Nonlinear dielectric response of periodic composite materials

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Abstract This paper addresses the rigorous treatment of
the tunability effect (dc electric field driven variation of the
permittivity) in a high-contrast two dimensional periodic
composite (a matrix of a large dielectric constant ferro-
electric material with linear dielectric inclusions). The
theoretical analysis here shows that the trend established
for the case of low linear dielectric concentrations (that the
dilution with a low permittivity dielectric does not result in
decrease of the tunability of the composite material), can
hold for appreciable dielectric concentrations. We have
even documented a pronounced increase of the tunability.
The results of our simulations are in qualitative agreement
with the experimental data on the composite effect in
ferroelectric/dielectric binary-phase systems. The result of
the numerical analysis gives no support to the "decoupled
approximation" in the effective medium approach often
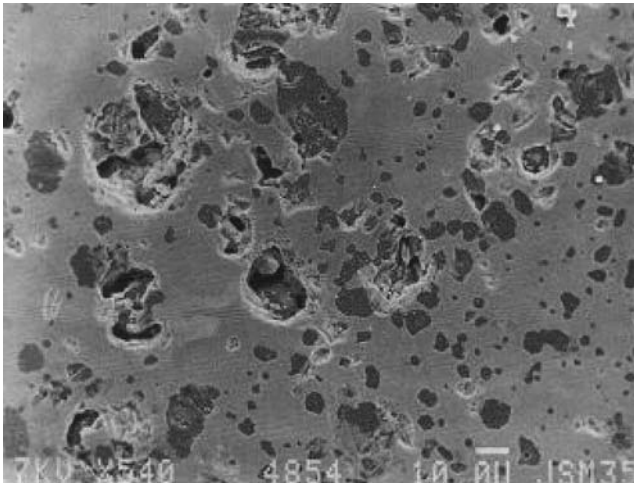used for the description of the dielectric non-linearity of
composites.

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1 Introduction

The potential utility of ferroelectric materials in high
frequency tunable devices was recognized early on in their
investigation. In general, these materials can appreciably
change their dielectric permittivity ε under the application
of a dc electric field, or in other words, these materials can
exhibit a high *relative tunability* defined as [1]

$$n_r = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} \qquad (1)$$

where $\varepsilon(E)$ is the dielectric permittivity of the material
corresponding to the field E applied to the material. It is this
property that can be used for fabrication of electronic
devices with parameters that can be tuned by the applica-
tion of a dc control voltage. However, for various reasons
related both to device electronics and materials technology,
only in the last few years have intensive development
efforts been made in this area. One of the directions of the
development in this field is the use of ferroelectric/dielectric
composites. A typical example is a $(Ba,Sr)TiO_3$ ceramic
fabricated with addition of MgO, which for volume
concentrations larger than 1–2% precipitates in a readily
distinguishable secondary phase. Figure 1 shows a SEM
image documenting the structure of the composite material
(Nenasheva and Dedyk, private communication). The
dielectric constants of these two phases are very different
(typically 1,000–2,000 for $(Ba,Sr)TiO_3$ and about 10 for
MgO), so that the dilution of ferroelectric with the dielectric
can obviously lead to an appreciable reduction the effective

Fig. 1 SEM images of a $(Ba,Sr)TiO_3 \times MgO$ sample at magnifications of ×540. Two phases of the composite material are clearly seen: the *dark* phase is MgO and the *light* one is BST with 1–5 μm crystallites (Nenasheva and Dedyk, private communication)

dielectric constant of the material. The tunability values of the two phases also differ significantly; for a ferroelectric one can readily achieve $n_r = 0.2 - 0.3$ whereas MgO does not exhibit any measurable tuning at realistic values of the electric field. Thus, one might expect some reduction of the tunability of the composite material as the concentration of the linear dielectric component increases. (For pure ferroelectrics, for example, according to the Landau theory a reduction of the permittivity should lead to a yet stronger reduction of the tunability.) At the same time experiment shows that the addition of the linear, low permittivity dielectric up to appreciable concentrations does not affect the tunability of the material at least as far as the effect of mechanical mixing of the two phases is concerned (Nenasheva and Dedyk, private communication), [2, 3]. This unexpected phenomenon has been addressed theoretically (see [1] for a review). It has been shown that in a model where a small concentration of spherical dielectric inclusions is incorporated into a ferroelectric, and tuning is still small, no decrease of tunability with dilution of the ferroelectric is expected. At the same time, a slight increase of tunability is predicted [1]

$$n_{r,eff} = n_r(1 + 0.2q)$$

whereas the same model predicts an appreciable reduction of the permittivity

$$\varepsilon_{eff} = \varepsilon(1 - 1.5q).$$

Here ε_{eff} and $n_{r,eff}$ are the permittivity and relative tunability of the composite containing a volume fraction q of a dielectric of much smaller permittivity than that of the ferroelectric matrix.

Although the qualitative agreement between the simple theory and experiment is encouraging, one should recognize the essential limitations of the theoretical result. First, the theory addresses only the limit of small concentrations, so that the comparison of the theoretical predictions with the experimental data (typically up to $q \approx 0.3$) is not fully justified. Second, the mathematical analysis used in the aforementioned theoretical treatment is not fully justified from the point of view of the rigorous mathematical theory of composites [4, 5].

