

Nonlinear alternating current responses of dipolar fluids

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The frequency-dependent nonlinear dielectric increment of dipolar fluids in nonpolar fluids is often measured by using a stationary relaxation method in which two electric fields are used: The static direct current (dc) field of high strength causing the dielectric nonlinearity, and the probing alternating current (ac) field of low strength and high frequency. When a nonlinear composite is subjected to a sinusoidal electric field, the electric response in the composite will, in general, consist of ac fields at frequencies of higher-order harmonics. Based on the Fröhlich model, we present a theory to investigate the nonlinear ac responses of dipolar fluids containing both polarizable monomers and dimers. In the case of monomers only, our theory reproduces the known results. We obtain the fundamental, second-, and third-order harmonics of the Fröhlich field by performing a perturbation expansion. The even-order harmonics are induced by the coupling between the ac and dc fields, although the system under consideration has a cubic nonlinearity only. The harmonics of the Fröhlich field can be affected by the field frequency, temperature, dispersion strength, and the characteristic frequency of the dipolar fluid, as well as the dielectric constant of the nonpolar fluid. The results are found to be in agreement with recent experimental observations.

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I. INTRODUCTION

Electric fields of high strength applied to dipolar fluids produce a nonlinearity in the dependence of the polarization on the field strength. On the other hand, when molecules are placed in alternating electric field, they display relaxation behavior—for small molecules that occurs typically at microwave frequencies. As studying the permittivity of molecules, or larger entities such as cells, yields detailed information about the structure and interactions in the system, frequency-dependent nonlinear dielectric increment of dipolar fluids has recently received much attention, see, e.g., Refs. [1–4] and references therein.

Nonlinear dielectric spectroscopy is a useful method for detecting intermolecular interactions and studying their kinetics due to its exceptional sensitivity to a large range of different aggregation processes in fluids. This method has been used, for example, to investigate the kinetics of *cis*-lactams cyclic dimerization [5,6], cholesterol aggregation [7] in nonpolar media, and it has been used to measure the nonlinear dielectric increment by using a stationary relaxation method [1–4]. Other recent and exciting developments in dielectric spectroscopy include, e.g., studies of phase transitions in liquid crystals [8], the dielectric properties of living cells using high- T_c SQUIDS at low frequencies [9], and combining it with microfluidic devices [10] to analyze cells, proteins, and bacteria noninvasively and without chemically modifying the system.

The nonlinear dielectric effect in dipolar fluids is not a result of a single mechanism, but it is caused by several

factors: (i) Langevin saturation of the orientation of the dipole due to a strong field; (ii) intermolecular interactions (e.g., dipole-dipole and hydrogen bonds) which lead to formation of aggregates with a compensated dipole moment, e.g., two monomers may form a dimer, $A+B \rightarrow AB$; and (iii) intramolecular processes may produce new dipoles, e.g., one dimer may dissociate to two monomers, $AB \rightarrow A+B$.

The first Langevin effect decreases the permittivity of the fluid, whereas the other two effects increase it. In fact, for aggregation and dissociation processes [(ii) and (iii) above] there is a dynamic equilibrium which may depend on the external field. Moreover, in the case of a field additional dimers have to be divided to reach a new equilibrium due to the activation energy of the field.

When a nonlinear composite is subjected to a sinusoidal electric field, the electric response in the composite will, in general, consist of alternating current (ac) fields at frequencies of higher-order harmonics [11–17]. In three previous papers [15–17], we studied the nonlinear ac responses of colloidal suspensions like electrorheological fluids, etc.

In this paper, we present a theory to investigate the nonlinear ac responses of dipolar fluids. We shall show the harmonics of the Fröhlich field can be affected by the field frequency, temperature, and dispersion strength and characteristic frequency of dipolar fluids, as well as the dielectric constant of the nonpolar fluid. Thus, by measuring the nonlinear ac responses of dipolar fluids, it is possible to investigate the frequency-dependent nonlinear dielectric increment.

This paper is organized as follows. In Sec. II, we derive the expression for the nonlinear dielectric increment of a dipolar fluid consisting of polarizable dimers and monomers, and obtain the desired fundamental, second-, and third-order harmonics of the Fröhlich field. In Sec. III, we numerically calculate the harmonics of the Fröhlich field for a simple case where there is no correlation between the orientations of the molecules. This is followed by a discussion and conclusion in Sec. IV.

