Second-order theory for nonlinear dielectric composites incorporating field fluctuations

P. Ponte Castañeda*
Department of Mechanical Engineering and Applied Mechanics, School of Engineering and Applied Science, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6315
(Received 2 June 2001; published 2 November 2001)

This paper deals with the development of an improved second-order theory for estimating the effective behavior of nonlinear composite dielectrics. The theory makes use of the field fluctuations in the phases of the relevant ''linear comparison composite'' to generate improved Maxwell-Garnett (MGA) and effective-medium (EMA) types of approximations for nonlinear media. Similar to the earlier version of the theory, the resulting MGA and EMA predictions are exact to second-order in the contrast, but—unlike the earlier version—the estimates satisfy all known bounds. In particular, the EMA estimates exhibit a nonlinearity-independent percolation threshold, and critical exponents that are consistent with recently developed bounds on these exponents. In addition, the MGA and EMA estimates are shown to yield reasonable predictions for strongly nonlinear composites with ''threshold-type'' nonlinearities, which are extreme cases where earlier methods have been known to sometimes fail.

DOI: 10.1103/PhysRevB.64.214205 PACS number(s): 77.84.Lf, 77.84.−s, 72.20.Ht, 05.40.−a

I. INTRODUCTION

In recent years, there have been numerous studies[1–30] concerned with the computation of the effective behavior of nonlinear dielectric (or conductor) composites (see also Refs. 31–33). In part, this has been due to theoretical interest in such material systems—after all, nonlinear effects are to be expected at sufficiently high field intensities, and the standard Maxwell-Garnett approximation[34] (MGA) (also known as the Claussius-Mossotti approximation) and effective-medium approximation[35] (EMA) apply only to linear systems. It should be emphasized that the extension to nonlinear systems is nontrivial, as the governing equations become nonlinear and the linear methods on which the standard MGA and EMA estimates are based are no longer applicable. The interest in these nonlinear heterogeneous material systems derives also, in part, due to their importance in the context of many different physical phenomena, including dielectric breakdown, fuse burn out, and nonlinear optical phenomena. Additional examples could be given in the realms of electric, magnetic and other physical and mechanical properties of matter.

The aim of this work is to propose a general method for deriving accurate estimates for nonlinear composites directly from corresponding estimates for suitably chosen linear composites. This is an approach that has been pioneered by the author and co-workers[9,10] in the so-called ''variational'' linear comparison method. In particular, one of the goals is to provide robust generalizations of the MGA and EMA estimates for nonlinear composites. As suggested recently by Barthelemy[27] and Pellegrini,[29] such generalizations must satisfy certain criteria: (i) They should be exact to second order in the contrast, and thus be in agreement with the perturbative small-contrast expansions of Blumenfeld and Bergman.[7] (ii) They should be in good agreement with known results[3,11,12] in the dilute (small concentration) limit. (iii) They should satisfy all known bounds.[2,9,24] (iv) For the particular case of the EMA estimates, a nonlinearity-independent percolation threshold should be predicted, with acceptable[28] values for the associated critical exponents. Furthermore, in two dimensions, duality theory[1,23] provides a condition on the critical exponents, as well as more restrictive conditions on the associated scaling functions. In addition to these criteria, one should also add the following: (v) The estimates should not degenerate for large values of the relevant nonlinearity parameter, and, in particular, for the important special cases of ''threshold-type'' nonlinearity. Of all the above requirements, the last one is perhaps the most strict.

To the knowledge of the author, the first general method to satisfy criterion (i) is the ''second-order'' method proposed by the author and co-workers.[19,20] As will be seen in more detail in the body of this paper, this method makes use of a second-order Taylor expansion for the energy-density functions of the constituent phases, leading to a ''linear comparison composite'' with spontaneous polarizations, which is then used to estimate the effective behavior of the nonlinear composite. While this method, when applied together with the EMA approximation, leads to nonlinearity-independent percolation thresholds, and initially appeared to give predictions consistent with all known bounds, it has been recently discovered[28] to violate the bounds provided by the ''variational'' method[9,10] sufficiently close to the percolation threshold.

