Electric field in nonlinear dielectrics

A. Morro

Dipartimento di Ingegneria Biofisica ed Elettronica, Università degli Studi di Genova, viale Causa 13, 16145 Genova, Italy
(Received 16 October 1990; revised manuscript received 8 January 1991)

Nonlinear dielectrics are investigated by allowing the permittivity to be a function of the modulus of the electric field. Such a function is examined subject to the requirement that the differential permittivity be positive definite. Then the electrostatic approximation is considered. A general relation is derived for the determination of the electric field that contains the space integral of a term involving the electric field and its gradient; the integrand vanishes when the permittivity is constant or the problem is endowed with particular symmetries. Next, a variational formulation is set up for a dielectric surrounding conductors, and the explicit form of the energy is determined. The solution to the electrostatic problem is shown to provide the minimum of a strictly convex functional. Besides being of interest conceptually, both the integral equation and the variational formulation are likely to be the basis for efficient numerical procedures.

I. INTRODUCTION

The electric polarization in matter is generally a function of the electric field. Such a function is usually taken to be linear, which amounts to regarding the electric susceptibility, and then the dielectric permittivity ϵ, as constant. The approximation of a constant permittivity fits the behavior of dielectrics very well to a large extent. This is certainly a reason why textbooks on electromagnetism in matter report that ϵ depends on the electric field but develop any pertinent topic by letting ϵ be constant.

However, there are substances and circumstances when the dependence on the electric field cannot be disregarded. For example, in water the limit value of the relative permittivity for weak electric fields is 80 and the limit value for strong electric fields is 6 (cf., e.g., Ref. 1). The transition is rather concentrated around a value $E_c \simeq 10^8$ V/m of the electric field. Also, a value $E_c \simeq 10^7$ V/m is appropriate for many substances (cf. Ref. 2). Then whenever the electric field reaches such values, or higher, we need a model of electric-field-dependent permittivity. In this regard I am unaware of any analytical model.

It might seem that the value of E_c is sufficiently high and then that the subject is hardly of practical interest. Apart from the conceptual interest in a model of field-dependent permittivity, it is not so rare to find situations when the electric field is of the same order as, or higher than, E_c. For example, when dissolved in water many macromolecules, such as proteins or nucleic acids, are dissociated into polyvalent macroions and a large number of small ions of opposite charge (counterions). In the vicinity of the ionized groups of the macroions, the counterions, as well as ions due to dissociation of other substances, experience a very high electric field such that the permittivity is estimated to be about 6 (cf., e.g., Ref. 3). In this connection, water solutions are of interest in two respects. First, the large permittivity of water enhances ionization by decreasing the force of attraction in ionic

bonds.[4] Second, the permittivity experiences a large change near the ions because of the high electric field.

The purpose of this paper is threefold. The first is to establish a reliable, albeit simple, dependence of the permittivity on the electric field. This is accomplished by having recourse to general properties of dielectrics and elaborating a one-parameter model of functional dependence. While the scheme applies to any dielectric, in the prominent case of water a quantitative model is elaborated by exploiting available data. The second is to establish a relation and a procedure for the determination of the electric field in a nonlinear dielectric. This topic involves only basic concepts of electrostatics. Nevertheless, a careful analysis leads to remarkable features which disappear in the standard case of constant permittivity or when the problem enjoys particular symmetries. The third is to frame the general electrostatic problem in a genuine variational form. Also in this case the result is remarkable for both the conceptual aspects and the practical advantages offered by related numerical procedures.

Specific remarks about nonlinear dielectrics have already appeared in the literature.[5,6] This paper, in addition to providing new results (Secs. IV–VIII), exhibits a systematic scheme for the subject of nonlinear dielectrics.

II. GENERAL PROPERTY OF PERMITTIVITY

Consider an isotropic dielectric for which the electric displacement $\mathbf{D}$ is related to the electric field $\mathbf{E}$ by

$$\mathbf{D} = \epsilon \mathbf{E} . \tag{2.1}$$

For the time being the permittivity ϵ is allowed to depend on the intensity of the electric field and we write

$$\epsilon = \epsilon(E^2) .$$

While such dependence is obviously related to the material under consideration, a general property can be derived by letting the differential permittivity be positive. Specifically, let the differential $d\mathbf{D}$ corresponding to the

