Nonlinear Dielectric Relaxation in AC and DC Electric Fields

P. M. Déjardin, W. T. Coffey, F. Ladieu and Yu. P. Kalmykov

Abstract Current theories of the nonlinear static and dynamic dielectric susceptibilities of polar fluids subjected to strong AC and DC electric fields are reviewed with specific emphasis on those extending Debye's theory of linear dielectric relaxation of an assembly of polar molecules. The inclusion of intermolecular interactions in this theory as well as nonlinear dielectric relaxation in the presence of time-dependent fields is discussed. In particular, we emphasize the role played by intermolecular interactions in the determination of the macroscopic dielectric properties of a polar fluid via microscopic calculations, in both the linear and nonlinear responses.

1 Introduction

A well-founded microscopic theory of the electric polarization (both static and dynamic) of polar fluids is essential to understanding many dielectric and electro-optical relaxation phenomena and as such was initiated by Debye [1]. He first calculated the static susceptibility of an assembly of noninteracting rigid dipoles obtaining a result which is essentially a replica of Langevin's theory of paramagnetism and so is called the Langevin–Debye theory. He then extended the calculation to include the linear dielectric susceptibility of noninteracting polar molecules subjected to a weak AC electric field, which unlike the static situation poses a nonequilibrium problem. In order to accomplish this, he treated the effects of the heat bath surrounding a dipole via the rotational diffusion model. This is based on a generalization of Einstein's 1905 [2] theory of the translational Brownian motion [3] to rotation on the unit sphere and to include the effects of a weak AC field applied along an axis chosen

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as the Z-axis. Thus, in the dynamical Debye theory as with that of Einstein, inertial effects are negligible and the rotation of the molecule is described by a random walk over small angular orientations. Later, his original calculation was generalized (using perturbation theory) to cover nonlinear phenomena in polar dielectrics subjected to strong AC and indeed other external fields [4–6]. As specific examples, we cite both the dynamic Kerr and nonlinear dielectric effects [4–8]. In particular, in nonlinear dielectric relaxation, depending on the particular form of the stimulus chosen, additional terms in the fundamental, third, etc., harmonic appear in the polarization response [5–7], which have been confirmed by experiment [4, 9–12]. Furthermore, the dynamical Debye theory has also been extended (by exact numerical solution using matrix continued fractions) to include nonlinear effects in *arbitrarily large* external fields [13–16]. Nevertheless, assemblies of *noninteracting* dipoles are still assumed implying that the Debye theory and its extensions may not be used for *dense* dipolar systems, where intermolecular interactions are significant. Although the treatment of the latter is much more involved, several methods are still available. For example, the dielectric relaxation of polar nematic liquid crystals may be regarded as the rotational Brownian motion in the Maier–Saupe uniaxial anisotropy potential [17, 18], leading to an Arrhenius-like escape over a barrier process due to the shuttling action of the rotational Brownian motion giving rise to reversal of a dipole occurring in all the dynamical responses. Such a mechanism was first identified by Kramers [19] in the context of the translational Brownian motion, and was recognized by Debye in the context of *normal* dispersion and absorption in solids. The method comprises the *static mean field* approach. However, such a treatment, although of restricted applicability because it ignores local order effects, is easily visualized and permits quantitative evaluation of dielectric parameters. Thus, it qualitatively demonstrates the effect of intermolecular interaction on these, an effect which must be included for the purpose of comparison with experimental data [20]. Yet another advantage is that it also yields the nonlinear response of assemblies of noninteracting uniaxial single-domain ferromagnetic particles [21]. Unfortunately, the static mean field method still ignores *dynamical effects* due to intermolecular interactions.

In contrast, the *dynamical mean field* method reveals dynamical effects due to intermolecular interactions manifesting themselves *at the nonlinear response level only* [22]. These novel predictions are interesting as they are *qualitatively* similar to observations of *supercooled* polar liquid nonlinear dielectric response measurements, namely non-monotonic behavior of the nonlinear response moduli, without corresponding modification of the linear response at low frequencies.

A succinct account of nonlinear dielectric effects in liquids has recently been given by Richert [23], who emphasized the growing importance of such measurements in so far as they can characterize many polar fluids in various states. Here, we review nonlinear dielectric response calculations based on further developments of the Debye theory which are accomplished by generalizing it to include both strong electric fields and intermolecular interactions. The chapter is organized as follows: in Sects. 2 and 3, we review the methods used in [7] for the nonlinear dynamic dielectric susceptibilities of a gas of noninteracting dipoles subjected to strong DC and AC electric fields. Next two mean field models of interaction are described in Sects. 4 and 5, while Sect. 6 is devoted to internal field corrections. These are the only corrections needed as a dielectric liquid always occupies the entire empty space between the electrodes of the measuring device. The depolarizing field effect is first discussed. Next, Sect. 7 shows how to include both static and dynamical intermolecular correlations.

2 Nonlinear Dielectric Response of Noninteracting Polar Molecules to a Strong AC Electric Field

We consider the *nonlinear* AC (alternating current) stationary response of an assembly of noninteracting polar molecules (electric dipoles) undergoing rotational Brownian motion due to the heat bath and also acted upon by a strong external AC field $\mathbf{E}(t)$. Moreover, we suppose without loss of generality that $\mathbf{E}$ is directed along the Z-axis of the laboratory coordinate system so that axial symmetry is preserved. This treatment is a simple extension of the work of Debye and is essentially due to Coffey and Paranjape [7]. The starting point of the theory is the rotational diffusion equation (the Smoluchowski equation, a particular form of the Fokker–Planck equation) due to Debye for the surface distribution function of the dipole orientations on the unit sphere when embedded in a heat bath, viz.,

$$2\tau_D \frac{\partial W}{\partial t} = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(\frac{\partial W}{\partial\vartheta} + \beta W \frac{\partial V}{\partial\vartheta}\right)\right]. \tag{1}$$

In Eq. (1) $T_D = \varsigma / (2kT)$ is the rotational diffusion time also called the Debye relaxation time, and expresses the given fluctuation–dissipation relation which exists between the magnitude of the Brownian *Schwankung* of the angle ϑ and the temperature T and friction constant ς, i.e., $\overline{\vartheta^2}/(4\delta t) = kT/\varsigma$. Here $\beta = (kT)^{-1}$, k is Boltzmann's constant, ϑ is the angle a (tagged) dipole moment makes with the externally applied uniform electric field $\mathbf{E}(t)$, $W(\vartheta, t)$ is the surface probability density of orientations of a dipole, and $V(\vartheta, t)$ is the potential of axially symmetric applied external torques. Here, it is simply that of the interaction of a dipole with the electric field, namely

$$V(\vartheta, t) = -\mu E(t)\cos\vartheta, \tag{2}$$

where $\boldsymbol{\mu}$ is the dipole moment of a molecule, and $E(t)$ is the amplitude of the electric field. The polarization in the field direction is then

$$P(t) = \rho_0 \mu \int_0^{\pi} \cos\vartheta\, W(\vartheta, t)\sin\vartheta d\vartheta. \tag{3}$$

Equation (3) is evaluated via the statistical moment method, which consists in expanding $W(\vartheta, t)$ as a series of Legendre polynomials $P_n(\cos\vartheta)$ [24], i.e.

$$W(\vartheta, t) = \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) f_n(t)\, P_n(\cos\vartheta), \tag{4}$$

and then using the recurrence and orthogonality properties of the P_n, thereby yielding an infinite hierarchy of differential-recurrence relations for the statistical moments $f_n(t)$, viz.,

$$\frac{2\tau_D}{n(n+1)} \dot{f}_n(t) + f_n(t) = \frac{\xi(t)}{2n+1} \left[f_{n-1}(t) - f_{n+1}(t)\right],\ \ n > 0 \tag{5}$$

Here $f_0 = 1, \xi(t) = \beta\mu E(t)$ and Eq. (3) by orthogonality can be rewritten using Eq. (4) as

$$P(t) = \rho_0 \mu f_1(t)\,. \tag{6}$$

Now, even for strong electric field intensities, $\xi(t) < 1$, thus the hierarchy of Eq. (5) may be solved by iterating a perturbation series, yielding

$$f_n(t) = f_n^{(0)} + \sum_{k=1}^{\infty} f_n^{(k)}(t), \tag{7}$$

where the superscript (k) indicates the desired order in the field strength, yielding the perturbed equations

$$n(n+1)\, f_n^{(0)} = 0, \tag{8}$$

$$\frac{2\tau_D}{n(n+1)} \dot{f}_n^{(k)}(t) + f_n^{(k)}(t) = \frac{\xi(t)}{2n+1} \left[f_{n-1}^{(k-1)}(t) - f_{n+1}^{(k-1)}(t)\right], \tag{9}$$

The hierarchy of recurrence Eq. (9) is solved subjected to the initial condition $f_n^{(k)}(-\infty) = 0$ since we are interested in the steady-state regime only. Now, the solution of Eq. (8) is obvious since it is a simple algebraic equation. Thus $f_n^{(0)} = 0$ for all $n \neq 0$. Moreover, $f_0^{(0)} = f_0 = 1$ and $f_0^{(k)} = 0,\ k > 0$. Hence, the linear response of the polarization is given explicitly by $f_1^{(1)}(t)$, that is

$$f_1^{(1)}(t) = \frac{1}{3\tau_D} \int_{-\infty}^{t} \mathrm{e}^{-\frac{t-t_1}{\tau_D}} \xi(t_1)\, \mathrm{d}t_1. \tag{10}$$

Since $f_n^{(1)}(-\infty) = 0$, we have

$$f_n^{(1)}(t) = 0,\ \ n \neq 1 \tag{11}$$

Likewise, we have the quadratic response functions $f_n^{(2)}(t)$, viz.,

$$f_n^{(2)}(t) = 0,\ n \neq 2, \tag{12}$$

and

$$f_2^{(2)}(t) = \frac{1}{5\tau_D^2} \int_{-\infty}^{t} \int_{-\infty}^{t_2} \mathrm{e}^{-\frac{3(t-t_2)}{\tau_D}} \xi(t_2)\, \mathrm{e}^{-\frac{t_2-t_1}{\tau_D}} \xi(t_1)\, \mathrm{d}t_1 \mathrm{d}t_2. \tag{13}$$

Moreover, via Eq. (9) for $n = 1$ and $k = 3$, we have the cubic polarization dynamical response, viz.,

$$f_1^{(3)}(t) = -\frac{1}{15\tau_D^3} \int_{-\infty}^{t} \int_{-\infty}^{t_3} \int_{-\infty}^{t_2} \mathrm{e}^{-\frac{t-t_3}{\tau_D}} \xi(t_3)\, \mathrm{e}^{-\frac{3(t_3-t_2)}{\tau_D}} \xi(t_2)\, \mathrm{e}^{-\frac{t_2-t_1}{\tau_D}} \xi(t_1)\, \mathrm{d}t_1 \mathrm{d}t_2 \mathrm{d}t_3 \tag{14}$$

Now, specializing to the pure AC field $E(t) = E_0 \cos \omega t$ so that $\xi(t) = \xi_0 \cos \omega t$ with $\xi_0 = \beta \mu E_0$, the polarization Eq. (6) can be written as

$$P(t) = P^{(1)}(t) + P^{(3)}(t),$$

where $P^{(1)}(t)$ is the linear polarization response given by

$$P^{(1)}(t) = \frac{\rho_0 \mu \xi_0}{3\left(1 + \omega^2 \tau_D^2\right)} \left(\cos \omega t + \omega \tau_D \sin \omega t\right), \tag{15}$$

which is the result of Debye, while the cubic polarization $P^{(3)}(t)$ is

$$\begin{aligned} P^{(3)}(t) = \frac{\rho_0 \mu \xi_0^3}{60\left(1 + \omega^2 \tau_D^2\right)\left(9 + 4\omega^2 \tau_D^2\right)} &\left\{ \frac{\left(13\omega^2 \tau_D^2 - 27\right) \cos \omega t - 2\omega \tau_D \left(21 + \omega^2 \tau_D^2\right) \sin \omega t}{3\left(1 + \omega^2 \tau_D^2\right)} \right. \\ &\left. + \frac{\left(17\omega^2 \tau_D^2 - 3\right) \cos 3\omega t + 2\omega \tau_D \left(3\omega^2 \tau_D^2 - 7\right) \sin 3\omega t}{\left(1 + 9\omega^2 \tau_D^2\right)} \right\}. \end{aligned} \tag{16}$$

This equation represents one of the most important results of the nonlinear Debye theory, demonstrating that for strong AC field amplitudes, the linear response (15) is corrected by the first term in the right-hand side of Eq. (16), while the second term predicts the existence of a third harmonic in the polarization response. This result was confirmed experimentally 20 years after its publication [12]. When $\omega = 0$, $P(t) = P_{\mathrm{s}}$ is time-independent and is given by the two first terms in the Taylor expansion of the Langevin function, viz.,

$$P_s = \rho_0 \mu \left(\frac{\xi_0}{3} - \frac{\xi_0^3}{45} \right), \tag{17}$$

The treatment described here must be further refined if the electric field comprises both a DC part and an AC part, since then the static conditions are no longer given by Eq. (8). This is the subject of the next section.

3 Nonlinear Dielectric Response in Superimposed AC and DC Electric Fields

The basic equation is still the rotational Smoluchowski Eq. (1) as given by Debye, with polarization given by Eq. (3) or (6), save that

$$V(\vartheta, t) = -\mu \left(E_S + E_0 \cos \omega t\right) \cos \vartheta, \tag{18}$$

where E_S is the static electric field amplitude, also supposed uniform and applied in the direction of the AC field. The differential-recurrence relations (5) now become

$$\frac{2\tau_D}{n(n+1)} \dot{f}_n(t) + f_n(t) = \frac{\xi_S + \xi(t)}{2n+1} \left[f_{n-1}(t) - f_{n+1}(t)\right], \; n > 0. \tag{19}$$

Where $\xi_S = \beta \mu E_S$.

