=\frac{\tilde{\epsilon}_1-\epsilon_2}{\tilde{\epsilon}_1+2\epsilon_2}=\frac{\epsilon_1+\chi_1\langle|\mathbf{E}_1|^2\rangle-\epsilon_2}{\epsilon_1+\chi_1\langle|\mathbf{E}_1|^2\rangle+2\epsilon_2}. \quad (3)$$

In order to obtain the effective dielectric constant $\tilde{\epsilon}_e$, we invoke the Maxwell–Garnett approximation (MGA) for anisotropic composites.[5,6] For the longitudinal field case when the ac field is applied along the uniaxial anisotropic axis, the MGA has the form

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

with f being the volume fraction of particles, whereas for an transverse field case when the ac field is applied perpendicular to the uniaxial anisotropic axis, the MGA expression is obtained by replacing β_L with $\beta_T=(3-\beta_L)/2$.[5,6] Here, β_L and β_T denote the local field factors parallel and perpendicular to the uniaxial anisotropic axis. These local field factors are defined as the ratio of the local field in the particles to the Lorentz cavity field.[5] 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. These β factors have been evaluated in a tetragonal lattice of dipole moments[5] and in various field-structured composites.[15]

We resort to the spectral representation approach[16] to represent the local field inside the particle:[3]

$$\langle|\mathbf{E}_1|^2\rangle=\frac{\mathbf{E}^2(t)}{f}\int_0^1\frac{|s|^2\mu(x)}{|s-x|^2}\mathrm{d}x, \quad (5)$$

with the material parameter $s=(1-\tilde{\epsilon}_1/\epsilon_2)^{-1}$ as well as the spectral density function $\mu(x)=f\delta[x-(1-f\beta)/3]$, which satisfies the sum rule $\int_0^1\mu(x)\mathrm{d}x=f$. Hence, Eq. (5) has the form

$$\langle|\mathbf{E}_1|^2\rangle=\frac{9|\epsilon_2|^2}{|\tilde{\epsilon}_1(1-f\beta)+\epsilon_2(2+f\beta)|^2}\mathbf{E}^2(t). \quad (6)$$

Actually, this is a self-consistent equation for $\langle|\mathbf{E}_1|^2\rangle$, which can be solved at least numerically.[6] In what follows, we will use a perturbation method instead to obtain analytic expressions for harmonics of the local electric field and the induced dipole moment.

On the other hand, due to the uniform local field in each particle, Eq. (6) can also be directly derived from[13,17]

$$\langle|\mathbf{E}_1|^2\rangle=\frac{1}{f}\mathbf{E}^2(t)\left|\frac{\partial\tilde{\epsilon}_e}{\partial\tilde{\epsilon}_1}\right|. \quad (7)$$

If we apply a sinusoidal electric field, i.e., $\mathbf{E}(t)=\mathbf{E}\sin(\omega t)$, 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

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

Also, the local electric field contains similar harmonics

$$\sqrt{\langle|\mathbf{E}_1|^2\rangle}=E_\omega\sin\omega t+E_{3\omega}\sin 3\omega t+\cdots. \quad (9)$$

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

III. ANALYTIC SOLUTIONS

In this section, we will apply the perturbation expansion[8,18] to extract the harmonics of the local electric field and the induced dipole moment. It is known that the perturbation expansion method is applicable to weak nonlinearity only, limited by the convergence of the series expansion.

We expand $\tilde{p}$ and $\sqrt{\chi_1\langle|\mathbf{E}_1|^2\rangle}$ into a Taylor expansion, taking $\chi_1\langle|\mathbf{E}_1|^2\rangle$ as a perturbative quantity:

$$\tilde{p}=\sum_{n=0}^{\infty}\frac{a^3E(t)}{n!}\frac{\partial^n}{\partial\tilde{\epsilon}_1^n}\times\left[\epsilon_2\tilde{b}\frac{\tilde{\epsilon}_1(1+3f-f\beta)+\epsilon_2(2-3f+f\beta)}{\tilde{\epsilon}_1(1-f\beta)+\epsilon_2(2+f\beta)}\right]_{\tilde{\epsilon}_1=\epsilon_1}\times(\chi_1\langle|\mathbf{E}_1|^2\rangle)^n, \quad (10)$$