II. FORMALISM

Let us consider a system in which polar molecules (dimers and monomers) are dissolved in a nonpolar fluid of dielectric constant ϵ_b . If one applies an external field, a dimer may dissociate to two monomers. We denote the dipole moment of a monomer by μ , that of a dimer by μ' , and assume that $\mu' \ll \mu$. In addition, we assume that only monomers and dimers exist (i.e., there are no multimers present) and that all dimers have the same dipole moment. Furthermore, we assume that the time chemical reactions need is short enough to be neglected, and that both dimers and monomers have an isotropic polarizability.

A. Nonlinear dielectric effect

At a high field intensity the dependence of the dielectric displacement \mathbf{D} on the field strength becomes nonlinear [18,19]

$$\mathbf{D} = \epsilon_0 \mathbf{E} + 4\pi\chi E^2 \mathbf{E}, \quad (1)$$

where \mathbf{E} is the electric field, ϵ_0 the field-independent part of the permittivity, and χ is the (nonlinear) susceptibility. To determine \mathbf{D} , one resorts to the Clausius-Mossotti equation for three components

$$\frac{\epsilon_0 - \epsilon_b}{\epsilon_0 + 2\epsilon_b} = \frac{4\pi}{3} \left[\eta N_1 \left(\alpha_1 + \frac{\mu'^2}{3k_B T} \frac{1}{1 + i\omega\tau_1} \right) + (1 - \eta) N_2 \left(\alpha_2 + \frac{\mu^2}{3k_B T} \frac{1}{1 + i\omega\tau_2} \right) \right],$$

where ϵ_b is dielectric constant of the nonpolar host fluid, $\eta = N_1 / (N_1 + N_2)$, and $i = \sqrt{-1}$. N_1 and N_2 are the number densities of dimers and monomers, respectively, k_B the Boltzmann constant, T the absolute temperature, ω angular frequency of the applied field, and τ_1 (τ_2) the relaxation time of dimers (monomers). The polarizabilities of dimers and monomers are denoted by α_1 and α_2 , respectively.

The desired field-dependent incremental dielectric constant ϵ_E is [18]

$$\epsilon_E = \frac{\partial D}{\partial E} = \epsilon_0 + 12\pi\chi E^2. \quad (2)$$

Then, the nonlinear dielectric effect is characterized by the ratio $\Delta\epsilon/E^2$ [18]

$$\frac{\Delta\epsilon}{E^2} = \frac{\epsilon_E - \epsilon_0}{E^2} = 12\pi\chi. \quad (3)$$

Next, we consider the orientation polarization p_{or} of a dielectric sphere of volume V , containing n_1 dimers and n_2 monomers with a dipole moment μ_d (see below) embedded in a continuum with dielectric constant ϵ_∞ (see below). The sphere is surrounded by an infinite dielectric with the same macroscopic properties as the sphere.

The average component of the dipole moment in the direction of the field due to the dipoles in the sphere is given by

$$\langle \mathbf{M}_d \cdot \mathbf{e} \rangle = V p_{or} = \frac{\int dX^{n_1+n_2} \mathbf{M}_d \cdot \mathbf{e} e^{-u/k_B T}}{\int dX^{n_1+n_2} e^{-u/k_B T}}, \quad (4)$$

where \mathbf{e} denotes the unit vector in the direction of the external field, and X stands for the set of positional and orientational variables of all monomers and dimers. Here, u is the energy related to the dipoles in the sphere, and it consists of four parts.

- (1) The energy of the dipoles in the external field.
- (2) The electrostatic interaction energy of the dipoles.
- (3) The nonelectrostatic interaction energy between the dipoles. This interaction is responsible for the short-range orientational and positional correlations.
- (4) The binding energy (denoted as u_B) between two "monomer dipoles" in the dimer dipoles.

In Eq. (4), \mathbf{M}_d is given by

$$\mathbf{M}_d = \sum_{i=1}^{n_2} (\boldsymbol{\mu}_d)_i + \sum_{i=1}^{n_1} (\boldsymbol{\mu}'_d)_i,$$

with $\boldsymbol{\mu}_d = \boldsymbol{\mu}(\epsilon_\infty + 2\epsilon_b)/3\epsilon_b$, and $\boldsymbol{\mu}'_d = \boldsymbol{\mu}'(\epsilon_\infty + 2\epsilon_b)/3\epsilon_b$. The number of monomers and dimers in the system are denoted by n_1 and n_2 . Parameter ϵ_∞ is the dielectric constant at frequencies at which the permanent dipoles (i.e., the orientational polarization) cannot follow the changes of the field, but in which the atomic and the electronic polarization are still the same as in the static field. Therefore, ϵ_∞ is the dielectric constant characteristic for the induced polarization. In practice, ϵ_∞ can be expressed using an expression containing an intrinsic dispersion

$$\epsilon_\infty = \epsilon_\infty(0) + \frac{\delta\epsilon}{1 + i\omega/\omega_c}, \quad (5)$$

where $\epsilon_\infty(0)$ is the dielectric constant at the high-frequency limit, and $\delta\epsilon$ stands for the dielectric dispersion strength with a characteristic frequency ω_c .

