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ABSTRACT

The nonlinear dielectric effect (NDE) is traditionally viewed as originating from saturation of the response of individual dipoles in a strong electric field. This mean-field view, mathematically described by the Langevin saturation function, predicts enhanced dielectric saturation at lower temperatures. In contrast, recent experiments for glycerol have shown a sharp increase of the NDE with increasing temperature. The formalism presented here splits the NDE into a sum of a term representing binary correlations of dipolar orientations and terms referring to three- and four-particle orientational correlations. Analysis of experimental data shows that the contribution of three- and four-particle correlations strongly increases at elevated temperatures. The mean-field picture of dielectric saturation as the origin of the NDE is inconsistent with observations. A positive NDE (increment of the field-dependent dielectric constant) is predicted for low-concentration solutions of polar molecules in nonpolar solvents. The dependence of the NDE on the concentration of the polar component is polynomial.

I. INTRODUCTION

Nonlinear dielectric effects are traditionally viewed as the result of saturation of the response of liquid dipoles when placed in a high electric field.[1,2] The standard argument invokes the Langevin saturation function specifying the average dipole of a single molecule aligned along the external electric field,

$$\langle m\rangle_E = mL(\beta m\chi_c E_0), \qquad L(x) = \coth x - 1/x. \tag{1}$$

Here, m is the gas-phase molecular dipole moment and the field of external free charges E_0 is modified by a generally unknown cavity-field susceptibility χ_c for a single molecule accounting for the modification of the field by the polarized surrounding liquid. The angular brackets $\langle\cdots\rangle_E$ refer to an ensemble average in the presence of the applied field and the energy of the dipole is scaled with inverse temperature $\beta = (k_B T)^{-1}$. This means that dielectric saturation becomes more pronounced at lower temperatures.

The Langevin saturation picture predicts a decrement of the dielectric constant with increasing electric field[3] as measured by the field-dependent dielectric function $\epsilon_E = \epsilon(E)$ in nonlinear dielectric experiments. The deviation of ϵ_E from the linear material dielectric constant ϵ is linear in the squared Maxwell field E in the lowest order. The proportionality constant a is the Piekara coefficient,[4–6]

$$\Delta\epsilon_E = \epsilon_E - \epsilon = aE^2. \tag{2}$$

The Langevin picture predicts $a < 0$ (dielectric saturation), as indeed observed in many cases with some notable exceptions.[6–8] Molecular dynamics simulations of water[9,10] and of dipolar fluids[11] also produced $a < 0$.

The Langevin picture is a mean-field view of dielectric phenomena when the complexity of interactions of a given tagged dipole with the surrounding liquid is replaced with a single parameter of the cavity-field susceptibility[12,13] χ_c in Eq. (1).The polarized liquid is viewed as a collection of independent dipoles $\langle m\rangle_E$. Fluctuations of the microscopic field and molecular cross-correlations are ignored in mean-field theories,[14] even though they are known to affect dielectric phenomena. In the case of the linear dielectric constant, cross-correlations account for the deviation of the Kirkwood factor from unity. The Kirkwood factor,[15]

$$g_K = \frac{1}{Nm^2}\langle \mathbf{M}^2\rangle = 1 + \sum_{i>1}\langle \mathbf{e}_1\cdot\mathbf{e}_i\rangle, \tag{3}$$

is defined through the variance of the dipole moment of a macroscopic sample $\mathbf{M}$ ($\langle\mathbf{M}\rangle = 0$) with N molecules (first equality). Alternatively, its deviation from unity comes from cross-correlations between the direction of a tagged dipole, specified by the unit vector $\mathbf{e}_1$, with the directions of the rest of the liquid dipoles specified by the unit vectors $\mathbf{e}_i$ (second equality). The angular brackets in Eq. (3) refer to an ensemble average in the absence of an external electric field. The ensemble average on the left-hand side of Eq. (3) can be written in terms of the binary correlation function of the isotropic liquid $h(1,2)$,[14,16]

$$\sum_{i>1}\langle \mathbf{e}_1\cdot\mathbf{e}_i\rangle = \frac{\rho}{V\Omega^2}\int d1d2\ (\mathbf{e}_1\cdot\mathbf{e}_2)h(1,2). \tag{4}$$

Here, ρ is the number density, 1, 2 stand for orientational and spatial coordinates,[16] V is the liquid volume, and $\Omega = 4\pi$ for linear molecules. When no orientational cross-correlations are present, the average in the above equation is zero and $g_K = 1$ in Eq. (3). The neglect of cross-correlations between the liquid dipoles leads to the Onsager mean-field result.[14] For brevity, cross-correlations between distinct dipoles in the liquid will be labeled in the rest of the article as "correlations."