differential $d\mathbf{E}$ satisfy

$$d\mathbf{D}\cdot d\mathbf{E} > 0$$

as $d\mathbf{E}\neq 0$. Equivalently, we might require that the tensor $\partial\mathbf{D}/\partial\mathbf{E}$ be positive definite. Letting ϵ' denote the derivative of ϵ with respect to the argument, by (2.1) we have

$$2\epsilon'(E^2)|\mathbf{E}\cdot d\mathbf{E}|^2+\epsilon(E^2)d\mathbf{E}\cdot d\mathbf{E} > 0 \tag{2.2}$$

for any vector $d\mathbf{E}$, which holds if and only if

$$2\epsilon'(E^2)E^2+\epsilon(E^2) > 0 \ . \tag{2.3}$$

Of course, if ϵ' would be positive then (2.3) would hold identically. However, this is usually not the case. In particular, in water ϵ is a decreasing function of E^2. Accordingly, (2.3) is to be viewed as a constraint on the function $\epsilon(E^2)$. In this regard observe that for hysteretic dielectrics (2.3) should hold for each branch. Here, though, we confine our discussion to nonhysteretic dielectrics.

Assume that the limit values

$$\epsilon_0=\epsilon(0), \quad \epsilon_\infty = \lim_{E\to\infty} \epsilon(E^2) \tag{2.4}$$

exist and are known. Then we look for functions $\epsilon(E^2)$ such that (2.3) and (2.4) hold. Among such functions we have, for example,

$$
\begin{aligned}
\epsilon &= \epsilon_\infty + \frac{\epsilon_0-\epsilon_\infty}{(1+\mu E^2)^{1/2}} \ , \\
\epsilon &= \left[\epsilon_\infty^2 + \frac{\epsilon_0^2-\epsilon_\infty^2}{1+\gamma E^2} \right]^{1/2} ,
\end{aligned}
\tag{2.5}
$$

where μ and γ are positive parameters. By adopting any of these models for the permittivity we allow the properties of the pertinent dielectric to be expressed by the three parameters ϵ_0, ϵ_∞, and, e.g., γ. The choice of one of them, or possibly of other functions, as the appropriate dependence of ϵ on E^2 is a matter of best fit with available data.

III. PERMITTIVITY OF WATER

Once we have chosen a particular dielectric, we have to assess the suitability of any function $\epsilon(E^2)$ compatible with (2.3) and then determine the pertinent parameters by the best-fit requirement. This is now performed in the case of water. Preliminarily, though, we observe that ϵ_0 and ϵ_∞ are affected, for instance, by temperature variation and ionic solvation (cf. Ref. 1, Secs. 2.5.7 and 2.5.8). We may reasonably assume that the ionic concentration is not too high (less than 1 mol/l, say) so that the influence on permittivity is negligible. As regards the temperature, we may well assume that it is constant during the phenomenon under consideration and then we have simply to take the values for ϵ_0 and ϵ_∞ which correspond to the fixed temperature. For instance, letting ϵ_v be the vacuum permittivity, the value $\epsilon_0=80\epsilon_v$ for water is relative to 20 °C.

For definiteness, in this section we confine the attention to water and take $\epsilon_0=80\epsilon_v$ and $\epsilon_\infty=6\epsilon_v$. It is difficult to find direct results on ϵ as a function of E^2. For example, the value for ϵ_∞ is obtained by measuring the permittivity at alternating field frequencies so high that the water dipoles cannot follow the alternating field and then remain aligned and fixed as for an infinite field. Obviously much more difficult to obtain are the values of ϵ which correspond to finite values of E. In any case, to have quantitative results also, consider the curve given in Ref. 1, p. 156, where ϵ/ϵ_v is expressed in terms of the distance r from an ion (proton). To obtain the values of the function $\epsilon(E^2)$ observe that the (radial) electric displacement at the distance r from (the center of) the ion is

$$D(r)=\frac{e}{4\pi r^2} \ , \tag{3.1}$$

where e is the proton charge, and then

$$E(r)=\frac{e}{4\pi\epsilon(r)r^2} \ .$$

Since $\epsilon(r)$ is given by the available curve, we can determine, for any value of r, the pair ϵ, E. We thus have the data for ϵ in terms of E^2. Comparison with the function (2.5) has shown a good fit and the best one occurs when $\gamma=6.49\times10^{-18}$ m²/V². Incidentally, this provides the critical field E_c as $E_c=(10/\sqrt{6.49})10^8$ V/m.