The external field in this model is equal to the field within the spherical cavity filled with a continuum of dielectric constant ϵ_∞ , while the cavity is situated in a dielectric with dielectric constant ϵ_0 . This field is called Fröhlich field E_F , as given by the Fröhlich model [20]

$$E_F = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} E + \frac{12\pi\chi\epsilon_\infty}{(2\epsilon_0 + \epsilon_\infty)^2} E^3. \quad (6)$$

In this equation, the higher-order terms have been omitted.

With the above definitions and using u as defined in Eq. (4), we now have

$$\frac{\partial u}{\partial E_F} = -\mathbf{M}_d \cdot \mathbf{e} + \beta. \quad (7)$$

Here, $\beta = \partial u_B / \partial E_F < 0$, and it is first assumed to be a quantity independent of E_F . Then, we obtain

$$\begin{aligned} \langle \mathbf{M}_d \cdot \mathbf{e} \rangle_{E_F=0} &= 0 \frac{\partial}{\partial E_F} \langle \mathbf{M}_d \cdot \mathbf{e} \rangle = \frac{1}{k_B T} [\langle \mathbf{M}_d \cdot \mathbf{e} (\mathbf{M}_d \cdot \mathbf{e} - \beta) \rangle - \langle \mathbf{M}_d \cdot \mathbf{e} \rangle \langle \mathbf{M}_d \cdot \mathbf{e} - \beta \rangle] \frac{\partial}{\partial E_F} \langle \mathbf{M}_d \cdot \mathbf{e} \rangle \Big|_{E_F=0} = \frac{1}{k_B T} \langle M_d^2 \rangle_0 \frac{\partial^3}{\partial E_F^3} \langle \mathbf{M}_d \cdot \mathbf{e} \rangle \\ &= \frac{1}{(k_B T)^3} [\langle \mathbf{M}_d \cdot \mathbf{e} (\mathbf{M}_d \cdot \mathbf{e} - \beta)^3 \rangle - 3 \langle \mathbf{M}_d \cdot \mathbf{e} (\mathbf{M}_d \cdot \mathbf{e} - \beta)^2 \rangle \langle \mathbf{M}_d \cdot \mathbf{e} - \beta \rangle + 6 \langle \mathbf{M}_d \cdot \mathbf{e} (\mathbf{M}_d \cdot \mathbf{e} - \beta) \rangle \langle \mathbf{M}_d \cdot \mathbf{e} - \beta \rangle^2 \\ &\quad - 3 \langle \mathbf{M}_d \cdot \mathbf{e} (\mathbf{M}_d \cdot \mathbf{e} - \beta) \rangle \langle \mathbf{M}_d \cdot \mathbf{e} - \beta \rangle^2 - 6 \langle \mathbf{M}_d \cdot \mathbf{e} \rangle \langle \mathbf{M}_d \cdot \mathbf{e} - \beta \rangle^3 + 6 \langle \mathbf{M}_d \cdot \mathbf{e} \rangle \langle \mathbf{M}_d \cdot \mathbf{e} - \beta \rangle \langle \mathbf{M}_d \cdot \mathbf{e} - \beta \rangle^2 - \langle \mathbf{M}_d \cdot \mathbf{e} \rangle \\ &\quad \times \langle (\mathbf{M}_d \cdot \mathbf{e} - \beta)^3 \rangle] \frac{\partial^3}{\partial E_F^3} \langle \mathbf{M}_d \cdot \mathbf{e} \rangle \Big|_{E_F=0} = \frac{1}{15(k_B T)^3} [3 \langle M_d^4 \rangle_0 - 5 \langle M_d^2 \rangle_0^2]. \end{aligned}$$

Note the subscript 0 indicates the absence of the field.