Concerning the case of non-linear response at significant dielectric concentrations, there exists a problem with the application of any analytic method. In order to proceed further, one usually has had to introduce additional assumptions into the theory. The rather popular "decoupled approximation" in the effective medium approach [6, 7] postulates that, for the spatial distribution of the electric field $E_i(x)$ in the composite, there is a relation

$$\langle E_i^4(x) \rangle = \langle E_i^2(x) \rangle^2,$$

where <...> stands for the spatial average.

In this paper, we present the results of rigorous mathematical treatment (analytical and numerical) of the problem of the dielectric non-linearity of the ferroelectric-dielectric composite. We present the results obtained for the case of a 2-D periodic composite, which corresponds to a material where a system of dielectric rods is embedded into a ferroelectric matrix and exposed to an electric field that is normal to the direction of the axes of the rods. Though this model is quite far from the real experimental situation in the common ferroelectric/dielectric composites under experimental investigation, we believe that our analysis represents a significant advance in presenting the first rigorous mathematical treatment of this problem.

2 Tunability of composite materials

The relative tunability of an electrically tunable material has been defined in Eq. 1. We will address the case in which the tuning is small so that the function $\varepsilon(E)$ can be approximated as (see e.g. [1])

$$\varepsilon(E) = \varepsilon(0) + \mu E^2. \qquad (2)$$

so that formula (1) takes the form

$$n_r = \frac{\mu}{\varepsilon(0)} E^2. \qquad (3)$$

The composite material is inhomogeneous (Fig. 1), i.e. a material whose properties depend on the spatial variable $\mathbf{x} = (x, y)$. Then, in Eq. 2 $\varepsilon(0)$ and μ are functions that depend
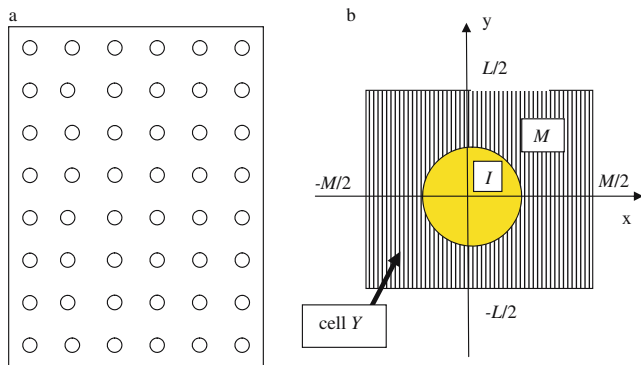
Fig. 2 Model of a composite material (**a**) and its unit cell (**b**). Y—cell, I—inclusion, M—matrix. For numerical cellular calculations $L=M=1$

on the spatial variable $\mathbf{x}$. Rewriting Eq. 2 in terms of the potential, we have

$$\varepsilon(\mathbf{x}, |\nabla\phi|) = \varepsilon(\mathbf{x}, 0) + \mu(\mathbf{x})|\nabla\phi|^2. \tag{4}$$

where $\phi(\mathbf{x})$ denotes the electrostatic potential $\left(\vec{E} = -\nabla\phi\right)$. The local dielectric displacement is related to $\nabla\phi$ by the formula

$$\vec{D} = \varepsilon(\mathbf{x}, |\nabla\phi|)\vec{\nabla}\phi$$

and satisfies the equation

$$div\ \vec{D} = 0. \tag{5}$$

Substituting Eq. 4 into Eq. 5, we obtain

$$div\ [\varepsilon(\mathbf{x}, |\nabla\phi|)\nabla\phi] = 0. \tag{6}$$

Solving Eq. 6 with the appropriate boundary conditions, we can in principle find the potential ϕ. It is however a very complex problem because of the inhomogeneity in $\mathbf{x}$.

A composite formed of many small components appears on macroscopic scales like a homogeneous material with its own material properties (referred to in the literature as *overall, microscopic, effective* or *homogeneous* characteristics).

Several authors have addressed computations of the overall properties for the composite materials similar to the one described here (see e.g. [6, 8]). We address specifically the case of the periodic composite illustrated in Fig. 2a in the weak nonlinearity limit, where the field-induced relative change of the dielectric constant is small $n_r \ll 1$. In this case, the overall dielectric constant of the composite can be written in the form [4]

$$\varepsilon_{\text{eff}}(E) = A + BE^2, \tag{7}$$

where

$$A = \frac{1}{|Y|} \int_Y \varepsilon(\mathbf{x}, 0)|\nabla N(\mathbf{x})|^2 d\mathbf{x} \tag{8}$$

and

$$B = \frac{1}{|Y|} \int_Y \mu(\mathbf{x})|\nabla N(\mathbf{x})|^4 d\mathbf{x}. \tag{9}$$

