Quantifying dielectric permittivities in the nonlinear regime

Ranko Richert [1] and Dmitry V. Matyushov [2]

[1] *School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287, USA*

[2] *Department of Physics and School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287, USA*

In contrast to the static dielectric permittivity, ε, associated with linear response, its high-field counterpart, ε_E, is not a material specific quantity, but rather depends on the experimental method used to determine the nonlinear dielectric effect (NDE). Here, we define ε_E in a manner consistent with how high field permittivities are typically derived from a capacitance measurement using high voltages. Based upon characterizing the materials nonlinear behavior via its third order susceptibility, χ_3, the relations between a given χ_3 and the observable ε_E is calculated for six different experimental or theoretical approaches to NDEs in the static limit. It is argued that the quantity χ_3 is superior over ε_E or the Piekara factor, $(\varepsilon_E - \varepsilon)/E^2$, because it facilitates an unambiguous comparison among different experimental techniques and it provides a more robust connection between experiment and theory.

Keywords: nonlinear dielectric effects, high electric fields, Piekara factor, supercooled liquids

I. INTRODUCTION

The experimental observation as well as the theoretical understanding of nonlinear dielectric effects (NDEs) has received increasing attention in recent years, particularly in the context of glass-forming materials [1,2,3,4,5,6,7,8,9,10].The work of Debye has laid the foundation for this field by showing that the dielectric constant, ε_s, depends on the magnitude of the externally applied electric field, E [11]. A prediction for the NDE in condensed polar materials is not available [12]. Measurements of the permittivity, $\hat{\varepsilon}(\omega)$, at high electric fields have revealed field-induced increases as well as reductions of the static permittivity, ε_s, [13,14] and shifts of the dielectric time constants in either direction have also been observed [6,7,15,16,17]. Which of these effects appears is a matter of the material and of the type of high field applied, alternating (ac) versus static (dc). The standard experimental approach to NDEs is to measure at a relatively high electric field, but then analyze the data in the same fashion as done in the case of linear responses associated with sufficiently low fields. A survey of the relevant literature shows that NDEs are being quantified in very different ways: as the high field permittivity, ε_E, relative to its linear response counterpart ε, as the Piekara factor $a = (\varepsilon_E - \varepsilon)/E^2$, as a relative change of permittivity, $(\varepsilon_E - \varepsilon)/\varepsilon \approx \ln(\varepsilon_E/\varepsilon)$, or in terms of higher order susceptibilities observed via the higher harmonics of the polarization response.

This work aims at providing a definition of the static limit of high field permittivity, ε_E, that i) is consistent with experimental approaches and ii) can be related unambiguously to the lowest order term, χ_3, of nonlinear polarization (in SI units),

$$\varepsilon_0^{-1} P = \chi E + \chi_3 E^3 , \tag{1}$$

where ε_0 is the permittivity of vacuum. We restrict our considerations to the static case, where $\chi = \chi' = \chi_s$ and $\chi'' = 0$. For a real system with $\hat{\chi}(\omega) = \chi'(\omega) + i\chi''(\omega)$, this implies that experiments that determine ε_E require the condition that dielectric relaxation is sufficiently fast to ensure that polarization P maintains equilibrium with the external field E. In other words, we address only situations for which the dielectric relaxation time τ is very short compared with the time scale of the experiment, usually defined by the radian frequency ω, i.e. $\omega\tau \ll 1$ is required. In this case, the real valued constant χ_3 characterizes the nonlinear dielectric behavior of the sample. We find that the high field permittivity, ε_E, as derived from impedance type experiments, does not have a unique connection to χ_3, but rather depends on how the nonlinear dielectric effect is measured. For six distinct field protocols, the relations between χ_3 and ε_E are determined, and it is argued that χ_3 is the best choice for quantifying NDEs in the static limit.

The sections below are organized as follows. First, we generalize permittivity to beyond the linear regime in a manner that is consistent with the typical experimental approach. The next step is to provide connections between χ_3 and ε_E, which is done separately for static and for oscillating fields. For the important case of high field impedance without a bias field, it is then shown that the χ_3 - ε_E relation can also be derived from nonlinear theory based on Kubo's formalism. These sections are followed by a discussion and conclusions.