More specifically, using standard notation[1,27] for power-law composite conductors (dielectrics), it has been recently found[28] that the critical exponents t and s, corresponding to metal/insulator (dielectric/insulator), and metal/superconductor (dielectric/conductor) mixtures, respectively, must satisfy the bounds

$$t \leqslant (1+m)/2 \quad \text{and} \quad s \geqslant (1+m)/2, \tag{1}$$

where the power exponent m, characterizing the nonlinearity of the material, has been assumed to be such that $m>1$. Note that m corresponds to $1/\alpha$ and $1+\kappa$ in the notations of Straley and Kenkel[1] and Barthélémy,[27] respectively, in such a way that $m=1$ corresponds to the linear case. The above

bounds also apply for the case where $0 \leqslant m < 1$, but the sense of the inequalities in Eq. (1) must be inverted. The predictions of the second-order[19,20] theory for the EMA estimates for power-law composites leads to the values $t = m$ and $s = 1$, which can be seen to violate the bounds described above for any value of m different from 1. It is interesting to remark that the critical exponents predicted by the second-order[19,20] theory are identical to those obtained by Barthelemy[27] in his ''path-integral'' approach to strongly nonlinear composites, as well as to those predicted by the theory of Bergman,[8] on which it is based. It should also be noted that the original EMA theory of Bergman,[8] in its full implementation,[13,21] was checked to satisfy criterion (i) numerically, while Barthélémy's theory was found[27] to satisfy this criterion exactly. However, unlike the second-order theory,[19,20] the EMA theories of Bergman and Barthélémy both exhibit nonlinearity-dependent percolation thresholds, and thus violate criterion (iv) above. It is interesting to remark,[27] however, that, in two dimensions, both sets of critical exponents satisfy the duality relation[1,23] $t(m) = ms(1/m)$.

It should also be remarked that there is a ''mean-field theory'' due to Wan, Lee, Hui, and Yu[14] (see also Refs. 16,17) that yields critical exponents that are consistent (in fact identical) to the above bounds. This is due to the fact[24] that the theory of Wan *et al.* gives predictions that are identical to the earlier ''variational'' theory,[9,10] when used together with the EMA approximation for the relevant linear comparison composite. However, both of these theories lead to predictions that are *only* exact to first order in the contrast and therefore violate criterion (i).

Concerning criterion (ii) for dilute systems, exact analytical estimates are unfortunately *not* available for strongly nonlinear dielectrics. The underlying one-inclusion problem being fully nonlinear, an exact analytical result is not expected, but numerical predictions are certainly feasible. Such estimations have been attempted in the mechanics literature, but mostly in three dimensions. However, dilute results are available[36] for the special case of power-law solids with aligned rigid fibers—where a well-known analogy permits the direct conversion to two-dimensional electrostatics. Ponte Castañeda and Kailasam have shown[20] (see Fig. 2 in that reference) that the predictions of the earlier ''second-order'' theory (given in a different form) are in excellent agreement with the numerical simulations in this case (for values of m between 1/10 and 1), while the corresponding predictions of the ''variational'' theory[9,10] progressively diverge from the numerical estimates with increasing nonlinearity, consistent with their bounding status. (Note that the corresponding dilute predictions of Hui and Wang,[15] being identical to the ''variational'' estimates, are also not very accurate for large nonlinearity.) As already mentioned, there are also results available for weakly nonlinear composites,[3,12] as well as an exact result for the (very special) case of strongly nonlinear inclusions embedded in a *linear* matrix.[11]

In this paper, an improved version of the ''second-order'' method[19,20] is proposed that incorporates field fluctuations in the selection of the linear comparison composite, following an analogous development in the context of the ''variational'' procedure.[9,10] This improved version, which will be presented in Sec. III, is found to be free of the limitations of the earlier version of the method, and provides a general and robust method satisfying all the criteria listed above, as will be demonstrated in Sec. IV for two-phase systems. In fact, it will be seen that the ''new'' second-order theory is some sort of interpolation between the earlier (''old'') second-order theory[19] and the ''variational'' linear comparison theory[9], preserving the relative advantages of both.

It is interesting to note that very recently Pellegrini[29] has proposed an alternative improved version of the ''second-order'' theory making use of a Gaussian approximation for the probability distributions of the fields in the phases, following similar developments in his earlier work[26] for weakly nonlinear composites. This innovative approach also leads quite naturally to the use of the field fluctuations in the determination of the relevant linear comparison composite. As this method is quite recent, detailed comparisons will be left for future work, but the method of Pellegrini appears to be quite promising, also satisfying all the criteria above, with the possible exception of criterion (v) which remains to be investigated[30] in the context of his theory.