It is important to stress that correlations responsible for g_K deviating from unity are binary, i.e., two particles are involved in each of the averages in Eqs. (3) and (4). The binary correlation function of the liquid[16] $h(1,2)$ is sufficient to calculate g_K. For dipolar fluids, i.e., liquids made of molecules carrying dipoles and no higher multipolar moments, $g_K(y)$ is a strongly increasing function[17–19] of the dipolar density parameter of dielectric theories[2,15] $y = (4\pi/9)\beta m^2\rho$. However, g_K does not strongly deviate from unity for many polar liquids because of the competing effect of molecular quadrupoles destroying orientational correlations.[18–20] Orientational correlations thus do not strongly affect the magnitude of the linear dielectric constant, which is the reason for a relative success of the Onsager theory[21] assuming $g_K = 1$.[14] A large dielectric constant of water is related to its ability to hydrogen bond[22] and thus to produce a substantial $g_K \simeq 2.5$–2.6. Similar values of g_K are found below for the low-temperature glycerol.

The question of the validity of Langevin's mean-field picture and the importance of correlations in the nonlinear dielectric effect has not been sufficiently studied because of the lack of direct experimental evidence, requiring a revision of this traditional view. However, the idea of the importance of correlations has been interrogated in the past and already Piekara considered binary correlations between neighboring parallel and antiparallel dipoles to explain $a > 0$ observed for nitrobenzene[4] ($a < 0$ for a sufficiently diluted solution of nitrobenzene in benzene[5,6]). The ideas of orientational correlations and "cooperative regions"[23,24] affecting the nonlinear dielectric response have been recently extended to molecular glass formers in an attempt to clarify the origin of their specific dynamics. Third- and fifth-order dynamic susceptibilities are viewed as tools to access the thermodynamic length of order in low-temperature liquids and amorphous materials.[25,26] Observations of $a > 0$ were also labeled as signatures of "cooperativity,"[27] although no quantitative model of this phenomenon has been offered. Density dependence $a(\rho)$ for a dilute solution of dipolar molecules relevant to solution measurements[5,6] is discussed below.

A direct scrutiny of the Langevin model is allowed by the temperature dependence of the Piekara coefficient, which would test the prediction of increasing dielectric saturation with lowering temperature. Such data are mostly unavailable with the exception of recent measurements by Thoms *et al.*,[28] where the results for $a(T)$ for glycerol were presented in a broad range of temperatures from 230 to 320 K. Surprisingly, these data showed a strong increase in the Piekara coefficient at temperatures above $\simeq 290$ K, in disagreement with the mean-field expectations. These measurements support the suggestion that orientational correlations involving three and four dipoles in the liquid are responsible for the nonlinear dielectric effect.[29,30]

The proposition that correlations must be essential for the nonlinear dielectric effect can be appreciated from the link between the Piekara coefficient and the fourth-order cumulant of the macroscopic dipole moment of the sample.[2,6,11,29,31] Assume an external electric field is applied perpendicular to the planes of the dielectric slab, as is commonly done in the plane capacitor setup of the dielectric experiment. If the z-axis of the laboratory frame is perpendicular to the slab's planes, one finds from the perturbation expansion[29] that the Piekara coefficient is proportional to the parameter involving the fourth-order cumulant of the z-projection of the sample dipole moment M_z,

$$a \propto N\left[1 - \langle M_z^4\rangle/(3\langle M_z^2\rangle^2)\right]. \tag{5}$$

The term in the brackets is the Binder parameter used to quantify deviations of the statistics of macroscopic thermodynamic variables from the Gaussian statistics near points of thermodynamic instability.[32] The Binder parameter tends to zero as N^{-1} in the thermodynamic limit when $N \to \infty$. This asymptote is eliminated by multiplying the bracketed term with N in Eq. (5). The Piekara coefficient thus quantifies the first-order correction to the Gaussian statistics of an extensive thermodynamic variable [M_z in Eq. (5)] stipulated by the central limit theorem. One can anticipate that deviations from this outcome should involve molecular correlations, as is the case at the points of structural instability.[32] The Piekara coefficient, like the Kirkwood factor, must, therefore, quantify statistical orientational correlations between dipoles in polar liquids.

The expansion of the fourth-order cumulant $\langle M_z^4\rangle$ in Eq. (5) in terms of individual unit vectors $\mathbf{e}_i$ along molecular dipoles shows[29] that it contains both binary correlations, in terms of the Kirkwood factor g_K, and nontrivial third- and fourth-order correlations between the dipoles not reducible to correlations of lower order (see more details below). The question addressed here is whether these higher-order correlations are essential for the nonlinear dielectric effect or, alternatively, it can be reduced to binary correlations described by g_K, as is the case for the linear dielectric constant. The present analysis thus does not offer a new theory of the nonlinear dielectric effect. It, instead, provides a formalism for separating the experimental static nonlinear dielectric susceptibility into contributions from binary and higher-order orientational correlations. The formulation is also limited to static nonlinear dielectric effects and does not address nonlinear frequency-dependent dielectric susceptibility.[27,33,34]