We further assume that all transients due to the (sudden) application of the DC field E_S have disappeared, so that the assembly of dipoles has reached equilibrium in the absence of the AC field. Furthermore, starting from this configuration which represents the stationary state of the system before $E_0 \cos \omega t$ is applied, we then consider the *new stationary state* (i.e., all transient effects due to the application of $E_0 \cos \omega t$ have also disappeared) obtained in the presence of *both* fields. Hence, we can also use the perturbation expansion, Eq. (7) yielding the perturbation equations

$$n(n+1) f_n^{(0)} = \frac{n(n+1)\xi_S}{2n+1} \left[f_{n-1}^{(0)} - f_{n+1}^{(0)}\right], \tag{20}$$

$$\begin{aligned} \tfrac{2\tau_D}{n(n+1)} \frac{\mathrm{d}}{\mathrm{d}t} f_n^{(k)}(t) + f_n^{(k)}(t) &= \tfrac{\xi_S}{2n+1} \left[f_{n-1}^{(k)}(t) - f_{n+1}^{(k)}(t)\right] \\ &+ \tfrac{\xi(t)}{2n+1} \left[f_{n-1}^{(k-1)}(t) - f_{n+1}^{(k-1)}(t)\right]. \end{aligned} \tag{21}$$

Equation (20) can be solved using continued fractions, allowing one to express the static moments as ratios of modified Bessel functions [3]. However, we avoid this here because we can use the condition $\xi_S < 1$, yielding a perturbation expansion of all the $f_n^{(k)}(t)$ in terms of the powers of the DC field strength. Thus, we write, in an obvious notation

$$f_n^{(0)} = \sum_{q=0}^{\infty} f_n^{(0,q)}, \tag{22}$$

$$f_n^{(k)}(t) = \sum_{q=0}^{\infty} f_n^{(k,q)}(t). \tag{23}$$

Thus, the perturbation Eqs. (20) and (21) become $\left(f_0^{(0,0)} = f_0^{(0)} = f_0 = 1\right)$,

$$n(n+1) f_n^{(0,q)} = \frac{n(n+1)\xi_S}{2n+1}\left[f_{n-1}^{(0,q-1)} - f_{n+1}^{(0,q-1)}\right], \tag{24}$$

$$\begin{aligned}\tfrac{2\tau_D}{n(n+1)} \dot{f}_n^{(k,q)}(t) + f_n^{(k,q)}(t) &= \tfrac{\xi_S}{2n+1}\left[f_{n-1}^{(k,q-1)}(t) - f_{n+1}^{(k,q-1)}(t)\right] \\ &+ \tfrac{\xi(t)}{2n+1}\left[f_{n-1}^{(k-1,q)}(t) - f_{n+1}^{(k-1,q)}(t)\right], \quad k > 0.\end{aligned} \tag{25}$$

The polarization response to third order in the field strength is

$$P(t) = P^{(1)}(t) + P^{(2)}(t) + P^{(3)}(t), \tag{26}$$

where

$$P^{(1)}(t) = \rho_0 \mu \left(f_1^{(1,0)}(t) + f_1^{(0,1)}\right) \tag{27}$$

is the linear polarization response, while

$$P^{(2)}(t) = \rho_0 \mu \left(f_1^{(2,0)}(t) + f_1^{(1,1)}(t) + f_1^{(0,2)}\right), \tag{28}$$

is the quadratic polarization response (expected to vanish), and finally

$$P^{(3)}(t) = \rho_0 \mu \left(f_1^{(3,0)}(t) + f_1^{(2,1)}(t) + f_1^{(1,2)}(t) + f_1^{(0,3)}\right) \tag{29}$$

is the cubic polarization response. The nonlinear polarization (26) is explicitly determined by solving Eq. (24) up to $q = 3$. For $q = 0$, we have $n(n+1) f_n^{(0,0)} = 0$ implying $f_n^{(0,0)} = 0, \ n \neq 0$. For $q = 1$, Eq. (24) become

$$n(n+1) f_n^{(0,1)} = \frac{n(n+1)\xi_S}{2n+1}\left[f_{n-1}^{(0,0)} - f_{n+1}^{(0,0)}\right], \tag{30}$$

with nonvanishing solution

$$f_1^{(0,1)} = \frac{\xi_S}{3}. \tag{31}$$

which is the first term in the Taylor expansion of the Langevin function. For $q = 2$, we have

$$n(n+1) f_n^{(0,2)} = \frac{n(n+1)\xi_S}{2n+1}\left[f_{n-1}^{(0,1)} - f_{n+1}^{(0,1)}\right], \tag{32}$$

with solution

$$f_2^{(0,2)} = \frac{\xi_S^2}{15}. \tag{33}$$

which is the first term in the Taylor expansion of $\langle P_2 \rangle_0$. Finally, for $q = 3$, we have

$$n\,(n+1)\,f_n^{(0,3)} = \frac{n\,(n+1)\,\xi_S}{2n+1}\left[f_{n-1}^{(0,2)} - f_{n+1}^{(0,2)}\right], \tag{34}$$

so that

$$f_1^{(0,3)} = -\frac{\xi_S^3}{45},\ f_3^{(0,3)} = \frac{\xi_S^3}{105}, \tag{35}$$

as expected.

Next, we evaluate $f_1^{(1,0)}(t)$, the linear response to the AC field. Obviously, we see that $f_n^{(1,0)}(t) = 0$ save for $n = 1$, thus Eq. (25) becomes

$$\tau_D \dot{f}_1^{(1,0)}(t) + f_1^{(1,0)}(t) = \frac{\xi\,(t)}{3}, \tag{36}$$

with steady-state solution the Debye response, viz.,

$$f_1^{(1,0)}(t) = \frac{\xi_0}{3\left(1+\omega^2\tau_D^2\right)}\left(\cos\omega t + \omega\tau_D \sin\omega t\right). \tag{37}$$

Thus the linear polarization is

$$P^{(1)}(t) = \frac{\rho_0\mu}{3}\left[\xi_S + \frac{\xi_0}{\left(1+\omega^2\tau_D^2\right)}\left(\cos\omega t + \omega\tau_D \sin\omega t\right)\right]. \tag{38}$$

This result is physically acceptable, since in the linear response approximation, the steady-state DC and AC responses simply *superimpose*.

We now calculate the quadratic polarization response (28). Clearly, $f_1^{(0,2)} = 0$ by our earlier arguments, while the two remaining functions in Eq. (28) must satisfy the differential equations

$$\tau_D \dot{f}_1^{(1,1)}(t) + f_1^{(1,1)}(t) = 0,$$
$$\tau_D \dot{f}_1^{(2,0)}(t) + f_1^{(2,0)}(t) = 0,$$

with steady-state solutions $f_1^{(1,1)}(t) = 0$ and $f_1^{(2,0)}(t) = 0$. Therefore, as expected,

$$P^{(2)}(t) = 0. \tag{39}$$

Finally, we evaluate $P^{(3)}(t)$ as given by Eq. (29). We already have $f_1^{(0,3)}$ since it is given by Eq. (35). The three remaining functions satisfy

$$\tau_D \dot{f}_1^{(3,0)}(t) + f_1^{(3,0)}(t) = -\frac{\xi(t)}{3} f_2^{(2,0)}(t), \tag{40}$$

$$\tau_D \dot{f}_1^{(2,1)}(t) + f_1^{(2,1)}(t) = -\frac{\xi_S}{3} f_2^{(2,0)}(t) - \frac{\xi(t)}{3} f_2^{(1,1)}(t), \tag{41}$$

$$\tau_D \dot{f}_1^{(1,2)}(t) + f_1^{(1,2)}(t) = -\frac{\xi_S}{3} f_2^{(1,1)}(t) - \frac{\xi(t)}{3} f_2^{(0,2)}. \tag{42}$$

The determination of $f_1^{(3,0)}(t)$, $f_1^{(2,1)}(t)$ and $f_1^{(1,2)}(t)$ requires knowledge of $f_2^{(2,0)}(t)$ and $f_2^{(1,1)}(t)$ which satisfy

$$\tau_D \dot{f}_2^{(2,0)}(t) + 3 f_2^{(2,0)}(t) = \frac{3\xi(t)}{5} f_1^{(1,0)}(t), \tag{43}$$

$$\tau_D \dot{f}_2^{(1,1)}(t) + 3 f_2^{(1,1)}(t) = \frac{3\xi_S}{5} f_1^{(1,0)}(t) + \frac{3\xi(t)}{5} f_1^{(0,1)}. \tag{44}$$

We infer that the DC field does not affect the 3ω component of the nonlinear polarization in the cubic response approximation, due to Eq. (37) and because $f_1^{(3,0)}(t)$ is the sole term in the nonlinear polarization containing 3ω terms. Equations (40)–(44) then yield

$$\begin{aligned} f_1^{(3,0)}(t) = \frac{\xi_0^3}{60\left(1+\omega^2\tau_D^2\right)\left(9+4\omega^2\tau_D^2\right)} & \left\{ \frac{\left(13\omega^2\tau_D^2-27\right)\cos\omega t - 2\omega\tau_D\left(21+\omega^2\tau_D^2\right)\sin\omega t}{3\left(1+\omega^2\tau_D^2\right)} \right. \\ & \left. + \frac{\left(17\omega^2\tau_D^2-3\right)\cos 3\omega t + 2\omega\tau_D\left(3\omega^2\tau_D^2-7\right)\sin 3\omega t}{\left(1+9\omega^2\tau_D^2\right)} \right\}, \end{aligned} \tag{45}$$

i.e., the original Coffey–Paranjape result, and along with this the additional terms

$$\begin{aligned} f_1^{(2,1)}(t) = & -\frac{\xi_0^2\xi_S}{90} \frac{\left(27+7\omega^2\tau_D^2\right)}{\left(1+\omega^2\tau_D^2\right)\left(9+\omega^2\tau_D^2\right)} \\ & + \frac{\xi_0^2\xi_S}{30} \frac{\left(8\omega^6\tau_D^6+62\omega^4\tau_D^4+153\omega^2\tau_D^2-81\right)\cos 2\omega t}{\left(1+\omega^2\tau_D^2\right)\left(9+\omega^2\tau_D^2\right)\left(1+4\omega^2\tau_D^2\right)\left(9+4\omega^2\tau_D^2\right)} \\ & - \frac{2\xi_0^2\xi_S}{15} \frac{\omega\tau_D\left(4\omega^4\tau_D^4+22\omega^2\tau_D^2+63\right)\sin 2\omega t}{\left(1+\omega^2\tau_D^2\right)\left(9+\omega^2\tau_D^2\right)\left(1+4\omega^2\tau_D^2\right)\left(9+4\omega^2\tau_D^2\right)}, \end{aligned} \tag{46}$$

$$f_1^{(1,2)}(t) = -\frac{\xi_0\xi_S^2}{45} \frac{\left(27+\omega^2\tau_D^2-2\omega^4\tau_D^4\right)\cos\omega t + \omega\tau_D\left(42+19\omega^2\tau_D^2+\omega^4\tau_D^4\right)\sin\omega t}{\left(1+\omega^2\tau_D^2\right)^2\left(9+\omega^2\tau_D^2\right)}. \tag{47}$$

Furthermore, for $\omega = 0$, we have

$$P^{(3)}(t) = -\frac{\rho_0\mu\left(\xi_0+\xi_S\right)^3}{45}. \tag{48}$$

This is simply the second term of the Taylor expansion for the Langevin function with two superimposed DC fields.

Now, Eqs. (45)–(47) should be commented upon. First, on inspection of Eq. (46), application of a DC field in addition to an AC one causes a 2ω harmonic term to appear on the resulting DC response. This nonlinear frequency-dependent effect is completely different, however, from that due to the dynamic Kerr effect because there, an AC field alone is required to create a frequency-dependent DC term (the square law nonlinearity rectifies the applied field). Nevertheless, the *qualitative* frequency behavior is the same for both phenomena. Second, on inspection of Eq. (45), an extra term oscillating at the fundamental is superimposed on the pure AC response. Third, these formulas pertain with obvious changes in notation to magnetic relaxation of blocked ferrofluids [3]. Finally, we see that the DC field does not affect the third harmonic term at all *at this level of approximation*. However, if the *pentic* response is considered, the fundamental and the third harmonic will also be affected. In contrast to the original Coffey–Paranjape formulas, these results have been obtained only recently [25].

4 Account of Interactions via a Mean Field Potential

We shall now treat intermolecular interactions via a mean field static potential. The basic idea has been alluded to by Fröhlich [26], and relies on the *Ansatz* that intermolecular interactions may be represented by a (mean field) symmetric double-well potential. Thus, a way of including them in the dynamical Eq. (1) is to choose a potential exhibiting two wells in a cycle of the motion. Then, guided by the work of Maier and Saupe [17] at equilibrium and Martin, Meier and Saupe [17] for time-dependent situations in nematic liquid crystals, we merely rewrite $V(\vartheta, t)$ as

$$V(\vartheta, t) = K \sin^2 \vartheta - \mu \left(E_S + E(t)\right) \cos \vartheta, \tag{49}$$

where K represents an intermolecular interaction strength. We remark that disparate physical problems can be modeled using Eqs. (1) and (49), e.g., the nonlinear relaxation of (noninteracting) magnetic nanoparticles, with application to magnetic hyperthermia and information storage, or equally well the dielectric relaxation of polar nematic liquid crystals. Numerical and analytical calculations have been undertaken recently [27], which we now summarize.

