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Effective properties of nonlinear inhomogeneous dielectrics

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We develop a general procedure for estimating the effective constitutive behavior of nonlinear dielectrics. The procedure is based on a variational principle expressing the effective energy function of a given nonlinear composite in terms of the effective energy functions of the class of *linear comparison composites.* This provides an automatic procedure for converting well-known information for linear composites, in the form of estimates and bounds for their effective dielectric constants, into corresponding estimates and bounds for the effective behavior of nonlinear composites. Further, the procedure is easily implemented, and leads in some cases to *exact* results. Thus, exact estimates are given herein for isotropic *weakly nonlinear* composites with general nonlinearity, and bounds of the Hashin-Shtrikman type are given for the class of two-phase, isotropic dielectric composites with *strongly* and *perfectly nonlinear* constitutive behavior. The optimality of the bounds is addressed briefly.

I. INTRODUCTION

An important problem in classical physics is that of estimating the effective transport properties of composite materials. For materials with linear constitutive behavior, and negligible interfacial effects, there exists a well developed theory, which is reviewed, for example, in the article by Landauer.[1] However, there are numerous phenomena where nonlinear constitutive effects are very important. These include dielectric breakdown, burning out of fuses, and nonlinear optics. Further, it is anticipated that the coupling between nonlinearity and inhomogeneity may lead to potentially important new applications.[2]

This paper is concerned with the theoretical prediction of the effective constitutive behavior of nonlinear inhomogeneous dielectrics, although the resulting theory will also be applicable (with appropriate reinterpretations) to nonlinear inhomogeneous conductors, ferromagnetic materials, and lasers. Thus, the emphasis will be placed on the theoretical aspects of the problem rather than on specific applications. Although the theory of nonlinear composites is not nearly as well developed as the corresponding linear theory, significant progress has been achieved over the past five years. Stroud and Hui[3] made use of a perturbation expansion to obtain an exact estimate, to first order in the nonlinear (cubic) susceptibility of the composite, for dilute concentrations of inhomogeneities. More recently, this result has been extended to nondilute concentrations of inhomogeneities.[4] In addition to these results for weakly nonlinear materials, Blumenfeld and Bergman[5] have obtained an estimate for the effective dielectric constant of a strongly nonlinear composite, which is exact to second order in the fluctuations (contrast) of the dielectric coefficients in the composite. While the previous authors concerned themselves with specific types of nonlinearities (cubic susceptibilities and pure-power-law nonlinearities, respectively), and perturbation expansions (in the weak nonlinearity and contrast, respectively), Willis[6] considered composites with general types of nonlinearity and isotropic microstructures to obtain bounds of the Hashin-Shtrikman[7] type for the effective energy functions of these nonlinear composites.

In this paper, we use a *variational* procedure for estimating the effective behavior of *nonlinear* composites in terms of the effective properties of the class of *linear comparison* composites. The distinct advantage of the method is that well-known *bounds* and *estimates* from the linear theory may then be used to generate corresponding information for nonlinear composites. Additionally, the method is straightforward, and of great generality, not being limited to special perturbation limits nor to special types of nonlinearities. In Sec. II, we briefly define the effective behavior of a general nonlinear composite, and develop a variational principle, from which the effective behavior of the nonlinear composite may be estimated. In Sec. III, the method is applied to two-phase, nonlinear composites with overall *isotropy,* and compared to the results of previous authors in the special cases considered by these authors. Finally, in Sec. IV, we summarize our findings, and provide some comments concerning future directions of research.

II. EFFECTIVE PROPERTIES

The nonlinear constitutive behavior of an inhomogeneous dielectric, occupying a region in space (of unit volume), Ω, may be characterized by means of an electric energy-density function, $w(\mathbf{x},\mathbf{E})$, depending on the position vector $\mathbf{x}$ and the electric field $\mathbf{E}(\mathbf{x})$, such that the electric displacement field $\mathbf{D}(\mathbf{x})$ is given by

$$\mathbf{D}(\mathbf{x})=\partial_{\mathbf{E}} w(\mathbf{x},\mathbf{E}) \ , \tag{1}$$

where $\partial_{\mathbf{E}}$ denotes differentiation with respect to $\mathbf{E}$. We assume further that the dielectric is locally isotropic, so that

$$w(\mathbf{x},\mathbf{E})=\phi(\mathbf{x},E) \ , \tag{2}$$

where ϕ is taken to be convex in the magnitude of the electric field E.