The use of (3.1) for the eventual determination of $\epsilon(E^2)$ is open to the objection that it is not strictly valid in electrolyte solutions, due to the presence of counterions around any ion. Indeed, according to the Debye-Hückel model, $D(r)=0$ as r is greater than Debye's length, which is proportional to the inverse of the counterion concentration. This, in turn, shows that permittivity is to be measured at low ion concentrations.

IV. GENERAL EQUATION
FOR THE ELECTRIC FIELD

Consider a dielectric in stationary conditions. In rationalized MKSA units we can write the pertinent Maxwell equations as

$$\nabla\cdot\mathbf{D}=\rho \ , \tag{4.1}$$

$$\nabla\times\mathbf{E}=0 \ , \tag{4.2}$$

ρ being the free-charge density. By (4.2), $\mathbf{E}$ is the gradient of a scalar field; let $\mathbf{E}=-\nabla\phi$. This representation is used in Secs. VI and VII.

By (4.1), $\mathbf{D}$ is determined up to a solenoidal field. In general, letting $\mathbf{D}_0$ be any solution to (4.1), the general solution to (4.1) is

$$\mathbf{D}=\mathbf{D}_0-\mathbf{G} \ , \tag{4.3}$$

where $\mathbf{G}$ is any solenoidal field. We can take $\mathbf{D}_0$ as irrotational while, in general, $\mathbf{D}$ is not. Then, in view of (4.2) and (2.1) we have

$$\nabla\cdot\mathbf{G}=0, \quad \nabla\times\mathbf{G}=-\epsilon'(E^2)\nabla E^2\times\mathbf{E} \ . \tag{4.4}$$

This shows that $\nabla\times\mathbf{G}$ (and then $\mathbf{G}$) vanishes whenever ϵ is constant or, by symmetry reasons, $\nabla E^2\times\mathbf{E}=0$. Such is the case for distributions of charges with plane, spherical, and cylindrical symmetries.

Assume that

$$\epsilon'(E^2)\nabla E^2 \times \mathbf{E} = o(1/r) \qquad (4.5)$$

as the distance r from a chosen point tends to infinity. In fact, this assumption is very weak in that usually $\epsilon'(E^2)\nabla E^2 \times \mathbf{E}$ vanishes much faster than $1/r$ as $r \to \infty$. In view of (4.5) the unique solution of (4.4) is given by

$$\mathbf{G}(\mathbf{x}) = \frac{1}{4\pi} \int_\Omega [\epsilon'(E^2)\nabla E^2 \times \mathbf{E}](\tilde{\mathbf{x}}) \times \frac{\tilde{\mathbf{x}} - \mathbf{x}}{|\tilde{\mathbf{x}} - \mathbf{x}|^3} d\tilde{x}$$

where $d\tilde{x}$ is the volume element and Ω is the three-dimensional physical space $\mathscr{E}^3$. Then, by (4.3), the elec-

tric field $\mathbf{E}$ turns out to satisfy the integral equation

$$[\epsilon(E^2)\mathbf{E}](\mathbf{x}) + \frac{1}{4\pi} \int_\Omega [\epsilon'(E^2)\nabla E^2 \times \mathbf{E}](\tilde{\mathbf{x}})$$

$$\times \frac{\tilde{\mathbf{x}} - \mathbf{x}}{|\tilde{\mathbf{x}} - \mathbf{x}|^3} d\tilde{x} = \mathbf{D}_0(\mathbf{x}) . \qquad (4.6)$$

Of course, if $\mathbf{E} = 0$ in $\Sigma \subset \Omega$, then the integral is, in fact, over $\Omega \setminus \Sigma$. Concerning the integral in (4.6) it is worth remarking that the singularity at $\tilde{\mathbf{x}} = \mathbf{x}$ leaves the integral bounded [provided (4.5) holds]. Indeed, use of the polar coordinates r, ϑ, φ with the origin at $\mathbf{x}$ allows us to write

$$\int_\Omega [\epsilon'(E^2)\nabla E^2 \times \mathbf{E}](\tilde{\mathbf{x}}) \times \frac{\tilde{\mathbf{x}} - \mathbf{x}}{|\tilde{\mathbf{x}} - \mathbf{x}|^3} d\tilde{x} = \int_0^\infty \int_0^\pi \int_0^{2\pi} [\epsilon'(E^2)\nabla E^2 \times \mathbf{E}](\mathbf{x} + \mathbf{n}r) \times \mathbf{n} \, dr \, \sin\vartheta \, d\vartheta \, d\varphi ,$$

where $\mathbf{n}$ is the unit vector with components $\sin\vartheta \cos\varphi$, $\sin\vartheta \sin\varphi$, and $\cos\vartheta$.