The electric polarization is still given by Eq. (3), however, the differential-recurrence relations become [3]

$$\begin{aligned} \frac{2\tau_D}{n(n+1)} \dot{f}_n(t) + \left[1 - \frac{2\sigma}{(2n-1)(2n+3)}\right] f_n(t) &= \frac{\xi_S + \xi(t)}{2n+1} \left[f_{n-1}(t) - f_{n+1}(t)\right] \\ &+ 2\sigma \left[\frac{(n-1)}{(2n-1)(2n+1)} f_{n-2}(t) - \frac{(n+2)}{(2n+1)(2n+3)} f_{n+2}(t)\right], \end{aligned} \tag{50}$$

where $\sigma = \beta K$. Again specializing to a pure AC field, we seek the solution of Eq. (50) as a perturbation series in the AC field amplitude (cf. Eq. 7), so yielding the perturbed equations

$$\begin{aligned} \tfrac{2\tau_D}{n(n+1)} \dot{f}_n^{(k)}(t) + f_n^{(k)}(t) &= \tfrac{\xi_S}{2n+1} \left[f_{n-1}^{(k)}(t) - f_{n+1}^{(k)}(t) \right] \\ &+ \tfrac{\xi(t)}{2n+1} \left[f_{n-1}^{(k-1)}(t) - f_{n+1}^{(k-1)}(t) \right] \\ +2\sigma \left[\tfrac{n-1}{(2n-1)(2n+1)} f_{n-2}^{(k)}(t) \right. &- \left. \tfrac{n+2}{(2n+1)(2n+3)} f_{n+2}^{(k)}(t) \right], \quad k > 0, \end{aligned} \tag{51}$$

with the stationary values

$$f_n^{(0)} = Z^{-1} \int_0^{\pi} P_n(\cos\vartheta)\, e^{-\sigma \sin^2\vartheta + \xi_S \cos\vartheta} \sin\vartheta \, \mathrm{d}\vartheta, \tag{52}$$

and the partition function

$$Z = \int_0^{\pi} \mathrm{e}^{-\sigma \sin^2\vartheta + \xi_S \cos\vartheta} \sin\vartheta \, \mathrm{d}\vartheta. \tag{53}$$

However, it is no longer possible to solve the hierarchy of Eq. (51) by simple straightforward iteration, because of the mathematical complexity caused by the coupling between the seven kinds of terms involved. Nevertheless, as demonstrated in [27], we may formally solve these equations by writing them in matrix form. Thus, we introduce the column vectors in which the n dependence is subsumed,

$$\mathbf{c}^{(0)} = \begin{pmatrix} f_1^{(0)} \\ f_2^{(0)} \\ \vdots \\ f_n^{(0)} \\ \vdots \end{pmatrix}, \quad \mathbf{c}^{(k)}(t) = \begin{pmatrix} f_1^{(k)}(t) \\ f_2^{(k)}(t) \\ \vdots \\ f_n^{(k)}(t) \\ \vdots \end{pmatrix}, \quad k > 0. \tag{54}$$

Hence, Eq. (51) become the forced matrix differential equations

$$\tau_D \dot{\mathbf{c}}^{(1)}(t) + \mathbf{A}\mathbf{c}^{(1)}(t) = \xi(t)\, \mathbf{c}_1, \tag{55}$$

$$\tau_D \dot{\mathbf{c}}^{(k)}(t) + \mathbf{A}\mathbf{c}^{(k)}(t) = \xi(t)\, \mathbf{B}\mathbf{c}^{(k-1)}(t), \tag{56}$$

where

$$\mathbf{c}_1 = \frac{1}{3}\begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \\ \vdots \end{pmatrix} + \mathbf{B}\mathbf{c}^{(0)}. \tag{57}$$

The matrix elements of the time-independent system matrix **A** and driving force matrix **B** in Eqs. (55)–(57) are thus given by

$$\begin{aligned}(\mathbf{A})_{nm} = \frac{n\,(n+1)}{2}\Bigg(&-\frac{2\sigma\,(n-1)}{(2n-1)\,(2n+1)}\delta_{nm+2} + \left[1 - \frac{2\sigma}{(2n-1)\,(2n+3)}\right]\delta_{nm} \\ &+ \frac{\xi_S}{2n+1}\left(\delta_{nm-1} - \delta_{nm+1}\right) + \frac{2\sigma\,(n+2)}{(2n+1)\,(2n+3)}\delta_{nm-2}\Bigg),\end{aligned} \tag{58}$$

$$(\mathbf{B})_{nm} = \frac{n\,(n+1)}{2\,(2n+1)}\left(\delta_{nm+1} - \delta_{nm-1}\right) \tag{59}$$

(δ_{nm} is Kronecker's delta). The solution of the matrix Eqs. (55) and (56) is obtained by quadratures. We have, as in the scalar case, with $\mathbf{c}^{(k)}\left(-\infty\right) = \mathbf{0},\ k > 0$,

$$\mathbf{c}^{(1)}\left(t\right) = \frac{1}{\tau_D}\int_{-\infty}^{t} \xi\left(t'\right) \mathrm{e}^{-\mathbf{A}\frac{t-t'}{\tau_D}}\mathbf{c}_1 \mathrm{d}t', \tag{60}$$

while

$$\mathbf{c}^{(k)}\left(t\right) = \frac{1}{\tau_D}\int_{-\infty}^{t} \xi\left(t'\right) \mathrm{e}^{-\mathbf{A}\frac{t-t'}{\tau_D}}\mathbf{B}\mathbf{c}^{(k-1)}\left(t'\right) \mathrm{d}t',\ k > 1. \tag{61}$$

Next, iterating Eq. (61) twice yields vector-valued time-ordered integral representations of the vector quadratic and cubic responses analogous to the scalar case. We have

$$\mathbf{c}^{(2)}\left(t\right) = \frac{1}{\tau_D^2}\int_{-\infty}^{t}\int_{-\infty}^{t'} \xi\left(t'\right)\xi\left(t''\right) \mathrm{e}^{-\mathbf{A}\frac{t-t'}{\tau_D}}\mathbf{B}\mathrm{e}^{-\mathbf{A}\frac{t'-t''}{\tau_D}}\mathbf{c}_1 \mathrm{d}t''\mathrm{d}t', \tag{62}$$

$$\mathbf{c}^{(3)}\left(t\right) = \frac{1}{\tau_D^3}\int_{-\infty}^{t}\int_{-\infty}^{t'}\int_{-\infty}^{t''} \xi\left(t'\right)\xi\left(t''\right)\xi\left(t'''\right) \mathrm{e}^{-\mathbf{A}\frac{t-t'}{\tau_D}}\mathbf{B}\mathrm{e}^{-\mathbf{A}\frac{t'-t''}{\tau_D}}\mathbf{B}\mathrm{e}^{-\mathbf{A}\frac{t''-t'''}{\tau_D}}\mathbf{c}_1 \mathrm{d}t'''\mathrm{d}t''\mathrm{d}t' \tag{63}$$

Furthermore, for $\xi(t) = \xi_0 \cos \omega t$, Eqs. (61), (62), and (63) can be written in forms suitable for numerical computational purposes [27]. We have from Eqs. (61)–(63):

$$\mathbf{c}^{(1)}(t) = \xi_0 \mathrm{Re}\left[\boldsymbol{\varphi}_1^{(1)}(\omega)\, e^{i\omega t}\right], \tag{64}$$

$$\mathbf{c}^{(2)}(t) = \frac{\xi_0^2}{2}\mathrm{Re}\left[\boldsymbol{\varphi}_0^{(2)}(\omega) + \boldsymbol{\Phi}_2^{(2)}(2\omega)\,\boldsymbol{\varphi}_0^{(2)}(\omega)\, e^{2i\omega t}\right], \tag{65}$$

$$\begin{aligned}\mathbf{c}^{(3)}(t) = \frac{\xi_0^3}{4}\mathrm{Re}\Big\{&\Big(2\mathrm{Re}\left[\boldsymbol{\Phi}_1^{(3)}(\omega)\right]\boldsymbol{\varphi}_0^{(2)}(\omega) + \boldsymbol{\Phi}_1^{(3)}(\omega)\,\boldsymbol{\Phi}_2^{(2)}(2\omega)\,\boldsymbol{\varphi}_0^{(2)}(\omega)\Big)\, e^{i\omega t} \\ &+ \boldsymbol{\Phi}_1^{(3)}(3\omega)\,\boldsymbol{\Phi}_2^{(2)}(2\omega)\,\boldsymbol{\varphi}_0^{(2)}(\omega)\, e^{3i\omega t}\Big\},\end{aligned} \tag{66}$$

where

$$\boldsymbol{\varphi}_1^{(1)}(\omega) = \mathbf{G}(\omega)\,\mathbf{c}_1,\ \ \boldsymbol{\varphi}_0^{(2)}(\omega) = \mathbf{A}^{-1}\mathbf{B}\,\boldsymbol{\varphi}_1^{(1)}(\omega), \tag{67}$$

$$\boldsymbol{\Phi}_2^{(2)}(\omega) = \mathbf{G}(\omega)\,\mathbf{A},\ \ \boldsymbol{\Phi}_1^{(3)}(\omega) = \mathbf{G}(\omega)\,\mathbf{B}, \tag{68}$$

$$\mathbf{G}(\omega) = (\mathbf{A} + i\omega\tau_D\mathbf{I})^{-1}, \tag{69}$$

and $\mathbf{I}$ is the identity matrix. In writing Eqs. (64)–(69), we have supposed that the transition matrix $\exp(\mathbf{A}t)$ satisfies the condition

$$\lim_{t\to-\infty} \mathrm{e}^{\mathbf{A}t} = \mathbf{0}, \tag{70}$$

because *all the eigenvalues of the system matrix* $\mathbf{A}$ *are real and positive due to the properties of the Smoluchowski operator* [28]. Furthermore, the vectors $\boldsymbol{\varphi}_1^{(1)}(\omega)$ and $\boldsymbol{\varphi}_0^{(2)}(\omega)$ in Eq. (67) can also be written as linear and second-order nonlinear generalized normalized susceptibilities $X_{n1}(\omega)$ and $X_{n0}^{(2)}(\omega)$, viz.,

$$\boldsymbol{\varphi}_1^{(1)}(\omega) = \begin{pmatrix} \chi_{11}X_{11}(\omega) \\ \chi_{21}X_{21}(\omega) \\ \chi_{31}X_{31}(\omega) \\ \vdots \end{pmatrix},\ \ \boldsymbol{\varphi}_0^{(2)}(\omega) = \begin{pmatrix} \chi_{12}X_{10}^{(2)}(\omega) \\ \chi_{22}X_{20}^{(2)}(\omega) \\ \chi_{32}X_{30}^{(2)}(\omega) \\ \vdots \end{pmatrix} \tag{71}$$

with $X_{n1}(0) = 1$ and $X_{n0}^{(2)}(0) = 1$, while $\chi_{n1} = \left[\boldsymbol{\varphi}_1^{(1)}(0)\right]_n$ and $\chi_{n2} = \left[\boldsymbol{\Phi}_1^{(3)}(0)\,\boldsymbol{\varphi}_0^{(2)}(0)\right]_n$ are the corresponding static susceptibilities.

Although the foregoing matrix solutions facilitate numerical evaluation of nonlinear responses, they do not permit a qualitative understanding of the relaxation dynamics. These can be qualitatively understood however via the so-called two-mode approximation, originating in the *large* separation of the timescales of the fast intra-well and slow over-barrier (or inter-well) relaxation modes in the asymmetric double-well mean field potential (i.e., Eq. 49) with $E(t) = 0$). Here, we simply write down these two-mode approximations for the first and second-order responses and deduce from them the cubic one. Details can be found in [27].

It has become well established in the last two decades [3, 29] that the linear AC response to of dipolar systems undergoing (overdamped) rotational Brownian motion in a field of force essentially comprises two processes, namely

(a) A slow Arrhenius over-barrier relaxation process, with the same timescale for all linear response functions, which is represented here by the slowest decaying eigenvalue of the transition matrix $\exp(-\mathbf{A}t) = L^{-1}\left[(s\mathbf{I}+\mathbf{A})^{-1}\right]$, where L^{-1} denotes the inverse Laplace transform,
(b) A fast intra-well relaxation process which is not thermally activated and is near degenerate, with a characteristic timescale depending on the order of the linear response function considered.

Thus, we write for the general matrix elements of the linear response

$$f_n^{(1)}(t) = \xi_0 \chi_{n1} \mathrm{Re}\left[X_{n1}(\omega)\,\mathrm{e}^{i\omega t}\right], \tag{72}$$

where the scalar representations of χ_{n1} and $X_{n1}(\omega)$ are [3]

$$\chi_{n1} = \langle P_n P_1\rangle_0 - \langle P_n\rangle_0 \langle P_1\rangle_0\,, \tag{73}$$

$$X_{n1}(\omega) = \frac{\Delta_{n1}}{1 + i\omega/\lambda_1} + \frac{1-\Delta_{n1}}{1 + i\omega\tau_W^{(n1)}}. \tag{74}$$

Here, Δ_{n1} is the weight of the thermally activated process specific to the function $f_n^{(1)}(t)$, and $\tau_W^{(n1)}$ is the timescale of the short time near degenerate intra-well processes also specific to the function $f_n^{(1)}(t)$. These parameters are defined by [3]

$$\Delta_{n1} = \frac{\tau_{n1}/\tau_{\mathrm{eff}}^{(n1)} - 1}{\lambda_1\tau_{n1} - 2 + \left(\lambda_1\tau_{\mathrm{eff}}^{(n1)}\right)^{-1}}, \tag{75}$$

$$\tau_W^{(n1)} = \tau_{\mathrm{eff}}^{(n1)} \frac{\lambda_1\tau_{n1} - 1}{\lambda_1\tau_{\mathrm{eff}}^{(n1)} - 1}, \tag{76}$$

where in terms of low and high frequency limits of the generalized linear susceptibility

$$\tau_{n1} = \lim_{\omega\to 0} (\omega\chi_{n1})^{-1}\, \mathrm{Im}\left(\left[\varphi_1^{(1)}(\omega)\right]_n\right), \tag{77}$$

$$\tau_{\mathrm{eff}}^{(n1)} = \lim_{\omega\to\infty} \frac{\chi_{n1}}{\omega} \mathrm{Im}\left(\left[\varphi_1^{(1)}(\omega)\right]_n\right)^{-1} \tag{78}$$

The quadratic response functions $f_n^{(2)}(t)$ can also be represented in similar scalar fashion using the two-mode approximation. For example, we cite $f_1^{(2)}(t)$ for the polarization of the quadratic nonlinear response that is given by

$$f_1^{(2)}(t) = \frac{\xi_0^2}{2}\chi_{12}\mathrm{Re}\left[X_{10}^{(2)}(\omega) + X_{12}(2\omega)\,X_{10}^{(2)}(\omega)\,\mathrm{e}^{2i\omega t}\right], \tag{79}$$

where

$$X_{10}^{(2)}(\omega) = \frac{\Delta_{10}}{1 + i\omega/\lambda_1} + \frac{1-\Delta_{10}}{1 + i\omega\tau_W^{(10)}}, \tag{80}$$

$$X_{10}^{\prime(2)}(\omega) = \frac{\Delta'_{10}}{1 + i\omega/\lambda_1} + \frac{1-\Delta'_{10}}{1 + i\omega\tau_W^{(10)}} \tag{81}$$

$$X_{12}(\omega) = \frac{\Delta_{12}}{1 + i\omega\tau_{12}} + \frac{1-\Delta_{12}}{1 + i\omega\tau_W^{(12)}} \tag{82}$$