To express the macroscopic saturation behavior in microscopic quantities, higher derivatives of the average dipole moment have to be taken into account

$$\begin{aligned} \langle \mathbf{M}_d \cdot \mathbf{e} \rangle &= \frac{\partial \langle \mathbf{M}_d \cdot \mathbf{e} \rangle}{\partial E_F} \Big|_{E_F=0} E_F + \frac{1}{6} \frac{\partial^3 \langle \mathbf{M}_d \cdot \mathbf{e} \rangle}{\partial E_F^3} \Big|_{E_F=0} E_F^3 \\ &= \frac{\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \frac{\langle M_d^2 \rangle_0}{k_B T} E + \frac{4\pi\chi\epsilon_\infty}{(2\epsilon_0 + \epsilon_\infty)^2} \frac{\langle M_d^2 \rangle_0}{k_B T} E^3 \\ &\quad + \frac{27\epsilon_0^3}{(2\epsilon_0 + \epsilon_\infty)^3} \frac{3 \langle M_d^4 \rangle_0 - 5 \langle M_d^2 \rangle_0^2}{90(k_B T)^3} E^3. \end{aligned}$$

Terms higher than third order are neglected.

In addition, we have a general relation

$$\langle \mathbf{M}_d \cdot \mathbf{e} \rangle = V p_{or} = \frac{\epsilon_0 - \epsilon_\infty}{4\pi} V E + \chi V E^3. \quad (8)$$

Using Eq. (3) and the terms in E^3 and E , we obtain

$$\begin{aligned} \frac{\Delta\epsilon}{E^2} &= \frac{18\pi}{5(k_B T)^3} \frac{\epsilon_0^4}{(2\epsilon_0 + \epsilon_\infty)^2 (2\epsilon_0^2 + \epsilon_\infty^2)} \times [3 \langle M_d^4 \rangle_0 / V \\ &\quad - 5 \langle M_d^2 \rangle_0^2 / V]. \end{aligned} \quad (9)$$

On the other hand, we may write

$$\begin{aligned} \frac{\langle M_d^2 \rangle_0}{V} &= \left(\frac{\epsilon_\infty + 2\epsilon_b}{3\epsilon_b} \right)^2 \left[N_2 \mu^2 \sum_{j=1}^{n_2} \langle \cos \theta_{ij} \rangle \right. \\ &\quad + N_1 \mu'^2 \sum_{m=1}^{n_1} \langle \cos \theta_{lm} \rangle + N_1 \mu \mu' \sum_{q=1, p \neq q}^{n_1} \langle \cos \theta_{pq} \rangle \\ &\quad \left. + N_2 \mu \mu' \sum_{h=1, g \neq h}^{n_2} \langle \cos \theta_{gh} \rangle \right], \end{aligned}$$

$$\begin{aligned} \frac{\langle M_d^4 \rangle_0}{V} &= \left(\frac{\epsilon_\infty + 2\epsilon_b}{3\epsilon_b} \right)^4 \left[N_2 \mu^4 \sum_{j=1}^{n_2} \langle \cos \theta_{ij} \sum_{r=1}^{n_2} \sum_{s=1}^{n_2} \cos \theta_{rs} \rangle \right. \\ &\quad + N_1 \mu'^4 \sum_{m=1}^{n_1} \langle \cos \theta_{lm} \sum_{u=1}^{n_1} \sum_{v=1}^{n_1} \cos \theta_{uv} \rangle \\ &\quad + N_1 \mu^2 \mu'^2 \sum_{q=1, p \neq q}^{n_1} \langle \cos \theta_{pq} \sum_{c=1}^{n_1} \sum_{d=1}^{n_1} \cos \theta_{cd} \rangle \\ &\quad \left. + N_2 \mu^2 \mu'^2 \sum_{h=1, g \neq h}^{n_2} \langle \cos \theta_{gh} \sum_{a=1}^{n_2} \sum_{b=1}^{n_2} \cos \theta_{ab} \rangle \right]. \end{aligned}$$

Hence, the nonlinear dielectric increment $\Delta\epsilon/E^2$ is explicitly expressed. By setting $N_1=0$, $\mu'=0$ and $\epsilon_b=1$ (no dimers in the system), Eq. (9) can be reduced to Eq. (7.40) of Ref. [18], where a polar fluid in vacuum is investigated.

It is worth noting that the expression for $\Delta\epsilon/E^2$ [Eq. (9)] contains no β , i.e., the binding energy has no effect on the nonlinear dielectric increment. In fact, even if $\beta = \beta(E_F)$, the same result is also obtained due to the fact that the binding energy is due to hydrogen bonds, rather than from the interaction between dipoles.