It can be shown[6] that the *effective* constitutive behavior of the inhomogeneous dielectric may be expressed in terms of the spatial averages (over Ω) of the fields, $\overline{\mathbf{D}}$ and $\overline{\mathbf{E}}$, via the relation

$$\overline{\mathbf{D}}=\partial_{\overline{\mathbf{E}}} \tilde{W}(\overline{\mathbf{E}}) \ , \tag{3}$$

where the effective energy-density function of the composite, $\tilde{W}$, is in turn given by the minimum-energy principle

$$\tilde{W}(\overline{\mathbf{E}})=\min_{\mathbf{E}\in K} \int_{\Omega} w[\mathbf{x},\mathbf{E}(\mathbf{x})]dx \ , \tag{4}$$

where K is the set of *admissible* electric fields, specified by

$$K=\{\mathbf{E}|\mathbf{E}=-\nabla\varphi(\mathbf{x}) \ \text{ in } \ \Omega, \text{ and } \varphi=-\overline{\mathbf{E}}\cdot\mathbf{x} \ \text{ on } \ \partial\Omega\} \ . \tag{5}$$

This variational formulation of the electrostatics problem for the composite is completely equivalent to the standard boundary-value-problem formulation in terms of Gauss's and Faraday's laws ($\nabla\cdot\mathbf{D}=0$ and $\nabla\times\mathbf{E}=0$, respectively), together with the uniform boundary condition

$$\varphi=-\overline{\mathbf{E}}\cdot\mathbf{x} \ \text{ on } \ \partial\Omega \ , \tag{6}$$

where φ is the electrostatic potential. The main advantage of the variational formulation is that the effective behavior of the nonlinear composite is then characterized in terms of only one scalar variable, namely, $\tilde{W}$.

In practice, the difficulty associated with the computation of the effective energy function of the composite (4) is that the exact admissible fields are usually difficult to determine in general for typical microstructures. However, numerous methods—both approximate and exact—have been devised to address this problem in the context of *linear* constitutive behavior for the composite. Next, we develop a variational principle that will allow us to make use of these known linear results to obtain corresponding estimates for nonlinear composites.

Our variational principle centers around a change of variables $u=E^2$, defining a function f, such that

$$f(\mathbf{x},u)=\phi(\mathbf{x},E)=w(\mathbf{x},\mathbf{E}) \ . \tag{7}$$

Note that the function f has the same dependence on $\mathbf{x}$ as ϕ and w. Then, assuming *convexity* of f, we have the following representation for w, namely,

$$w(\mathbf{x},\mathbf{E})=\max_{\varepsilon_0\geq 0}\{w_0(\mathbf{x},\mathbf{E})-v(\mathbf{x},\varepsilon_0)\} \ , \tag{8}$$

where

$$v(\mathbf{x},\varepsilon_0)=\max_{\mathbf{E}}\{w_0(\mathbf{x},\mathbf{E})-w(\mathbf{x},\mathbf{E})\} \ , \tag{9}$$

and where $w_0(\mathbf{x},\mathbf{E})=\frac{1}{2}\varepsilon_0(\mathbf{x})E^2$ corresponds to the local energy-density function of a *linear comparison* composite with arbitrary non-negative dielectric coefficient (not constant) $\varepsilon_0(\mathbf{x})$. This representation is based on Legendre duality for the function f; in fact,[8] $v(\mathbf{x},\varepsilon_0)=f^*(\mathbf{x},\frac{1}{2}\varepsilon_0)$, where f^* denotes the Legendre transform of f, as given by

$$f^*(\mathbf{x},p)=\max_{u}\{up-f(\mathbf{x},u)\} \ . \tag{10}$$

Relations (8) and (9) form the basis for this variational principle, which is obtained by making use of (8) in the context of (4) to obtain the result[8]

$$\tilde{W}(\overline{\mathbf{E}})=\max_{\varepsilon_0(\mathbf{x})\geq 0}\{\tilde{W}_0(\overline{\mathbf{E}})-V(\varepsilon_0)\} \ , \tag{11}$$

where V is the functional generated by the function $v(\mathbf{x},\varepsilon_0)$,

$$V(\varepsilon_0)=\int_{\Omega} v[\mathbf{x},\varepsilon_0(\mathbf{x})]dx \ , \tag{12}$$

and where $\tilde{W}_0$ denotes the effective energy function of the linear comparison composite, with local energy function w_0, so that

$$\tilde{W}_0(\overline{\mathbf{E}})=\min_{\mathbf{E}\in K}\int_{\Omega} w_0(\mathbf{x},\mathbf{E})dx \tag{13}$$

[cf. (4)]. Thus, prescription (11), together with (12) and (13), provide an alternative way of determining the effective energy function of the nonlinear composite in terms of the effective energy function of a suitably optimized, *linear*, inhomogeneous, comparison material. We emphasize that the dielectric coefficient of the comparison material in (11) $[\varepsilon_0(\mathbf{x})]$ is a non-negative function of position.

The assumption that the function f in (7) is convex is essential in the above derivation. However, it can be demonstrated that a dual result exists for concave f.[8] Otherwise, the equality in (11) must be replaced by a strict inequality. Here, for simplicity, we will consider only examples for which f is convex.

III. APPLICATIONS TO TWO-PHASE ISOTROPIC COMPOSITES

In this section, we consider the application of the general variational principle to two-phase composite dielectrics with nonlinear constitutive behavior characterized by

$$\phi(\mathbf{x},E)=\sum_{r=1}^{2}\theta^{(r)}(\mathbf{x})\phi^{(r)}(E) \ , \tag{14}$$

where $\phi^{(r)}(E)$ and $\theta^{(r)}(\mathbf{x})$ $(r=1,2)$ are, respectively, the energy function and the characteristic function (which vanishes, unless $\mathbf{x}$ is in phase r, in which case it equals 1) of phase r. We assume further that the corresponding volume fractions $c^{(r)}$, given by

$$c^{(r)}=\int_{\Omega}\theta^{(r)}(\mathbf{x})dx \ , \tag{15}$$

are fixed, and such that $\sum_{r=1}^{2}c^{(r)}=1$.