Here $|Y|$ denotes the volume of the elementary cell of the composite Y and $N(\mathbf{x})$ is a solution of the so-called cellular problem (see Appendix for details)

$$\begin{aligned} &\text{div}[\varepsilon(\mathbf{x}, 0)\nabla N] = 0 \text{ in } Y, \\ &N(x, -1/2) = -1/2, N(x, 1/2) = 1/2, \\ &\frac{\partial N}{\partial \mathbf{n}}(x, y) = 0 \text{ for } x = -1/2 \text{ and } x = 1/2. \end{aligned} \tag{10}$$

Note that the average value of ∇N over the elementary cell of the composite Y is equal to unity. Taking into account the second equality from Eq. 10, the periodicity of N in the variable y, and the direction of the normal vector $\mathbf{n}$ on the boundary ∂Y of the cell, we have

$$\int_Y \nabla N(\mathbf{x})d\mathbf{x} = \int_{\partial Y} N(\mathbf{x})n d\mathbf{x} = 1/2 - (-1/2) = 1.$$

Since A and B are independent of the scaling transformation of the potential, the above equation can be written in dimensionless form.

Relations analogous to Eq. 7 and 8 have been obtained for the case of an arbitrary composite by Stroud and coworkers (see e.g. [8]); the method that they used, however, cannot be considered to be fully mathematically rigorous. Our derivation of this relation for the 2-D periodic composite based on the homogenization method [4] guaranties validity of formulae (7), (8) and (9) in the small field limit.

The overall tunability of composite described by Eq. 7 is then

$$n_{r,\text{eff}} = -\frac{B}{A}E^2. \tag{11}$$

3 Analysis of the overall properties of composite

Observing formulas (8), (9) and (10) for the overall characteristics of the composite, we find that the main difficulty in the calculation of these properties is the computation of the function $N(\mathbf{x})$. For the materials under consideration, our analysis is carried out for a two-phase composite, which consists of a nonlinear matrix M with linear inclusions I (Fig. 2). In accordance with the data presented in the introduction, we can assume that the dielectric constant of the inclusions is small compared to the dielectric constant of the matrix. Then, we can approximately take $\varepsilon(x) \approx 0$ inside the inclusions I, and $\varepsilon(X)=\varepsilon(0)$

in the matrix M. Then defining $\mu(X)=0$ in I, and $\mu(X)=\mu$ in M, we obtain from Eqs. 8, 11, and 13 the following formula for the parameters A, B and $n_{r,\text{eff}}$:

$$A = \varepsilon(0)I_2 \; B = \mu I_4, \tag{12}$$

$$n_{r,\text{eff}} = \frac{\mu}{\varepsilon(0)} JE^2, \tag{13}$$

where

$$I_2 = \frac{1}{|Y|} \int_M |\nabla N(\boldsymbol{x})|^2 d\boldsymbol{x} \;,\; I_4 = \frac{1}{|Y|} \int_M |\nabla N(\boldsymbol{x})|^4 d\boldsymbol{x},$$
$$J = \frac{I_4}{I_2}.$$

Note that the tunability of the pure ferroelectric is $\frac{\mu}{\varepsilon(0)} E^2$; from Eq. 13, J is then equal to the ratio of the tunability of composite to the tunability of the pure ferroelectric.

$$J = \frac{n_{r,\text{eff}}}{n_r}. \tag{14}$$

It is noted in [9] that J has the meaning of tunability amplification factor in inhomogeneous structure.

Formula (14) enables us to evaluate the impact of dilution on the effective tunability $n_{r,\text{eff}}$.

4 Estimates for the homogenized tunability of a high-contrast composite

For a high-contrast composite, the value of the tunability in accordance with formulas (12), (13) and (14) can be expressed through the values of the integral functionals

$$I_2 = \frac{1}{|Y|} \int_M |\nabla N|^2 d\boldsymbol{x}$$

and

$$I_4 = \frac{1}{|Y|} \int_M |\nabla N|^4 d\boldsymbol{x}$$

for the solution of the problem (10).

As mentioned in the introduction above, a popular method (the so-called decoupled approximation) has been used for evaluation of the dielectric non-linearity of composites. It was postulated that for the spatial distribution of the electric field in the composite $E_i(X)$, there is a relation $\langle E_i^4(x) \rangle = \langle E_i^2(x) \rangle^2$. It terms of our variables, this means that $I_4 = I_2^2$. Below we present our estimates for the quantities I_2 and I_4. In the next section it will be demonstrated that I_2^2 does not approximate I_4 for the local field determined from the electrostatic problem solution.