Let us choose a simple case for numerical calculations. It is assumed that there are no correlations between the orientations of the molecules. Thus, we have

$$\begin{aligned} \sum_{j=1}^{n_2} \langle \cos \theta_{ij} \rangle &= 1, \\ \sum_{j=1}^{n_2} \langle \cos \theta_{ij} \sum_{r=1}^{n_2} \sum_{s=1}^{n_2} \cos \theta_{rs} \rangle &= \frac{1}{3} (5n_2 - 2), \\ \sum_{m=1}^{n_1} \langle \cos \theta_{lm} \rangle &= 1, \end{aligned}$$

$$\sum_{m=1}^{n_1} \langle \cos \theta_{lm} \sum_{u=1}^{n_1} \sum_{v=1}^{n_1} \cos \theta_{uv} \rangle = \frac{1}{3}(5n_1 - 2),$$

$$\sum_{q=1, p \neq q}^{n_1} \langle \cos \theta_{pq} \rangle = 0,$$

$$\sum_{q=1, p \neq q}^{n_1} \langle \cos \theta_{pq} \sum_{c=1}^{n_1} \sum_{d=1}^{n_1} \cos \theta_{cd} \rangle = \frac{2}{3}(n_1 - 1),$$

$$\sum_{h=1, g \neq h}^{n_2} \langle \cos \theta_{gh} \rangle = 0,$$

$$\sum_{h=1, g \neq h}^{n_2} \langle \cos \theta_{gh} \sum_{a=1}^{n_2} \sum_{b=1}^{n_2} \cos \theta_{ab} \rangle = \frac{2}{3}(n_2 - 1).$$

In this regard, the nonlinear dielectric increment is given by

$$\frac{\Delta \epsilon}{E^2} = \frac{18\pi}{5(k_B T)^3} \frac{\epsilon_0^4}{(2\epsilon_0 + \epsilon_\infty)^2 (2\epsilon_0^2 + \epsilon_\infty^2)} \times \left(\frac{\epsilon_\infty + 2\epsilon_b}{3\epsilon_b} \right)^4 \phi, \quad (10)$$

where

$$\phi = -2N_2\mu^4 - 2N_1\mu'^4 + 2\mu^2\mu'^2(N_1n_1 - N_1 + N_2n_2 - N_2 - 5n_1N_2).$$

B. Nonlinear ac responses

Next, we perform a perturbation expansion approach [21] to investigate the nonlinear ac response of the dipolar fluid. In this case, the applied field is $\mathbf{E} = \mathbf{E}_{dc} + \mathbf{E}_{ac}(\omega)$, where \mathbf{E}_{dc} denotes the DC field, and $\mathbf{E}_{ac}(\omega)$ the sinusoidal ac field, namely $\mathbf{E}_{ac}(\omega) = \mathbf{E}_{ac} \sin(\omega t)$. As a result, the Fröhlich field is expressed in terms of the harmonics [14,15,17,22] as

$$E_F = E_F^{(dc)} + E_\omega \sin(\omega t) + E_{2\omega} \cos(2\omega t) + E_{3\omega} \sin(3\omega t) + \dots, \quad (11)$$

where the dc component ($E_F^{(dc)}$) and the fundamental, second-, and third- order harmonics (E_ω , $E_{2\omega}$ and $E_{3\omega}$) are analytically given by

$$E_F^{(dc)} = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} E_{dc} + \frac{12\pi\chi\epsilon_\infty}{(2\epsilon_0 + \epsilon_\infty)^2} E_{dc}^3 + \frac{18\pi\chi\epsilon_\infty}{(2\epsilon_0 + \epsilon_\infty)^2} E_{dc} E_{ac}^2, \quad (12)$$

$$E_\omega = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} E_{ac} + \frac{36\pi\chi\epsilon_\infty}{(2\epsilon_0 + \epsilon_\infty)^2} E_{dc}^2 E_{ac} + \frac{9\pi\chi\epsilon_\infty}{(2\epsilon_0 + \epsilon_\infty)^2} E_{ac}^3, \quad (13)$$

$$E_{2\omega} = -\frac{18\pi\chi\epsilon_\infty}{(2\epsilon_0 + \epsilon_\infty)^2} E_{dc} E_{ac}^2, \quad (14)$$

$$E_{3\omega} = -\frac{3\pi\chi\epsilon_\infty}{(2\epsilon_0 + \epsilon_\infty)^2} E_{ac}^3. \quad (15)$$

In the above derivation, we have used two identities, $\sin^2(\omega t) = [1 - \cos(2\omega t)]/2$ and $\sin^3(\omega t) = (3/4)\sin(\omega t) - (1/4)\sin(3\omega t)$. It is worth noting that the Fröhlich field [Eq. (11)] is a superposition of both odd and even harmonics, even though there is initially a cubic nonlinearity only [see, Eq. (1)]. Actually, the occurrence of both odd and even harmonics is simply due to the coupling between the dc and the ac fields [22]. In Eq. (11), we have omitted higher-order harmonics (e.g., fourth order, fifth order, and so on).