II. HIGH FIELD PERMITTIVITY

Generally, measurements of permittivity at high fields are based upon the determination of a capacitance. This obviously holds for impedance type experiments, where permittivity is derived from a capacitance, which in turn is obtained from voltage and current data [18,19]. Capacitance is also the basis for permittivities determined via the resonance frequency of an LC circuit [2,10]. Moreover, the permittivity associated with a high field experiment is generally calculated using the relations that are strictly valid only in the low field limit, i.e., within the regime of linear response. Therefore, a practical definition of high field permittivity is given by

$$\varepsilon_E = \frac{C_E(\omega)}{C_{geo}}, \tag{2}$$

analogous to the linear response (low field limit) counterpart $\varepsilon = 1 + \chi = C(\omega)/C_{geo}$, but accounting for the feature that the capacitance changes with field in case of a nonlinear dielectric. Here, the geometrical capacitance is given by $C_{geo} = \varepsilon_0 A/d$, where A is the surface area and d the uniform distance of the pair of planar electrodes forming the capacitor. The notation $C_E(\omega)$ instead of C_E is meant to indicate that in practice the capacitance is determined at a given frequency ω, and not that C depends on ω as long as the condition $\omega\tau \ll 1$ is preserved. The usual relations among impedance Z, admittance Y, current $I = jA$, voltage $V = Ed$, charge $\partial Q = C\partial V$, and capacitance $C = \partial Q/\partial V$ remain field amplitude invariant:

$$Y_E(\omega) = \frac{1}{Z_E(\omega)} = \frac{I_E(\omega)}{V_E(\omega)} = i\omega C_E(\omega)\,, \tag{3}$$

with $C_E(\omega) = |Q(\omega)|/|V(\omega)| = |I(\omega)|/(\omega V_0)$.

III. RELATION TO NONLINEAR POLARIZATION

A. Field step approaches

In the regime of linear response, polarization follows $\varepsilon_0^{-1}P = \chi E$ with a field invariant susceptibility χ. Beyond the linear regime, Eq. (1) relates P and E, provided that higher order terms such as χ_5 are negligible. This leaves the field independent quantity χ_3 for characterizing the extent of nonlinearity, and the goal is to establish a well defined connection between χ_3 and the ε_E defined in Eq. (2). To this end, we assume constant temperature ($\partial T = 0$), constant volume ($\partial \upsilon = 0$), and the reversibility of the processes involved ($T\partial S = q$). In this case, we have for the change ∂F in free energy ($F = U - TS$):

$$\partial F = \partial U - S\partial T - T\partial S = q - p\partial v + \partial w_{el} - S\partial T - T\partial S = \partial w_{el}\,, \tag{4}$$

where U the internal energy, S the entropy, T the temperature, q the heat, p the pressure, and w_{el} the electrostatic work. Thus, the change in free energy is entirely determined by the electrostatic work w_{el}.

The field induced free energy change is $\partial F_E = vE\partial D_E$, with υ being the volume and D_E the electric displacement defined as $D_E = \varepsilon\varepsilon_0 E = \varepsilon_0 E + P$, which leads to

$$\varepsilon_0^{-1} D_E = E + \chi E + \chi_3 E^3\,. \tag{5}$$

Now, the free energy change can be expressed in terms of susceptibilities, which yields

$$\partial F_E = vE\partial D_E = v\varepsilon_0(E + \chi E + 3\chi_3 E^3)\partial E\,, \tag{6}$$

where ∂F_E is equal to

$$\partial w_{el} = vE\partial D_E = V\partial Q_E = C_E V\partial V = \frac{1}{2}C_E\partial V^2 = \frac{d^2}{2}C_E\partial E^2\,. \tag{7}$$

The capacitance measured via a large field step from $E = 0$ to $E = E_B$, or $E(t) = E_B\theta(t)$, can now be obtained via $\Delta F_E = \int_0^{E_B} dF_E = \frac{v\varepsilon_0}{2}\left(\varepsilon E_B^2 + \frac{3}{2}\chi_3 E_B^4\right)$ and $C_E = \frac{2}{v\varepsilon_0}(\Delta F_E/E_B^2)$, which together with Eq. (2) results in .

$$\varepsilon_E = \varepsilon + \frac{3}{2}\chi_3 E_B^2\,. \tag{8}$$

An alternative approach is to obtain ε_E from a small field step at E_B, i.e., using a step from $E = E_B$ to $E = E_B + \delta E$, The above Eq. (2) together with Eq. (6) and Eq. (7) provides the result for this case:

$$\varepsilon_E = \frac{C_E}{C_{geo}} = \frac{2}{v\varepsilon_0}\frac{\partial w_{el}}{\partial E^2}\bigg|_{E=E_B} = \frac{2}{v\varepsilon_0}\frac{\partial F_E}{\partial E^2}\bigg|_{E=E_B} = \varepsilon + 3\chi_3 E_B^2\,. \tag{9}$$

Clearly, the relation between ε_E and χ_3 depends on the manner in which the measurement is performed.