4.1 Low-sided estimate

Let us apply the Cauchy–Schwartz–Bunyakovsky inequality to the integral $\int_M |\nabla N(x)|^2 dx$ in the following way:

$$\int_M |\nabla N(\boldsymbol{x})|^2 1 d\boldsymbol{x} \leq \left(\int_M |\nabla N(\boldsymbol{x})|^4 1 d\boldsymbol{x} \right)^{1/2} \left(\int_M 1 d\boldsymbol{x} \right)^{1/2}$$

$$= \left(\int_M |\nabla N(\boldsymbol{x})|^4 1 d\boldsymbol{x} \right)^{1/2} |M|^{1/2}.$$

Then

$$\left(\int_M |\nabla N(\boldsymbol{x})|^2 d\boldsymbol{x} \right)^2 \leq \int_M |\nabla N(\boldsymbol{x})|^4 d\boldsymbol{x} |M|.$$

Dividing by $|Y|^2$, we obtain

$$\left(\frac{1}{|Y|} \int_Y |\nabla N(\boldsymbol{x})|^2 d\boldsymbol{x} \right)^2 \leq \frac{1}{|Y|} \int_Y |\nabla N(\boldsymbol{x})|^4 d\boldsymbol{x} \frac{|M|}{|Y|}.$$

Thus

$$\frac{I_2^2}{I_4} \leq \frac{|M|}{|Y|}$$

Taking into account that $\frac{|M|}{|Y|} = 1 - q < 1$, where q is volume fraction of the dielectric inclusion, we conclude that the relation $I_4 = I_2^2$, which is the basic assumption of the decoupled approximation, can never be satisfied in this system. However, the result obtained does not exclude $I_4 \approx I_2^2$. We will return to this later when treating the problem numerically.

4.2 Upper-sided estimate

Now let us apply the CSB inequality to the integral $\int_M |\nabla N(x)|^4 dx$ in the following way

$$\int_M |\nabla N(\boldsymbol{x})|^4 1 d\boldsymbol{x} \leq \left(\int_M |\nabla N(\boldsymbol{x})|^8 d\boldsymbol{x} \right)^{1/2} \left(\int_M 1 d\boldsymbol{x} \right)^{1/2}$$

$$= \left(\int_M |\nabla N(\boldsymbol{x})|^8 d\boldsymbol{x} \right)^{1/2} |M|^{1/2}.$$

Then

$$\left(\int_M |\nabla N(\boldsymbol{x})|^4 d\boldsymbol{x} \right)^2 \leq \int_M |\nabla N(\boldsymbol{x})|^8 d\boldsymbol{x} |M|.$$

Table 1 Values of parameters controlling the dielectric properties of the non-linear periodic composite calculated as functions of the dielectric volume concentration q.

q	I_2	I_4	$J=I_4/I_2$	$J*$	I_4/I_2^2
0.03	0.94	0.98	1.04	1.04	1.11
0.05	0.91	0.96	1.06	1.06	1.17
0.07	0.87	0.94	1.08	1.08	1.24
0.09	0.84	0.92	1.10	1.09	1.31
0.13	0.78	0.87	1.12	1.12	1.45
0.19	0.68	0.79	1.16	1.16	1.71
0.20	0.67	0.79	1.17	1.16	1.75
0.28	0.56	0.68	1.22	1.21	2.18
0.35	0.48	0.60	1.25	1.25	2.60
0.39	0.40	0.57	1.30	1.27	2.94
0.46	0.36	0.50	1.38	1.35	3.79

Dividing the expression above by $|Y|^2$, one can obtain

$$\left(\frac{1}{|Y|}\int_Y |\nabla N(\boldsymbol{x})|^4 d\boldsymbol{x}\right)^2 \leq \frac{1}{|Y|}\int_Y |\nabla N(\boldsymbol{x})|^8 dx \frac{|M|}{|Y|}.$$

Thus

$$I_4^2 \leq \frac{1}{|Y|}\int_Y |\nabla N(\boldsymbol{x})|^8 dx \frac{|M|}{|Y|}$$

or

$$I_4^2 \leq \frac{1}{|Y|}\int_Y |\nabla N(\boldsymbol{x})|^8 d\boldsymbol{x}(1-q).$$

Another upper-sided estimate can be obtained as follows. We apply CSB to the integral $\int_M |\nabla N(\boldsymbol{x})|^4 d\boldsymbol{x}$ in the following way

$$\int_M |\nabla N(\mathbf{x})|^4 d\mathbf{x} = \int_M |\nabla N(\mathbf{x})|^3 |\nabla N(\mathbf{x})| d\mathbf{x} \leq$$

$$\leq \left(\int_M |\nabla N(\mathbf{x})|^6 d\mathbf{x}\right)^{1/2}\left(\int_M |\nabla N(\mathbf{x})|^2 d\mathbf{x}\right)^{1/2}.$$

Then

$$\left(\int_M |\nabla N(\boldsymbol{x})|^4 d\boldsymbol{x}\right)^2 \leq \left(\int_M |\nabla N(\boldsymbol{x})|^6 d\boldsymbol{x}\right)\left(\int_M |\nabla N(\boldsymbol{x})|^2 d\boldsymbol{x}\right).$$

Dividing again by $|Y|^2$, we obtain

$$\left(\frac{1}{|Y|}\int_Y |\nabla N(\mathbf{x})|^4 d\mathbf{x}\right)^2 \leq \left(\frac{1}{|Y|}\int_M |\nabla N(\mathbf{x})|^6 d\mathbf{x}\right)\left(\frac{1}{|Y|}\int_M |\nabla N(\mathbf{x})|^2 d\mathbf{x}\right).$$

The last factor on the right-hand side of this inequality is equal to A. Then, we have

$$I_4^2 \leq A\left(\frac{1}{|Y|}\int_Y |\nabla N(\boldsymbol{x})|^6 d\boldsymbol{x}\right).$$