Next we recall that even though the properties of the nonlinear phases are homogeneous [as assumed in (14)], the solutions for the comparison dielectric coefficients $\varepsilon_0(\mathbf{x})$ in the variational principle (11) will not, in general, be constant over the individual phases, unless the actual fields happen to be constant over the phases. However, we can obtain a lower bound for $\widetilde{W}$ by restricting the class of admissible comparison dielectric coefficients to be constant within each phase, i.e., $\varepsilon_0(\mathbf{x})=\sum_{r=1}^{2}\theta^{(r)}(\mathbf{x})\varepsilon_0^{(r)}$ (with constant $\varepsilon_0^{(r)}$). This follows from the fact that the minimum over any set is in general larger than the minimum over a subset of the original set. Therefore, we have that

$$\widetilde{W}(\overline{\mathbf{E}})\geq \max_{\varepsilon_0^{(r)}>0}\left\{\widetilde{W}_0(\overline{\mathbf{E}})-\sum_{r=1}^{2}c^{(r)}v^{(r)}(\varepsilon_0^{(r)})\right\} , \tag{16}$$

where $\widetilde{W}_0$ now corresponds to a linear comparison composite with the same microstructure as the nonlinear composite, that is, with dielectric constants $\varepsilon_0^{(r)}$ in volume fractions $c^{(r)}$. Also, the functions $v^{(r)}$ are obtained from relation (9), specialized to phase r, i.e., $v(\mathbf{x},\varepsilon_0)=\sum_{r=1}^{2}\theta^{(r)}(\mathbf{x})v^{(r)}(\varepsilon_0^{(r)})$.

Finally, if we limit our consideration to the class of *isotropic* nonlinear composites, we are justified in writing $\widetilde{W}_0(\overline{\mathbf{E}})=\frac{1}{2}\tilde{\varepsilon}_0\overline{E}^2$, where $\tilde{\varepsilon}_0$ is a function of the comparison dielectric constants $\varepsilon_0^{(r)}$, the volume fractions $c^{(r)}$, and any other available information about the specific microstructure, or *class* of microstructures under consideration. Of particular interest in this connection is the Maxwell-Garnett[9] approximation for *particulate* composites with a distinct matrix phase (say, phase 2) and an inclusion phase (1). This estimate, which may be expressed in the form

$$\tilde{\varepsilon}_0=\left[\sum_{r=1}^{2}\frac{c^{(r)}}{\varepsilon_0^{(r)}+(d-1)\varepsilon_0^{(2)}}\right]^{-1}-(d-1)\varepsilon_0^{(2)} \tag{17}$$

(where d stands for the dimension of the underlying Euclidean space), has alternatively been shown to be a bound for the class of two-phase, linear isotropic composites by Hashin and Shtrikman[7] [it is a lower (upper) bound if $\varepsilon_0^{(1)}>\varepsilon_0^{(2)}(\varepsilon_0^{(2)}>\varepsilon_0^{(1)})$]. This bound is further known[7] to be *optimal* (i.e., no better bound is possible for this class of materials). Additionally, the above estimate is *exact* to first order in the dilute limit (as $c^{(1)}\rightarrow 0$), and also to second order in the contrast (as $\delta\varepsilon=\varepsilon_0^{(2)}-\varepsilon_0^{(1)}\rightarrow 0$). Other linear estimates, such as the effective-medium approximation,[10] and bounds, such as the Beran bounds,[11] are also available, but the corresponding nonlinear estimates and bounds will be considered elsewhere.

In the next subsections, we will limit our consideration to three cases: general estimates for weakly nonlinear composites, and Hashin-Shtrikman bounds for strongly and perfectly nonlinear composites, respectively. We will assume the following constitutive behavior for the phases:

$$\phi^{(r)}(E)=\tfrac{1}{2}\varepsilon^{(r)}E^2+\chi^{(r)}\psi^{(r)}(E) \ , \tag{18}$$

where the first term corresponds to linear dielectric behavior, and the second to a nonlinear susceptibility function (if $\psi^{(r)}$ is quadratic, and $\varepsilon^{(r)}$ is set equal to the permittivity of free space, then $\chi^{(r)}$ is the standard dielectric susceptibility of phase r). Finally, in the last subsection, we consider briefly the question of optimality of the bounds for the perfectly nonlinear composite.