The theoretical formalism is next applied to the experimental data for the Piekara coefficient of glycerol by Thoms *et al.*[28] The static nonlinear susceptibility of glycerol close to the glass transition is often viewed as "trivial" and comparable to the response of the ideal gas of dipoles.[25,35] It was previously noted[30] that for most polar liquids, the nonlinear dielectric susceptibility at higher temperatures significantly exceeds the corresponding low-temperature limit. However, direct measurements of the temperature dependence of the Piekara coefficients were absent in the literature until the recent method development[36] that allowed collecting glycerol data.[28] The analysis of these data presented here shows that third- and fourth-order correlations dominate in the Piekara coefficient at elevated temperatures and are responsible for its sharp temperature rise. They cannot be neglected even at lower temperatures since they exceed, in magnitude, the binary terms by a factor of two. The "trivial" model[25,35] of the ideal gas of dipoles thus does not perform quantitatively well even at the lowest temperatures analyzed here.

Overall, the nonlinear dielectric effect reflects multi-body (binary and higher-order) orientational correlations in polar liquids. Binary correlations, probed by linear dielectric techniques, are insufficient to describe the nonlinear response. The mean-field (Langevin) picture of dielectric saturation neglecting correlations altogether is inconsistent with observations.

II. NONLINEAR DIELECTRIC EFFECT

The linear dielectric constant of dielectric theories establishes the constitutive relation, $D = \epsilon E$ (Gaussian units), connecting the electric displacement D with the Maxwell electric field E, where no anisotropy of the dielectric constant is required for isotropic polar liquids.[37,38] This definition is extended to nonlinear dielectrics in the differential form[2,39]

$$\delta D = \epsilon_E \delta E, \tag{6}$$

where $D = D(E)$ is now an arbitrary function of E. In contrast, Booth,[3] Kusalik,[11] and Scaife[40] used an alternative definition $\epsilon_E = \epsilon' = D(E)/E$; see a relevant discussion in Ref. 2. The definition through Eq. (6) yields the capacitance of the plane capacitor equal to $C = A\epsilon_E/(4\pi d)$ in which ϵ_E replaces ϵ in the standard equation (A and d are the capacitor area and the distance between the plates, respectively).

From Eq. (6), one draws the relation between ϵ_E and the third-order polarization susceptibility χ_3. It enters the series expansion of the induced electric polarization $\langle P\rangle_E$ in terms of E truncated after the second expansion term,

$$\langle P\rangle_E = \rho\langle m\rangle_E = \chi_1 E + \chi_3 E^3. \tag{7}$$

The relation between $\Delta\epsilon_E$ and the nonlinear cubic susceptibility χ_3 becomes[2,30,39,41]

$$\Delta\epsilon_E = 12\pi\chi_3 E^2. \tag{8}$$

This result applies to experiments in which a constant field bias is applied to the dielectric sample. When, instead, an oscillatory field with amplitude E_m is used, one needs to replace E^2 with $E_m^2/4$ in Eq. (8).[41] We next want to establish a connection between χ_3 and dipolar correlations in a polar liquid.

The response of a dielectric slab to an applied electric field is anisotropic and requires separate consideration of the field applied perpendicular to the slab planes (z-axis) and parallel to the planes (x, y-axes). The two responses are then combined to obtain the rotationally invariant variance of the vector dipole moment $\langle \mathbf{M}^2\rangle$, which should be independent of the sample shape if the dielectric constant is a material property.[14,42] In the derivation presented below, we will assume that the nonlinear dielectric susceptibility is a local property independent of the direction of the applied field such that the precautions required for the linear polar response, related to the long-range character of dipolar interactions, are not required for the nonlinear dielectric response. The results obtained here, stressing the importance of multiparticle correlations, support this assumption.

Applying the field of external charges E_0 along the z-axis, one obtains from the statistical perturbation expansion[29] in terms of the weak perturbation $\beta M_z E_0$,

$$\langle P_z\rangle_E = \beta E_0 \frac{\langle M_z^2\rangle}{V} + (\beta E_0)^3 \frac{K_4^z}{6V}, \tag{9}$$

where the fourth-order cumulant is

$$K_4^z = \langle M_z^4\rangle - 3\langle M_z^2\rangle^2. \tag{10}$$

Assuming isotropy (locality) of the fourth cumulant, K_4^z can be written in terms of the vector dipole moment $15K_4^z = 3\langle \mathbf{M}^4\rangle - 5\langle \mathbf{M}^2\rangle^2$ as appears in a number of formulations of the nonlinear dielectric response.[2,6,11,31,40,43] The isotropy assumption does not apply to the second cumulant $\langle M_z^2\rangle$ in Eq. (9) and application of the external field along z- and x-axes separately is required.