II. EFFECTIVE BEHAVIOR

The nonlinear composite dielectric occupies a region in space Ω, and its constitutive behavior is characterized by an energy-density function w, depending on the position vector $\mathbf{x}$ and the electric field $\mathbf{E}$, such that the electric displacement field $\mathbf{D}$ is given by

$$\mathbf{D}(\mathbf{x}) = \frac{\partial w}{\partial \mathbf{E}}(\mathbf{x}, \mathbf{E}). \tag{2}$$

It is assumed that the composite dielectric is made up of N homogeneous phases, so that

$$w(\mathbf{x}, \mathbf{E}) = \sum_{r=1}^{N} \theta^{(r)}(\mathbf{x}) w^{(r)}(\mathbf{E}), \tag{3}$$

where the functions $\theta^{(r)}$ $(r = 1, \ldots, N)$, characterizing the distribution of the phases in Ω, are such that $\theta^{(r)} = 1$ if $\mathbf{x}$ is in phase r and 0 otherwise. The phases are assumed here to be isotropic so that the energy functions $w^{(r)}$ depend only on the magnitude of the electric field $E = |\mathbf{E}|$. In addition, the functions $w^{(r)}$ are taken to be convex in the electric field E and such that $w^{(r)}(E) \geqslant 0$ and $w^{(r)}(0) = 0$.

A commonly used form for the phase energy functions is the power-law (usually referred[31] to as ''strongly nonlinear'') form

$$w(E) = \frac{1}{m+1} \chi E^{m+1}, \tag{4}$$

such that $D = \chi E^m$, where χ is the nonlinear susceptibility, and the nonlinearity exponent m is taken to be between 0 and ∞, with $m = 1$ corresponding to linear behavior. As depicted in Fig. 1, the limits as m tends to 0 and ∞ correspond to ''thresholds,'' D_0 and E_0, in the electric displacement and

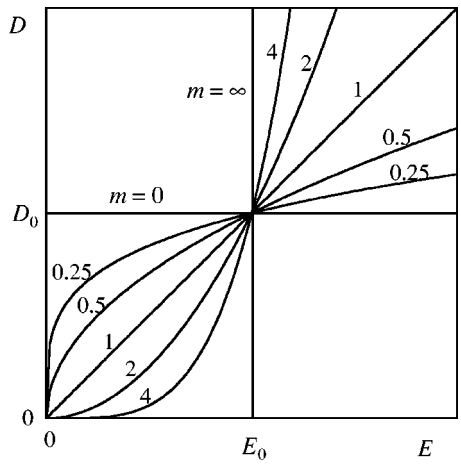

FIG. 1. Power-law dielectric with nonlinearity exponent m ranging from 0 to ∞. Here, $m=1$ corresponds to linear behavior, 0 to a threshold in the electric displacement field D_0, and ∞ to a threshold in the electric field E_0.

electric fields, respectively. In this connection, note that χ tends to D_0 in the limit as m tends to 0. On the other hand, $\chi^{-1/m}$ tends to E_0 in the limit as m tends to ∞, so that $\chi^{-1/m}$ is the physically meaningful variable in this limit. For the conductivity analog, the limits as m tends to 0 and ∞ physically correspond[1] to the behaviors of a saturating conductor and a varistor, respectively.

It is known[31,32] that the *effective* constitutive behavior of the composite dielectric may be expressed in terms of the averages of the fields $\overline{\mathbf{D}}=\langle\mathbf{D}\rangle$ and $\overline{\mathbf{E}}=\langle\mathbf{E}\rangle$, where angular brackets are used to denote volume averages over Ω, as

$$\overline{\mathbf{D}}=\frac{\partial\tilde{W}}{\partial\overline{\mathbf{E}}}(\overline{\mathbf{E}}). \tag{5}$$