5 Computer simulations

We consider a periodic cell with a circular inclusion. To determine the function $N(\mathbf{x})$ it suffices to solve the so-called "cellular problem" for the periodicity cell of the composite. The cellular problem is equivalent to the problem of minimization of the integral functional

$$\int_Y \varepsilon_0(\mathbf{x})|\nabla N|^2 d\mathbf{x}$$

over the set of function satisfying following boundary conditions

$$N(x,-1/2) = -1/2, \ N(x,1/2) = 1/2$$

and

$$\frac{\partial N}{\partial \mathbf{n}}(x,y) = 0 \quad \text{for} \quad x = 1/2 \quad \text{and} \quad x = -1/2.$$

Using a symmetry approach, one can solve the corresponding problem for 1/4 of the periodicity cell. The derivatives $\frac{\partial N}{\partial x}$ and $\frac{\partial N}{\partial y}$ are approximated using finite-differences by $\frac{N^{i+1,i}-N^{i,j}}{h}$ and $\frac{N^{i,i+1}-N^{i,j}}{h}$, respectively, where h is the size of the discretization. As a result, we obtain a quadratic function of finite variables. Minimizing this function by an iterative method, we obtain an approximate solution of the problem above. We then compute the integrals (8) and (9) numerically.

A computer code for solution to the 2-D cellular problem has been developed. The computational results are presented in Table 1.

Table 1 shows the values of the integrals

$$I_2 = \frac{1}{|Y|} \int\limits_M |\nabla N|^2 d\boldsymbol{x}$$
$$I_4 = \frac{1}{|Y|} \int\limits_M |\nabla N|^4 d\boldsymbol{x},$$

as functions of the volume fraction q of dielectric inclusion for the high-contrast composite ($\varepsilon_{diel}=0$). The quantities $I_2 = \frac{A}{\varepsilon(0)}$ and $I_4 = \frac{B}{\mu}$ are the ratio of the dielectric constant of the composite to the dielectric constant of the pure ferroelectric (matrix) and for the coefficient describing the quadratic non-linearity of the material, respectively The quantity

$$J = \frac{I_4}{I_2} = \frac{n_{r,\text{eff}}}{n_r}$$

is the ratio of the tunability of the composite to that of the pure ferroelectric. Table 1 also gives the values of the parameter J^*=B/A calculated according to Eqs. 8 and 9 for a finite dielectric contrast between the matrix and inclusions ($\varepsilon_{diel}=10$ and $\varepsilon_{matrix}=2,000$).

The data presented in Table 1 shows that, in a 2-D periodic composite, the decrease of the effective linear permittivity with the dilution of the matrix is accompanied with an appreciable increase of the tunability. Comparing the calculated values of J and J^*, one finds them to be nearly equal. This shows that the high-contrast composite approximation ($\varepsilon_{diel}=0$) remains appropriate up to rather high dielectric concentrations.

Our numerical simulation also enables evaluation of the validity of the basic assumption of "decoupled approximation" in the effective medium approach [6, 7], which assumes that $\langle E_i^4(x) \rangle = \langle E_i^2(x) \rangle^2$. It terms of our variable this means that $I_4 = I_2^2$. As is clear form Table 1, I_4 is much closer to I_2 than to I_2^2. Thus, our calculations give no support to the "decoupled approximation" in the effective medium approach.

6 Conclusions

We have carried out a theoretical analysis of weak dielectric non-linearity in a high-contrast nonlinear composite 2-D periodic structure. The analysis was done using the rigorous homogenization method earlier developed for the mathematical treatment of composites. For the model considered, this approach provides a full mathematical justification of the relations obtained earlier for the dielectric non-linearity of a weakly nonlinear ferroelectric composite [1, 8]. Our numerical treatment of 2-D periodic composites of this kind has shown that the trend established for the case of low concentrations (namely, the dilution with a low permittivity dielectric does not result in the decrease of the tunability),

can hold for appreciable dielectric concentrations. Rather, in the case of our model we have documented a pronounced *increase* of the tunability. Qualitatively similar behavior has been experimentally documented for Ba$_x$Sr$_{1-x}$TiO$_3$ (BST) ferroelectric with Mg-based additives [1–3], but where the additional effect of chemical doping of the matrix [1] makes the phenomenon more complicated. Using the results of our numerical simulations we have also probed the principal assumption of the "decoupled approximation" in the effective medium approach to find no support for this assumption for the system considered in this paper.

Appendix

Homogenization procedure for the electrostatic problem (with arbitrary volume fraction of inclusions)

Assume that the permittivity of the nonlinear material has the form

$$A(|\nabla\varphi|) = a + \lambda b(|\nabla\varphi|),$$

where λ is a small parameter, so that the nonlinearity is weak. The small nonlinearity can be used as model of a significantly nonlinear material provided that the electric field magnitude is rather small as well.