As a simple example, suppose that ρ is determined by N spherical particles, of charge q_i, centered at the positions $\mathbf{x}_i$, $i = 1, \ldots, N$. In such a case, outside the charges themselves, we have

$$\mathbf{D}_0(\mathbf{x}) = \frac{1}{4\pi} \sum_i q_i \frac{\mathbf{x} - \mathbf{x}_i}{|\mathbf{x} - \mathbf{x}_i|^3} .$$

V. ITERATIVE METHOD

A closed-form solution $\mathbf{E}(\mathbf{x})$ to (4.6) seems to be out of the question. For practical purposes it may then be of interest to develop a procedure for determining approximate solutions. Here we elaborate on an iterative procedure which is likely to be the most efficient one when a reference field $\mathbf{D}_0(\mathbf{x})$ is available.

By letting

$$\mathbf{f}(\mathbf{E}) = \epsilon(E^2)\mathbf{E}, \quad \mathbf{g} = -\mathbf{G} ,$$

we can write (4.6) as

$$\mathbf{f}(\mathbf{E}) = \mathbf{g}(\mathbf{E}) + \mathbf{D}_0 . \qquad (5.1)$$

Since $\mathbf{f}$ is a differentiable vector operator we can apply Newton's method[7] to the iterative algorithm

$$\mathbf{f}(\mathbf{E}_{n+1}) = \mathbf{g}(\mathbf{E}_n) + \mathbf{D}_0, \quad n = 0, 1, \ldots .$$

The linear approximation

$$\mathbf{f}(\mathbf{E}_{n+1}) = \mathbf{f}(\mathbf{E}_n) + \frac{\partial \mathbf{f}}{\partial \mathbf{E}}(\mathbf{E}_n)(\mathbf{E}_{n+1} - \mathbf{E}_n)$$

yields

$$\frac{\partial \mathbf{f}}{\partial \mathbf{E}}(\mathbf{E}_n)\mathbf{E}_{n+1} = -\mathbf{f}(\mathbf{E}_n) + \frac{\partial \mathbf{f}}{\partial \mathbf{E}}(\mathbf{E}_n)\mathbf{E}_n + \mathbf{g}(\mathbf{E}_n) + \mathbf{D}_0 .$$

$$(5.2)$$

Now,

$$\frac{\partial \mathbf{f}}{\partial \mathbf{E}} = -2\epsilon'\mathbf{E} \otimes \mathbf{E} + \epsilon \mathbf{1} ,$$

where $\otimes$ denotes the dyadic product. Then (5.2) becomes

$$2\epsilon'(E_n^2)(\mathbf{E}_n \cdot \mathbf{E}_{n+1})\mathbf{E}_n + \epsilon(E_n^2)\mathbf{E}_{n+1} = \mathbf{a}(\mathbf{E}_n) , \qquad (5.3)$$

where

$$\mathbf{a}(\mathbf{E}) = -\epsilon(E^2)\mathbf{E} + \frac{\partial \mathbf{f}}{\partial \mathbf{E}}\mathbf{E} + \mathbf{g}(\mathbf{E}) + \mathbf{D}_0 .$$

Inner multiplication of (5.3) by $\mathbf{E}_n$ yields

$$\mathbf{E}_n \cdot \mathbf{E}_{n+1} = \frac{\mathbf{a}(\mathbf{E}_n) \cdot \mathbf{E}_n}{\epsilon(E_n^2) + 2\epsilon'(E_n^2)E_n^2}$$

and hence, by (5.3),

$$\mathbf{E}_{n+1} = \frac{\epsilon(E_n^2)\mathbf{a}(\mathbf{E}_n) + 2\epsilon'(E_n^2)\mathbf{E}_n \times [\mathbf{a}(\mathbf{E}_n) \times \mathbf{E}_n]}{\epsilon(E_n^2)[\epsilon(E_n^2) + 2\epsilon'(E_n^2)E_n^2]} . \qquad (5.4)$$

Incidentally, the condition (2.3) enables (5.4) to be written for any electric field $\mathbf{E}_n$.