B. Oscillating field approaches

The goal of this section is to determine ε_E for a given χ_3 for the more common impedance experiments, which apply an oscillating field, $E(t) = E_B + E_\omega \cos(\omega t)$, possibly in combination with a large bias field E_B. The measured quantity is the current, $I(t) = I_{n\omega} \cos(n\omega t + \varphi)$, either at the fundamental frequency ($n = 1$) or at the higher harmonics ($n > 1$). The connection between current and displacement is given by $D_E(t) = \int I(t)dt/A$, or for sinusoidal signals by $D_E(\omega) = I(\omega)/(\omega A)$. We calculate the electric displacement $D_E(t)$ by inserting $E(t)$ into

$$D_E(t) = \varepsilon_0 E(t) + \chi \varepsilon_0 E(t) + \chi_3 \varepsilon_0 E(t)^3 = D_B + \sum_{n=1}^{3} D_n(\omega) \tag{10}$$

and express the outcome as a static term D_B and the harmonics $D_n(\omega)$ which are associated with frequencies $n\omega$:

$$D_1(\omega) = \varepsilon_0 E_\omega \left(\varepsilon + 3\chi_3 E_B^2 + \frac{3}{4}\chi_3 E_\omega^2\right) \cos(\omega t)\,, \tag{11a}$$

$$D_2(\omega) = \varepsilon_0 E_B \left(\frac{3}{2}\chi_3 E_\omega^2\right) \cos(2\omega t)\,, \tag{11b}$$

$$D_3(\omega) = \varepsilon_0 E_\omega \left(\frac{1}{4}\chi_3 E_\omega^2\right) \cos(3\omega t)\,. \tag{11c}$$

For the fundamental frequency, $n = 1$, an impedance measurement based on $\varepsilon = |Y(\omega)|/|Y_{geo}| = |I(\omega)|d/(\omega \varepsilon_0 A V_0)$ results in

$$\varepsilon_{E,1} = \frac{C_{E,1}}{C_{geo}} = \frac{|D_1(\omega)|}{\varepsilon_0 E_\omega} = \varepsilon + \frac{3}{4}\chi_3 E_\omega^2 + 3\chi_3 E_B^2\,. \tag{12}$$

Here and in the following, we use the notation $\varepsilon_{E,n}$ for the 'permittivity' derived from the n^{th} harmonic signal. For typical experiments, there are two limiting cases of interest: a small sinusoidal field with large amplitude bias, and a large oscillating field with zero bias as illustrated in Fig. 1. The former case yields

$$\lim_{E_\omega \to 0} \varepsilon_{E,1} = \varepsilon + 3\chi_3 E_B^2\,, \tag{13}$$

consistent with the previous results of a small field step superposed onto a high static field E_B, Eq. (9). The latter case assumes $E_B = 0$ and gives a different result:

$$\lim_{E_B \to 0} \varepsilon_{E,1} = \varepsilon + \frac{3}{4}\chi_3 E_\omega^2 , \tag{14}$$

where the effect of χ_3 on $\varepsilon_{E,1}$ is reduced relative to the high bias field case of Eq. (13) because much of the polarization response occurs near the linear regime.

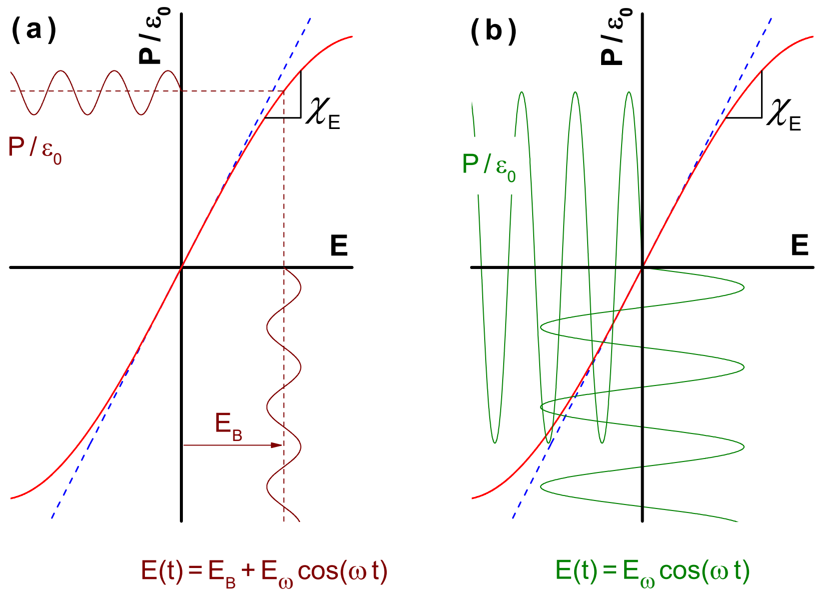

FIG. 1. Schematic representation of polarization P versus E curves for a nonlinear system, characterized by the nonlinear solid (red) line wit slope χ_E. Panel (a) is for a case of a high bias field E_B with a relatively small E_ω. Panel (b) reflects a situation with zero bias ($E_B = 0$) and high amplitude, E_ω, of the oscillating field.