$$\sqrt{\chi_1\langle|\mathbf{E}_1|^2\rangle}=\sum_{m=0}^{\infty}\frac{1}{m!}\frac{\partial^m}{\partial\tilde{\epsilon}_1^m}\left[\frac{3|\epsilon_2|\sqrt{\chi_1\mathbf{E}^2(t)}}{|(1-f\beta)\tilde{\epsilon}_1+(2+f\beta)\epsilon_2|}\right]_{\tilde{\epsilon}_1=\epsilon_1}\times(\chi_1\langle|\mathbf{E}_1|^2\rangle)^m. \quad (11)$$

In view of weak nonlinearity, we can rewrite Eqs. (10) and (11), keeping the lowest orders of $\chi_1\langle|\mathbf{E}_1|^2\rangle$ and $\chi_1\mathbf{E}^2(t)$:

$$\tilde{p}\approx h_1E(t)+h_3\chi_1E^3(t),$$
$$\sqrt{\chi_1\langle|\mathbf{E}_1^2|\rangle}\approx j_1\sqrt{\chi_1\mathbf{E}^2(t)}+j_3(\sqrt{\chi_1\mathbf{E}^2(t)})^3, \quad (12)$$

where

$$h_1=a^3\epsilon_2\frac{\epsilon_1-\epsilon_2}{\epsilon_1+2\epsilon_2}\frac{\rho+3f(\epsilon_1-\epsilon_2)}{\rho},$$