Quite naturally we choose as the reference field $\mathbf{E}_0$ the electric field in the dielectric with constant permittivity ϵ_0, i.e.,

$$\mathbf{E}_0 = \frac{1}{\epsilon_0}\mathbf{D}_0 .$$

With this in mind we proceed to the estimate of the next approximation $\mathbf{E}_1$ to the electric field $\mathbf{E}$.

The expression of $\mathbf{a}(\mathbf{E}_0)$ turns out to be given by

$$\mathbf{a}(\mathbf{E}_0) = [\epsilon_0 + 2\epsilon'(E_0^2)E_0^2]\mathbf{E}_0 + \mathbf{g}(\mathbf{E}_0) . \qquad (5.5)$$

By (5.5) we see that there is a part of $\mathbf{a}(\mathbf{E}_0)$ which is parallel to $\mathbf{E}_0$ and then

$$\mathbf{a}(\mathbf{E}_0) \times \mathbf{E}_0 = \mathbf{g}(\mathbf{E}_0) \times \mathbf{E}_0 .$$

Substitution in (5.4) gives

$$\mathbf{E}_1 = \frac{\epsilon_0 + 2\epsilon'(E_0^2)E_0^2}{\epsilon(E_0^2) + 2\epsilon'(E_0^2)E_0^2}\mathbf{E}_0 + \frac{1}{\epsilon(E_0^2)}\mathbf{g}(\mathbf{E}_0)$$

$$- \frac{2\epsilon'(E_0^2)}{\epsilon(E_0^2)[\epsilon(E_0^2) + 2\epsilon'(E_0^2)E_0^2]}[\mathbf{E}_0 \cdot \mathbf{g}(\mathbf{E}_0)]\mathbf{E}_0 . \qquad (5.6)$$

As a consistency requirement, we expect that if ϵ is constant, then, at any order of approximation, $\mathbf{E}=\mathbf{E}_0$. The relation (5.6) meets this requirement.

Since ϵ is a monotonically decreasing function, then

$$\epsilon_0 + 2\epsilon'(E_0^2)E_0^2 > \epsilon(E_0^2) + 2\epsilon'(E_0^2)E_0^2 > 0, \quad E_0^2 \in (0, \infty) \ .$$

This implies that the parallel part (to $\mathbf{E}_0$) of the first-order electric field $\mathbf{E}_1$ is everywhere greater than the zeroth-order electric field $\mathbf{E}_0$. In this sense the nonlinearity of the dielectric enhances the effective electric field. This property, ascertained for the parallel part of the (approximate) field (5.6), is consistent with the general feature that, in essence, the electric displacement depends on the charges; the lower the dielectric permittivity, the higher the electric field. This feature may be extended to the whole electric field $\mathbf{E}_1$ if the perpendicular part (to $\mathbf{E}_0$) is much smaller than the parallel part, which is usually the case.

VI. VARIATIONAL FORMULATION

Consider a dielectric occupying a region $\Omega \subset \mathcal{E}^3$ and surrounding conductors, labeled by $i=1,\ldots,N$, with net charge q_i, $i=1,\ldots,N$. The charge distribution inside any conductor is unknown; we know only that the flux of $\mathbf{D}$ through the surface S_i of the ith body equals the net charge q_i. Letting ν be the unit outward normal (to S_i), we have

$$\int_{S_i} \mathbf{D} \cdot \nu \, da = q_i$$

and then

$$\int_{S_i} \epsilon \frac{\partial \phi}{\partial \nu} da = -q_i \ . \tag{6.1}$$

Further, the potential ϕ has a constant value on each body, i.e.,

$$\phi = \phi_i \quad \text{on } S_i \ . \tag{6.2}$$

The values ϕ_i are unknown. The potential ϕ satisfies Gauss's law in the differential form

$$\nabla \cdot [\epsilon(|\nabla \phi|^2)\nabla \phi] = 0 \quad \text{in } \Omega \ . \tag{6.3}$$

Finding the solution ϕ to (6.1)–(6.3) means solving the electrostatic problem. In the linear case, i.e., $\epsilon = \text{const}$, the electrostatic problem (6.1)–(6.3) has a unique solution (cf. Ref. 8).