A. Estimates for weakly nonlinear composites

We define the weakly nonlinear composite as one for which $\chi^{(r)}\ll 1$ in relations (18). Then, the case considered by Zeng *et al.*[4] corresponds to the special case of (18) with quartic $\psi^{(r)}$ (i.e., cubic susceptibility). Thus, given a *specific* isotropic microstructure for the nonlinear dielectric, if we assume that we have an estimate for the effective dielectric constant of a linear comparison composite with the *same* microstructure (as the nonlinear composite), specified by

$$\tilde{\varepsilon}_0=F(\varepsilon_0^{(r)},c^{(r)}) \ , \tag{19}$$

where the function F depends on the properties of the linear comparison composite $\varepsilon_0^{(r)}$ and the volume fractions $c^{(r)}$ [e.g., (17)], then we can determine a corresponding estimate for the nonlinear composite. Such an estimate may be obtained from relation (16), by making use of (9), which leads to

$$v^{(r)}(\varepsilon_0^{(r)})=\chi^{(r)}(g^{(r)})^*(\tfrac{1}{2}\delta\varepsilon^{(r)}) \ , \tag{20}$$

where $g^{(r)}(u)=\psi^{(r)}(E)$ $(u=E^2)$ and $\delta\varepsilon^{(r)}=(\varepsilon_0^{(r)}-\varepsilon^{(r)})/\chi^{(r)}$, and of a Taylor-series expansion of F about $\varepsilon_0^{(r)}=\varepsilon^{(r)}$, given by

$$\tilde{\varepsilon}_0=F(\varepsilon^{(r)},c^{(r)})+\sum_{r=1}^{2}\chi^{(r)}\frac{\partial F}{\partial\varepsilon^{(r)}}(\varepsilon^{(r)},c^{(r)})\delta\varepsilon^{(r)} + O[(\chi^{(r)})^2] \ . \tag{21}$$

This calculation yields the following result for the effective energy function of the weakly nonlinear composite, namely,

$$\widetilde{W}(\overline{\mathbf{E}})\geq\tfrac{1}{2}F(\varepsilon^{(r)},c^{(r)})\overline{E}^2+\sum_{r=1}^{2}\chi^{(r)}c^{(r)}\psi^{(r)}\left[\left[\frac{1}{c^{(r)}}\frac{\partial F}{\partial\varepsilon^{(r)}}(\varepsilon^{(r)},c^{(r)})\right]^{1/2}\overline{E}\right]+O[(\chi^{(r)})^2] \ , \tag{22}$$

where we have assumed (for simplicity) that $\partial F/\partial\varepsilon^{(r)}\geq 0$. By specializing this result for *general* weak nonlinearity to the case of a quartic weak nonlinearity, we recover the specific results of Zeng *et al.*[4]

B. Hashin-Shtrikman bounds and estimates for strongly nonlinear composites

As mentioned earlier, Hashin and Shtrikman[7] determined optimal bounds for the class of two-phase, *linear* isotropic composites with prescribed volume fractions. In this section, we will make use of these results to obtain a corresponding lower bound for the effective energy of the class of two-phase, *nonlinear* isotropic composites. We note that such a nonlinear Hashin-Shtrikman bound can also be given the interpretation of a Maxwell-Garnett approximation for nonlinear composites with particulate microstructures. In order to achieve a simple form for the nonlinear bound, we make use of the following identity:

$$\left[\sum_{r=1}^{2}\frac{c^{(r)}}{\varepsilon_0^{(r)}}\right]^{-1}=\min_{\omega}\{c^{(1)}\varepsilon_0^{(1)}(1-c^{(2)}\omega)^2+c^{(2)}\varepsilon_0^{(2)}(1+c^{(1)}\omega)^2\}\ . \tag{23}$$

Then, application of (23) to (17), together with (16), leads to

$$\tilde{W}(\bar{\mathbf{E}})\geq\max_{\varepsilon_0^{(1)},\varepsilon_0^{(2)}>0}\left(\min_{\omega}\{c^{(1)}[\tfrac{1}{2}\varepsilon_0^{(1)}(s^{(1)})^2-v^{(1)}(\varepsilon_0^{(1)})]+c^{(2)}[\tfrac{1}{2}\varepsilon_0^{(2)}(s^{(2)})^2-v^{(2)}(\varepsilon_0^{(2)})]\}\right)\ ,$$

where

$$s^{(1)}=|1-c^{(2)}\omega|\bar{E}$$

and

$$s^{(2)}=\sqrt{(1+c^{(1)}\omega)^2+(d-1)c^{(1)}\omega^2}\,\bar{E}\ ,$$

or

$$s^{(1)}=\sqrt{(1-c^{(2)}\omega)^2+(d-1)c^{(2)}\omega^2}\,\bar{E}$$

and

$$s^{(2)}=|1+c^{(1)}\omega|\bar{E}\ ,$$

depending on whether $\varepsilon_0^{(1)}>\varepsilon_0^{(2)}$ or $\varepsilon_0^{(1)}<\varepsilon_0^{(2)}$ [so that (17) is a lower bound for $\tilde{\varepsilon}_0$]. Finally, noticing that the argument of the minimum function is convex in ω and concave in $\varepsilon_0^{(1)}$ and $\varepsilon_0^{(2)}$, application of the saddle-point theorem, and of result (8) applied to each phase, leads to a simple bound for $\tilde{W}$, given by

$$\tilde{W}(\bar{\mathbf{E}})\geq\min_{\omega}\{c^{(1)}\phi^{(1)}(s^{(1)})+c^{(2)}\phi^{(2)}(s^{(2)})\}\ , \tag{24}$$

where $s^{(1)}$ and $s^{(2)}$ are given by the pair above yielding the smallest minima in (24). Alternatively, it can be shown that choosing the pair $s^{(1)}$ and $s^{(2)}$ yielding the largest minima in the right-hand side of (24) results in an *upper estimate* for the effective energy function of the nonlinear composite $\tilde{W}$. This Hashin-Shtrikman upper estimate is not in general a rigorous upper bound for $\tilde{W}$ because the approximation made in relation (16) is strictly one sided. On the other hand, the Hashin-Shtrikman upper estimate may also be given the interpretation of a Maxwell-Garnett approximation for particulate composites with the more conducting phase serving the role of the matrix phase.