In this relation, the effective energy-density function of the composite $\tilde{W}$ is most naturally described in terms of the minimum energy principle

$$\tilde{W}(\overline{\mathbf{E}})=\min_{\mathbf{E}\in K}\langle w(\mathbf{x},\mathbf{E})\rangle=\min_{\mathbf{E}\in K}\left\{\sum_{r=1}^{N}c^{(r)}\langle w^{(r)}(\mathbf{E})\rangle^{(r)}\right\}, \tag{6}$$

where K is the set of trial electric fields, defined by

$$K=\{\mathbf{E}|\mathbf{E}=-\nabla\varphi(\mathbf{x})\ \text{ in }\ \Omega,\ \text{ and }\ \varphi=-\overline{\mathbf{E}}\cdot\mathbf{x}\ \text{ on }\ \partial\Omega\}, \tag{7}$$

$c^{(r)}=\langle\theta^{(r)}\rangle$ is the volume fraction of phase r, and the symbol $\langle\cdot\rangle^{(r)}$ is used to denote a volume average over phase r. An equivalent formulation in terms of the complementary energy-density function u, such that $\mathbf{E}=\partial u/\partial\mathbf{D}$ is available.[31,32] For convenience, the details are summarized in the Appendix.

The main difficulty associated with the computation of the effective energy function $\tilde{W}$ of the composite (6) lies in the fact that the relevant fields are impossible to determine exactly in general. However, approximate methods have been developed to address this problem for composites with *linear* constitutive behavior. In the following section, a variational method allowing the use of known estimates for linear composites to obtain corresponding estimates for nonlinear composites is developed and compared with earlier homogenization methods.

III. THE VARIATIONAL ESTIMATES

Following earlier work,[19,20] a ''linear comparison composite'' is introduced with energy-density function w_T given by

$$w_T(\mathbf{x},\mathbf{E})=\sum_{r=1}^{N}\theta^{(r)}(\mathbf{x})w_T^{(r)}(\mathbf{E}), \tag{8}$$

where the phase energy function $w_T^{(r)}$ is given by the second-order Taylor approximation to the nonlinear phase energy function $w^{(r)}$:

$$w_T^{(r)}(\mathbf{E})=w^{(r)}(\mathbf{E}^{(r)})+\frac{\partial w^{(r)}}{\partial\mathbf{E}}(\mathbf{E}^{(r)})\cdot(\mathbf{E}-\mathbf{E}^{(r)})$$
$$+\frac{1}{2}(\mathbf{E}-\mathbf{E}^{(r)})\cdot\boldsymbol{\varepsilon}_0^{(r)}(\mathbf{E}-\mathbf{E}^{(r)}). \tag{9}$$

In this relation, $\mathbf{E}^{(r)}$ is a uniform reference electric field and $\boldsymbol{\varepsilon}_0^{(r)}$ is a symmetric, positive definite tensor of dielectric constants, both of which are taken to be otherwise arbitrary at this stage.

It is useful to note here that the phase energy function (9) corresponds to a fictitious linear dielectric with ''spontaneous'' polarizations $\mathbf{P}^{(r)}=\partial w^{(r)}/\partial\mathbf{E}^{(r)}-\boldsymbol{\varepsilon}_0^{(r)}\mathbf{E}^{(r)}$ in the phases, such that its constitutive behavior is given by

$$\mathbf{D}=\mathbf{P}^{(r)}+\boldsymbol{\varepsilon}_0^{(r)}\mathbf{E}. \tag{10}$$

Ponte Castañeda and co-workers[19,20] made use of expressions (9) to estimate the local energy-density functions $w^{(r)}$ directly in expression (6) for the effective energy function $\tilde{W}$. Here, instead, ''error'' functions $V^{(r)}$, depending on the reference fields $\mathbf{E}^{(r)}$ and dielectric tensors $\boldsymbol{\varepsilon}_0^{(r)}$, are introduced such that the phase energy functions $w^{(r)}$ may be approximated as

$$w^{(r)}(\mathbf{E})=w_T^{(r)}(\mathbf{E})+V^{(r)}(\mathbf{E}^{(r)},\boldsymbol{\varepsilon}_0^{(r)}), \tag{11}$$

for any value of the electric field $\mathbf{E}$.