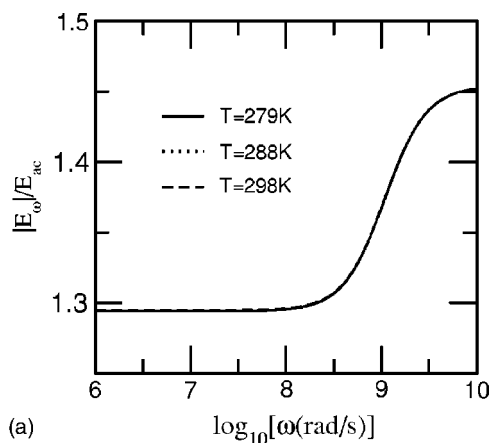
III. NUMERICAL RESULTS

Based on Eqs. (3), (10), and (11), we are now in a position to perform numerical calculations. Without loss of generality, we choose the following parameters: $V = 5.0 \times 10^5 \text{ cm}^3$, $n_1 = 0.25 \times 10^{15}$, $n_2 = 1.0 \times 10^{15}$, $\mu = 2.5D$, $\mu' = 0.05D$, $\tau_1 = 0.018 \text{ ns}$, $\tau_2 = 0.02 \text{ ns}$, $\alpha_1 = 8 \times 10^{-25} \text{ cm}^3$, $\alpha_2 = 2 \times 10^{-25} \text{ cm}^3$, $T = 300 \text{ K}$, $\epsilon_b = 40$, $\epsilon_\infty(0) = 2.5$, $\delta\epsilon = 10$, $\omega_c = 10^9 \text{ rad/s}$, $E_{ac} = 1 \text{ V/cm}$, and $E_{dc} = 10^5 \text{ V/cm}$, unless otherwise mentioned. Here, D is Debye unit (10^{-18} e.s.u. of electric moment).

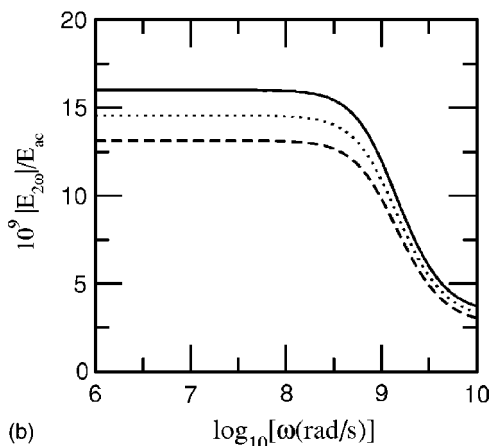
Figure 1 displays the fundamental, second-, and third-order harmonics of the Fröhlich field as a function of the field frequency. It is shown that the harmonics of the Fröhlich field is sensitive to the frequency of the field. Decreasing the frequency causes the second- and third-order (fundamental) harmonics to increase (decrease). Thus, it is possible to investigate the frequency-dependent nonlinear dielectric increment ($\Delta\epsilon/E^2$) of dipolar fluids by detecting the nonlinear ac responses. We also find that decreasing the temperature T causes the second- and third-order harmonics to increase due to the change in the Fröhlich field. This result is in qualitative agreement with the experimental findings by Hellemans *et al.* [2]. In their experiment, they measured the nonlinear dielectric relaxation spectra for 10-TPEB dissolved in benzene at three different temperatures, 279, 288, and 298 K. In addition, it is shown that the temperature has no effect on the fundamental harmonics [note that the three curves in Fig. 1(a) overlap].

In Fig. 2, we investigate the effect of the dielectric constant of the nonpolar fluid ϵ_b on the harmonics, and find that decreasing ϵ_b leads to increasing second- and third- order harmonics, but decreasing fundamental harmonics. This is due to the change of Fröhlich field. However, decreasing $\delta\epsilon$ has exactly the opposite effect; see Fig. 3).

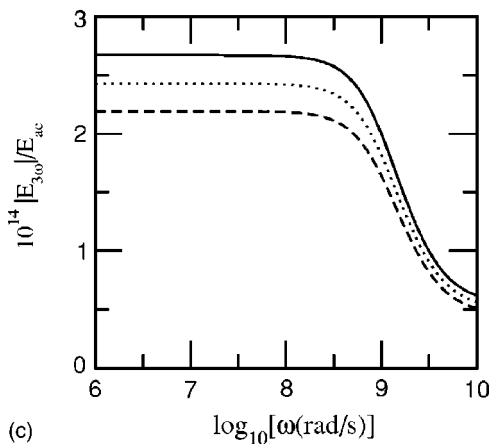
Figure 4 shows the effect of the intrinsic characteristic frequency ω_c . From this figure, we can conclude that the characteristic frequency for the harmonics is strongly dependent on the intrinsic characteristic frequency of the dipolar fluid.