Bounds and estimates of this type for nonlinear composites have also been obtained by Willis[7] by making use of an extension of the Hashin-Shtrikman variational principle (which makes use of a *homogeneous* comparison material) for nonlinear constitutive behavior. However, the form for the nonlinear bound that has emerged in this work in terms of a one-dimensional optimization problem is simpler.

It is interesting to compare the predictions of our lower bound with the *exact* second-order perturbation result of Blumenfeld and Bergman[5] for *pure-power-law* strongly nonlinear composites [i.e., $\varepsilon^{(r)}=0$ and $\psi^{(r)}(E)=E^{n+1}/(n+1)$ $(n\geq1)$ in (18)] in the small-contrast limit ($\delta\chi\to0$, where $\chi^{(1)}=\chi^{(0)}$, $\chi^{(2)}=\chi^{(0)}+\delta\chi$). Their result may be expressed in the form (with $d=3$)

$$\tilde{\chi}=\langle\chi\rangle-\frac{n+1}{2(n-1)\chi^{(0)}}\left[1-\frac{\sin^{-1}\sqrt{(n-1)/n}}{\sqrt{n-1}}\right]\times(\langle\chi^2\rangle-\langle\chi\rangle^2)+O(\delta\chi^3)\ , \tag{25}$$

where the effective nonlinear susceptibility $\tilde{\chi}$ of the pure-power-law composite is defined by $\tilde{W}(\bar{\mathbf{E}})=\tilde{\chi}\bar{E}^{n+1}/(n+1)$,[5] and where the angular brackets denote spatial averages over the composite. By comparison, our result (24), in the corresponding limit, reduces to (with $d=3$)

$$\tilde{\chi}\geq\langle\chi\rangle-\frac{n+1}{2(n+2)\chi^{(0)}}(\langle\chi^2\rangle-\langle\chi\rangle^2)+O(\delta\chi^3)\ . \tag{26}$$

We note that this result is in general exact only to *first* order in the contrast $\delta\chi$. However, in the limits as $n\to1$ and ∞ (corresponding, respectively, to the linear and "perfectly"[12] nonlinear limits), we find that the two results [(25) and (26)] agree to *second* order in $\delta\chi$. In between these two limits, we find that our bound (26) lies below the exact result (25). It is important to emphasize at this stage that result (25) is one of the few exact results available for nonlinear composites, but also that it is special in that corresponding results are not available for general nonlinearity. On the other hand, our results for the nonlinear Hashin-Shtrikman bound (24) apply for general nonlinearity and arbitrary contrast for the composite.

Finally, we note that when the above Hashin-Shtrikman bound is applied to composites with constitutive behavior given by (18), it leads to a result that agrees, in the small nonlinearity limit, with our weakly nonlinear result (22). However, more generally, the weakly nonlinear result is not a good approximation for strongly nonlinear composites.

C. Hashin-Shtrikman bounds and estimates for perfectly nonlinear composites

In this section, we are concerned with the determination of Hashin-Shtrikman bounds and estimates for the effective behavior of the class of two-phase, isotropic *perfectly nonlinear* composites. As we have seen, this class of composites is a special case of the class of strongly nonlinear composites, where the constitutive behavior of the phases is of the pure-power type with $n \to \infty$. However, the function $\psi^{(r)}(E) = E^{n+1}/(n+1)$ needs to be properly interpreted in the limit as $n \to \infty$. This can be accomplished rigorously via convex analysis, but in the interest of brevity, we will simply introduce some appropriate notation. Thus, we define the "threshold" electric field $E_n^{(r)}$ (analogous to the "yield stress"[12]) from the relation

$$\phi^{(r)}(E) = \frac{1}{n+1} E_n^{(r)} \left[\frac{E}{E_n^{(r)}} \right]^{n+1} . \tag{27}$$

Note that, with this definition, $E_n^{(r)} = (\chi^{(r)})^{-1/n}$ in (18). Then, in the limit as $n \to \infty$, the corresponding constitutive relation (1) is given by $\mathbf{E} = \mathbf{0}$ and $\mathbf{D} = \mathbf{0}$; or $E = E_\infty^{(r)}$ and $\mathbf{D}$ is parallel to $\mathbf{E}$, but otherwise indeterminate. We continue by formally applying the general expression for the lower bound (24) to the perfectly nonlinear composite to obtain an upper bound (lower bound for $\tilde{W}$) for the corresponding threshold electric field for the composite $\tilde{E}_\infty$, namely,

$$\tilde{E}_\infty \le \frac{dc^{(1)}}{c^{(2)} + dc^{(1)}} \left[E_\infty^{(1)} + \frac{c^{(2)}}{dc^{(1)}} \sqrt{(c^{(2)} + dc^{(1)})(E_\infty^{(2)})^2 - (d-1)c^{(1)}(E_\infty^{(1)})^2} \right] , \tag{28}$$

where we have assumed that $E_\infty^{(1)} \le E_\infty^{(2)}$. We note that, for $d=3$, in the small-contrast limit ($\delta E_\infty = E_\infty^{(1)} - E_\infty^{(2)} \to 0$), this result (28) is consistent (to second order) with results (25) and (26), as $n \to \infty$. However, the bound (28) for perfectly nonlinear composites is valid more generally, with no restrictions placed on the concentration of the inhomogeneities, nor on the contrast between the phases.