The fourth-order cumulant K_4^z can be written in the form of correlations of individual unit vectors $\mathbf{e}_j$ specifying orientations of the dipoles in the liquid,

$$\begin{aligned} m^{-4}\langle M_z^4\rangle = \frac{N}{5} &+ \sum_{i\neq j}\left[3\langle e_{iz}^2 e_{jz}^2\rangle + 4\langle e_{iz}e_{jz}^3\rangle\right] \\ &+ 6\sum_{i\neq j\neq k}\langle e_{iz}e_{jz}e_{kz}^2\rangle + \sum_{i\neq j\neq k\neq m}\langle e_{iz}e_{jz}e_{kz}e_{mz}\rangle, \end{aligned} \tag{11}$$

where e_{iz} is the z-projection of the unit vector of the molecular dipole. The fourth-order cumulant separates into the component involving binary correlations (second term) and nontrivial correlations between three (third term) and four (last term) distinct dipoles. The binary term can be explicitly evaluated[29] with the higher-order terms left unspecified. The result is

$$K_4^z = \frac{2m^4 N}{15}\left[H_z^{(2)} + H_z^{(3)} + H_z^{(4)}\right], \tag{12}$$

where

$$H_z^{(2)} = 6(g_K^L - 1) + \frac{5}{2}\beta^{-1}\rho\chi_T - 1,$$
$$H_z^{(3)} = \frac{45}{N}\sum_{i\neq j\neq k}\langle e_{iz}e_{jz}e_{kz}^2\rangle - 5N(g_K^L - 1), \quad (13)$$
$$H_z^{(4)} = \frac{15}{2N}\sum_{i\neq j\neq k\neq m}\langle e_{iz}e_{jz}e_{kz}e_{mz}\rangle - \frac{5N}{2}(g_K^L - 1)^2.$$

In Eq. (13),

$$g_K^L = \frac{\langle M_z^2\rangle}{Nm^2} = \frac{\epsilon - 1}{3y\epsilon} \quad (14)$$

is the longitudinal Kirkwood factor equal to the $k = 0$ value, $S^L = S^L(0)$, of the longitudinal dipolar structure factor[44,45] and $\beta^{-1}\rho\chi_T$ is the $k = 0$ value of the density structure factor expressed[46] in terms of the liquid isothermal compressibility χ_T. Identical equations were derived in Ref. 29. However, g_K notation was incorrectly used there in place of g_K^L as noted by Fulton.[47]

The terms linear in N are included in $H^{(3)}$ and $H^{(4)}$ since they must cancel out with the correlation terms reducible to lower-order correlations. For instance, third-order correlations in $H^{(3)}$ require the three-particle distribution function $g(1, 2, 3)$, where the numbers $1, 2, 3$ specify both positions and orientations of molecules in the liquid. If the superposition approximation[16] $g(1, 2, 3) \simeq g(1, 2)g(1, 3)g(2, 3)$, factorizing the three-particle distribution function into the product of binary functions, is applied, the first and second terms in the equation for $H^{(3)}$ become equal and this correlation vanishes. Therefore, only correlations of three and four dipoles nonreducible to correlations of lower order contribute to $H^{(3)}$ and $H^{(4)}$. Overall, K_4^z must scale as $\propto N$ for the induced polarization $\langle P_z\rangle_E$ in Eq. (9) to be an intensive thermodynamic variable. This means that the terms linear in N in $H^{(3)}$ and $H^{(4)}$ must vanish. Because of the importance of nonreducible multiparticle correlations, constructing approximate theories[48–50] for the nonlinear dielectric susceptibility is challenging. For instance, the quadratic hypernetted chain closure for dipolar liquids[39] produces $a > 0$, through the account for electrostriction, in disagreement with simulations.[11]

Turning to the electric field applied along the x-axis, one obtains the results identical to Eqs. (9)–(13) provided that the subscript z is replaced with the subscript x. Since probing a polar liquid along the x-axis allows access to the transverse polar response,[51] the x-projection of the binary term in the nonlinear susceptibility in Eq. (13) becomes

$$H_x^{(2)} = 6(g_K^T - 1) + \frac{5}{2}\beta^{-1}\rho\chi_T - 1. \quad (15)$$

Here, $g_K^T = (\epsilon - 1)/(3y)$ is the transverse Kirkwood factor equal to the $k = 0$ value of the transverse dipolar structure factor of the polar liquid $S^T = S^T(0)$. Accordingly, g_K^L in equations for $H_z^{(3,4)}$ in Eq. (13) is replaced with g_K^T in the corresponding equations for $H_x^{(3,4)}$. As anticipated from standard dielectric theories,[15] anisotropy of the dielectric response applies to binary correlations related to longitudinal and transverse projections of the Kirkwood factor.[51] For instance, the variances of z- and x-projections of the dipole moment [the first term in Eq. (9)] are not equal[47,51] and are related to the total variance by the following formulas:

$$\langle M_z^2\rangle = \frac{1}{2\epsilon + 1}\langle \mathbf{M}^2\rangle, \qquad \langle M_x^2\rangle = \frac{\epsilon}{2\epsilon + 1}\langle \mathbf{M}^2\rangle. \quad (16)$$