There are different ways to define the error functions $V^{(r)}$. Ponte Castañeda[9] defined the functions

$$V^{(r)}(\mathbf{E}^{(r)},\boldsymbol{\varepsilon}_0^{(r)})=\min_{\hat{\mathbf{E}}^{(r)}}[w^{(r)}(\hat{\mathbf{E}}^{(r)})-w_T^{(r)}(\hat{\mathbf{E}}^{(r)})], \tag{12}$$

where m has been assumed to be greater than 1 in expression (4) for the energy functions $w^{(r)}$. Then, it is obvious from Fig. 2, which shows a one-dimensional sketch of the function $w^{(r)}-w_T^{(r)}$ (that we seek to minimize) for the special case $m=4$, that $V^{(r)}$ is negative and also that

$$w^{(r)}(\mathbf{E})\geqslant w_T^{(r)}(\mathbf{E})+V^{(r)}(\mathbf{E}^{(r)},\boldsymbol{\varepsilon}_0^{(r)}). \tag{13}$$

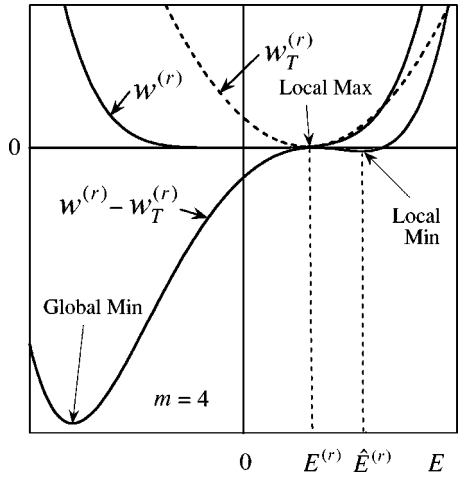

FIG. 2. One-dimensional sketch of the function $w^{(r)}-w_T^{(r)}$ and its stationary points for a power-law material with $m=4$.

A generalization of the definition (12) is to take

$$V^{(r)}(\mathbf{E}^{(r)},\boldsymbol{\varepsilon}_0^{(r)}) = \underset{\hat{\mathbf{E}}^{(r)}}{\text{stat}}[\,w^{(r)}(\hat{\mathbf{E}}^{(r)}) - w_T^{(r)}(\hat{\mathbf{E}}^{(r)})\,], \qquad (14)$$

where ''stat'' corresponds to the *optimization* operation consisting in taking derivatives of the terms inside the square brackets, setting the result equal to zero and solving for the variables $\hat{\mathbf{E}}^{(r)}$. Referring again to Fig. 2, it is observed that, in this case with $1 \leqslant m < \infty$, the function $w^{(r)}-w_T^{(r)}$ has other stationary points in addition to the global minimum discussed in the context of definition (12). Thus, it can be seen that the function additionally admits a local minimum, as well as a local maximum, with $\hat{\mathbf{E}}^{(r)}=\mathbf{E}^{(r)}$. In the alternative case, when $0<m\leqslant 1$, the function $w^{(r)}-w_T^{(r)}$ (not shown in the figure) also has three stationary points, but with the leftmost one now being a global maximum, the rightmost, a local maximum, and the middle one, a local minimum at $\hat{\mathbf{E}}^{(r)}=\mathbf{E}^{(r)}$. It is important to emphasize here that, because of the multidimensional character of the problem, there are in fact several other possible stationary points, including saddle points. It is not essential at this stage to catalog the different possibilities; it is only important to realize that there are possibilities *other than* the trivial choice $\hat{\mathbf{E}}^{(r)}=\mathbf{E}^{(r)}$ and the extremal points (global maxima and minima).

It is also useful here to spell out the stationarity conditions for the variables $\hat{\mathbf{E}}^{(r)}$ in the definition (14) of the functions $V^{(r)}$, which may be written in the form

$$\frac{\partial w^{(r)}}{\partial \mathbf{E}}(\hat{\mathbf{E}}^{(r)}) - \frac{\partial w^{(r)}}{\partial \mathbf{E}}(\mathbf{E}^{(r)}) = \boldsymbol{\varepsilon}_0^{(r)}(\hat{\mathbf{E}}^{(r)} - \mathbf{E}^{(r)}). \qquad (15)$$