For the higher harmonics, $n > 1$, admittances at frequencies $n\omega$ can no longer be defined as $Y(n\omega) = I(n\omega)/V(n\omega)$, since $V(n\omega) = 0$ for $n > 1$. However, if we follow common practice and use $\tilde{Y}(n\omega) = I(n\omega)/V(\omega)$, higher harmonic permittivities can be defined analogously as

$$\left|\varepsilon_{E,2}\right| = \frac{C_{E,2}}{C_{geo}} = \frac{|D_2(\omega)|}{\varepsilon_0 E_\omega} = \frac{3}{2}|\chi_3| E_B E_\omega , \tag{15a}$$

$$\left|\varepsilon_{E,3}\right| = \frac{C_{E,3}}{C_{geo}} = \frac{|D_3(\omega)|}{\varepsilon_0 E_\omega} = \frac{1}{4}|\chi_3| E_\omega^2 . \tag{15b}$$

Note that $\varepsilon_{E,2}$ vanishes for $E_B = 0$, while $\varepsilon_{E,3}$ is independent of E_B.

IV. NONLINEAR RESPONSE THEORY

This section addresses the case of a sinusoidal field of large amplitude with zero bias, $E_B = 0$. The expansion of the medium polarization in Eq. (1) is performed in powers of the electric field E. It represents the combined field of the free charges at the plates of the capacitor and the electric field of the polarized dielectric (Maxwell field). In contrast, perturbation theories of dynamical observables operate in terms of the perturbation induced by the field of charges external to the material, which is the field E_0 of the free carriers at the plates of the capacitor in the case of the dielectric experiment. The reason is that the time-dependent perturbation of the dielectric is given by the perturbation Hamiltonian

$$H'(t) = -ME_0(t)\,, \tag{16}$$

where M is the instantaneous total dipole moment of the sample projected on the direction of the field. The linear polarization of the sample follows from the standard Kubo's formalism [20], in terms of the time-dependent response function $\chi^0(t-\tau)$

$$P(t) = \varepsilon_0 \int_{-\infty}^{t} \chi^0(t-\tau)E_0(\tau)d\tau\,. \tag{17}$$

This equation assumes that the perturbation was turned on at the time $t_0 \to -\infty$.

The standard manipulations relate the Fourier-Laplace transform of $\chi^0(t)$ to the dielectric function $\varepsilon(\omega)$

$$\varepsilon(\omega) = [1 - \tilde{\chi}^0(\omega)]^{-1}\,, \tag{18}$$

where

$$\tilde{\chi}^0(\omega) = \int_0^\infty \chi^0(t)e^{i\omega t}dt\,. \tag{19}$$

Further, the response function is expressed in terms of the correlation function between the dipole moment $M(t)$ at time t and its time derivative $\dot{M}(0)$ at $t = 0$

$$\chi^0(t) = \frac{\beta}{\varepsilon_0 V}\langle M(t)\dot{M}(0)\rangle\,, \tag{20}$$

where $\beta = 1/(k_B T)$.

The experimental conditions applied here assume an oscillatory external field $E_0(t) = E_\omega^0 cos(\omega t)$ and the static limit for the dielectric susceptibility $\chi^0 = \tilde{\chi}(0)$. Taking this limit, the amplitude of the polarization density oscillating with the principal frequency ω becomes

$$\varepsilon_0^{-1} P_\omega = \chi^0 E_\omega^0 \,. \tag{21}$$

The same set of approximations can be applied to the Kubo perturbation expansion truncated after the third-order polarization term (see Appendix). The sum of the first and third order polarization responses becomes

$$\varepsilon_0^{-1} P_\omega = \chi^0 E_\omega^0 + \frac{3}{4} \chi_3^0 (E_\omega^0)^3 \,. \tag{22}$$

This equation is the analog of Eq. (1) expressed in terms of the vacuum field. To convert it to the expansion in terms of the amplitude of the Maxwell field E_ω one notices the following connection,

$$E_\omega^0 = \frac{D_\omega}{\varepsilon_0} = E_\omega + \varepsilon_0^{-1} P_\omega \,. \tag{23}$$