Correspondingly, a lower estimate may also be established for the effective threshold electric field $\tilde{E}_\infty$ of this class of composites. The result is obtained in the same way as (28), and is given by the right-hand side of expression (28), with superscripts 1 and 2 interchanged if

$$(1 - 1/d)\sqrt{1 + c^{(2)}/(d-1)}\, E_\infty^{(2)} \le E_\infty^{(1)} \le E_\infty^{(2)} ,$$

or alternatively, by

$$\tilde{E}_\infty = \sqrt{1 + c^{(2)}/(d-1)}\, E_\infty^{(1)}$$

if

$$E_\infty^{(1)} \le (1 - 1/d)\sqrt{1 + c^{(2)}/(d-1)}\, E_\infty^{(2)} .$$

Figure 1(a) is a plot of the upper bound (HS+) and lower estimate (HS−) for the effective threshold electric field of the perfectly nonlinear composite, $\tilde{E}_\infty$ (appropriately normalized by $E_\infty^{(2)}$, as a function of the contrast between the two phases $E_\infty^{(1)}/E_\infty^{(2)}$, for $c^{(1)} = c^{(2)} = 0.5$. Additionally, the classical bounds of Weiner,[13] obtained directly from the minimum-energy principle (4) and its dual, the complementary energy principle, are shown for comparison. These are given in this case by $\tilde{E}_\infty = E_\infty^{(1)}$ and $\tilde{E}_\infty = c^{(1)}E_\infty^{(1)} + c^{(2)}E_\infty^{(2)}$, respectively, for the lower and upper bounds. We note that the rigorous Hashin-Shtrikman upper bound (HS+) is a significant improvement over the classical Weiner bound (W+), which gets progressively better as the contrast between the phases increases. On the other hand, the Hashin-Shtrikman lower estimate (HS−) is stronger than the Weiner lower bound (W−), but the Hashin-Shtrikman estimate gets progressively weaker (relative to the Weiner bound) as the contrast increases. We also give in Figs. 1(b) and 1(c) the corresponding plots for the threshold electric fields $\tilde{E}_n$ of the pure-power-law nonlinear composite [cf. (27)], as functions of the contrast, for $n = 10$ and 3, respectively. These plots are given for comparison with the perfectly nonlinear results of Fig. 1(a) ($n = \infty$). The results for the Hashin-Shtrikman upper bound and lower estimate are obtained by evaluating numerically the minima implied by relations (24). The corresponding Weiner lower and upper bounds are given by $\tilde{E}_\infty = [c^{(1)}(E_\infty^{(1)})^{-n} + c^{(2)}(E_\infty^{(2)})^{-n}]^{-1/n}$ and $\tilde{E}_\infty = c^{(1)}E_\infty^{(1)} + c^{(2)}E_\infty^{(2)}$, respectively. Finally, in Fig. 1(d), again for the purpose of comparison with the previous results, we depict the corresponding results for the linear composite ($n = 1$). In this case both the upper and lower Hashin-Shtrikman estimates are rigorous optimal bounds.

D. On the optimality of the bounds for perfectly nonlinear composites

The fact that the small-contrast bound (26) for the effective nonlinear susceptibility of the pure-power composite reduces to the corresponding linear result in the limit as $n \to 1$ is, of course, expected. More surprising, however, is that the bound (26) also appears to be exact in the limit as $n \to \infty$ (to second order in the contrast). Motivated by this finding, we investigate next the possibility that the more general bound (28) [obtained from (24)] may, in fact, be *optimal* for the class of two-phase, isotropic *perfectly nonlinear* composites. This is accomplished by applying the exact version of the variational principle (11) to a *sequentially laminated material* (Fig. 2),[14] which we will show has an effective energy function attaining the bound (24), at least for certain special loading conditions.