Note that in general $\hat{\mathbf{E}}^{(r)}$ need not be aligned with $\mathbf{E}^{(r)}$. The various possible conditions are depicted schematically in Fig. 3 for a one-dimensional energy function with $m=4$. They can be seen to correspond to various types of *linear* approximations to the constitutive relation for the nonlinear dielectric relating D to E. Thus, it can be seen that the case where $\hat{\mathbf{E}}^{(r)} \neq \mathbf{E}^{(r)}$ and $\mathbf{E}^{(r)} \neq \mathbf{0}$ corresponds to a ''generalized secant'' approximation, which is different from the more standard ''secant'' and ''tangent'' approximations that have been used in the context of earlier theories.[9,19]

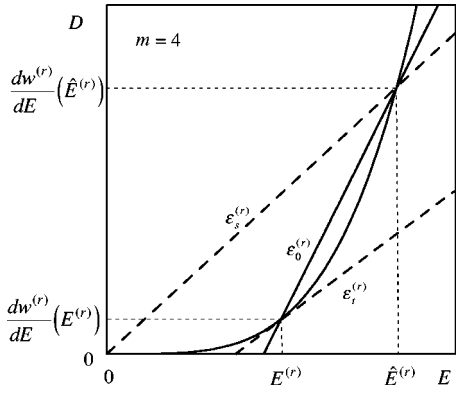

FIG. 3. The ''generalized secant'' approximation (15) for the linear comparison composite, with dielectric constant $\boldsymbol{\varepsilon}_0^{(r)}$, versus the ''secant'' and ''tangent'' approximations, with dielectric constants $\boldsymbol{\varepsilon}_s^{(r)}$ and $\boldsymbol{\varepsilon}_t^{(r)}$, respectively.

Now, use of the various estimates (11) for the phase energies $w^{(r)}$ in expression (6) leads to the following approximations for the effective energy function $\tilde{W}$:

$$\tilde{W}(\overline{\mathbf{E}}) = \tilde{W}_T(\overline{\mathbf{E}};\mathbf{E}^{(s)},\boldsymbol{\varepsilon}_0^{(s)}) + \sum_{r=1}^{N} c^{(r)} V^{(r)}(\mathbf{E}^{(r)},\boldsymbol{\varepsilon}_0^{(r)}), \quad (16)$$

where $\tilde{W}_T$ is the effective energy function associated with the linear composite with local energy-density function given by Eqs. (8) and (9), such that

$$\tilde{W}_T(\overline{\mathbf{E}};\mathbf{E}^{(s)},\boldsymbol{\varepsilon}_0^{(s)}) = \min_{\mathbf{E}\in K} \langle w_T(\mathbf{x},\mathbf{E}) \rangle. \qquad (17)$$

The approximations (16) are valid for any choice of the reference variables $\mathbf{E}^{(s)}$ and $\boldsymbol{\varepsilon}_0^{(s)}$ $(s=1,\ldots,N)$, which suggests *optimizing* with respect to them by evaluating the appropriate stationary conditions with respect to these variables. Depending on the choice of the error functions $V^{(r)}$, it will be seen that there are several possible different ways to select these reference variables. However, the important point is that the expression (16) allows the computation of the effective energy function $\tilde{W}$ for the nonlinear composite in terms of the effective energy function $\tilde{W}_T$ of a linear comparison composite with dielectric tensors $\boldsymbol{\varepsilon}_0^{(s)}$ and spontaneous polarizations $\mathbf{P}^{(s)}$ distributed with the same statistics as the original nonlinear composite. In the next subsections, it will be shown how the general variational statement (16) can be used to recover earlier estimates, as well as to generate improved estimates for $\tilde{W}$.

A. The variational bound

If the stationary point leading to the extremum value of the function $w^{(r)}-w_T^{(r)}$ is used in definition (14) for the function $V^{(r)}$, the estimate (16) can be shown[9,10] to be a bound. The best bound is obtained by optimizing with respect to the variables $\mathbf{E}^{(s)}$ and $\boldsymbol{\varepsilon}_0^{(s)}$. However, it has been shown[9,37] that

the optimal choice of the tensors $\mathbf{E}^{(s)}$ is identically zero for typical material behaviors, including of the power-law type. Thus, for the case when $1<m\leqslant\infty$, a *lower* bound is given by[9,10]

$$\tilde{W}(\overline{\mathbf{E}})\geqslant\max_{\boldsymbol{\varepsilon}_0^{(s)}}\left\{\tilde{W}_0(\overline{\mathbf{E}};\boldsymbol{\varepsilon}_0^{(s)})+\sum_{r=1}^{N}c^{(r)}V^{(r)}(\mathbf{0},\boldsymbol{\varepsilon}_0^{(r)})\right\},\quad(18)$$