When Eq. (22) is substituted in the above equation, one obtains

$$E_\omega^0 = \varepsilon E_\omega + \frac{3\varepsilon}{4} \chi_3^0 (E_\omega^0)^3 \,. \tag{24}$$

This equation can be solved in terms of E_ω by iterations. Truncating after the third order-term leads to

$$E_\omega^0 = \varepsilon E_\omega + \frac{3\varepsilon^4}{4} \chi_3^0 E_\omega^3 \,. \tag{25}$$

This relation between the vacuum and Maxwell field can now be used in Eq. (22), from which one arrives at the final result for the polarization density in terms of the Maxwell field

$$\varepsilon_0^{-1} P_\omega = \chi E_\omega + \frac{3\varepsilon^4}{4} \chi_3^0 E_\omega^3 \,, \tag{26}$$

where $\chi = \varepsilon \chi^0$ was used. We therefore recover Eq. (14) for the dielectric constant in the limit of zero bias field,

$$\varepsilon_E = \varepsilon + \frac{3\varepsilon^4}{4} \chi_3^0 E_\omega^2 = \varepsilon + \frac{3}{4} \chi_3 E_\omega^2 \,, \tag{27}$$

with $\chi_3 = \varepsilon^4 \chi_3^0$.

V. DISCUSSION

For the calculations outlined above, we have assumed an ideal dielectric in the sense that dc-conductivity is absent. This eliminates problems such as electrode polarization, i.e., the accumulation of charges near blocking electrodes, which can interfere with high field experiments performed on real systems. Also, an ideal dielectric does not absorb energy from a time dependent electric field with $\omega\tau \ll 1$. By contrast, the loss, $\varepsilon'' > 0$, of a real sample leads to heating and thus violates the present assumption of a constant temperature. Moreover, C_{geo} has been used as a field invariant quantity, implying that electrostriction is negligible. As a result, it is well established that there are several obstacles to measuring ε_E precisely [21,22,23,24].

A common metric for quantifying the degree of dielectric nonlinearity in the static limit is the Piekara factor a [25], defined as:

$$a = \frac{\varepsilon_E - \varepsilon}{E^2}, \tag{28}$$

where E refers to the magnitude of the field, either E_B or E_ω. Implicit in this quantity a is the expectation that ε_E varies linearly with E^2, i.e., that susceptibilities χ_5 and orders beyond may be disregarded. Having demonstrated above that different experimental approaches to measuring ε_E lead to distinct relations between ε_E and χ_3, it appears advantageous to compare results on the basis of the material specific quantity χ_3, rather than using the high-field permittivity ε_E or the Piekara factor a. Similar to defining a high-field permittivity, ε_E, we can also define a high-field susceptibility, χ_E, for instance via

$$\chi_E = \frac{\partial P}{\varepsilon_0 \partial E} = \chi + 3\chi_3 E^2 , \tag{29}$$

provided that higher order terms are negligible.

The case of a large field step, $E(t) = E_B\theta(t)$, resulted in $\chi_3 = 2a/3$, while a small step superposed onto a high field, $E(t) = E_B + \delta E\theta(t)$, gave $\chi_3 = a/3$. From an experimental point of view, a field step is unrealistic because it leads to extreme current surges, and establishing a high field more slowly will lead to electrode polarization interfering with the result. Consequently, the various approaches involving oscillating fields with $E(t) = E_B + E_\omega\, cos(\omega t)$ are the experimental methods commonly found in the literature [2,6,7,10,13,15,21,23]. As illustrated in Fig. 1, extending the field into the nonlinear regime can be a matter of either E_B or E_ω.

With the above notation of $\varepsilon_{E,n}$ designating high-field permittivity derived from the n^{th} harmonic, how to calculate χ_3 from experimental results is compiled as follows:

$$\lim_{E_\omega \to 0} \varepsilon_{E,1} \quad \Longrightarrow \quad \chi_3 = \frac{(\varepsilon_{E,1} - \varepsilon)}{3E_B^2} = \frac{a}{3}, \tag{30a}$$

$$\lim_{E_B \to 0} \varepsilon_{E,1} \quad \Longrightarrow \quad \chi_3 = \frac{4(\varepsilon_{E,1} - \varepsilon)}{3E_\omega^2} = \frac{4a}{3}, \tag{30b}$$

$$\varepsilon_{E,2} \quad \Longrightarrow \quad |\chi_3| = \frac{2|\varepsilon_{E,2}|}{3E_B E_\omega}, \tag{30c}$$

$$\varepsilon_{E,3} \quad \Longrightarrow \quad |\chi_3| = \frac{4|\varepsilon_{E,3}|}{E_\omega^2}. \tag{30d}$$