If, instead, some conductors are placed at known potentials, e.g., grounded, the corresponding conditions (6.1) are replaced with

$$\phi = \phi_i \quad \text{on } S_i \ .$$

The problem (6.1)–(6.3) can be framed in a genuine variational form. By applying the theory pertaining to the inverse problem of the calculus of variations,[9,10] or by direct check, we can see that the differential equation (6.3) is the Euler-Lagrange equation of the functional

$$\int_\Omega \int_0^{|\nabla \phi|^2} \epsilon(\xi) d\xi \, dx \ .$$

Furthermore, the whole problem (6.1)–(6.3) has a solution which corresponds to the global minimum of the functional

$$f(\phi) = \frac{1}{2} \int_\Omega \int_0^{|\nabla \phi|^2} \epsilon(\xi) d\xi \, dx - \sum_i q_i \phi_i \ . \tag{6.4}$$

To show that this is so, consider the Hilbert space

$$K = \{\psi : \nabla \psi \in L^2(\Omega), \ \psi = \psi_i \text{ on } S_i\} \ .$$

By the theory of Sobolev's spaces we can say that there exists $c > 0$ such that

$$\|\phi\|_{L^6(\Omega)} < c \|\nabla \phi\|_{L^2(\Omega)} \ .$$

Then we can write

$$|\phi_i| < c \|\nabla \phi\|_{L^2(\Omega)} \ .$$

This implies that f is bounded from below, which gives meaning to the search for minima of f. Let $\phi, h \in K$ and consider the functional $f(\phi + \alpha h)$ as a function of $\alpha \in [0,1]$. Then

$$\frac{df(\phi + \alpha h)}{d\alpha} = \int_\Omega \epsilon(|\nabla \phi + \alpha \nabla h|^2)$$
$$\times (\nabla \phi + \alpha \nabla h) \cdot \nabla h \, dx - \sum_i q_i h_i \ .$$

At $\alpha = 0$ an integration by parts and the assumption $\phi \in C^2(\Omega)$ yield

$$\frac{df}{d\alpha}(0) = -\int_\Omega \nabla \cdot [\epsilon(|\nabla \phi|^2)\nabla \phi] h \, dx$$
$$- \sum_i \left[\int_{S_i} \epsilon \frac{\partial \phi}{\partial \nu} da + q_i\right] h_i \ .$$

The arbitrariness of $h \in K$ and the functional lemma of the calculus of variations show that f is stationary at $\alpha = 0$, namely at ϕ, if and only if ϕ is a solution to the problem (6.1)–(6.3). Indeed, the solution to the problem (6.1)–(6.3) minimizes the functional f and the minimum is unique. To prove that this is so, we evaluate the second-order derivative $d^2 f/d\alpha^2$ at any value of α. We have

$$\frac{d^2 f}{d\alpha^2} = \int_\Omega \{ 2\epsilon'(|\nabla \phi + \alpha \nabla h|^2)[(\nabla \phi + \alpha \nabla h) \cdot \nabla h]^2$$
$$+ \epsilon(|\nabla \phi + \alpha \nabla h|^2)|\nabla h|^2\} dx \ .$$

By (2.2), with the identifications $\nabla \phi + \alpha \nabla h = \mathbf{E}$ and $\nabla h = d\mathbf{E}$, it follows that f is a strictly convex functional, in K, whence the uniqueness of the solution to (6.1)–(6.3).

VII. ENERGY

A natural question arises as to the expression of the energy density associated with a set of charges producing an electric field in a nonlinear dielectric. To answer this question, we begin by recalling, or generalizing, well-known properties.[11] Consider the N conductors with charges q_i and potentials ϕ_i, $i=1,\ldots,N$. By varying any charge q_i of a quantity dq_i, we need to perform a work $\sum_i \phi_i dq_i$. Now, by (6.1) we have

$$dq_i = \int_{S_i} d\mathbf{D} \cdot \mathbf{v} \, da$$

and, by (6.2),

$$\phi_i dq_i = \int_{S_i} \phi \, d\mathbf{D} \cdot \mathbf{v} \, da \ .$$

Then the divergence theorem and (6.3) yield

$$\sum_i \phi_i dq_i = \sum_i \int_{S_i} \phi \, d\mathbf{D} \cdot \mathbf{v} \, da = -\int_\Omega \nabla \cdot (\phi \, d\mathbf{D}) dx$$