The parameters Δ_{10} and $\tau_W^{(10)}$ can be evaluated via

$$\Delta_{10} = \frac{\tau_{10}/\tau_{10}^{\mathrm{eff}} - 1}{\lambda_1\tau_{10} - 2 + \left(\lambda_1\tau_{10}^{\mathrm{eff}}\right)^{-1}}, \tag{83}$$

$$\tau_W^{(10)} = \tau_{\mathrm{eff}}^{(10)}\frac{\lambda_1\tau_{10} - 1}{\lambda_1\tau_{\mathrm{eff}}^{(10)} - 1}, \tag{84}$$

where the characteristic times τ_{10} and $\tau_{\mathrm{eff}}^{(10)}$ are determined by

$$\tau_{10} = \lim_{\omega\to 0}(\omega\chi_{12})^{-1}\,\mathrm{Im}\left(\left[\varphi_0^{(2)}(\omega)\right]_1\right), \tag{85}$$

$$\tau_{\mathrm{eff}}^{(10)} = \lim_{\omega\to\infty}\frac{\chi_{12}}{\omega}\mathrm{Im}\left(\left[\varphi_0^{(2)}(\omega)\right]_1\right)^{-1} \tag{86}$$

However, unlike Eqs. (75) and (76), analytic equations for the parameters Δ'_{10}, $\tau_W^{\prime(10)}$, Δ_{12}, τ_{12} and $\tau_W^{(12)}$ are unknown. Therefore, in Eqs. (81) and (82), they are treated as adjustable. In this way, the cubic polarization response $f_1^{(3)}(t)$ can be rewritten as

$$\begin{aligned} f_1^{(3)}(t) = \frac{\xi_0^3}{4}\chi_{13}\mathrm{Re}\Big\{&\Big(2\mathrm{Re}\left[X_{13}(\omega)\right]X_{10}^{\prime(2)}(\omega) + X_{13}(\omega)\,X_{12}(\omega)\,X_{10}^{\prime(2)}(\omega)\Big)\,\mathrm{e}^{i\omega t} \\ &+ X_{13}(3\omega)\,X_{12}(2\omega)\,X_{10}^{\prime(2)}(\omega)\,\mathrm{e}^{3i\omega t}\Big\} \end{aligned} \tag{87}$$

with $X_{10}^{\prime(2)}(\omega)$ given by Eq. (81) and

$$X_{13}(\omega) = \frac{\Delta_{13}}{1 + i\omega/\lambda_1} + \frac{1-\Delta_{13}}{1 + i\omega\tau_W^{(13)}}, \tag{88}$$

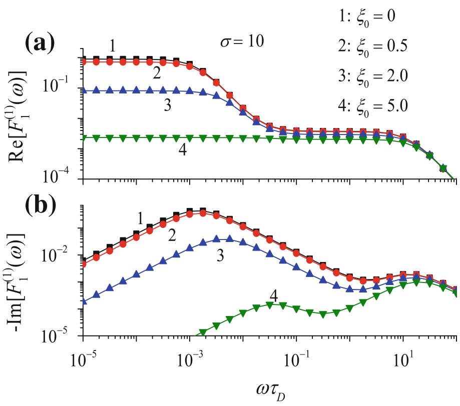

Fig. 1 (Color on line) Real (**a**) and imaginary (**b**) parts of the linear susceptibility $F_1^{(1)}(\omega) = \chi_{11} X_{11}(\omega)$ versus the normalized frequency $\omega\tau_D$ for various DC field amplitudes ξ_0 with anisotropy parameter $\sigma = 10$. Solid lines: the matrix solution. Symbols: the two-mode approximation

where Δ_{13} and $\tau_W^{(13)}$ are again adjustable parameters.

As indicated by Figs. 1 and 2, the two-mode approximation formulas yield excellent agreement with the exact numerical solution obtained via various matrix methods. The introduction of a distribution of relaxation times in the above calculations is discussed in [27]. The treatment as outlined may be used to any order in perturbation theory in the field strength. Thus, it may directly be applied both to nonlinear dielectric relaxation of polar nematic liquid crystals and to nonlinear magnetic relaxation of noninteracting single-domain ferromagnetic particles, and indeed to all polar systems where the interaction field is static. However, if this field is replaced by a *mean* field accounting for the *dynamics* of the dipole, then pronounced new features appear which are revealed *in the nonlinear response only*. We now review these.

5 Dynamical Mean Field Effects in the Nonlinear Dielectric Response

Here, dynamical effects due to interactions are accounted for in first approximation, as inspired by Berne [30]. He, by solving the Poisson equation with natural boundary conditions, demonstrated that the collective tumbling of an assembly of interacting dipoles was described by a nonlinear Fokker–Planck equation, where the orientational pair distribution function is systematically unity. Consequently, the potential has dynamical features related to the time-dependent orientational probability density. The Fokker–Planck (Smoluchowski) Eq. (1) is formally unchanged, however V is now replaced by

$$V(\vartheta, t) = U_s(\vartheta, t) + V_{\text{int}}(\vartheta, t)\,, \tag{89}$$

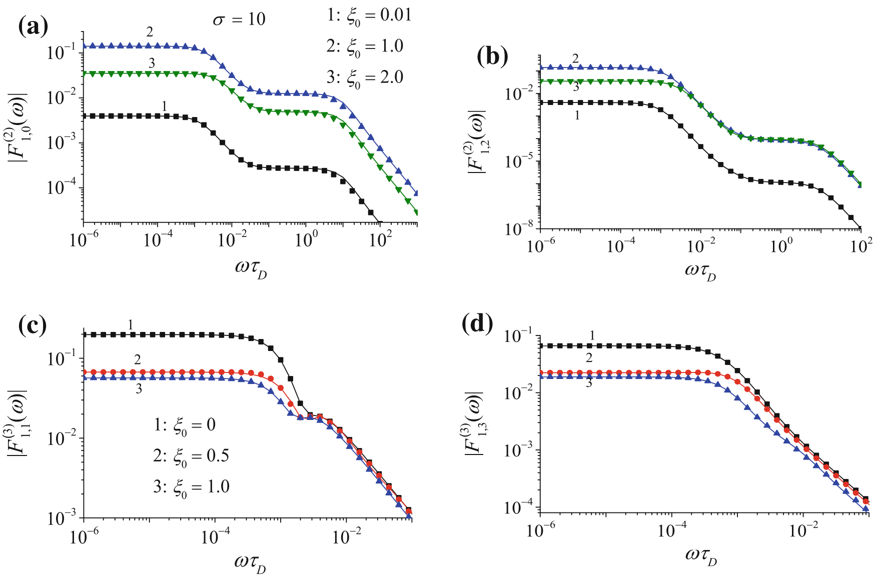

Fig. 2 (Color on line) Modulus of **a** the DC component of the nonlinear dielectric response $\left|F^{(2)}_{1,0}(\omega)\right|$, **b** the second harmonic component of the nonlinear dielectric response $\left|F^{(2)}_{1,2}(\omega)\right|$, **c** the fundamental component of that response $\left|F^{(3)}_{1,1}(\omega)\right|$, and **d** the third harmonic component $\left|F^{(3)}_{1,3}(\omega)\right|$ versus $\omega\tau_D$ for various DC field amplitudes ξ_0 with $\sigma = 10$. Solid lines: matrix solution. Symbols: two-mode approximation using the fitting parameters as described in the text

where U_s in Eq. (89) as usual contains the orientational terms due to the externally applied fields, while in the dipolar approximation [22], the interaction field is represented by

$$V_{\text{int}}(\vartheta, t) = \frac{4\pi\rho_0\mu^2}{3}\cos\vartheta f_1(t)\,. \tag{90}$$

Under these conditions, we may write

$$\beta V(\vartheta, t) = -\xi(t)\cos\vartheta + \lambda\cos\vartheta f_1(t)\,, \tag{91}$$

where

$$\lambda = 4\pi\beta\rho_0\mu^2/3 \tag{92}$$

is 4π times the linear Langevin susceptibility of an ideal gas of dipoles. Thus, using Eqs. (1) and (91), we have the intrinsically *nonlinear* differential-recurrence relations as opposed to the linear result Eq. (5)

$$\frac{2\tau_D}{n(n+1)}\dot{f}_n(t) + f_n(t) = \frac{1}{2n+1}\left[\xi(t) - \lambda f_1(t)\right]\left[f_{n-1}(t) - f_{n+1}(t)\right]. \tag{93}$$

The perturbation expansion (7) to cubic order in the field strength then yields the scheme

$$f_n^{(0)} = \frac{\lambda f_1^{(0)}}{2n+1}\left[f_{n+1}^{(0)} - f_{n-1}^{(0)}\right], \tag{94}$$

$$\frac{2\tau_D \dot{f}_n^{(1)}(t)}{n(n+1)} + f_n^{(1)}(t) = \frac{\xi(t) - \lambda f_1^{(1)}(t)}{2n+1}\left[f_{n-1}^{(0)} - f_{n+1}^{(0)}\right] + \frac{\lambda f_1^{(0)}}{2n+1}\left[f_{n+1}^{(1)}(t) - f_{n-1}^{(1)}(t)\right], \tag{95}$$

$$\begin{aligned}\frac{2\tau_D \dot{f}_n^{(2)}(t)}{n(n+1)} + f_n^{(2)}(t) = {} & \frac{\xi(t) - \lambda f_1^{(1)}(t)}{2n+1}\left[f_{n-1}^{(1)}(t) - f_{n+1}^{(1)}(t)\right] + \frac{\lambda f_1^{(2)}(t)}{2n+1}\left[f_{n+1}^{(0)} - f_{n-1}^{(0)}\right] \\ & + \frac{\lambda f_1^{(0)}}{2n+1}\left[f_{n+1}^{(2)}(t) - f_{n-1}^{(2)}(t)\right],\end{aligned} \tag{96}$$

and

$$\begin{aligned}\frac{2\tau_D \dot{f}_n^{(3)}(t)}{n(n+1)} + f_n^{(3)}(t) = {} & \frac{\xi(t) - \lambda f_1^{(1)}(t)}{2n+1}\left[f_{n-1}^{(2)}(t) - f_{n+1}^{(2)}(t)\right] + \frac{\lambda f_1^{(3)}(t)}{2n+1}\left[f_{n+1}^{(0)} - f_{n-1}^{(0)}\right] \\ & + \frac{\lambda f_1^{(2)}(t)}{2n+1}\left[f_{n+1}^{(1)}(t) - f_{n-1}^{(1)}(t)\right] + \frac{\lambda f_1^{(0)}}{2n+1}\left[f_{n+1}^{(3)}(t) - f_{n-1}^{(3)}(t)\right].\end{aligned} \tag{97}$$

We desire $f_1^{(1)}(t)$ and $f_1^{(3)}(t)$. Thus [22] we have, specializing to a pure AC field

$$f_1^{(1)}(t) = \xi_0\left[\alpha_1'^{(1)}(\omega)\cos\omega t + \alpha_1''^{(1)}(\omega)\sin\omega t\right] \tag{98}$$

with

$$\alpha_1'^{(1)}(\omega) = \frac{1}{(3+\lambda)(1+\omega^2\tau_1^2)}, \tag{99}$$

$$\alpha_1''^{(1)}(\omega) = \frac{\omega\tau_1}{(3+\lambda)(1+\omega^2\tau_1^2)}, \tag{100}$$

and

$$\tau_1 = \frac{3\tau_D}{3+\lambda}. \tag{101}$$

Clearly, the linear response to the AC stimulus in the dynamical mean field picture is still essentially of Debye type. In contrast, however, the nonlinear response $f_1^{(3)}(t)$ is now given by

$$f_1^{(3)}(t) = \xi_0^3\left[\alpha_3'^{(1)}(\omega)\cos\omega t + \alpha_3''^{(1)}(\omega)\sin\omega t + \alpha_3'^{(3)}(\omega)\cos 3\omega t + \alpha_3''^{(3)}(\omega)\sin 3\omega t\right], \tag{102}$$

where

$$\alpha_3'^{(1)}(\omega) = -\frac{3}{20}\,\frac{(3+\lambda)^2(4\lambda-39)\,\omega^4\tau_1^4 + (378+522\lambda+51\lambda^2)\omega^2\tau_1^2 + 729}{(3+\lambda)^4\,[81+4(3+\lambda)^2\,\omega^2\tau_1^2](1+\omega^2\tau_1^2)^3}, \tag{103}$$

$$\alpha_3''^{(1)}(\omega) = \frac{\omega\tau_1\left\{81(2\lambda-21) + 3(3+\lambda)\left[(\lambda(\lambda-45)-198) - (3+\lambda)^2\omega^2\tau_1^2\right]\omega^2\tau_1^2\right\}}{10(3+\lambda)^4\left(81+4(3+\lambda)^4\,\omega^2\tau_1^2\right)\left(1+\omega^2\tau_1^2\right)^3}, \tag{104}$$

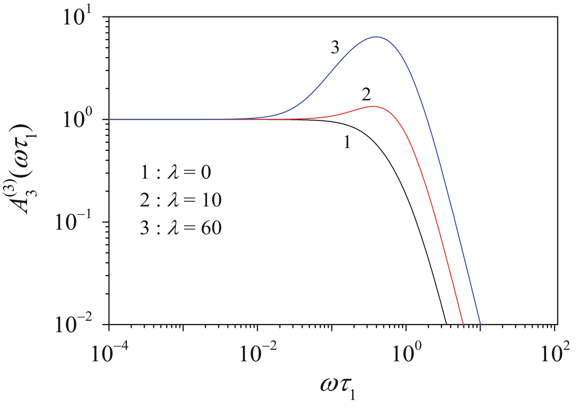

Fig. 3 Normalized modulus of the normalized nonlinear response 3ω component $A_3^{(3)}(\omega\tau_1) = \frac{1}{\alpha_3'^{(3)}(0)}\sqrt{\left(\alpha_3'^{(3)}(\omega\tau_1)\right)^2 + \left(\alpha_3''^{(3)}(\omega\tau_1)\right)^2}$ as a function of $\omega\tau_1$ for various λ. Note that $\alpha_3'^{(3)}(0) \propto (3+\lambda)^{-4}$, i.e., decreases upon cooling. The value $\lambda = 0$ is the Coffey–Paranjape result

$$\alpha_3'^{(3)}(\omega) = \frac{9\left[(3+\lambda)^2(51+20\lambda)\,\omega^6\tau_1^6 + 3\,(279 - 4\lambda\,(\lambda\,(6+\lambda) - 21))\,\omega^4\tau_1^4 - 3\,(\lambda\,(78+\lambda) - 99)\,\omega^2\tau_1^2 - 81\right]}{20\,(3+\lambda)^4\left[81 + 4\,(3+\lambda)^2\,\omega^2\tau_1^2\right]\left[1+\omega^2\tau_1^2\right]^3\left[1+9\omega^2\tau_1^2\right]} \tag{105}$$

$$\alpha_3''^{(3)}(\omega) = \frac{9\omega\tau_1\left\{9\,(2\lambda - 21) + \left(\lambda^3 - 243\lambda - 297\right)\omega^2\tau_1^2 - 3\,(3+\lambda)\left[(3+\lambda\,(19+4\lambda)) - (3+\lambda)^2\,\omega^2\tau_1^2\right]\omega^4\tau_1^4\right\}}{10\,(3+\lambda)^4\left[81 + 4\,(3+\lambda)^2\,\omega^2\tau_1^2\right]\left[1+\omega^2\tau_1^2\right]^3\left[1+9\omega^2\tau_1^2\right]} \tag{106}$$

For $\lambda = 0$, these formulas become the usual nonlinear response of noninteracting dipoles to alternating electric fields. However, cf. Figures 3 and 4, they strongly deviate from the *known results for large interactions*, thereby revealing pronounced dynamical effects due to intermolecular interactions, which must be investigated via nonlinear response measurements. In particular, the humped-back shape of the nonlinear response moduli found at large λ reveals the non-monotonic behavior of that response for interacting molecules.