(a)



(b)



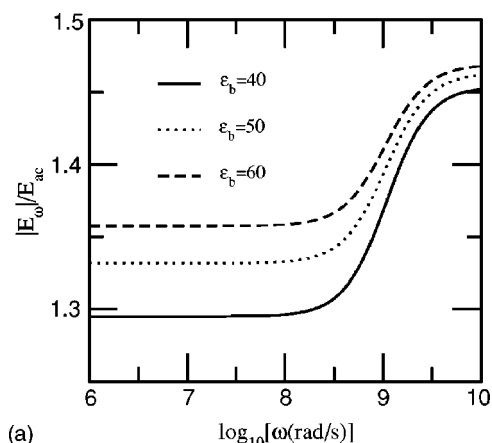
(c)

FIG. 1. The fundamental, second-, and third-order harmonics of the Fröhlich field as a function of the field frequency for three different temperatures.

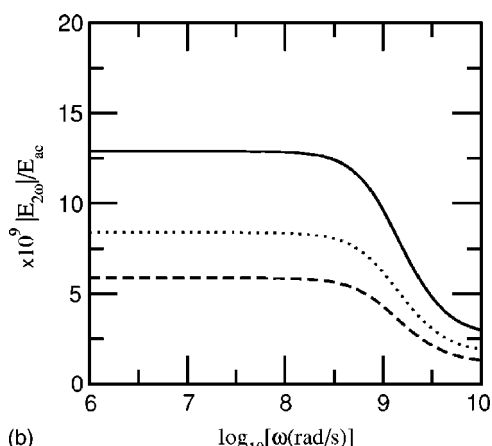
IV. DISCUSSIONS AND CONCLUSIONS

In the present paper, we have studied the system containing polarizable monomers and dimers. Our theory can be extended to deal with multimers as well. Here, we have studied the fundamental, second-, and third- order harmonics. The extension to higher-order harmonics is interesting and the present theory can be extended to include them simply by keeping the higher-order terms in Eqs. (6) and (11).

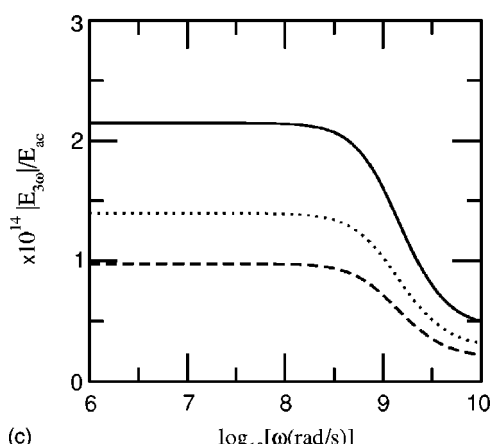
Throughout this paper, we have discussed the case of weak nonlinearity. The spherical inclusion is assumed to be



(a)



(b)

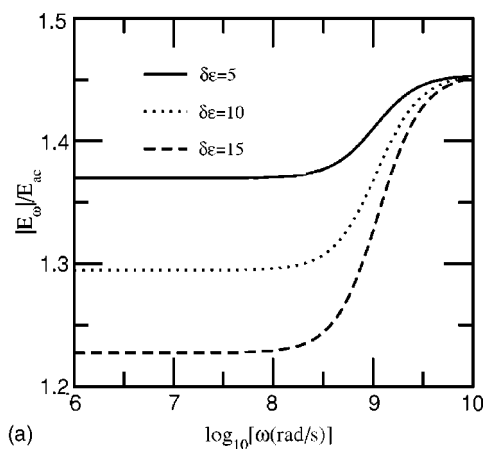


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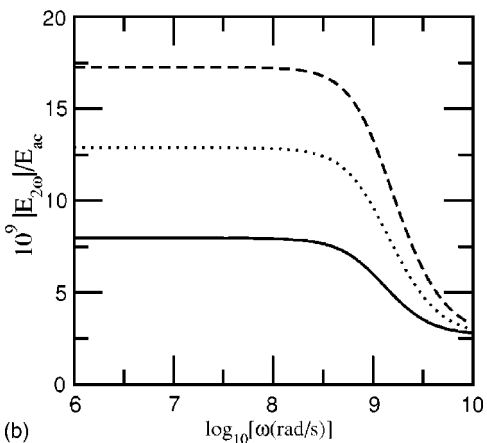
FIG. 2. Same as Fig. 1, but for three different ϵ_b (dielectric constant of the host fluid).

nonlinear, but only weakly so. Thus, for extracting the harmonics, a perturbation expansion approach was performed. In the case of strong nonlinearity, this approach is no longer valid, and we might need to resort to a self-consistent method [15,23]. In addition, the dipolar fluid considered here is seen as dispersive. In fact, in real systems, the nonpolar fluid is also dispersive. The present theory can be extended for that case as well.