Let particles of another material to be introduced into the nonlinear material. Then

$$A = A(\mathbf{x}, |\nabla\varphi|) = a(\mathbf{x}) + \lambda b(\mathbf{x}, |\nabla\varphi|). \tag{A1}$$

The potential of the electric field in the composite satisfies the following differential equation

$$\text{div } [A(\mathbf{x}, |\nabla\varphi|)\nabla\varphi] = 0. \tag{A2}$$

We consider a 2-D composite possessing a periodic structure for which computation of the homogenized characteristics can be reduced to the analysis of a problem for one periodicity cell only. We assume that the periodicity cell is rectangular with the center at the origin of the coordinate axes and with the lengths of the sides equal to L and M. We assume that it contains one inclusion, which is symmetric with respect to the origin corresponding to the cell of the composite illustrated in Fig. 2b. These assumptions are made in order to simplify the mathematical evaluations to be presented below.

We assume that the horizontal pair of sides are subjected to voltage $\pm EL$ (these values correspond to the average field magnitude E) and on the other pair of sides the potential is

periodic (see. Fig. 2b). Because of the symmetry and equivalence of all periodic cells, we obtain the following conditions on the boundary of one cell:

$$\varphi(x, \pm L/2) = \pm EL/2, \tag{A3}$$

$$\frac{\partial \varphi}{\partial n}(\pm M/2, y) = 0. \tag{A4}$$

The total flux of the dielectric displacement

$$\mathbf{D} = A(|\nabla \varphi|)\nabla \varphi$$

through the specimen is the sum of the fluxes through all its sides. The flux through the upper side $\Gamma = \{-L/2 < x < L/2, y = M/2\}$ of the periodicity cell Y, corresponding to the potential difference U in Eq. A3 is equal to

$$F = \int_\Gamma A(\mathbf{x}, |\nabla \varphi|)\frac{\partial \varphi}{\partial \mathbf{n}}d\mathbf{x}. \tag{A5}$$

Multiplying Eq. A2 by φ and integrating by parts, we obtain with regard to Eqs. A3 and A4

$$-\int_Y A(\mathbf{x}, |\nabla \varphi|)|\nabla \varphi|^2 d\mathbf{x} + \int_\Gamma A(\mathbf{x}, |\nabla \varphi|)\varphi d\mathbf{x} = 0. \tag{A6}$$

The flux through the lateral sides of the cell is then equal to zero (see Eq. A4)

$$\int_{x=\pm L/2} A(\pmb{x}, |\nabla \varphi|)\varphi \, d\pmb{x} = 0. \tag{A7}$$

Taking into account Eq. A7 and boundary condition (A3) we obtain from Eq. A6 that

$$-\int_Y A(\mathbf{x}, |\nabla \varphi|)|\nabla \varphi|^2 d\mathbf{x}$$

$$+ \int_{y=\pm L/2} A(\mathbf{x}, |\nabla \varphi|)\frac{\partial \varphi}{\partial \mathbf{n}}[\pm EL/2] \, d\mathbf{x} = 0. \tag{A8}$$

The fluxes through the upper and low sides of the cell Y are equal to

$$\int_{y=L/2} A(\mathbf{x}, |\nabla \varphi|)\frac{\partial \varphi}{\partial \mathbf{n}} \, d\pmb{x} = \int_{y=-L/2} A(\mathbf{x}, |\nabla \varphi|)\frac{\partial \varphi}{\partial \mathbf{n}}d\pmb{x}. \tag{A9}$$

From Eqs. A8 and A9 we obtain

$$\int_{y=\pm 1/2} A(\mathbf{x}, |\nabla \varphi|)\nabla \varphi \, d\mathbf{x}$$

$$= EL \int_{y=1/2} A(\mathbf{x}, |\nabla \varphi|)\frac{\partial \varphi}{\partial \mathbf{n}} \, d\mathbf{x}. \tag{A10}$$

From Eqs. A8 and A10 (flux corresponds to the potential difference U) we obtain

$$D_{\text{total}} = \int_\Gamma A(\mathbf{x}, |\nabla \varphi|)\frac{\partial \varphi}{\partial \mathbf{n}}d\mathbf{x}$$

$$= \frac{1}{EL} \int_Y A(\mathbf{x}, |\nabla \varphi|)|\nabla \varphi|^2 d\mathbf{x}. \tag{A11}$$

The specific flux D (flux per unit length of the horizontal boundary $y=L/2$ of the periodicity cell) is

$$D = \frac{1}{ELM} \int_Y A(\mathbf{x}, |\nabla \varphi|)|\nabla \varphi|^2 d\mathbf{x}. \tag{A12}$$

Formula (A12) corresponds to the homogenization theory [5] if we define

$$|Y| = LM,$$

the measure (the square in the case under consideration) of the periodicity cell Y.