Note that the higher harmonics ($n > 1$) provide more direct measures of χ_3 in the sense that the extent of nonlinearity can be determined without knowledge of ε. Clearly, for a given value of χ_3, each technique referred to in Eq. (30) leads to a different high-field permittivity as derived in the usual manner from an impedance measurement. In other words, there is no simple relation connecting ε_E to χ_E, especially $\varepsilon_E \neq 1 + \chi_E$, unless ε_E is determined from a small field step or oscillation superposed on a high amplitude static field. Note that the notation $|\chi_3|$ is commonly used in the context of reporting frequency dependent NDEs derived from third harmonic responses [26,27,28,29], but even in the static limit those quantities are not necessarily identical to the present χ_3 as defined in Eq. (1).

Another argument in favor of χ_3 being the key quantity for characterizing deviations from simple dynamics is its relation to dipole moment fluctuations and their departure from the Gaussian limit. Eq. (26) was derived by taking the zero frequency limit in the response functions to an oscillatory perturbation. One can alternatively calculate the static polarization of the dielectric in response to a static field E_0 by applying the cumulant expansion in the statistical averages [30]. This approach allows one to represent the cubic polarization susceptibility in terms of a fundamental physical parameter B_V (the subscript V stands for constant-volume conditions) which enumerates the deviation of the statistics of dipole moment fluctuations from the Gaussian limit

$$B_V = NU_N = N\left[1 - \frac{\langle M^4 \rangle}{3\langle M^2 \rangle^2}\right]. \tag{31}$$

The relation of χ_3 to B_V is given by the following equation [12]

$$\chi_3 = -\frac{\beta\varepsilon_0\varepsilon^2(\varepsilon-1)^2}{2\rho} B_V\,, \tag{31}$$

where $\rho = N/V$ is the number density.

The Binder parameter, U_N, [31] in the brackets of Eq. (31) tends to zero as $1/N$ in the leading order when the thermodynamic limit $N \to \infty$ is taken and the statistics of the macroscopic dipole moment becomes Gaussian. The nonlinear susceptibility χ_3 thus quantifies the first-order correction to the Gaussian statistics of the dipole moment fluctuations. It tends to a finite value even in the thermodynamic limit because B_V is taken as a product of N and U_N. Given this fundamental connection, it is the cubic susceptibility χ_3 that should be the primary parameter connecting experiment to statistical theories of medium polarization.

VI. CONCLUSIONS

We have established a definition of high-field permittivity ε_E that is consistent with thermodynamics and with experimental approaches to permittivity outside the linear regime. This definition of ε_E accounts for a common feature of permittivities reported for high-field impedance measurements, namely that data is derived from capacitances and analyzed in the same manner as low field data. Unlike ε derived from linear responses, it turns out that its high-field counterpart, ε_E, is not material specific. Instead, its relation to χ_3 is a matter of how the experiment is conducted, where χ_3 characterizes the nonlinear dielectric behavior of the material via its field induced polarization at high field magnitudes. The relation between ε_E and χ_3 is calculated for a variety of experimental or theoretical approaches to nonlinear dielectric behavior in the static limit, and each case results in a different coefficient. Note that one could have used an alternative approach to ε_E by defining it as $1 + \chi_E$, i.e., as $\varepsilon_E = \varepsilon + 3\chi_3 E^2$. However, such a definition of high field permittivity would not always match the experimental values typically reported in the literature.

The present results facilitate not only the quantitative connection among different types of experimental approaches to NDEs in the static limit, but also relate measured permittivities to the more fundamental material variables such as the cubic polarization susceptibility, χ_3, and the Binder parameter, U_N, associated with theoretical approaches to nonlinear responses. The conditions that were assumed in the present calculations are the lack of electrostriction ($\partial C_{geo}/\partial E = 0$), constant temperature ($\partial T = 0$), and constant volume ($\partial \upsilon = 0$). Meeting these conditions in a real experiment is not trivial. Reducing effects of electrostriction requires a capacitor whose electrode separation is not changed by the electrostatic forces, which can be considerable [32]. Maintaining a constant temperature calls for rapid heat transport to heat sinks, to avoid temperature changes from energy absorbed from time dependent fields (sinusoidal or step-like) [16,33] and from electrocaloric effects [34]. The constant volume assumption inherent in the present calculation contrasts the constant pressure situation of most experiments, but the difference may be minor for most materials [30]. The dielectric loss and conductivity of real samples is considered the main source of the notorious inconsistencies regarding values reported for NDEs in the static limit [22]. The present results may help improving this situation, because obtaining the same value for χ_3 from distinct field protocols will increase the reliability of the NDE result.