Given that the x- and y-projections are equivalent in the slab geometry, one can next combine the z- and x-projections of the polarization field as $\langle P_z\rangle_E + 2\langle P_x\rangle_E$ to arrive at the variance of the total dipole moment of the sample $\mathbf{M}$ in the first term of the perturbation series in Eq. (9). This linear combination eliminates the long-range, $\propto r^{-3}$, component in the dipolar correlation function and thus eliminates the dependence of the result on the sample shape for the linear dielectric response.[14,18,42]

The resulting linear combination of two Cartesian projections is

$$\langle P_z\rangle_E + 2\langle P_x\rangle_E = \beta E_0\frac{\langle \mathbf{M}^2\rangle}{V} + (\beta E_0)^3\frac{K_4}{2V}. \quad (17)$$

In this equation, the fourth-order cumulant is given as a sum of the binary and higher-order correlation terms,

$$K_4 = \frac{2m^4N}{15}\Big[H^{(2)} + H^{(3,4)}\Big]. \quad (18)$$

The binary term in Eq. (18) is given by a closed-form expression allowing direct calculation from experimentally accessible parameters of polar liquids,

$$H^{(2)} = 6(g_K - 1) + \frac{5}{2}\beta^{-1}\rho\chi_T - 1. \quad (19)$$

Here, $g_K = (g_K^L + 2g_K^T)/3$ is the Kirkwood factor [Eq. (3)] satisfying the Kirkwood–Onsager equation,[2,15]

$$(\epsilon - 1)(2\epsilon + 1) = 9y\epsilon g_K. \quad (20)$$

As mentioned above, the higher-order correlations are assumed to be independent of the sample shape and are collected into the term $H^{(3,4)}$ in Eq. (18).

We note that the often employed replacement of $\langle \mathbf{M}^2\rangle$ in the Kirkwood–Onsager equation with the dipole variance in the electric field $\langle \mathbf{M}^2\rangle_E$ as a starting point for developing a theory of the nonlinear dielectric effect is not justified. For spherical samples, this type of approximation amounts to assuming that the cavity field in a sample is given by the solution of the linear boundary value problem with an effective nonlinear dielectric constant $\epsilon' = D(E)/E$ [Eq. (7.31) in Ref. 2]. The issue here is to construct a formalism eliminating the long-range $\propto r^{-3}$ dipolar correlations, making the result depend on the sample shape.[42] A combination of longitudinal (z-projection for the slab) and transverse (x-projection for the slab) susceptibilities constructed for a specific sample to achieve this goal within the linear response approximation does not automatically extend to the case of nonlinear response. A complete perturbation expansion in powers of the electric field should be used instead, either for a spherical or slab samples. The use of slab geometry in the present framework avoids the need for a cavity field[2] in a nonlinearly polarized dielectric. It is also important to stress that this algorithm eliminates the shape-dependent long-range correlations in the binary term $H^{(2)}$, thus producing g_K in Eq. (19) affected by short-range correlations only.[18,52]

To connect the fourth-order cumulant to the third-order dielectric susceptibility χ_3, one rewrites Eq. (7) for two polarization projections by applying the boundary condition $E_0 = E$ to the x-projection,

$$\begin{aligned}\langle P_z\rangle_E &= \chi_1 E + \chi_3 E^3,\\ \langle P_x\rangle_E &= \chi_1 E_0 + \chi_3 E_0^3.\end{aligned} \tag{21}$$

These equations are supplemented with $\epsilon = 1 + 4\pi\chi_1$ and the connection between $E_0 = D$ and E when the field is applied along the z-axis,

$$E_0 = \epsilon E + 4\pi\chi_3 E^3. \tag{22}$$

Note that the term cubic in the field was missing from the connection between E_0 and E in the derivation presented by Kusalik.[11]

By combining the polarization components from Eq. (21) according to the rule on the left-hand side of Eq. (17), one obtains

$$\chi_1 = \frac{\epsilon - 1}{4\pi} = \frac{\epsilon}{2\epsilon + 1}\frac{\beta\langle \mathbf{M}^2\rangle}{V} \tag{23}$$

and

$$\chi_3 = \frac{\epsilon^4}{2\epsilon^4 + 1}\frac{\beta^3 K_4}{2V} \simeq \frac{\beta^3 K_4}{4V}. \tag{24}$$

Given the definition of the Kirkwood factor in Eq. (3), the equation for the linear susceptibility χ_1 is the Kirkwood–Onsager equation [Eq. (20)]. The equation for χ_3 allows one to relate K_4 to the experimentally measurable Piekara coefficient through Eq. (8). Since $H^{(2)}(T)$ in Eq. (18) can be accessed from experimental data, experimental $a(T)$ provides access to the higher-order term $H^{(3,4)}(T)$. This term turns out to dominate at high temperatures and is responsible for a sharp rise in the Piekara coefficient of glycerol with rising temperature.