Considering small nonlinearity, we will carry out the homogenization analysis in combination with the classical method of small parameters. Following [6], we find the solution of Eqs. A2, A3 and A4 in the form

$$\varphi = \varphi_0 + \lambda\varphi_1 + \ldots \tag{A13}$$

Substituting Eq. A13) in Eqs. A2, A3 and A4, we then have

$$\text{div}\,[a(\mathbf{x}) + \lambda b(\mathbf{x}, |\nabla\varphi_0 + \lambda\varphi_1 + \ldots|)\nabla(\varphi_0 + \lambda\varphi_1 + \ldots)]$$

$$= 0, \tag{A14}$$

$$\varphi_0 + \lambda\varphi_1 + \ldots (x, \pm 1/2) = \pm U, \tag{A15}$$

$$\frac{\partial}{\partial \mathbf{n}}(\varphi_0 + \lambda\varphi_1 + \ldots)(\pm 1/2, y) = 0. \tag{A16}$$

From Eqs. A14, A15 and A16) we obtain the equations of the 0th order (terms corresponding to λ^0)

$$\text{div}\,[a(\mathbf{x})\nabla\varphi_0] = 0, \tag{A17}$$

$$\varphi_0(x, \pm 1/2) = \pm E/2, \tag{A18}$$

$$\frac{\partial \varphi_0}{\partial \mathbf{n}}(\pm 1/2, y) = 0, \tag{A19}$$

and the equations of the 1st order (terms corresponding to λ^1)

$$\text{div}\,[a(\mathbf{x})\nabla\varphi_1 + b(\mathbf{x}, |\nabla\varphi_0|)\nabla\varphi_0] = 0, \tag{A20}$$

$$\varphi_1(x, \pm 1/2) = 0, \tag{A21}$$

$$\frac{\partial \varphi_0}{\partial \mathbf{n}}(\pm 1/2, y) = 0. \tag{A22}$$

Substituting Eq. A13 in Eq. A11, we obtain
$$F = \frac{1}{E}\int_Y A(\mathbf{x}, |\nabla(\varphi_0 + \lambda\varphi_1 + \ldots)|)|\nabla(\varphi_0 + \lambda\varphi_1 + \ldots)|^2 d\mathbf{x}.$$

Saving terms in which the order is not higher than the first order in μ, we obtain

$$\begin{aligned} F = \tfrac{1}{E}\int_Y A(\mathbf{x}, |\nabla\varphi_0)|)|\nabla\varphi_0|^2 d\mathbf{x}+ \\ + \tfrac{\lambda}{E}\int_Y [a(\mathbf{x})\nabla\varphi_0\nabla\varphi_1 + b(\mathbf{x}, |\nabla\varphi_0|)\nabla\varphi_0\nabla\varphi_0] d\mathbf{x}. \end{aligned} \tag{A23}$$

In Eq. A23 we omit the terms of the highest order.

Now we apply some transformations. Multiplying Eq. A17 by φ_1 and integrating, we obtain

$$\int_Y \text{div}\,[a(x)\nabla\varphi_0]\varphi_1 d\mathbf{x} = 0.$$

Integrating by parts, we have

$$-\int_Y a(\mathbf{x})\nabla\varphi_0\nabla\varphi_1 d\mathbf{x} + \int_{\partial Y} a(\mathbf{x})\frac{\partial \varphi_0}{\partial \mathbf{n}}\varphi_1 d\mathbf{x} = 0. \tag{A24}$$

Consider the first boundary integral in Eq. A25. For the upper and lower sides of the cell, we have

$$\int_{y=\pm 1/2} a(\mathbf{x})\frac{\partial \varphi_0}{\partial \mathbf{n}}\varphi_1(x, y) d\mathbf{x} = 0. \tag{A25}$$

The last equality results from $\varphi_1(x, \pm L/2) = 0$ in accordance with Eq. A21. For the lateral sides of the cell

$$\int_{x=\pm 1/2} a(\mathbf{x})\frac{\partial \varphi_0}{\partial \mathbf{n}}(x, y)\varphi_1(x, y) d\mathbf{x} = 0.$$

The equality results from $\frac{\partial \varphi_0}{\partial \mathbf{n}}(\pm M/2, y) = 0$ in accordance with Eq. A19.

Then the boundary integral in Eq. A24 is equal to zero and from Eq. A24 it follows that

$$-\int_Y a(\mathbf{x})\nabla\varphi_0\nabla\varphi_1 d\mathbf{x} = 0. \tag{A26}$$

Note that we cannot obtain an analogous expression for the equality (A26) for an arbitrary function. We obtain (A26) using the fact that the sides on which φ_1 and $\frac{\partial \varphi_0}{\partial \mathbf{n}}$ are zero cover the entire boundary of the cell Y.

Using Eq. A26 we can rewrite Eq. A23 as

$$\begin{aligned} F = \frac{1}{EML}\int_Y A(\mathbf{x}, |\nabla\varphi_0)|)|\nabla\varphi_0|^2 d\mathbf{x}+\frac{\lambda}{EML} \\ \int_Y b(\mathbf{x}, |\nabla\varphi_0|)|\nabla\varphi_0|^2 d\mathbf{x}. \end{aligned} \tag{A27}$$

The specific flux of the electric field through the periodicity cell Y has the form $F = F_0 + \mu F_1$, where

$$F_0 = \frac{1}{EML}\int_Y A(\mathbf{x}, |\nabla\varphi_0)|)|\nabla\varphi_0|^2 d\mathbf{x}, \tag{A28}$$

$$F_1 = \frac{\mu}{EML}\int_Y b(\mathbf{x}, |\nabla\varphi_0|)|\nabla\varphi_0|^2 d\mathbf{x}. \tag{A29}$$