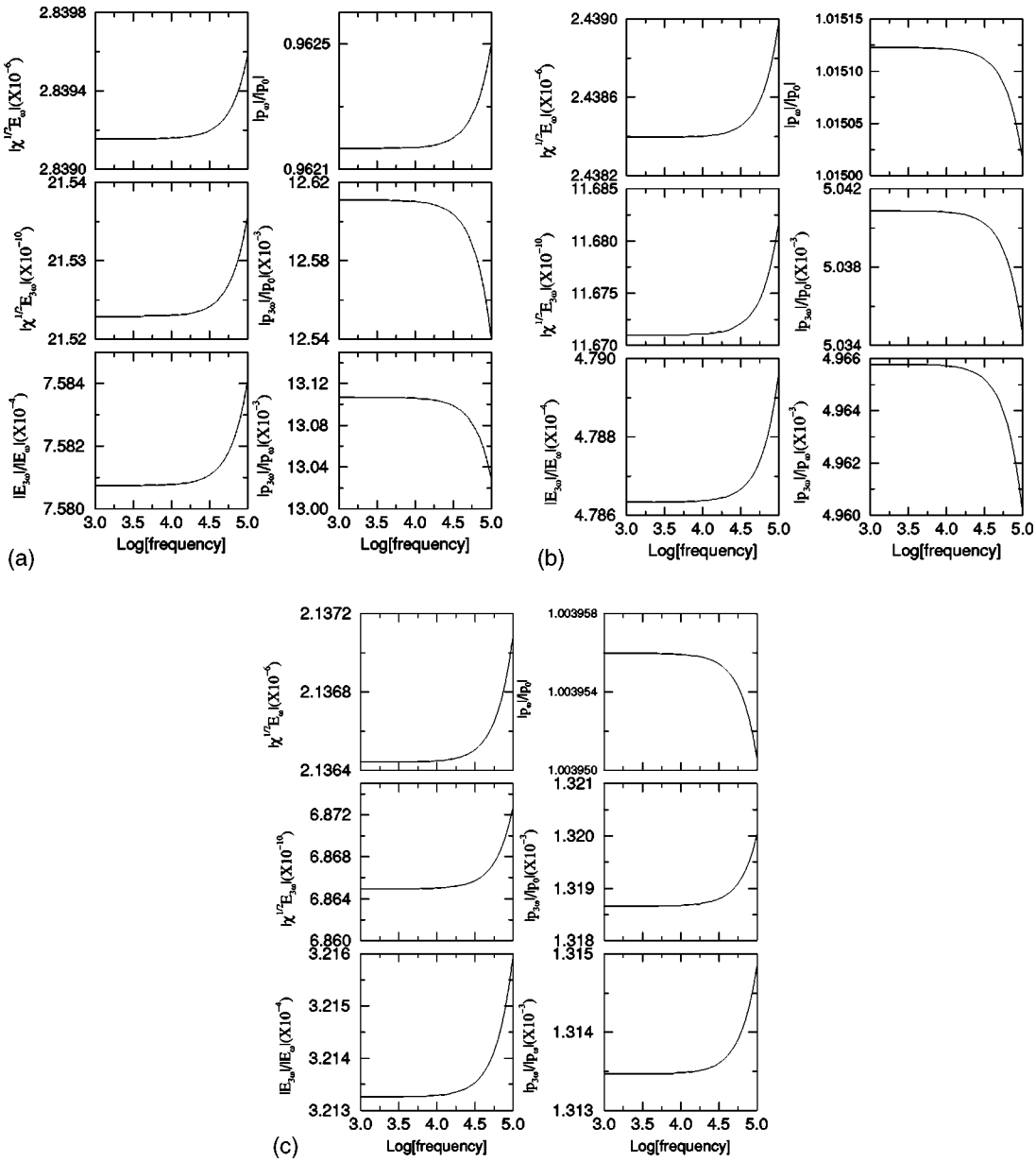

FIG. 1. Harmonics of the local electric field and the induced dipole moment vs frequency for $\tau_0=10^{-6.5}$ s and $\beta_L=2$, for different intrinsic dispersion strengths. (a) $\Delta\epsilon_1=50\epsilon_0$; (b) $\Delta\epsilon_1=100\epsilon_0$; and (c) $\Delta\epsilon_1=150\epsilon_0$.

$$h_3=\frac{27a^3|\epsilon_2|^2\epsilon_2^2}{\rho|\rho|^2(\epsilon_1+2\epsilon_2)}\left[\frac{3f(\epsilon_1-\epsilon_2)}{\rho}+\frac{\rho+3f(\epsilon_1-\epsilon_2)}{\epsilon_1+2\epsilon_2}\right],$$

$$j_1=\frac{3|\epsilon_2|}{\rho},\quad j_3=\frac{27}{2}|\epsilon_2|^3\frac{f\beta-1}{\rho|\rho|}\left(\frac{1}{|\rho|^2}+\frac{1}{(\rho^2)^*}\right),$$

with $\rho=(1-f\beta)\epsilon_1+(2+f\beta)\epsilon_2$.

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

$$p_\omega=h_1E+\tfrac{3}{4}h_3\chi_1E^3,\quad p_{3\omega}=-\tfrac{1}{4}h_3\chi_1E^3. \tag{13}$$

Similarly, we find the harmonics of the local electric field

$$\chi_1^{1/2}E_\omega=j_1\chi_1^{1/2}E+\tfrac{3}{4}j_3(\chi_1^{1/2}E)^3, \tag{14}$$

$$\chi_1^{1/2}E_{3\omega}=-\tfrac{1}{4}j_3(\chi_1^{1/2}E)^3.$$

In the above analysis, we have used the identity $\sin^3\omega t=(3/4)\sin\omega t-(1/4)\sin 3\omega t$ to obtain the first and the third harmonics. Similar analysis can be used to extract the higher-order harmonics, by retaining more terms in the series expansion. For instance, to obtain fifth harmonics, we may take into account the identity $\sin^5\omega t=(5/8)\sin\omega t-(5/16)\sin 3\omega t+(1/16)\sin 5\omega t$, and then obtain the harmonics of induced dipole moment and local electric field, respectively:

$$p_\omega=h_1E+\tfrac{3}{4}h_3\chi_1E^3+\tfrac{5}{8}h_5\chi_1^2E^5,$$

$$p_{3\omega}=-\tfrac{1}{4}h_3\chi_1E^3-\tfrac{5}{16}h_5\chi_1^2E^5,$$

$$p_{5\omega}=\tfrac{1}{16}h_5\chi_1^2E^5, \tag{15}$$

where

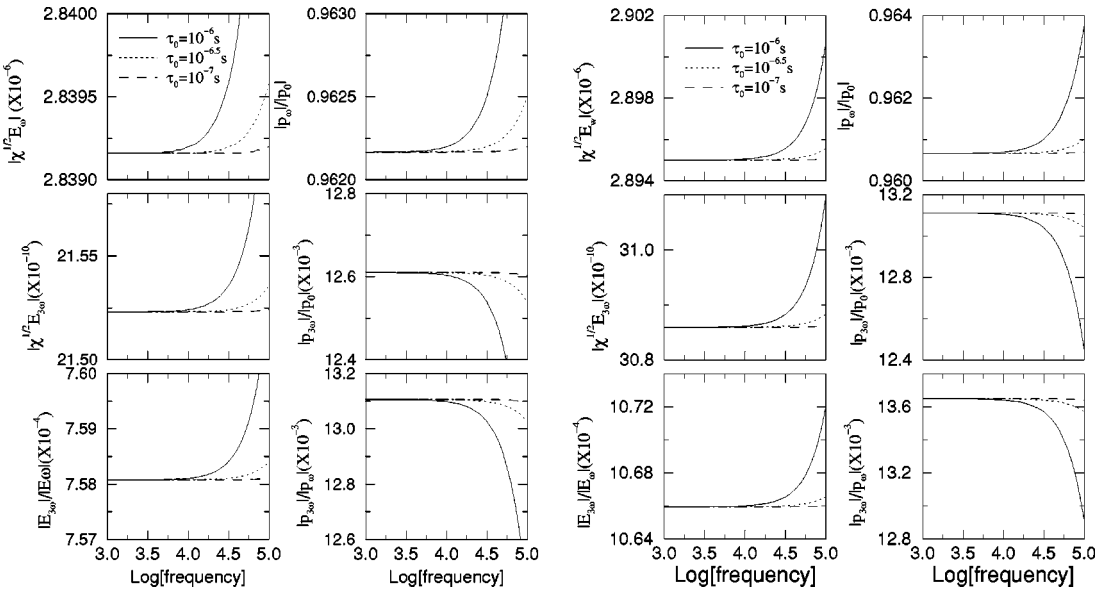

FIG. 2. Harmonics of the local electric field and the induced dipole moment vs frequency for $\Delta\epsilon_1=50\epsilon_0$, for different intrinsic relaxation times τ_0. (a) $\beta_L=2$; (b) $\beta_T=0.5$.

$$h_5=\frac{81}{2}\frac{a^3|\epsilon_2|^4}{|\rho|^4}\left\{\frac{9f\epsilon_2^2}{\rho^2(\epsilon_1+2\epsilon_2)}\left[\frac{-2(1-f\beta)(\epsilon_1-\epsilon_2)}{\rho}+\frac{3\epsilon_2}{\epsilon_1+2\epsilon_2}\right]\right.$$
$$\left.+\frac{3\epsilon_2^2}{\rho(\epsilon_1+2\epsilon_2)^2}\left[\frac{(1+3f-f\beta)\rho-(1-f\beta)(\rho+3f\epsilon_1-3f\epsilon_2)}{\rho}-\frac{2\rho+6f(\epsilon_1-\epsilon_2)}{\epsilon_1+2\epsilon_2}\right]\right\},$$

and

$$\chi_1^{1/2}E_\omega=j_1\chi_1^{1/2}E+\tfrac{3}{4}j_3(\chi_1^{1/2}E)^3+\tfrac{5}{8}j_5(\chi_1^{1/2}E)^5,$$
$$\chi_1^{1/2}E_{3\omega}=-\tfrac{1}{4}j_3(\chi_1^{1/2}E)^3-\tfrac{5}{16}j_5(\chi_1^{1/2}E)^5,$$
$$\chi_1^{1/2}E_{5\omega}=\tfrac{1}{16}j_5(\chi_1^{1/2}E)^5,$$

where

$$j_5=\frac{243}{4}\frac{(1-f\beta)^2|\epsilon_2|^5}{|\rho|^4}\left(\frac{3}{2}\frac{1}{\rho^2|\rho|}+\frac{1}{|\rho|^3}+\frac{3}{2}\frac{\rho^2}{|\rho|^5}\right).$$

Because of the weak nonlinearity under consideration, the effect of high-order harmonics is quite small. Thus, without loss of generality, we only consider the Taylor expansion up to the second term. In this regard, we will use Eqs. (13) and (14) to investigate the nonlinear ac response in the numerical calculations in next section.