This finding is in marked contrast to that of the previous section, where the modulus of the nonlinear response is *monotonic* for all interaction strengths. Now, recalling that the mean field approximation is a poor representation of long range intermolecular interactions, shorter interaction ranges could be modeled using the model under discussion by superimposing a $P_2(\cos\vartheta)\,f_2(t)$ term in the interaction potential (90). This Ansatz then leads to a Martin–Maier–Saupe-type model as pertains to dielectric relaxation of polar nematic liquid crystals. In particular, as the amplitude of the P_2 term is increased, the humped-back shape disappears, implying that Eqs. (103)–(106) can represent at best the "trivial" contribution to Ladieu's toy model of nonlinear dielectric relaxation of supercooled liquids [31]. This conclusion may be drawn because according to the present theory, on decreasing the temperature, the humped-back behavior of the nonlinear response spectrum vanishes, while experimental data on glycerol exhibit the *opposite* behavior [22, 32]. Finally, quantitative comparison

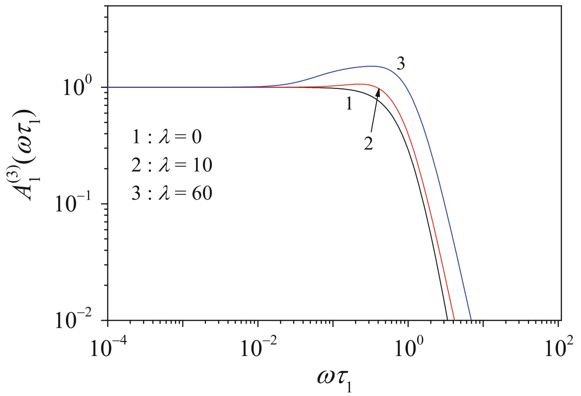

Fig. 4 Normalized modulus of the ω nonlinear polarizability component $A_3^{(1)}(\omega\tau_1) = \frac{1}{\alpha_3'^{(1)}(0)}\sqrt{\left(\alpha_3'^{(1)}(\omega\tau_1)\right)^2 + \left(\alpha_3''^{(1)}(\omega\tau_1)\right)^2}$ as a function of $\omega\tau_1$ for various λ. Note that $\alpha_3'^{(1)}(0) \propto (3+\lambda)^{-4}$, i.e., decreases upon cooling. $\lambda = 0$ is the Coffey–Paranjape result

of Eqs. (103)–(106) with experiment implies that we are using them for $-3 < \lambda \leq 3$, meaning that they can now only pertain to *low densities*. This behavior agrees with that expected from the mean field (or random phase) approximation [33], although that occasionally predicts a large density effect. Consequently, the only feasible way to treat dynamical effects of the intermolecular interactions in the above calculation is to abandon the mean field approximation entirely so that intermolecular orientational correlations can be fully included. This task is much more involved and is beyond the scope of our review.

6 Depolarizing Field and Internal Field

First, we recall various electrostatic concepts, e.g., the depolarizing and internal fields, as they may be important in explaining experimental data. We start with the depolarizing field. As much as possible, we loosely follow Brown's excellent presentation of the subject [34].

(a) The depolarizing field.

Consider a capacitor polarized due to a constant voltage imposed between its electrodes in vacuo. Consequently, an electric field $\mathbf{E}_{\text{vac}}$ exists between the electrodes. However, insertion of a dielectric will cause a decrease in the voltage between the electrodes (with respect to the field measured in vacuo). The origin of the decrease is that polarization charges (of opposite signs) appear at the surfaces of the dielectric which interface with the electrodes in order to ensure global electro-neutrality of the overall structure (capacitor + dielectric). Consequently, one says that the dielectric is polarized, and the electric field inside the dielectric $\mathbf{E}_{\mathrm{d}}$ has an opposite direction to that of $\mathbf{E}_{\mathrm{vac}}$. Hence, the overall electric field between the plates is decreased, thereby explaining the voltage decrease due to the insertion of the dielectric, hence the name "depolarizing field" for $\mathbf{E}_{\mathrm{d}}$ [35]. Standard electrostatics shows that the depolarizing field $\mathbf{E}_{\mathrm{d}}$ is systematically proportional to the polarization vector of the substance, and points in an opposite direction to that of the polarization vector of the dielectric. Moreover, $\mathbf{E}_{\mathrm{d}}$ depends on the sample shape. Thus

$$\mathbf{E}_{\mathrm{d}} = -\overset{\leftrightarrow}{D}_p \cdot \mathbf{P}, \tag{107}$$

where $\overset{\leftrightarrow}{D}_p$ is the depolarization tensor. The total field *inside* the dielectric (called the Maxwell field) is then $\mathbf{E} = \mathbf{E}_{\mathrm{vac}} + \mathbf{E}_{\mathrm{d}}$, and the various electric susceptibilities as well as the linear and nonlinear permittivities in electromagnetic theory are defined *with respect to this field*. For example, in the linear case in the AC regime, we have

$$\mathbf{P}^{(1)}(\omega) = \overset{\leftrightarrow}{\boldsymbol{\chi}}^{(1)}(\omega) \cdot \mathbf{E}(\omega), \tag{108}$$

where $\overset{\leftrightarrow}{\boldsymbol{\chi}}^{(1)}(\omega)$ is the linear susceptibility Cartesian tensor. For a macroscopic spherical isotropic sample, this tensor becomes a scalar so that the linear polarization can be linked to the vacuum field $\mathbf{E}_{\mathrm{vac}}$, e.g., for a pure AC field in vacuo, we have

$$\mathbf{P}^{(1)}(\omega) = \frac{3}{4\pi}\left(\frac{4\pi\chi^{(1)}(\omega)}{3 + 4\pi\chi^{(1)}(\omega)}\right) \cdot \mathbf{E}_{\mathrm{vac}}. \tag{109}$$

Since it is believed that the linear susceptibility (and therefore the linear complex permittivity) of a sample is an intensive quantity, determining it under the assumption of a specific shape is relatively unimportant since calculations for two different shapes lead to the same expression [22, 36]. In particular, the expression for the linear complex permittivity is the same both for an infinite thin dielectric sheet and for a sphere, yielding [22, 36]

$$\varepsilon(\omega) - 1 = 4\pi\chi^{(1)}(\omega) = \frac{\lambda}{1 + i\omega\tau_D}, \tag{110}$$

where λ is given by Eq. (92). This equation yields in particular the Langevin–Debye equation for an assembly of purely polar molecules $\varepsilon(0) - 1 = \lambda$ in the static regime. Now, the nonlinear susceptibilities may depend on the sample shape; however, if a liquid completely fills the vacuum between the electrodes, such corrections are unnecessary, because then *the applied field coincides with the Maxwell field*. However, for strongly polar liquids, the Langevin–Debye equation $\varepsilon(0) - 1 = \lambda$ noticeably disagrees with experiment, if the actual value of the dipole moment is used. This is also true for any trivial modification of this equation. An explanation of this discrepancy was given by Lorentz. He conjectured that a typical molecule in a *dense* system does not experience the applied field as a consequence of the discrete nature of matter, instead it experiences that field plus the sum of the electric fields due to all the other molecules, thus automatically leading to the concept of *internal or local field*.

(b) *The internal field*.

We have seen that this field was introduced into the literature by Lorentz. Furthermore, it is a convenient tool in the *classical microscopic theory of dielectrics* [36] because at the molecular level, matter can no longer be regarded as continuous. Although, strictly speaking, the calculation of this field should be quantum-mechanical, nevertheless the translational and rotational motion of the molecules does not depart markedly from classical behavior. Thus, we will continue with the classical treatment, and again following Brown's discussion [34], excluding the motion of atoms or ions *within* the molecules.

By definition, the internal field $\mathbf{E}_\ell$ is the field at the position of a specific (tagged) molecule *due to all charges* except those attached to that molecule. Now, although writing a general expression for the polarization (i.e., a *macroscopic quantity*) in *microscopic* terms is relatively straightforward (i.e., the statistical average of the vector sum of all molecular dipoles times the number of molecules per unit volume or concentration), it is not at all simple to relate the internal field $\mathbf{E}_\ell$ to the Maxwell field $\mathbf{E}$, or even to its average value [34]. Only for solutions of polar molecules in nonpolar solvents is this distinction unimportant and then only in the simplest cases can such a relation be established. These have been considered in detail by Lorentz and later by Onsager.

(i) *Outline of the Lorentz method for* $\mathbf{E}_\ell$ *for polar dielectrics*

We proceed as follows [34]: we construct a macroscopic sphere of radius R (i.e., *large* with respect to intermolecular distances, but *small* with respect to the overall macroscopic size of our sample), with center taken as the location of a typical molecule where the local field is calculated. The local field can then be divided into two parts: that due to matter *outside* the sphere $\mathbf{E}_{\text{out}}$ and that due to matter *inside* it $\mathbf{E}_{\text{in}}$. Under quite general conditions, we have from electrostatics

$$\mathbf{E}_{\text{out}} = \mathbf{E} + \frac{4\pi \mathbf{P}}{3}. \tag{111}$$

The computation of $\mathbf{E}_{\text{in}}$ is more difficult, as it must account in some way for the spatial arrangement of the molecules near the (tagged) one at which $\mathbf{E}_\ell$ is calculated. Lorentz showed, assuming that the molecules are arranged at the sites of a simple cubic lattice, that

$$\mathbf{E}_{\text{in}} = \mathbf{0}. \tag{112}$$

Hence, if the molecules near our (tagged) one are also situated at the sites of such a lattice, Lorentz finds that

$$\mathbf{E}_\ell = \mathbf{E}_{\text{in}} + \mathbf{E}_{\text{out}} = \mathbf{E} + \frac{4\pi \mathbf{P}}{3}. \tag{113}$$

If the arrangement differs from the simple cubic one, then we have

$$\mathbf{E}_\ell = \mathbf{E} + \frac{4\pi \mathbf{P}}{3} + \mathbf{E}_{\text{in}}, \tag{114}$$

where $\mathbf{E}_{\text{in}}$ is unknown. For a dielectric consisting of purely polar molecules, Eq. (113) leads to the Debye–Lorentz equation of state, viz.

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\lambda}{3}, \tag{115}$$

where $\varepsilon = \varepsilon\,(0)$. Since $\lambda \propto T^{-1}$, Eq. (115) predicts a transition from an *unpolarized* to a *spontaneous polarized* state at a finite temperature. For water in particular, this temperature coincides with room temperature, therefore giving rise to a fundamental criterion whereby Eqs. (113) and (115) must be rejected for polar dielectric liquids with large dielectric constants. Finally, Eq. (114) is not used in practice because of the extreme difficulty in evaluating $\mathbf{E}_{\text{in}}$.