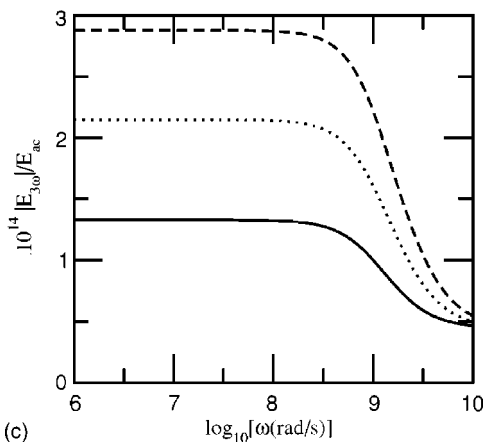
To summarize, we have presented a theory to investigate the nonlinear ac responses of dipolar fluids based on the



(a)



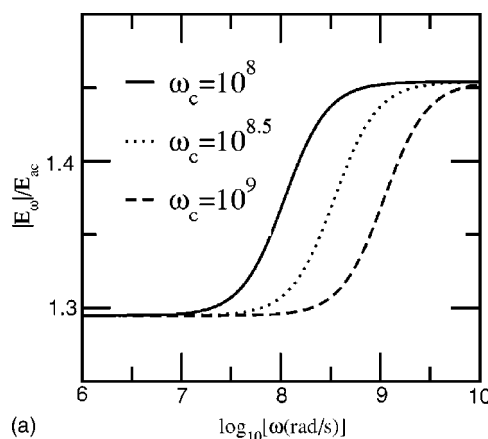
(b)



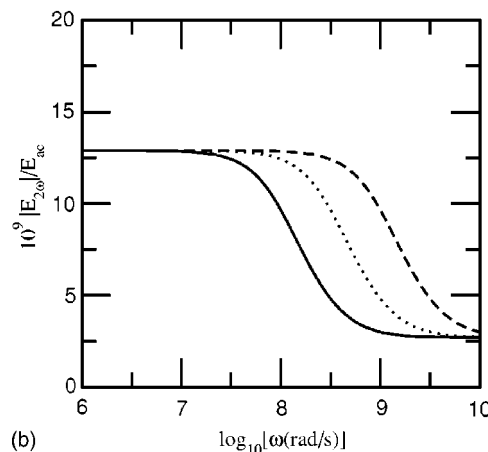
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FIG. 3. Same as Fig. 1, but for three different $\delta\epsilon$.

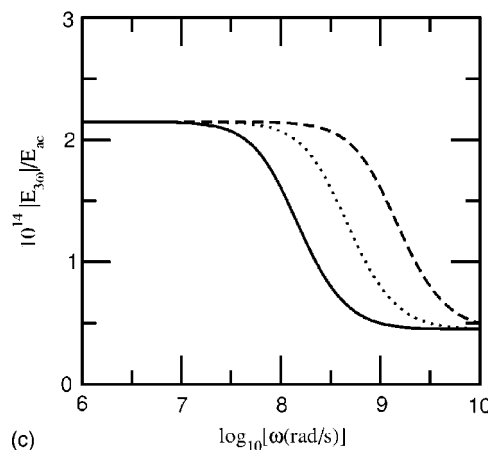
Fröhlich model. It was shown that our theory reproduces the known results of a polar fluid in vacuum [18], and is consistent with the experimental observations of Hellemans *et al.* [2] for the nonlinear dielectric relaxation spectra of 10-TPEB dissolved in benzene. For the simple case where there is no correlation between the orientation of the molecules, we have obtained the harmonics of the Fröhlich field analytically by performing a perturbation expansion approach. It has been found that the harmonics of the Fröhlich field is affected by the field frequency, temperature, dispersion strength, and characteristic frequency of dipolar fluids, as well as the dielectric constant of the nonpolar host fluid. The



(a)



(b)



(c)

FIG. 4. Same as Fig. 1, but for three different ω_c .

results are found to be in agreement with experimental observations. Thus, by measuring the nonlinear ac responses of dipolar fluids, it is possible to investigate the frequency-dependent nonlinear dielectric increment.

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