The homogenized dielectric constant D of the composite is introduced as ratio of the total flux F of the electric field to the corresponding (initiating this flux) potential difference E. In the case under consideration

$$D = \frac{F}{E} = D_0 + \mu D_1,$$

where

$$\begin{aligned} D_0 &= \frac{1}{2E^2 ML}\int_Y a(\mathbf{x})|\nabla\varphi_0|^2 d\mathbf{x} \\ &= \frac{1}{2ML}\int_Y a(\mathbf{x})\left|\frac{\nabla\varphi_0}{U}\right|^2 d\mathbf{x}, \end{aligned} \tag{A30}$$

$$\begin{aligned} D_1 &= \frac{\lambda}{E^2 ML}\int_Y b(\mathbf{x}, |\nabla\varphi_0|)|\nabla\varphi_0|^2 d\mathbf{x} \\ &= \lambda\frac{1}{ML}\int_Y b(\mathbf{x}, |\nabla\varphi_0|)\left|\frac{\nabla\varphi_0}{U}\right|^2 d\mathbf{x} \end{aligned} \tag{A31}$$

We introduce $N(x, y)$ as solution of the linear cellular problem (A17), (A18) and (A19) with $E=1/2$. Then

$$\varphi_0(\mathbf{x}) = EN(\mathbf{x}), \tag{A32}$$

and we can write formulas (A30) and (A31) in the following form

$$D_0 = \frac{1}{2ML} \int_Y a(\boldsymbol{x})|\nabla N|^2 d\boldsymbol{x}, \tag{A33}$$

where

$$D_1 = \lambda \frac{1}{ML} \int_Y b(\boldsymbol{x},|U\nabla N|)|\nabla N|^2 d\boldsymbol{x}, \tag{A34}$$

The cellular problem has the following form

$$\begin{aligned} &\text{div}[a(\mathbf{x})\nabla N] = 0, \\ &N(x, \pm L/2) = \pm L/2, \\ &\frac{\partial N}{\partial \boldsymbol{n}}(\pm M/2, y) = 0. \end{aligned} \tag{A35}$$

This problem corresponds to a potential difference equal to 1.

Let us discuss the formulas obtained above. Formula (A33) is known from paper [5]. It introduces the homogenized dielectric constant of a linear composite.

Let us consider the composite nonlinear matrix—linear inclusion. In this case

$$\begin{aligned} &b(\mathbf{x},|\mathbf{E}|) \neq 0 \quad \text{in the matrix,} \\ &b(\mathbf{x},|\mathbf{E}|) = 0 \quad \text{in the inclusion.} \end{aligned}$$

Then formula (A34) takes the form

$$D_1 = \lambda \frac{1}{ML} \int_M b(|U\nabla N|)|\nabla N|^2 d\boldsymbol{x}, \tag{A36}$$

so that we integrate over the matrix only. In this case a and $b(|U\nabla N|)$ do not depend on the spatial variables, but take values corresponding to the matrix.

Assume that $b(\mathbf{x},0)=0$. Under this assumption the tunability $n_{r,\text{eff}}$ is computed in accordance with the formula

$$n_{r,\text{eff}} = \lambda \frac{D_1(U)}{D_0} = \lambda \frac{\int_M b(|U\nabla N|)|\nabla N|^2 d\boldsymbol{x}}{\int_M a|\nabla N|^2 d\boldsymbol{x}}, \tag{A37}$$

The tunability of the material of the matrix is

$$n_r = \lambda \frac{b(|U|)}{a}.$$

Diluting a matrix which has a large dielectric constant with particles which have low dielectric constant, we find that the overall dielectric constant D_0 decreases as well. When D_0 and $D_1(U)$ decrease as a function of a and $b(|U|)$, the ratio (A37) can increase or decrease against $\frac{b(|U|)}{a}$.

We can write

$$\begin{aligned} \frac{D_1(U)}{D_0} - \frac{b(|U|)}{a} &= \\ &= \frac{\int_M b(|U\nabla N|)|\nabla N|^2 d\mathbf{x}}{\int_M a|\nabla N|^2 d\mathbf{x}} - \frac{b(|U|)}{a} = \\ &= \frac{a\int_M [b(|U\nabla N|)-b(|U|)]|\nabla N|^2 d\mathbf{x}}{aD_0}. \end{aligned} \tag{A38}$$

From Eq. A38 the tunability is determined by the distribution of the local electric field (solution of the cellular problem (A35).

The quadratic function A. In applications A is often taken in the form of a quadratic function. In this case

$$b(U) = \mu U^2,$$

so that (A34) becomes

$$D_1 = \lambda U^2 \int_M \mu(\mathbf{x})|\nabla N|^4 d\mathbf{x}. \tag{A39}$$

The case when the periodicity cell $Y = 1 \times 1$ was considered. Every square can be transformed into the cell $Y = 1 \times 1$. As a result of this transformation we obtain that for an arbitrary square all integrals over Y and M must be divided by the square of the cell Y. This conclusion is in accordance with general homogenization theory [5].

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