III. DATA ANALYSIS

The data reported by Thoms *et al.*[28,36] were collected with a large amplitude oscillatory field and zero bias field. One, therefore, has to apply $E^2 \to E_m^2/4$ in Eq. (8) with the following result for the Piekara coefficient $\Delta\epsilon_E/E_m^2$ expressed in terms of the binary and higher-order orientational correlations:

$$a = \frac{\pi\beta^3 m^4\rho}{10}\left[H^{(2)} + H^{(3,4)}\right]. \tag{25}$$

As mentioned above, K_4 can be alternatively written in the form of the fourth cumulant of the vector dipole moment,[11,31,48,49]

$$K_4 = \frac{1}{15}\left[3\langle \mathbf{M}^4\rangle - 5\langle \mathbf{M}^2\rangle^2\right], \tag{26}$$

which produces an alternative expression for a,

$$a = \frac{\pi\beta^3}{20V}\left[3\langle \mathbf{M}^4\rangle - 5\langle \mathbf{M}^2\rangle^2\right]. \tag{27}$$

The derivation presented above applies to a nonpolarizable dipolar liquid. To apply the theory to experimental data, electronic polarization due to molecular polarizability needs to be included. This can be achieved by adopting the Fröhlich model[15] viewing a polar liquid as an ensemble of permanent dipoles immersed in the dielectric continuum with the dielectric constant ϵ_∞ equal to the liquid refractive index squared. The vacuum external field E_0 in the above derivation is then replaced with the Maxwell field in the electronically polarized continuum $E_\infty = E_0/\epsilon_\infty$. The perturbation expansion in Eq. (17) is performed in terms of the field E_∞, and the boundary condition for the field applied along the x-axis reads $E_\infty = E$.

Repeating the above analysis in terms of fields E_∞ and E, one finds that the linear polarization susceptibility in Eq. (23) becomes

$$\chi_1 = \frac{\epsilon - \epsilon_\infty}{4\pi} = \frac{\epsilon}{2\epsilon + \epsilon_\infty}\frac{\beta\langle \mathbf{M}'^2\rangle}{V}, \tag{28}$$

where now the total dipole moment $\mathbf{M}'$ is a sum of all permanent dipoles $\mathbf{m}'$ modified by electronic polarization of the molecule. Assuming that each molecule carries an effective dipole

$$\mathbf{m}' = \mathbf{m}\frac{\epsilon_\infty + 2}{3} \tag{29}$$

corrected by the Lorenz cavity field,[2,15] one arrives at the Kirkwood–Fröhlich equation,[15] given by

$$\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} = y g_K, \tag{30}$$

or, alternatively,

$$\Delta\epsilon(2\epsilon + \epsilon_\infty) = 9y'\epsilon g_K. \tag{31}$$

Here, $\Delta\epsilon = \epsilon - \epsilon_\infty$ is the dielectric strength and $y' = (4\pi/9)\beta\rho(m')^2$.

The formula for the third-order susceptibility modifies to

$$\chi_3 = \frac{\epsilon^4}{2\epsilon^4 + \epsilon_\infty^4}\frac{\beta^3 K_4}{2V} \simeq \frac{\beta^3 K_4}{4V} \tag{32}$$

and is less affected by the polarizability corrections [compare to Eq. (24)]. Equation (25) remains intact except for the replacement of the gas-phase permanent dipole m with the effective condensed-phase dipole m'.

A number of recent studies[23,25,27,53] identified a dimensionless third-order dielectric susceptibility $X_3 = (4\pi)^2\rho|\chi_3|/(\beta\Delta\epsilon^2)$. Expressed in terms of dipolar correlations, this static susceptibility becomes

$$X_3 = \frac{1}{30}\left(\frac{2\epsilon + \epsilon_\infty}{\epsilon g_K}\right)^2\left|H^{(2)} + H^{(3,4)}\right|. \tag{33}$$

To separate $H^{(3,4)}$ from the binary term $H^{(2)}$, the experimental results for the density[55] and compressibility[56] of glycerol were used in Eq. (19). The compression term [second term in Eq. (19)] makes a small, $\simeq 8\times 10^{-3}$, contribution to $H^{(2)}$ in the case of glycerol (see the supplementary material). The Kirkwood factor is more essential and it can be calculated from Eq. (30). An alternative route to $g_K(T)$ can be established through the mean-field

Wertheim theory,[18,54] which—in contrast to the Kirkwood–Fröhlich equation applying the continuum form of the medium electronic polarization—provides the effective molecular dipole and polarizability in the liquid in terms of functions derived from liquid-state perturbation theories.[16,57] It therefore replaces the dipolar density y in the Kirkwood–Onsager equation [Eq. (20)] with the effective dipolar density

$$y_{\text{eff}} = (4\pi/9)\beta\rho(m')^2 + (4\pi/3)\rho\alpha' \tag{34}$$

through a formalism for calculating the liquid-state permanent dipole m' and the liquid-state polarizability α'. They are altered from their corresponding gas-phase values due to electronic polarization of a given tagged molecule by the local electric field of the surrounding liquid. These two approaches produce consistent results for glycerol (Fig. 1), with Wertheim's formalism yielding a somewhat lower temperature slope for $g_K(T)$. Similar results for the Kirkwood–Fröhlich route were recently reported by Gabriel *et al.*[58]