IV. NUMERICAL RESULTS

We are now in a position to perform numerical calculations to investigate the dispersion effect on the harmonics of local electric field as well as induced dipole moment. We let $f=0.15$, $\epsilon_{1H}=6\epsilon_0$, $\epsilon_2=75\epsilon_0$, where ϵ_0 is the dielectric constant of free space. Additionally, set $\mathbf{p}_0=\epsilon_e a^3(\epsilon_1-\epsilon_2)/(\epsilon_1+2\epsilon_2)\mathbf{E}$ to normalize the induced dipole moment, where ϵ_e is given by the anisotropic MGA [Eq. (4)] without the nonlinear characteristic. Obviously, the expressions for the normalized local electric field and the normalized induced dipole moment are functions of a single variable $\chi_1^{1/2}E$.[9] In view of the weak nonlinearity, we set $\chi_1^{1/2}E=0.9\sqrt{\epsilon_0}$ for our calculation.

In Figs. 1(a)–1(c), we investigate the harmonics of the local field and induced dipole moment versus frequency for different intrinsic dispersion strengths $\Delta\epsilon_1$. It is obvious that increasing the dispersion strength reduces the harmonics of both the local field and the induced dipole moment. We find that, for increasing frequency, the harmonics of the local field always increases. However, the harmonics of the induced dipole moment exhibit a more complicated behavior. For small $\Delta\epsilon_1$, the ratio of the third to first harmonics of the induced dipole moment decreases as the frequency increases, which is qualitatively in good agreement with the experimental data.[4] However, for large $\Delta\epsilon_1$, its harmonic ratio also increases as the frequency increases. We expect this behavior can be demonstrated by experiment in the future.

In Fig. 2, we investigate the harmonics of the local field and induced dipole moment versus frequency for different intrinsic relaxation times τ_0. A longitudinal field case ($\beta_L=2$) is discussed in Fig. 2(a), while a transverse field case ($\beta_T=0.5$) is discussed in Fig. 2(b). It is shown that, in either case, increasing relaxation time τ_0 may enhance the harmonics of both the local field and induced dipole moment. In addition, the transverse field case may predict stronger harmonics than the longitudinal field case within the high-frequency region, which is actually valid for different dispersion strengths as well (no figures shown herein).

On the other hand, Klingenberg claimed that increasing the external electric field leads to increasing the harmonics of the electric current.[4] In this sense, we have also calculated the effect of the external electric field on the nonlinear ac response of the induced dipole moment (no figures shown herein). Obviously, our calculations qualitatively demonstrate the experimental results[4] as well.

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. Our considerations may be extended to a nonlinear host medium.[11]

We have studied the effect of intrinsic dispersion on the nonlinear ac response of a colloidal suspension. Actually, our formalism can be readily generalized to discuss two or more intrinsic dielectric dispersions of particles (or host fluid). In view of the fact that the intrinsic dielectric dispersion often occurs due to the surface conductivity or the inhomogeneous structure (e.g., the coating effect[12]), we believe such an effect also plays an important role in the dielectric behavior of biological cells, such as the electrorotation, dielectrophoresis, and electro-orientation.

The perturbation method is used in the present work, but we believe similar results may also be predicted by self-consistent theory.[6]

In summary, a perturbation method has been employed to compute the local electric field and the induced dipole moment for suspensions in which the suspended particles have a nonlinear characteristic and an intrinsic dispersion, in an attempt to investigate the frequency effect on the nonlinear ac response. The results showed for weak intrinsic dispersion strength the ratio of the third to first harmonics of the induced dipole moment decreases as the frequency increases, which is qualitatively in agreement with experiment. However, for strong dispersion strength, the harmonics ratio increases as the frequency increases. Moreover, an increase in the intrinsic relaxation time may increase the strength of the harmonics.

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