A sequentially laminated material (or laminate, for short) is an iterative construction obtained by layering laminated materials (which in turn have been obtained from lower-order lamination procedures) with one of the homogeneous phases that make up the composite, in such a way as to produce hierarchical microstructures of increasing complexity. One important property of this construction is that the length scale of the embedded laminates is assumed to be small compared to the length scale of the embedding laminates (for example, in Fig. 2, $\delta_1 \ll \delta_2 \ll 1$). This assumption derives from the fact that the effective properties of simple laminates can be computed exactly, and hence, by treating the sequential laminate as a simple laminate (where the embedded laminate is replaced by a homogeneous material with the effective properties of the embedded laminate), the effective properties of the sequential laminate can also be computed exactly. This property, together with the flexibility with which their microstructure can be controlled (by varying the proportion of the phases within each elemental layer, as well as the orientation of the layering directions), makes them useful theoretical tools, and they have been

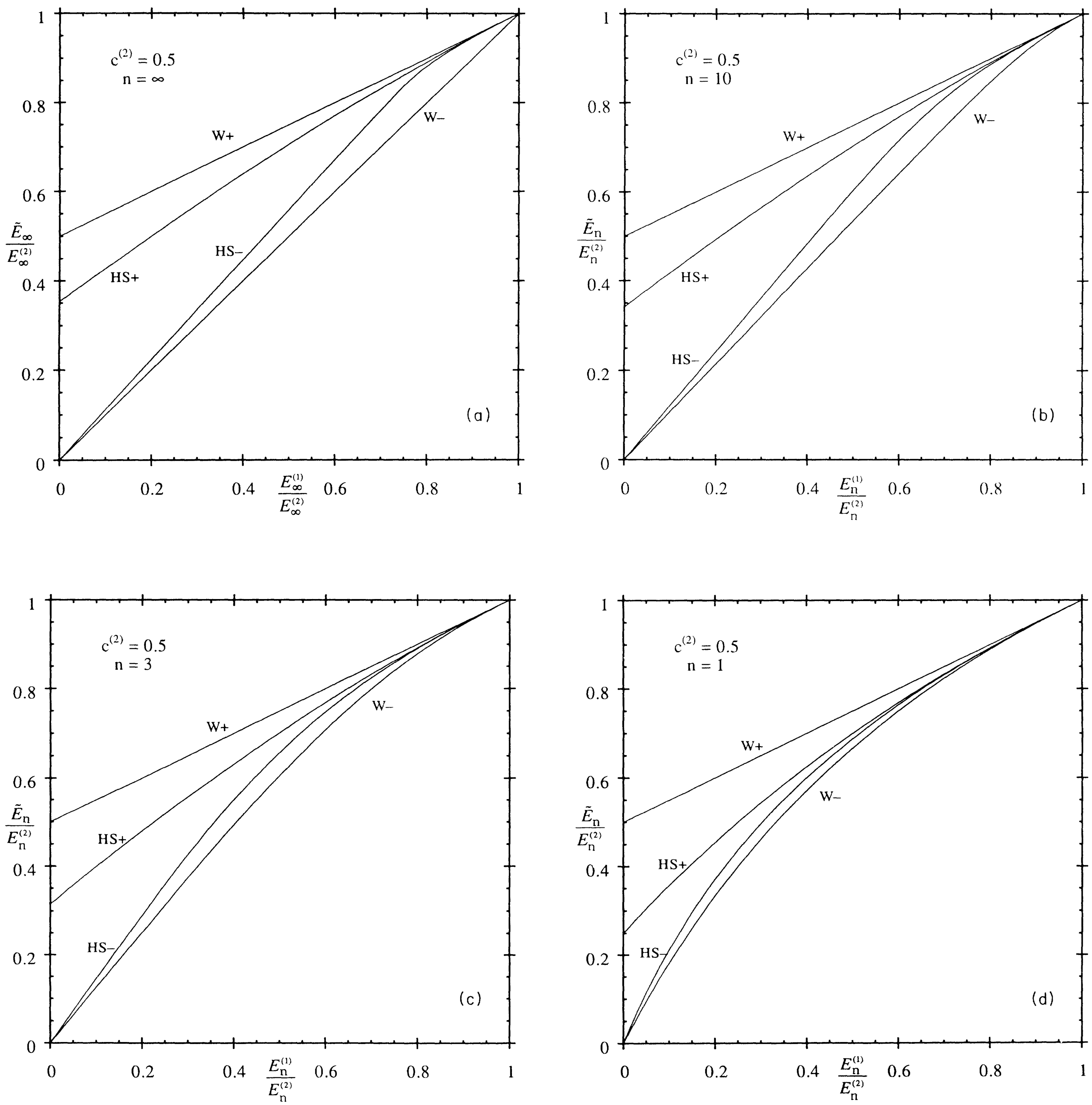

FIG. 1. Plots of the effective threshold electric field ($\tilde{E}_n/E_n^{(2)}$) as a function of the contrast ($E_n^{(1)}/E_n^{(2)}$) for (a) the *perfectly nonlinear* composite ($n=\infty$), (b) the *pure-power-law* composite ($n=10$), (c) the *pure-power-law* composite ($n=3$), and (d) the *linear* composite ($n=1$). The proportions of the two phases are identical ($c^{(1)}=c^{(2)}=0.5$).

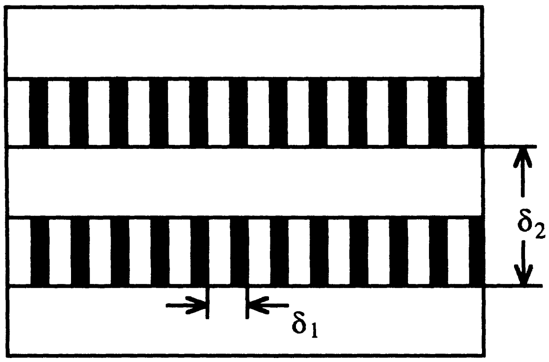

FIG. 2. A sequentially laminated composite material of rank two.

used extensively[14] in the *linear* theories of composites to demonstrate optimality of bounds.