The binary correlation term $H^{(2)}$ in Eq. (25) was calculated from experimental parameters of glycerol and is shown by the solid line in Fig. 2. The experimental $a(T)$ were used to calculate $H^{(2)} + H^{(3,4)}$ (red points) from Eq. (25). The correlation term $H^{(3,4)}$ (blue points) was calculated from these results by substituting m' in place of m and taking $H^{(2)}$ from Eq. (19). The dielectric constant $\epsilon_\infty(T)$ was calculated from $\rho(T)$[55] and the molecular polarizability of glycerol[59] $\alpha = 8.17$ Å^3 according to the Clausius–Mossotti equation; $\epsilon(T)$ is from Ref. 60 (see the supplementary material). The molecular dipole moment is $m = 2.67$ D[61,62] ($m = 2.56$ D was listed in Ref. 63).

It is clear that higher-order correlations specified by $H^{(3,4)}$ dominate in the Piekara coefficient at elevated temperatures: The magnitude of this term increases by a factor of ≃40 at the end of the temperature scale compared to the low-temperature values (lower panel in Fig. 2). The higher-order and binary correlations are of opposite sign, incompletely compensating each other below ≃280 K. One empirically finds $H^{(2)} + H^{(3,4)} \simeq -H^{(2)}$ (dashed line in the lower panel in Fig. 2). Adopting this approximation, one obtains from Eq. (33)

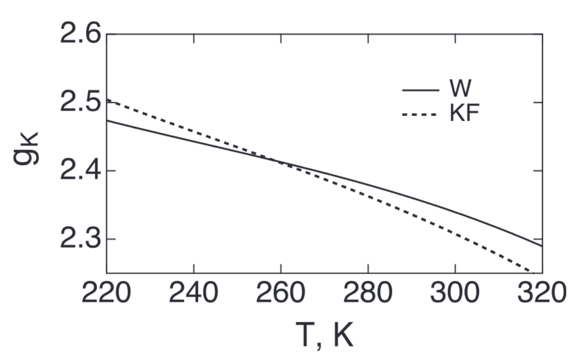

FIG. 1. $g_K(T)$ calculated from the Kirkwood–Fröhlich equation [Eq. (30), KF, dashed] and from the Wertheim theory[54] (W, solid) vs T with the molecular parameters of glycerol.

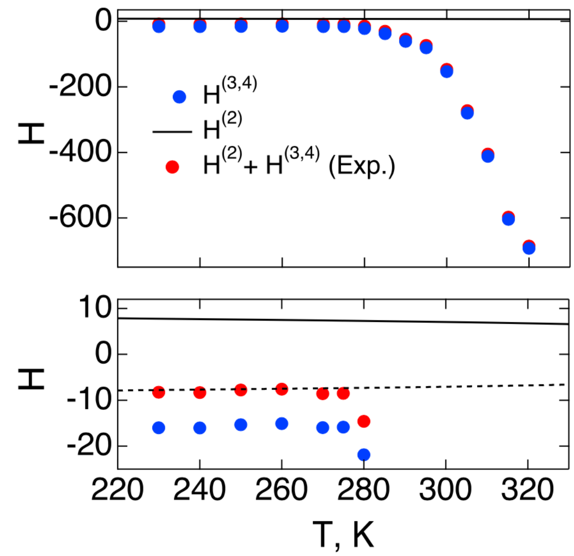

FIG. 2. $H^{(2)}$ (solid line), $H^{(3,4)}$ (blue points), and $H^{(2)} + H^{(3,4)}$ (red points) from experimental[28] Piekara coefficients $a(T)$ used in Eq. (25) where m is replaced with m' calculated according to Wertheim's algorithm[54] also used to calculate $g_K(T)$ in Eq. (19). Average values of experimental[28,36] $a(T)$ were taken at each temperature. The lower panel shows the magnified part of the plot at low temperatures; the dashed line refers to $-H^{(2)}$ and the solid line to $H^{(2)}$.

$$X_3 \simeq \frac{1}{30}\left(\frac{2\epsilon + \epsilon_\infty}{\epsilon g_K}\right)^2 |6g_K - 7|. \tag{35}$$

From this equation, $X_3 \simeq 0.17$ for glycerol at $T \simeq 210$ K, in agreement with the value ≃0.16 reported from measurements.[35] The theory thus predicts a possibility of $X_3 = 0$ at $g_K = 7/6$.