(ii) *Outline of Onsager's method of calculating* $\mathbf{E}_\ell$ *for polar dielectrics.*

As already alluded to above, the Lorentz method of calculating ε for polar substances must be rejected. Now, Onsager [37] remarked (full details are available in [39]) that the effect of long range dipole–dipole interactions is not accounted for properly in Lorentz's computation of $\mathbf{E}_\ell$. In effect, he modified Lorentz's method to include the effects of the *surroundings of the tagged molecule of permanent dipole moment* $\boldsymbol{\mu}$ *on the local field at this molecule*. In order to calculate ε, he used a model originally proposed by Bell [38] for a spherical dipolar molecule *embedded in a dielectric*. This model is a rigid point dipole situated at the center of a *macroscopic* empty spherical cavity of radius a in a dielectric continuum with permittivity equal to the bulk permittivity ε. The radius of the cavity is determined from the close-packing condition

$$\frac{4\pi \rho_0 a^3}{3} = 1,$$

so that the volume of the cavity is that available to each molecule. Now the dipole $\boldsymbol{\mu}$ itself creates a dipolar field that *polarizes the surroundings*. The resulting polarization of the surroundings in turn *induces a uniform field in the cavity* which is called *the reaction field* $\mathbf{R}$. For a spherical cavity, the uniform field $\mathbf{R}$ has the same direction as the dipole moment in the cavity (if the cavity is not spherical, this is not so), thus, for purely polar molecules, Onsager can write $\mathbf{R} = f\boldsymbol{\mu}$. Furthermore, if a uniform electric field $\mathbf{E}$ is imposed on the dielectric by external sources, standard electrostatics [35] shows that the field in the *empty* cavity (i.e., with no dipole in it) is not equal to $\mathbf{E}$. This field is called the cavity field $\mathbf{G}$ and for a spherical cavity, is collinear with

$\mathbf{E}$, so that we have $\mathbf{G} = g\mathbf{E}$. Then Onsager writes the *overall* field in the *spherical* cavity in the presence of $\mathbf{E}$ and the tagged dipole $\boldsymbol{\mu}$ *due to the surroundings* as

$$\mathbf{E}_\ell = \mathbf{G} + \mathbf{R} = g\mathbf{E} + f\boldsymbol{\mu}, \tag{116}$$

The coefficients g and f can be calculated via electrostatics [35]. For a spherical cavity of radius a in an *infinite* dielectric, we have (details in [39, 47])

$$g = \frac{3\varepsilon}{2\varepsilon + 1}, \quad f = \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)\,a^3}. \tag{117}$$

Now, at equilibrium, the reaction field gives rise to zero torque on the tagged dipole because the term $-\boldsymbol{\mu} \cdot \mathbf{R}$ contributes only a constant to its orientational potential energy. Then, by *equating* the macroscopic polarization from electrostatics with that obtained via statistical mechanics, Onsager finds (in the linear regime)

$$(\varepsilon - 1)\,\mathbf{E} = \lambda g \mathbf{E}. \tag{118}$$

Thus, by using Eq. (117), we have Onsager's equation describing dielectrics consisting of pure polar molecules, viz.,

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{3\varepsilon} = \lambda. \tag{119}$$

For polar and *isotropically* polarizable molecules, Eq. (119) is only slightly modified. Using $\varepsilon_\infty = n^2$ (where n is the refractive index of the medium) and the Lorenz–Lorentz equation [39], Onsager finds

$$\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon\,(\varepsilon_\infty + 2)^2} = \frac{\lambda}{3}. \tag{120}$$

Equation (120) may be used to determine the permittivity of assemblies of pure polar molecules. However, for water at 25 °C, Eq. (120) yields $\varepsilon \approx 30$, while the experimental value is 78.5. Nevertheless, Onsager's method has the great advantage of removing the unphysical ferroelectric Curie point predicted by the Lorentz–Debye formula (115). The lack of full agreement with the experimental value of ε suggests that Eq. (120) should be improved.

(iii) *The Kirkwood–Fröhlich formula for the relative permittivity*

Onsager's Eq. (120) was generalized by Kirkwood [40] to a cavity containing a very large number of interacting molecules and he obtained in so doing a much more acceptable value for the relative permittivity of water. However, Fröhlich [39] presented a more systematic derivation valid for all assemblies of polar molecules, which may be summarized as follows. We regard our entire macroscopic specimen as a very large sphere of radius b placed in a uniform field and select from it a smaller yet still macroscopic sphere of radius a, such as $a << b$. The inner sphere is treated on a *microscopic* basis (i.e., via *statistical mechanics*), while the large surrounding shell is treated as a *continuous* dielectric medium, i.e., on a macroscopic basis. The entire system (inner sphere + surroundings) is assumed to obey the laws of classical statistical mechanics. Regarding the inner sphere, the total dipole moment of an ensemble of N charges is

$$\mathbf{M}(\mathbf{X}) = \sum_{i=1}^{N} \mathrm{e}_i \mathbf{r}_i , \tag{121}$$

where $\mathbf{r}_i$ is the displacement of charge number i and e_i is its charge. Now, an atom or molecule contains several elementary charges (s in total) and $\mathbf{X}$ is the ensemble of the associated displacements $\mathbf{r}_i$. Following Fröhlich, we term an atom or molecule of the inner sphere *a cell* and label such a cell j, and assume that each cell makes *the same contribution to the polarization* in the direction of the applied field $\mathbf{E}$ inside the shell. The dipole moment of the cell j is, applying Eq. (121) to the cell j

$$\mathbf{m}\left(\mathbf{x}_j\right) = \sum_{k=1}^{s} \mathrm{e}_{jk} \mathbf{r}_{jk} \tag{122}$$

with obvious notations. Then, the total dipole moment of the inner sphere comprising N cells is

$$\mathbf{M}(\mathbf{X}) = \sum_{j=1}^{N} \mathbf{m}\left(\mathbf{x}_j\right) = \sum_{j=1}^{N} \sum_{k=1}^{s} e_{jk} \mathbf{r}_{jk} \tag{123}$$

Now the mean total dipole moment of the inner sphere in the direction of $\mathbf{E}$ is

$$\langle \mathbf{M} \cdot \mathbf{e} \rangle = \frac{1}{Z} \int_0^{\pi} \int_N (\mathbf{M}(\mathbf{X}) \cdot \mathbf{e})\, \mathrm{e}^{-\beta U(\mathbf{X},\mathbf{E})} \sin\vartheta\, d\mathbf{X} d\vartheta , \tag{124}$$

where $U(\mathbf{X}, \mathbf{E})$ is the potential energy of the system of molecules inside the inner sphere in the presence of $\mathbf{E}$, ϑ is the angle between $\mathbf{M}$ and $\mathbf{E}$, $\mathbf{e}$ is a unit vector in the direction of $\mathbf{E}$, and Z is the partition function defined by

$$Z = \int_0^{\pi} \int_N \mathrm{e}^{-\beta U(\mathbf{X},\mathbf{E})} \sin\vartheta\, \mathrm{d}\mathbf{X} \mathrm{d}\vartheta .$$

Hence, in the linear approximation in $\mathbf{E}$, we have (details in [39])

$$\langle \mathbf{M} \cdot \mathbf{e} \rangle = \frac{3\varepsilon}{2\varepsilon + 1} \frac{\beta}{3} \left\langle M^2 \right\rangle_0 , \tag{125}$$

where $\langle M^2 \rangle_0$ *is the mean square value of the dipole moment of the inner sphere in the absence of the electric field*. By equating the (macroscopic) polarization obtained via electrostatics with that given by Eq. (125), we then have

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{3\varepsilon} = \frac{4\pi\beta}{3\upsilon} \langle M^2 \rangle_0 , \tag{126}$$

where υ is the volume of the dielectric. The last equation is a perfectly general result, and is *the equation of state for linear dielectrics*. Put succinctly, it yields ε in terms of the mean square fluctuations of the dipole moment of a *macroscopic* spherical specimen of the dielectric *embedded in a large volume of the same dielectric*. These fluctuations in the dipole moment are the *total fluctuations* from *all causes*, because in the dielectric several mechanisms of polarization may be operative [39].

Equation (126) may further be specialized to identify a specific mechanism, namely the contribution of the displacement (or distortional) polarization to the total dipole moment of a molecule, which is the sum of the permanent and the induced dipole moment. This postulate assumes that the contribution of this mechanism to the permittivity may be treated by separating the overall polarization into a systematic term essentially due to the permanent dipoles of the molecules and a term due to the elastic displacement of all charges. For simplicity, the latter mechanism is then treated on a continuous basis, assuming that *for this mechanism* only the inner sphere is filled with material having static relative permittivity ε_∞. The sum of the cavity and reaction fields yields

$$\mathbf{E}_\ell = \frac{3\varepsilon \mathbf{E}}{2\varepsilon + \varepsilon_\infty} + \frac{2(\varepsilon - \varepsilon_\infty)}{a^3 (2\varepsilon + \varepsilon_\infty)} \mathbf{M}, \tag{127}$$

plus the field of the dipole **M**. Since both the dipole and the reaction fields contribute only a constant to the orientational potential energy, Eq. (126) becomes (details again in [39])

$$\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{3\varepsilon} = \frac{4\pi\beta \langle M^2 \rangle_0}{3\upsilon}. \tag{128}$$

Now, the evaluation of the static permittivity from Eq. (128) requires the calculation of $\langle M^2 \rangle_0$. On using Eq. (123) and confining ourselves to terms linear in **E**, we have

$$\langle M^2 \rangle_0 = \sum_{j=1}^{N} Z_0^{-1} \int_N \mathbf{m}(\mathbf{x}_j) \cdot \mathbf{M}(\mathbf{X})\, \mathrm{e}^{-\beta U(\mathbf{X}, \mathbf{0})} \mathrm{d}\mathbf{X}, \tag{129}$$

where

$$Z_0 = \int_N \mathrm{e}^{-\beta U(\mathbf{X}, \mathbf{0})} \mathrm{d}\mathbf{X}$$

is the partition function in the absence of the external field. On introducing the notation

$$\mathrm{d}\mathbf{X}_j = \mathrm{d}\mathbf{x}_1 \ldots \mathrm{d}\mathbf{x}_{j-1}\mathrm{d}\mathbf{x}_{j+1} \ldots \mathrm{d}\mathbf{x}_N$$

so that

$$\mathrm{d}\mathbf{X} = \mathrm{d}\mathbf{X}_j \mathrm{d}\mathbf{x}_j,$$

we can rewrite Eq. (129) with some algebra as

$$\left\langle M^2 \right\rangle_0 = \sum_{j=1}^{N} \int\limits_j \mathrm{d}\mathbf{x}_j \mathbf{m}\left(\mathbf{x}_j\right) \cdot \frac{\int\limits_{N-1} \mathbf{M}\left(\mathbf{X}\right) \mathrm{e}^{-\beta U(\mathbf{X},\mathbf{0})} \mathrm{d}\mathbf{X}_j}{\int\limits_{N-1} \mathrm{e}^{-\beta U(\mathbf{X},\mathbf{0})} \mathrm{d}\mathbf{X}_j} \frac{\int\limits_{N-1} \mathrm{e}^{-\beta U(\mathbf{X},\mathbf{0})} \mathrm{d}\mathbf{X}_j}{\int\limits_{N} \mathrm{e}^{-\beta U(\mathbf{X},\mathbf{0})} \mathrm{d}\mathbf{X}}.$$

Next, by introducing the probability $p\left(\mathbf{x}_j\right)$ of finding the jth cell with the set of displacements $\mathbf{x}_j$

$$p\left(\mathbf{x}_j\right) = \frac{\int\limits_{N-1} \mathrm{e}^{-\beta U(\mathbf{X},\mathbf{0})} \mathrm{d}\mathbf{X}_j}{\int\limits_{N} \mathrm{e}^{-\beta U(\mathbf{X},\mathbf{0})} \mathrm{d}\mathbf{X}}$$

and $\mathbf{m}^*\left(\mathbf{x}_j\right)$ the mean moment of the sphere given that its jth cell has a set of *fixed* displacements $\mathbf{x}_j$ so that

$$\mathbf{m}^*\left(\mathbf{x}_j\right) = \frac{\int\limits_{N-1} \mathbf{M}\left(\mathbf{X}\right) \mathrm{e}^{-\beta U(\mathbf{X},\mathbf{0})} \mathrm{d}\mathbf{X}_j}{\int\limits_{N-1} \mathrm{e}^{-\beta U(\mathbf{X},\mathbf{0})} \mathrm{d}\mathbf{X}_j},$$

one may express the mean square dipole fluctuations $\left\langle M^2 \right\rangle_0$ as *a sum of statistical averages* over the *jth cell only*. In other words, we have

$$\left\langle M^2 \right\rangle_0 = \sum_{j=1}^{N} \int\limits_j \mathrm{d}\mathbf{x}_j \mathbf{m}\left(\mathbf{x}_j\right) \cdot \mathbf{m}^*\left(\mathbf{x}_j\right) p\left(\mathbf{x}_j\right) \mathrm{d}\mathbf{x}_j. \tag{130}$$

Next, it may be shown from electrostatics [41] that the dipole moment induced in a sphere by a dipole residing in a cavity in that sphere is independent of the size of the latter. This result is extremely important because ε is an intensive quantity (therefore independent of the size and shape of the dielectric, and the calculations are easiest for spherical shapes). This result is true even if the cavity is not concentric with the surrounding spherical shell, so that the precise location of the cavity in the dielectric is unimportant provided *it is taken as spherical*. Next, let $\mathbf{m}_s^*$ denote the dipole moment of a sphere surrounding the jth cell. Thus, if $\mathbf{m}_s^*$ can be obtained by treating the jth cell *as a point dipole in a spherical cavity surrounded by a continuous dielectric*, then

$$\mathbf{m}_s^* = \mathbf{m}^*,$$

where by definition $\mathbf{m}^*$ is the dipole moment of the *entire sphere*. Thus, we have

$$\mathbf{m}^* = \mathbf{m},$$

so that Eq. (128) reduces to Onsager's Eq. (120). Therefore, *we must assume that* $\mathbf{m}^* \neq \mathbf{m}$, since Onsager's equation *does not predict* ε *quantitatively*, meaning that it is impossible to treat the jth cell as a point dipole *surrounded by a continuous dielectric*. In other words, $\mathbf{m}^* \neq \mathbf{m}$ if and only if

- The shape of the jth cell differs from that of a sphere, a hypothesis that we do not make, otherwise the electrostatic part of the calculation becomes very difficult,
- The region surrounding the jth cell *cannot be treated on a macroscopic basis*, a hypothesis that we will maintain in our calculation of ε because then we can handle the surroundings of the jth cell by the methods of (classical) statistical mechanics.