APPENDIX: DERIVATION OF NONLINEAR RESPONSE

The time-dependent Hamiltonian of the system is a sum of the unperturbed time-independent Hamiltonian H_0 and the external perturbation $H'(t)$: $H(t) = H_0 + H'(t)$, see Eq. (16). One writes the time-dependent probability density in the phase space (distribution function) as a sum of perturbations of increasing order,

$$f_t = \sum_{i=0}^{\infty} f_t^{(i)} \, , \tag{A1}$$

where $f_t^{(0)} = f_{eq}$ is the equilibrium Gibbs distribution of the unperturbed dielectric, $f_{eq} = Z^{-1} e^{-\beta H_0}$.

The Liouville equation allows to write the time evolution relations for each order in perturbation [35]

$$\partial_t f_t^{(i)} = iL f_t^{(i)} - E_0(t)\left(M, f_t^{(i-1)}\right), \tag{A2}$$

where $(\ldots)$ are Poisson brackets and $iL{=}(H_0, f)$ is the Liouville operator. This set of differential equations can be recursively integrated to obtain the response of the dipole moment of n^{th} order. We are mainly interested in the third-order response,

$$\langle M^{(3)} \rangle_t = \int M f_t^{(3)} \, d\Gamma \, , \tag{A3}$$

where $d\Gamma$ implies integration over the entire phase space of the system. One obtains from Eq. (A2) and Eq. (A3)

$$\langle M^{(3)}\rangle_t = \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' \int_{-\infty}^{t''} dt''' \\ E_0(t')E_0(t'')E_0(t''')\chi_3^0(t-t',t'-t'',t''-t''')\,, \tag{A4}$$

where the third-order susceptibility is

$$\chi_3^0(t-t',t'-t'',t''-t''') = \beta\,\langle M(t-t')\left(M, e^{iL(t'-t'')}\left(M, e^{iL(t''-t''')}\dot{M}(0)\right)\right)\rangle\,. \tag{A5}$$

We consider the oscillatory electric field $E(t) = E_\omega^0\, cos(\omega t)$ and use it in Eq. (A4). The result is

$$\langle M^{(3)}\rangle_t = \tfrac{1}{4}(E_\omega^0)^3\ \mathrm{Re}\left[\chi_3^{(1)}(\omega)e^{3i\omega t} + \chi_3^{(2)}(\omega)e^{i\omega t}\right], \tag{A6}$$

where

$$\begin{aligned} \chi_3^{(1)}(\omega) &= \tilde{\chi}_3(-3\omega,-2\omega,-\omega)\,, \\ \chi_3^{(2)}(\omega) &= \tilde{\chi}_3(-\omega,-2\omega,-\omega) + \tilde{\chi}_3(-\omega,0,-\omega) + \tilde{\chi}_3(-\omega,0,\omega)\,, \end{aligned} \tag{A7}$$

and the Fourier-Laplace transform of the response function is

$$\tilde{\chi}_3(\omega_1,\omega_2,\omega_3) = \int_0^\infty dt' \int_0^\infty dt'' \int_0^\infty dt''' \\ \chi_3(t',t'',t''')e^{i\omega_1 t' + i\omega_2 t'' + i\omega_3 t'''}\,. \tag{A8}$$

If the frequency of the experiment is much below the relaxation frequency of the response function, one can apply the limits ω_1, ω_2, $\omega_3 \to 0$ in Eq. (A8) with the result for the third-order polarization density:

$$P^{(3)}(t) = \frac{1}{V}\langle M^{(3)}\rangle_t = \frac{1}{4}\chi_3^0(E_\omega^0)^3\ [\cos(3\omega t) + 3\cos(\omega t)]\,. \tag{A9}$$

Consistent with Eq. (15), the second harmonic does not appear in the response. When the response at the principal frequency ω is concerned, the polarization density becomes

$$P(t) = \left[\chi^0 E_\omega^0 + \frac{3}{4}\chi_3^0(E_\omega^0)^3\right]\ \cos(\omega t)\,, \tag{A10}$$

where the notation $\chi_3^0 = \tilde{\chi}_3(0,0,0)/V$ is used.

Similar expressions were obtained by Brun *et al.* [27]. Their derivation, however, does not explicitly incorporate causality of the third order susceptibility function, and the result is somewhat different from ours. Our derivation is fully consistent with the third-order optical susceptibility from the quantum Liouville equation, using

$$\chi_3(t_3,t_2,t_1) = \left(\frac{i}{\hbar}\right)^3 \theta(t_1)\theta(t_2)\theta(t_3) \times \langle P(t_3+t_2+t_1)\left[P(t_2+t_1),\left[P(t_1),\left[P(0),\rho_{eq}\right]\right]\right]\rangle\,, \tag{A11}$$

see equation (5.16a) in [36], where ρ_{eq} is the equilibrium density matrix.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under grant numbers CHE-1800243 (DVM) and DMR-1904601 (RR).