In the interest of brevity, we will not discuss sequentially laminated materials in any further detail, and we will simply borrow a result from the linear theory, which is needed in our investigation of the optimality of the nonlinear Hashin-Shtrikman bound for two-phase, isotropic, perfectly nonlinear composite dielectrics. This result is[14] that there exists a sequential laminate of rank d (the rank is the number of layering operations) attaining the Hashin-Shtrikman lower bound (17) for two-phase, *linear,* isotropic composite dielectrics in d dimensions. Figure 2 is a schematic representation of the pertinent rank-2 laminate in two dimensions. We note that, to obtain the lower bound for $\tilde{\varepsilon}_0$, the weaker phase (phase 2), with the smaller dielectric constant $\varepsilon_0^{(2)}$, must play the role of the matrix, and correspondingly, the stronger phase (phase 1), with the larger dielectric constant $\varepsilon_0^{(1)}$, must play the role of the inclusion.

The above result suggests that the same rank-d, sequentially laminated microstructure (with the material with the larger threshold electric field occupying the matrix phase) may attain the Hashin-Shtrikman upper bound (28) for the class of two-phase, perfectly nonlinear, isotropic composite dielectrics in d dimensions. Indeed, if we *assume* that all the phases in the perfectly nonlinear, rank-d laminate become simultaneously active ($E=E_\infty^{(r)}$ in each part of each phase r), we can show that the corresponding expression for the energy function of the laminate is precisely the same as the expression for the Hashin-Shtrikman nonlinear bound (28). To see this, we make use of the exact version of the variational principle (11). Because the fields within the perfectly nonlinear sequentially laminated composite are constant, it follows that the inequality in (16) may be replaced by an equality for such a microstructure. Then, the effective energy function of the nonlinear iterated laminate $\tilde{W}$ is given by (16), with $\tilde{W}_0$ corresponding to the effective energy function of the two-phase, linear comparison laminate. But, the expression for $\tilde{W}_0$ is precisely the same as that for the corresponding linear Hashin-Shtrikman bound, and therefore the energy function of the nonlinear sequential laminate is the same as that for the nonlinear Hashin-Shtrikman bound (28).

It is important in the above construction to note that there are only two optimization variables $\varepsilon_0^{(1)}$ and $\varepsilon_0^{(2)}$. This is because the magnitudes of the electric fields in the perfectly nonlinear phases can only take on two values in each phase r: 0 or $E_\infty^{(r)}$. For a *general* nonlinear composite, we would require more optimization variables (one for the inclusion phase, and one for each lamination operation in the matrix phase). Then, the above procedure for a rank-d sequential laminate would not result in the nonlinear Hashin-Shtrikman bound. Thus, the bound (24) for general nonlinearity is not expected to be optimal.

However, even for perfectly nonlinear composites, the above argument does not allow us to conclude that the Hashin-Shtrikman upper bound for $\tilde{E}_\infty$ is optimal. This is because the assumption that *all* parts of the phases that make up the rank-d laminate become simultaneously active, under all possible loading conditions, is not valid. Thus, for example, for the rank-2 laminate of Fig. 2, application of an electric field in the horizontal direction would lead to an overall electric displacement for the composite as soon as the part of the matrix phase, within the embedded rank-1 laminate, becomes active (this does not require the other portion of the matrix phase, outside the embedded rank-1 laminate, to become active). Thus, the effective threshold electric field for the rank-2 laminate in the horizontal direction is less than that predicted by the Hashin-Shtrikman bound (28). In the context of the minimum energy principle (4), defining the effective properties of the laminated composite, both solutions (the solution with the fully active matrix phase and the solution with the partially active matrix) are stationary points of the minimum principle, but the second solution yields the minimum energy, and is therefore preferred.

Hence, the above simple example demonstrates that the rank-d laminate does not, in general, attain the Hashin-Shtrikman bound (in fact, it is not even isotropic, essentially for the same reason that it is not extremal). Therefore, we cannot conclude that the Hashin-Shtrikman bound (28) is optimal, although it may well be.

IV. CONCLUDING REMARKS

We have shown that the method proposed herein for determining the effective properties of nonlinear composite dielectrics is not only capable of reproducing the results of particular asymptotic expansions in the weakly nonlinear and small contrast limits for specific types of nonlinearities, but it is also able to deliver results for general types of nonlinearities, without limitation to dilute, weakly nonlinear, or small-contrast limits. Further, it is found that the results of the method, either in the form of estimates or rigorous bounds, are in some cases exact, and in other cases allow the possibility of investigating the optimality of the bounds. A more exhaustive treatment of the applications considered here, as well as applications to higher-order bounds and other types of estimates, will be given elsewhere. Applications to the nonlinear mechanical behavior of solids has also been considered elsewhere.[15] Extensions to anisotropic behavior and multiple phases are also under consideration. However, many issues, including the determination of *upper* bounds (for the effective energy functions), and the optimality of the bounds, still remain unresolved.

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