Furthermore, an important consequence of all the electrostatic considerations made above is that $\mathbf{m}^*$ is independent of the position of the jth cell as long as this cell is so far removed from the bounding surface of the dielectric so that it *allows its interaction with the outside to be treated on a macroscopic basis*. Of course, for an infinite dielectric, this last condition is always true. Bearing in mind all the above hypotheses, we have

$$\left\langle M^2 \right\rangle_0 = N \left\langle \mathbf{m} \cdot \mathbf{m}^* \right\rangle_0,$$

since each cell contributes equally to the polarization. Consequently, Eq. (128) becomes

$$\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{3\varepsilon} = \frac{4\pi\beta\rho_0}{3} \left\langle \mathbf{m} \cdot \mathbf{m}^* \right\rangle_0. \tag{131}$$

In this equation, $\rho_0 = N/v$ is the *number of cells* per unit volume of the dielectric, and $\mathbf{m}$ and $\mathbf{m}^*$ now refer to nonelectronic displacements. Having derived Eq. (131), we can obtain the so-called Kirkwood–Fröhlich equation by first choosing the cell j in such a way that it contains only one dipolar molecule of dipole moment $\boldsymbol{\mu}$, meaning that the orientations of the dipoles are the only variables. We now define

$$\mathbf{m}^* = \boldsymbol{\mu}^*, \tag{132}$$

where $\boldsymbol{\mu}^*$ is the average dipole moment of the sphere when the tagged dipole $\boldsymbol{\mu}$ is held in a *fixed* orientation. Now, in a liquid, in the absence of an applied field, all dipolar directions are equivalent therefore

$$\left\langle \mathbf{m} \cdot \mathbf{m}^* \right\rangle_0 = \left\langle \boldsymbol{\mu} \cdot \boldsymbol{\mu}^* \right\rangle_0$$

and we must also have

$$\left\langle \boldsymbol{\mu} \cdot \boldsymbol{\mu}^* \right\rangle_0 = \boldsymbol{\mu} \cdot \boldsymbol{\mu}^*. \tag{133}$$

Finally, if the interactions with *nearest* neighbors only are considered, then $\boldsymbol{\mu}^*$ is the sum of the moment $\boldsymbol{\mu}$ of the tagged dipole held in a *fixed orientation* relative to its neighbors and the *average of the sum of the moments of its nearest neighbors*. Hence, if z represents the average number of nearest neighbors, we have

$$\boldsymbol{\mu} \cdot \boldsymbol{\mu}^* = \mu^2 \left(1 + z \left\langle \cos\gamma \right\rangle_{Av}\right) = \mu^2 g_K,$$

where γ is the angle between neighboring dipoles, and g_K is called the Kirkwood correlation factor, so that Eq. (128) becomes

$$\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{3\varepsilon} = \frac{4\pi\rho_0\mu^2 g_K}{3kT}. \tag{134}$$

Furthermore, the value of the dipole moment to be used in Eq. (134) is the dipole moment of a molecule embedded in a medium of dielectric constant ε_∞. This moment is related to the vacuum moment by the equation [39]

$$\mu = \frac{\varepsilon_\infty + 2}{3}\mu_g, \tag{135}$$

where μ_g is the dipole moment of the molecule in vacuo. Hence, by combining Eqs. (134) and (135), we finally have the Kirkwood–Fröhlich equation, viz.,

$$\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} = \frac{\lambda g_K}{3}. \tag{136}$$

By accounting for nearest neighbor contributions as described above, Kirkwood obtained $\varepsilon = 67$ for water at 25 °C, a far more acceptable value. By including both nearest and next-nearest neighbors in the evaluation of g_K, Oster and Kirkwood [42] found $\varepsilon = 78.5$, in excellent agreement with experiment. Now, we describe the generalization of the Kirkwood–Fröhlich equation to the frequency-dependent (complex) permittivity in the linear approximation.

(iv) The dynamical equation for the linear complex permittivity

Any theory of the linear complex permittivity $\varepsilon(\omega)$ of polar fluids must include the effect of the local field at the dynamical level. This calculation is much more involved than its static counterpart, because the dynamics of the internal field are generally unknown [39] and in addition are a function of $\varepsilon(\omega)$, i.e., the property one is trying to calculate. However, we may proceed in a general sense by establishing a relation between the *time-dependent* dipole moment of the dielectric and the complex permittivity. The dipole moment induced in a dielectric body induced by a very small time-dependent external electric field is, at any time (assuming that both quasi-electrostatics and linear response obtain)

$$\mathbf{M}(t) = \int_0^t \mathbf{E}(t-x)\,\frac{\mathrm{d}a}{\mathrm{d}x}(x)\,\mathrm{d}x, \tag{137}$$

where $a(t)$ is the step response of the body and $\mathbf{E}(t) = \mathbf{0}$ for $t < 0$. Following Scaife [41], we introduce the *aftereffect function* $b(t)$ defined by

$$b(t) = \begin{cases} a(\infty) - a(t) & (t > 0) \\ 0 & (t < 0) \end{cases}, \tag{138}$$

so that the polarizability $\alpha(\omega)$ of the body is given by

$$\alpha(\omega) = \int_0^\infty \dot{a}(t)\,\mathrm{e}^{-i\omega t}\mathrm{d}t = -\int_0^\infty \dot{b}(t)\,\mathrm{e}^{-i\omega t}\mathrm{d}t. \tag{139}$$

We must now relate $a(t)$ (or $b(t)$) to the induced time-dependent dipole moment $\mathbf{M}(t)$. This is accomplished by via the fluctuation–dissipation theorem which we explain as follows. First, we remark that by applying the Kramers–Kronig relations to $\alpha(\omega) = \alpha'(\omega) - i\alpha''(\omega)$, viz.,

$$\alpha'(\omega) = \frac{2}{\pi}\int_0^\infty \frac{z\alpha''(z)}{z^2-\omega^2}\mathrm{d}z, \quad \alpha''(\omega) = -\frac{2}{\pi}\int_0^\infty \frac{\omega\alpha'(z)}{z^2-\omega^2}\mathrm{d}z,$$

we have, at zero frequency

$$\alpha'(0) = \frac{2}{\pi}\int_0^\infty \frac{\alpha''(\omega)}{\omega}\mathrm{d}\omega = \frac{\beta}{3}\left\langle M^2\right\rangle_0. \tag{140}$$

Now, denoting time averages by an overbar, we have by ergodicity

$$\left\langle M^2\right\rangle_0 = \overline{M^2} = \lim_{T'\to\infty}\frac{1}{T'}\int_{-T'/2}^{T'/2} \mathbf{M}(t)\cdot\mathbf{M}(t)\,\mathrm{d}t$$

However, by the Parseval–Plancherel theorem, we must also have

$$\left\langle M^2 \right\rangle_0 = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} \lim_{T' \to \infty} \frac{\left| \tilde{\mathbf{M}}(\omega) \cdot \tilde{\mathbf{M}}^*(-\omega) \right|}{T'} \mathrm{d}\omega = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} S_M(\omega)\, \mathrm{d}\omega, \tag{141}$$

where the star denotes the complex conjugate, the tilde denotes the Fourier transform of $\mathbf{M}(t)$, i.e.,

$$\tilde{\mathbf{M}}(\omega) = \int\limits_{-T'/2}^{T'/2} \mathbf{M}(t)\, \mathrm{e}^{-i\omega t} \mathrm{d}t, \ T' \to \infty,$$

and $S_M(\omega)$ is by definition the spectral density of the fluctuations of the dipole $\mathbf{M}$. Hence via Eqs. (140) and (141), we then have the fluctuation–dissipation theorem (FDT),

$$6\alpha''(\omega) = \beta\omega S_M(\omega). \tag{142}$$

Thus, we have related the *dissipative part* $\alpha''(\omega)$ *of the frequency-dependent complex polarizability* to the *spectral density of the spontaneous fluctuations in the dipole moment at equilibrium* of the dielectric body. In deriving the FDT, we have asserted that *macroscopic fluctuations decay according to macroscopic laws*.

Now, on introducing the autocorrelation function of the dipole $C_M(t)$ defined by

$$C_M(t) = \lim_{T' \to \infty} \frac{1}{T'} \int\limits_{-T'/2}^{T'/2} \mathbf{M}\left(t - t'\right) \cdot \mathbf{M}\left(t'\right) \mathrm{d}t' = \overline{\mathbf{M}(t - t') \cdot \mathbf{M}(t')}. \tag{143}$$

so that by the Wiener–Khintchine theorem [3], $C_M(t)$ and $S_M(\omega)$ are Fourier cosine transform pairs, hence recalling that $C_M(t)$ is *even* in time and $S_M(\omega)$ is *even* in frequency we have

$$C_M(t) = \frac{1}{\pi} \int\limits_0^{\infty} S_M(\omega) \cos(\omega t)\, \mathrm{d}\omega = \frac{6}{\pi\beta} \int\limits_0^{\infty} \frac{\alpha''(\omega)}{\omega} \cos(\omega t)\, \mathrm{d}\omega \tag{144}$$

In writing the foregoing equation, we have used the FDT Eq. (142). Thus, by Fourier inversion, Eq. (144) obviously yields $\alpha''(\omega)$ in terms of the Fourier cosine transform of the aftereffect function $b(t)$, viz.,

$$\alpha''(\omega) = \frac{\beta\omega}{3} \int\limits_0^{\infty} C_M(t) \cos(\omega t)\, \mathrm{d}t = \omega \int\limits_0^{\infty} b(t) \cos(\omega t)\, \mathrm{d}t$$

where we have used Eq. (139). Thus $b(t)$ and $\mathbf{M}(t)$ are related via

$$3b(t) = \beta C_M(t) \tag{145}$$

Now, by ergodicity and stationarity in time, we also have

$$C_M(t) = \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle_0 .$$

Thus, the polarizability may be expressed in terms of the total dipole moment fluctuations as

$$\alpha(\omega) = \frac{\beta}{3} \left\{ \left\langle M^2 \right\rangle_0 - i\omega \int\limits_0^\infty \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle_0 \, \mathrm{e}^{-i\omega t} \mathrm{d}t \right\} . \tag{146}$$

This is the commonly known Kubo relation generalizing that of Fröhlich at zero frequency, viz., $\alpha'(0) = \beta \left\langle M^2 \right\rangle_0 /3$ to the frequency-dependent case, as obtained using the new method of Scaife [47]. Furthermore Scaife (see [47], Chap. 7, Eq. (7.217) has also shown by means of rather involved calculations that Eq. (128) may be generalized to the frequency-dependent case yielding

$$\frac{[\varepsilon(\omega) - \varepsilon_\infty][2\varepsilon^*(\omega) + \varepsilon_\infty][2\varepsilon(\omega) + 1]}{\varepsilon(\omega)[2\varepsilon^*(\omega) + 1](\varepsilon_\infty + 2)^2} = \frac{4\pi\alpha(\omega)}{3\upsilon}. \tag{147}$$

Here, we have separated the displacement polarization mechanism as before, and $\alpha(\omega)$ is the polarizability of a sphere in vacuo (i.e., calculated by means of classical statistical mechanics). Any further calculation necessitates a detailed investigation of the dynamics of the fluctuation phenomena at the microscopic level.

In this context, Nee and Zwanzig [43] included the fact that in the time-dependent situation the reaction field **R** lags behind the dipole. Thus, they obtained, for the dynamical Onsager model (i.e., ignoring dynamical correlations) the Fatuzzo–Mason equation [44], viz.,

$$\frac{[\varepsilon(\omega) - \varepsilon_\infty][2\varepsilon(\omega) + \varepsilon_\infty]}{3\lambda\varepsilon(\omega)} = \frac{1}{1 - i\omega\tau_D - \left(1 - \frac{\varepsilon_\infty}{\varepsilon}\right)\left(\frac{\varepsilon(\omega) - \varepsilon}{2\varepsilon(\omega) + \varepsilon_\infty}\right)}. \tag{148}$$

Hence, they were able to reproduce the experimental complex permittivity of glycerol at −60 °C. However, their derivation of Eq. (148) is open to objection. In effect, when a dipole rotates, it produces a time-dependent field outside the cavity, and energy is dissipated to the surroundings because of dielectric loss. Therefore, the dipole moment slows down: this is dielectric friction. This frictional effect is in addition to the local effects of van der Waals forces, which are usually represented by the frictional term in the Langevin equation [3]. The problem is then to determine how dielectric friction combines with the Stokes–Einstein friction of the rotational Brownian motion [39]. Therefore, the most rigorous treatment of the linear complex permittivity to date is that of Scaife, Eq. (147) [47].

(v) *The nonlinear static susceptibilities and the local field*

The range of validity of both the Onsager and the Kirkwood–Fröhlich equations has been described in Fröhlich's own words [39]: a molecule occupies a sphere of radius a, its polarizability is isotropic and no saturation effects can take place. In other words, provided the external field is small and static, the above treatment of the local field holds. If the field is increased so that the dielectric behaves nonlinearly, all the above treatment must be revisited. Here, we summarize the inclusion of internal field effects on nonlinear susceptibilities. Thus, we briefly review the main results already obtained for the cubic dielectric increment of polar fluids. In this context, Onsager mentions that his local field formula (116) is not suitable for estimating nonlinear effects due to strong electric fields. The reason for that is in the absence of free charges, the electric displacement vector **D** obeys the Maxwell equation:

$$\nabla \cdot \mathbf{D} = 0, \tag{149}$$

while the Maxwell field obeys the irrotational condition

$$\nabla \times \mathbf{E} = \mathbf{0} \tag{150}$$

so that $\mathbf{E} = -\nabla\Phi$, where Φ is the electrostatic potential. However, Eqs. (149) and (150) cannot be solved without a constitutive equation linking **D** and **E**, which for nonlinear dielectrics is

$$\mathbf{D} = \varepsilon_R \left(E^2\right) \mathbf{E}. \tag{151}$$

Furthermore, we are interested in the cubic dielectric increment only, thus we may expand the field-dependent permittivity $\varepsilon_R \left(E^2\right)$ as

$$\varepsilon_R \left(E^2\right) \approx \varepsilon \left(1 - \kappa E^2\right), \tag{152}$$

where κ is the relative cubic nonlinear dielectric increment and ε is the constant linear permittivity as before. Now, it is found [45] that κ is of the order of 10^{-18} $\mathrm{m}^2/\mathrm{V}^2$ and is usually positive (normal saturation), however, negative values have also been observed (anomalous saturation) [45–47]. By analogy with the Langevin theory of paramagnetism, the phenomenon described by Eq. (152) is called dielectric saturation. From Eqs. (149)–(152), we see that the electrostatic potential Φ no longer satisfies Laplace's equation, instead satisfying [45]

$$\left(1 - \kappa \left(\nabla\Phi\right)^2\right) \nabla^2\Phi = \kappa \left(\nabla\Phi \cdot \nabla\right) \left(\nabla\Phi\right)^2 \tag{153}$$