REFERENCES

[1] J. L. Déjardin and Y. P. Kalmykov, Phys. Rev. E **61**, 1211 (2000).

[2] S. J. Rzoska and V. P. Zhelezny (Eds.), *Nonlinear Dielectric Phenomena in Complex Liquids*, (Kluwer Academic Publishers, Dordrecht, 2004).

[3] L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hôte, F. Ladieu, and M. Pierno, Science **310**, 1797 (2005).

[4] R. L. Fulton, J. Chem. Phys. **130**, 204503 (2009).

[5] I. Szalai, S. Nagy, and S. Dietrich, J. Chem. Phys. **131**, 154905 (2009).

[6] D. L'Hôte, R. Tourbot, F. Ladieu, and P. Gadige, Phys. Rev. B **90**, 104202 (2014).

[7] S. Samanta and R. Richert, J. Chem. Phys. **142**, 044504 (2015).

[8] D. V. Matyushov, J. Chem. Phys. **142**, 244502 (2015).

[9] S. Albert, Th. Bauer, M. Michl, G. Biroli, J.-P. Bouchaud, A. Loidl, P. Lunkenheimer, R. Tourbot, C. Wiertel-Gasquet, and F. Ladieu, Science **352**, 1308 (2016).

[10] R. Richert (Ed.), *Nonlinear Dielectric Spectroscopy* (Springer, Cham, 2018).

[11] P. Debye, *Polar Molecules* (Chemical Catalog Company, New York, 1929).

[12] D. Matyushov, in: R. Richert (Ed.), *Nonlinear Dielectric Spectroscopy* (Springer, Cham, 2018).

[13] A. Piekara and A. Chelkowski, J. Chem. Phys. **25**, 794 (1956).

[14] R. Richert, J. Phys.: Condens. Matter **29**, 363001 (2017).

[15] R. Richert and S. Weinstein, Phys. Rev. Lett. **97**, 095703 (2006).

[16] W. Huang and R. Richert, J. Chem. Phys. **130**, 194509 (2009).

[17] R. Richert, J. Chem. Phys. **149**, 240901 (2018).

[18] J. R. Macdonald (Ed.), *Impedance Spectroscopy: Emphasizing Solid Materials and Systems* (Wiley, New York, 1987).

[19] R. Richert, Adv. Chem. Phys. **156**, 101 (2014).

[20] R. Kubo, Rep. Prog. Phys. **29**, 255 (1966).

[21] J. A. Schellman, J. Chem. Phys. **24**, 912 (1956).

[22] A. Chełkowski, *Dielectric Physics* (Elsevier, Amsterdam, 1980).

[23] M. Gorny, J. Ziolo, and S. J. Rzoska, Rev. Sci. Instrum. **67**, 4290 (1996).

[24] K. Orzechowski and A. Burakowski, Measurement **131**, 219 (2019).

[25] A. Piekara, J. Chem. Phys. **36**, 2145 (1962).

[26] C. Crauste-Thibierge, C. Brun, F. Ladieu, D. L'Hôte, G. Biroli, and J.-P. Bouchaud, Phys. Rev. Lett. **104**, 165703 (2010).

[27] C. Brun, F. Ladieu, D. L'Hôte, M. Tarzia, G. Biroli, and J.-P. Bouchaud, Phys. Rev. B **84**, 104204 (2011).

[28] Th. Bauer, P. Lunkenheimer, and A. Loidl, Phys. Rev. Lett. **111**, 225702 (2013).

[29] P. Kim, A. R. Young-Gonzales, and R. Richert, J. Chem. Phys. **145**, 064510 (2016).

[30] D. V. Matyushov, J. Chem. Phys. **142**, 244502 (2015).

[31] D. P. Landau and K. Binder, *Monte Carlo Simulations in Statistical Physics* (Cambridge University Press, Cambridge, UK, 2000).

[32] S. Weinstein and R. Richert, Phys. Rev. B **75**, 064302 (2007).

[33] A. R. Young-Gonzales, S. Samanta, and R. Richert, J. Chem. Phys. **143**, 104504 (2015).

[34] J. F. Scott, Annu. Rev. Mater. Res. **41**, 229 (2011).

[35] O. Nakada, J. Phys. Soc. Jpn. **15**, 2280 (1960).

[36] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, Oxford, 1995).