$$= -\int_\Omega \nabla \phi \cdot d\mathbf{D} \, dx \ .$$

Accordingly, the sought energy density, say, w is such that

$$dw = \mathbf{E} \cdot d\mathbf{D} \ . \tag{7.1}$$

We can phrase (7.1) by saying that a function $w(\mathbf{D})$ is to be determined, if it exists, such that $\mathbf{E} \cdot d\mathbf{D}$ is its differential. Because of the nonlinearity in the law (2.1), it is more convenient to regard $\mathbf{E}$ as the independent variable. This is obtained by considering

$$dw = d(\mathbf{D} \cdot \mathbf{E}) - \mathbf{D} \cdot d\mathbf{E} \ ,$$

and the problem is to find a possible function whose differential is $\mathbf{D} \cdot d\mathbf{E}$. This means that a function u is needed such that

$$\epsilon(E^2)\mathbf{E} = \frac{\partial u}{\partial \mathbf{E}} \ .$$

By the integrability conditions, such a function u exists if and only if the tensor $\partial \mathbf{D}/\partial \mathbf{E}$ is symmetric. In fact, by (2.1)

$$\frac{\partial \mathbf{D}}{\partial \mathbf{E}} = 2\epsilon' \mathbf{E} \otimes \mathbf{E} + \epsilon \mathbf{1} \ ,$$

which is obviously symmetric. Incidentally, this symmetry condition is also necessary and sufficient for the existence of a variational formulation.[5]

A trivial integration of $du = \epsilon(E^2)\mathbf{E} \cdot d\mathbf{E}$ yields

$$u(\mathbf{E}) - u(0) = \int_0^1 \epsilon(\alpha E^2)\alpha \mathbf{E} \cdot \mathbf{E} \, d\alpha = \tfrac{1}{2} \int_0^{E^2} \epsilon(\xi) d\xi \ .$$

Then, letting $w = 0$ as $\mathbf{E} = 0$ we have

$$w = \epsilon(E^2)E^2 - \tfrac{1}{2} \int_0^{E^2} \epsilon(\xi) d\xi \ . \tag{7.2}$$

If ϵ is constant, then w simplifies—as it must—to the well-known relation

$$w = \tfrac{1}{2}\epsilon E^2 \ .$$

Quite naturally one expects that increasing (the modulus of) the electric fields results in the increasing of the energy density w. Now, by (7.2)

$$\frac{dw}{dE^2} = \epsilon' E^2 + \tfrac{1}{2}\epsilon \ .$$

In view of (2.3) we have the expected result $dw/dE^2 > 0$. Indeed, this shows which paradoxical result we might have, i.e., $dw/dE^2 < 0$, if we would have not required the positive definiteness of the differential permittivity.

VIII. CONCLUSIONS

The theory presented in this paper exhibits some remarkable features of the electric field in nonlinear dielectrics. The general solution for $\mathbf{E}$ is given by the integral equation (4.6). The term $\epsilon(E^2)\mathbf{E}$ is the obvious generalization of $\epsilon\mathbf{E}$ for linear dielectrics. The integral for $\mathbf{G}(\mathbf{E})$ is a direct consequence of Maxwell's equations for nonlinear dielectrics: it vanishes if the permittivity is constant and if the problem is endowed with particular symmetries. Usually, researchers devote attention to such particular symmetries and, presumably, that is the reason why this term has not appeared in the literature yet. Quantitatively, $\mathbf{G}(\mathbf{E})$ may be predominant on $\epsilon\mathbf{E}$, depending on the geometry and the parameters under consideration. Usually, though, the contribution of $\mathbf{G}(\mathbf{E})$ is quite smaller and this makes the iterative method (of Sec. V) efficient in a few steps, if not only one. For this procedure we need only a starting reference field $\mathbf{E}_0$. In this regard it is worth mentioning that the iterative method has recently been applied[12] to the electric field produced by a dipole (modeling the hydrophilic heads of a lipid) in pure water by letting $\mathbf{E}_0$ be the field produced when $\epsilon = \epsilon_0 \epsilon_v$. In such a case the nonlinearity turns out to be effective up to a distance of about 10 Å from the ions.

The variational formulation of Sec. VI allows us to say that the electrostatic problem has a unique solution which minimizes the functional f. This feature is certainly of conceptual interest, but it is also remarkable for practical purposes. It allows us to develop and apply variational methods by which approximate solutions are determined in correspondence with any geometry of the conductors. In such a case we need not know any reference field $\mathbf{E}_0$ as in the previous procedure. Such variational formulation is likely to be the most general way to determine the electric field in nonlinear dielectrics.

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