The details of the approximate perturbative solution of the nonlinear Eq. (153) are given elsewhere [45], and may be summarized as follows. Because of the smallness of κ, one may seek the solution of Eq. (153) by perturbation methods, i.e., we may write

$$\Phi = \Phi^{(0)} + \kappa\,\Phi^{(1)}. \tag{154}$$

Here, $\Phi^{(0)}$ is the solution of Laplace's equation while $\Phi^{(1)}$ is the perturbed part of the electrostatic potential because the dielectric is no longer linear. Including the effect of the polarizability of the molecules, we then find that the Kirkwood–Fröhlich equation is modified to (details in [45])

$$\begin{aligned}\varepsilon - \varepsilon_\infty = {} & \left(\frac{3\varepsilon}{2\varepsilon + \varepsilon_\infty}\right)\frac{4\pi\beta\left\langle M^2\right\rangle_0}{3\upsilon} + 2\kappa\varepsilon\left(\frac{2\varepsilon - 5\varepsilon_\infty}{(2\varepsilon+\varepsilon_\infty)^4}\right)\frac{(4\pi)^3\,\beta\left\langle M^4\right\rangle_0}{15\upsilon^3} \\ & + \frac{(4\pi)^2\,\kappa\varepsilon\,(\varepsilon_\infty - 1)\left\langle M^2\right\rangle_0}{(2\varepsilon+1)\,\upsilon^2}\left[\frac{2}{3}\,\frac{2\varepsilon - 5\varepsilon_\infty}{(2\varepsilon+\varepsilon_\infty)^3} - \frac{32\pi\beta\varepsilon}{5\,(2\varepsilon+\varepsilon_\infty)^4}\,\frac{\left\langle M^4\right\rangle_0}{\upsilon\left\langle M^2\right\rangle_0}\right],\end{aligned} \tag{155}$$

while the nonlinear dielectric increment is

$$\frac{\Delta\varepsilon}{E^2} = \kappa\varepsilon = -\frac{4\pi\beta^3}{90\upsilon Q}\left(\frac{2\varepsilon+1}{2\varepsilon+\varepsilon_\infty}\right)\left(\frac{3\varepsilon}{2\varepsilon+\varepsilon_\infty}\right)^3\left(3\left\langle M^4\right\rangle_0 - 5\left\langle M^2\right\rangle_0^2\right) \tag{156}$$

where $\Delta\varepsilon$ is the absolute nonlinear dielectric increment, and

$$\begin{aligned} Q = {} & 1 + \frac{1}{5}\,\frac{(\varepsilon_\infty - 1)\left(28\varepsilon^3 - 66\varepsilon^2\varepsilon_\infty - 60\varepsilon\varepsilon_\infty^2 - 37\varepsilon_\infty^3\right)}{(2\varepsilon+\varepsilon_\infty)^4} \\ & + \frac{4\pi\beta\left\langle M^2\right\rangle_0}{15\upsilon\,(2\varepsilon+\varepsilon_\infty)^5}\left\{\left(28\varepsilon^3 - 66\varepsilon^2\varepsilon_\infty - 60\varepsilon\varepsilon_\infty^2 - 37\varepsilon_\infty^3\right)(2\varepsilon+1)\ -54\varepsilon\,(\varepsilon_\infty - 1)\left(4\varepsilon^2 + 2\varepsilon\varepsilon_\infty + 3\varepsilon_\infty^2\right)\right\} \\ & + \frac{(4\pi)^2\,\beta^2\left(9\left\langle M^4\right\rangle_0 - 5\left\langle M^2\right\rangle_0^2\right)}{75\upsilon^2\,(2\varepsilon+\varepsilon_\infty)^6}\left\{6\varepsilon^2\,(\varepsilon_\infty - 1)\,(2\varepsilon - 5\varepsilon_\infty)\ -\varepsilon\,(2\varepsilon+1)\left(4\varepsilon^2 - 8\varepsilon\varepsilon_\infty + 13\varepsilon_\infty^2\right)\right\} \\ & + 3\,\frac{(4\pi)^3\,\beta^3\varepsilon^2\left(3\left\langle M^6\right\rangle_0 - 5\left\langle M^2\right\rangle_0^2\left\langle M^4\right\rangle_0\right)}{25\upsilon^3\,(2\varepsilon+\varepsilon_\infty)^7}\left(4\varepsilon^2 - 18\varepsilon\varepsilon_\infty + 10\varepsilon - 5\varepsilon_\infty\right).\end{aligned} \tag{157}$$

Now, the extra terms in the modified Kirkwood–Fröhlich Eq. (155) can usually be ignored in practice, especially for liquids with large permittivity. In contrast, the expression for the nonlinear dielectric increment cannot be simplified. Here, it is impossible to proceed without a statistical model allowing the calculation of the statistical averages in Eqs. (156) and (157).

Other attempts to calculate $\Delta\varepsilon/E^2$ were made before that of Coffey and Scaife. Following an earlier remark of Van Vleck [48], a first calculation of the nonlinear dielectric increment was attempted by Thiébaut [49], assuming that intermolecular correlations are negligible. Orientational correlations were included in the formula derived with the assumptions of Van Vleck by Kielich [50] before Thiébaut's work, then later by Barriol and Greffe [51], and Böttcher [46], with the result

$$\frac{\Delta\varepsilon}{E^2} = \kappa\varepsilon = \frac{4\pi\rho_0\beta^3\mu^4}{45}\,\frac{\varepsilon^4\,(\varepsilon_\infty+2)^4}{(2\varepsilon+\varepsilon_\infty)^2\left(2\varepsilon^2+\varepsilon_\infty^2\right)}R_S, \tag{158}$$

where

$$R_S = \frac{3\left\langle M^4\right\rangle_0 - 5\left\langle M^2\right\rangle_0^2}{2\rho_0 \upsilon \mu^4} \tag{159}$$

is called the Piekara–Kielich correlation factor [46, 50], which also arises in the Coffey–Scaife formula. However, unlike the Kirkwood factor, R_S may be negative or positive, indicating that an anomalous saturation effect may on occasion dominate the normal saturation effect. Now, Van Vleck's derivation [48] assumes that

$$\varepsilon_R\left(E^2\right) \approx \varepsilon\left(1 - \kappa E^{(0)2}\right), \tag{160}$$

where $\mathbf{E}^{(0)} = -\nabla\Phi^{(0)}$ is the field existing in a *linear* dielectric. However, as already pointed out by Onsager and later by Brown [34], no logical grounds exist for making this assumption about a nonlinear dielectric and then replacing $\varepsilon_R\left(E^2\right)$ by $\varepsilon_R\left(E^{(0)2}\right)$ both in the cavity and reaction field factors (117), because this is equivalent to assuming that *the dielectric is linear in the overall sense*, despite the fact that one is attempting to calculate *a nonlinear property*. Hence, *one cannot merely assume that Eq.* (160) *holds for a nonlinear dielectric*. A more complete theoretical discussion is given in [45].

Now, although Eq. (160) is, stricto sensu, incorrect, comparison of Eq. (158) with experiment (with $R_s = 1$) shows that agreement may sometimes be achieved, especially in substances where the Kirkwood correlation factor has value 1 [45]. Marked differences between the Thiébaut [49] and Coffey–Scaife formulas and experimental data occur occasionally [45], nevertheless the disagreement arises for both formulas from the same sources of uncertainty, namely, either experimental errors or the lack of accounting for orientational correlations. Thus, Eq. (156) demonstrates clearly that the local field manifests itself quite differently for the relative permittivity and for the nonlinear cubic dielectric increment.

Regarding dynamical susceptibilities, all we may anticipate is that the single dielectric increment splits in two dynamical responses: one at the fundamental and one at the third harmonic.

7 A Perspective: The Dean-Kawasaki Approach

As alluded to previously, it is very difficult, if not impossible, to calculate the dynamics of the internal field exactly. Nevertheless, the various correlation effects may still be calculated by using a specific many-body method, comprising the Dean-Kawasaki method [52, 53]. The latter naturally extends Berne's approach [54] so far as the mean field approximation is relaxed. For simplicity, we consider an assembly of dipoles that are distributed at random however with positions fixed in space so that only the rotational degrees of freedom are relevant. The stochastic equation describing the collective tumbling of the dipoles is then [53]

$$2\tau_D \frac{\partial \rho}{\partial t}(\mathbf{u}, t) = \nabla_{\mathbf{u}} \cdot \left[\beta\rho(\mathbf{u}, t)\,\nabla_{\mathbf{u}} \frac{\delta F}{\delta \rho}(\mathbf{u}, t) + \boldsymbol{\gamma}(\mathbf{u}, t) \right], \tag{161}$$

where $\boldsymbol{\gamma}(\mathbf{u}, t)$ is a random Gaussian white noise vector field with statistical properties

$$\overline{\boldsymbol{\gamma}(\mathbf{u}, t)} = \mathbf{0}, \tag{162}$$

$$\overline{\gamma_i(\mathbf{u}, t)\,\gamma_j(\mathbf{u}', t)} = \tau_D^{-1}\overline{\rho(\mathbf{u}, t)}\delta_{ij}\delta\left(\mathbf{u} - \mathbf{u}'\right)\delta\left(t - t'\right),\ (i, j) = x, y, z. \tag{163}$$

Here, the overbar denotes an average over the distribution of the realizations of the noise field $\boldsymbol{\gamma}$, δ_{ij} is Kronecker's delta while $\delta\left(\mathbf{u} - \mathbf{u}'\right)$ and $\delta\left(t - t'\right)$ are Dirac delta functions, ρ is defined by

$$\rho(\mathbf{u}, t) = \sum_{i=1}^{N} \delta(\mathbf{u} - \mathbf{u}_i(t)), \tag{164}$$

$\mathbf{u}_i(t)$ is the orientation of dipole i with dynamics governed by its individual rotational Langevin equation, $F = F[\rho]$ is a free energy functional and is also a (stochastic) functional of ρ (the compact notation $\delta F/\delta\rho$ holds for a functional derivative taken in the usual way for deterministic quantities). If only pair interactions are retained, the free energy functional F for a pure species may be restricted to just an entropic term, a field orientational term and (long range) pair intermolecular interactions, viz.,

$$\begin{aligned} F[\rho](t) = kT \int \rho(\mathbf{u}, t) \ln \rho(\mathbf{u}, t)\, d\mathbf{u} - \mu E(t) \int (\mathbf{u} \cdot \mathbf{e})\, \rho(\mathbf{u}, t)\, d\mathbf{u} \\ + \frac{1}{2} \int \int \rho(\mathbf{u}, t)\, U_m\left(\mathbf{u}, \mathbf{u}'\right) \rho\left(\mathbf{u}', t\right) d\mathbf{u} d\mathbf{u}', \end{aligned} \tag{165}$$

where $U_m\left(\mathbf{u}, \mathbf{u}'\right)$ is the interaction energy for a single pair of dipoles. By defining the orientational one-body and pair densities W and W_2 by the equations

$$\overline{\rho(\mathbf{u}, t)} = W(\mathbf{u}, t),\ \overline{\rho(\mathbf{u}, t)\,\rho(\mathbf{u}', t)} = W_2\left(\mathbf{u}, \mathbf{u}', t\right), \tag{166}$$

and averaging Eq. (161) over the distribution of the realizations of the noise field, we have the partial integrodifferential equation

$$\begin{aligned} 2\tau_D \frac{\partial W}{\partial t}(\mathbf{u}, t) = \nabla_{\mathbf{u}} \cdot \left[\nabla_{\mathbf{u}} W(\mathbf{u}, t) + \beta W(\mathbf{u}, t)\, \nabla_{\mathbf{u}} V_i(\mathbf{u})\right] \\ + \beta \nabla_{\mathbf{u}} \cdot \int \nabla_{\mathbf{u}} U_m\left(\mathbf{u}, \mathbf{u}'\right) W_2\left(\mathbf{u}, \mathbf{u}', t\right) d\mathbf{u}', \end{aligned} \tag{167}$$

where $V_i(\mathbf{u}, t) = -\mu E(t)(\mathbf{u} \cdot \mathbf{e})$ is the mean electrostatic orientational energy due to the molecular field (i.e., the orientational electrostatic energy as seen by a molecule). As written, Eq. (167) is just a rotational Fokker–Planck (Smoluchowski) equation forced by pair interactions. However, it may also be regarded as a nonlinear integrodifferential equation for W the orientational single-body density, because W_2 may be written in most general form as

$$W_2\left(\mathbf{u}, \mathbf{u}', t\right) = W(\mathbf{u}, t)\, W\left(\mathbf{u}', t\right) g\left(\mathbf{u}, \mathbf{u}', t\right),$$

where $g\left(\mathbf{u}, \mathbf{u}', t\right)$ is the dynamical orientational pair distribution function. In particular, Eq. (167) has been used to evaluate the temperature dependence of the dielectric constant of water and methanol, giving satisfactory agreement between the Kirkwood–Fröhlich formula and experimental data without any fitting parameter [55]. Thus, it appears that higher nonlinear correlation factors could also be computed with this method.

8 Conclusion

We have reviewed a number of methods for the calculation of the linear and nonlinear polarization responses to externally applied fields, both for noninteracting and interacting molecules. In this way, we have emphasized the role that may be played by dynamical interaction effects and the possible importance of the internal field effects in these nonlinear responses. In particular, we have given a simple method whereby thermally activated effects could be included in the theory. Moreover, we have also indicated how dynamical effects due to intermolecular interactions may alter the nonlinear polarizability spectra *without affecting the linear response*. The inclusion of internal field effects in these nonlinear spectra is absolutely nontrivial and is left for future investigation. Here, we have accounted for intermolecular interactions at the mean field level only, thereby effectively neglecting intermolecular interactions. However, we have also indicated how the collective tumbling of the dipolar system may be treated on the basis of the Dean-Kawasaki formalism, because this allows the inclusion of static and dynamic correlations at the molecular level. This formalism is essentially equivalent to the Bogolyubov–Born–Green–Kirkwood–Yvon formalism [33] treatment by diffusion processes, in which inertial effects are neglected completely. In effect, the short-range van der Waals forces are accounted for using a white noise approximation in the manner of Langevin [3], while the long range forces are treated explicitly. In particular, the Dean-Kawasaki formalism is able to reproduce the nonlinear integrodifferential equation obeyed by the equilibrium pair distribution function [32], in turn reducing to the Born–Green equation [33] when the Kirkwood superposition principle is used. Therefore, for the purpose of modeling long range interaction potentials, the various correlation factors occurring in Eqs. (136) and (156) can be computed. These tasks are left for future research.

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