If the mean-field view, neglecting dipolar correlations, is alternatively adopted, one obtains $H^{(2)} \simeq -1$ at $g_K = 1$ and a small compression term in $H^{(2)}$ dropped. Even though this approximation, used in the past,[2,40] yields the correct sign for the nonlinear dielectric effect, it is still not justified: Even at low temperatures, the overall negative sign of the Piekara coefficient comes from the negative $H^{(3,4)}$ term representing higher-order correlations totally neglected in the mean-field framework. The approximation of the ideal gas of dipoles is not quantitatively correct even at low temperatures.

Rotations of individual dipoles produce non-Gaussian polarization noise because rotational matrices involve nonlinear trigonometric functions converting Gaussian fluctuations of the molecular angles to non-Gaussian fluctuations of polarization Cartesian components. This is the reason why the approximation of statistically independent dipoles yields $K_4 \neq 0$, i.e., non-Gaussian fluctuations. For the same reason, rotational transformations from the body to the laboratory frame make the mobility dynamics non-Gaussian for particles undergoing both translational and rotational diffusion.[64,65] Despite producing a qualitatively correct result, the approximation of uncorrelated dipoles is quantitatively incorrect in the entire range of temperatures studied for glycerol. It also predicts $a \propto \beta^3$ [Eq. (25)], which implies a lower nonlinear dielectric effect at elevated temperatures, in contrast to what has been observed. The rise of the Piekara coefficient at elevated temperatures is controlled by higher-order correlations, which project the increasing—approximately as $\propto T$—variance of the Gaussian angle fluctuations into increasingly non-Gaussian fluctuations of the dipole moment.

The present theory makes specific predictions for the solution of polar molecules in nonpolar solvents. When the density of dipoles is low, one can apply liquid-state perturbation theories[17,19,66] to obtain an expansion of g_K in the powers of y characterizing the density of polar molecules. The lowest-order expansion yields the following result for dipolar hard spheres:[66]

$$g_K \simeq 1 + (17/16)y^2. \tag{36}$$

The higher-order correlations vanish for a dilute solution and the binary term becomes

$$H^{(2)} = \frac{3}{2}\left[\frac{17}{4}y^2 + 1 - \frac{5}{3}B_\rho \rho\right], \tag{37}$$

where B_ρ is the second-order virial coefficient for the interactions between polar molecules dissolved in a nonpolar solvent [$\beta^{-1}\rho\chi_T = 1$ in Eq. (19) for an ideal solution].

The $\rho \to 0$ limit is $H^{(2)} \to 3/2$ and the theory predicts an increment of $\Delta\epsilon_E$ [$a > 0$ in Eq. (25)] in the limit of very dilute solutions. At higher concentrations, the dependence on the density of polar solutes ρ is more complex,

$$a(\rho) \propto \rho\left[1 - c_1\rho + c_2\rho^2\right]. \tag{38}$$

In particular, this function predicts a negative minimum of $a(\rho)$ at $B_\rho > 0$, as indeed observed for the solutions of nitrobenzene[5,6] and 4-heptyl-4′-nitro-biphenyl[67] in benzene. In other cases, such as 1,2-dichloroethane and 1,2-dibromoethane in carbon tetrachloride,[5] a monotonic nonlinear increase of a positive Piekara coefficient with the rising concentration of polar molecules was found. Modeling specific systems will require calculating the three-particle perturbation integrals[19] $I(\rho)$ to obtain $g_K = 1 + y^2 I(\rho)$ in Eq. (36). The density expansion $I(\rho) \simeq 17\pi^2/9 - c\rho$, $c > 0$ (Lennard-Jones, Ref. 66) will add an additional linear in density term to the second virial coefficient in Eq. (37).

IV. CONCLUSIONS

In conclusion, recent experimental measurements of the temperature-dependent Piekara coefficient have put in doubt the view that nonlinear dielectric effects represent saturation of the dipolar response. The present analysis provides a formalism for separating the component arising from three- and four-particle orientational correlations in the Piekara coefficient from the component due to binary correlations. From the data for glycerol, the higher-order correlations strongly increase in magnitude with increasing temperature and produce the main contribution to the Piekara coefficient at elevated temperatures. This phenomenology is in disagreement with the mean-field view of the nonlinear dielectric effect as originating from saturation of orientations of separate dipoles in the liquid and neglecting correlations altogether.

A microscopic theory of the temperature effect on many-particle orientational correlations in polar liquids is still missing. The present analysis does not attempt to develop such a theory and, instead, focuses on a formalism to extract the impact of higher-order correlations from observations. The formulation is limited only by the truncation of the expansion for the medium polarization in terms of the linear and first nonlinear susceptibilities and the assumption of locality of the fourth cumulant of the dipole moment. The analytical result for the binary term in the Piekara coefficient becomes the basis for the theory of nonlinear dielectric response of dilute solutions of polar molecules in nonpolar solvents. This term also provides an analytical expression for the third-order dielectric susceptibility at low temperatures [Eq. (35)].

SUPPLEMENTARY MATERIAL

See the supplementary material for the parameters for glycerol and details of calculations.

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AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

Dmitry V. Matyushov: Conceptualization (lead); Investigation (lead); Writing – original draft (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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