where $\tilde{W}_0$ is the effective energy associated with a linear comparison composite dielectric with phase energy functions given by

$$w_0^{(r)}(\mathbf{E})=\frac{1}{2}\mathbf{E}\cdot\boldsymbol{\varepsilon}_0^{(r)}\mathbf{E},\quad(19)$$

and the functions $V^{(r)}$ are given by expressions (12). On the other hand, for the case when $0\leqslant m<1$, an *upper* bound is generated, which is similar in form to the right-hand side of Eq. (18), except that the *max* must be replaced by the corresponding *min*.

It is also noted here that the choice $\mathbf{E}^{(r)}=\mathbf{0}$ in expression (15) leads to the classical secant condition: (see Fig. 3), defining the ''secant'' dielectric tensors $\boldsymbol{\varepsilon}_s^{(r)}$ by

$$\frac{\partial w^{(r)}}{\partial\mathbf{E}}(\hat{\mathbf{E}}^{(r)})=\boldsymbol{\varepsilon}_s^{(r)}\hat{\mathbf{E}}^{(r)}.\quad(20)$$

It follows from the assumed isotropy of the constituent phases that these secant tensors are isotropic.

On the other hand, optimality with respect to the variables $\boldsymbol{\varepsilon}_0^{(s)}$ in expression (18) leads[38,24] to the following conditions:

$$\hat{E}^{(r)}=\sqrt{\langle E^2\rangle^{(r)}}\quad(21)$$

for the magnitude of the variables $\hat{\mathbf{E}}^{(r)}$. Note that these expressions identify the variables $\hat{E}^{(r)}$ with the isotropic trace of the second moments $\langle\mathbf{E}\otimes\mathbf{E}\rangle^{(r)}$ of the electric field in the phases of the linear comparison composite, which in turn can be estimated from the effective dielectric tensor of the linear comparison composite using a well known result.[39] It then follows[38,24] that the effective energy function for the nonlinear composite may be expressed as

$$\tilde{W}(\overline{\mathbf{E}})=\sum_{r=1}^{N}c^{(r)}w^{(r)}(\hat{E}^{(r)}).\quad(22)$$

Note that the final answer does not depend on the direction of $\hat{E}^{(r)}$, which is indeterminate from the secant condition (20).

B. The second-order estimate

As already mentioned, another possible solution to relations (15) is the choice $\hat{\mathbf{E}}^{(r)}=\mathbf{E}^{(r)}$, which makes the functions $V^{(r)}$ vanish identically. Then, holding the variables $\boldsymbol{\varepsilon}_0^{(s)}$ fixed in expression (16), and optimizing with respect to the variables $\mathbf{E}^{(s)}$, leads to the estimate (which is not a bound):

$$\tilde{W}(\overline{\mathbf{E}})=\operatorname*{stat}_{\mathbf{E}^{(s)}}\{\tilde{W}_T(\overline{\mathbf{E}};\mathbf{E}^{(s)},\boldsymbol{\varepsilon}_0^{(s)})\},\quad(23)$$

where $\tilde{W}_T$ is still given by relation (17). The stationarity condition with respect to the variables $\mathbf{E}^{(s)}$ in this expression then leads to the conditions[20,25]

$$[\boldsymbol{\varepsilon}_t^{(s)}(\mathbf{E}^{(s)})-\boldsymbol{\varepsilon}_0^{(s)}](\langle\mathbf{E}\rangle^{(s)}-\mathbf{E}^{(s)})=0,\quad(24)$$

where $\boldsymbol{\varepsilon}_t^{(r)}\doteq\partial^2 w^{(r)}/\partial\mathbf{E}\partial\mathbf{E}$ is the ''tangent'' approximation to the nonlinear constitutive relation for phase r. This condition can be satisfied by setting

$$\mathbf{E}^{(s)}=\overline{\mathbf{E}}^{(s)},\quad(25)$$

where the symbol $\overline{\mathbf{E}}^{(s)}$ has been used to denote the phase averages of the electric field $\langle\mathbf{E}\rangle^{(s)}$. The estimate (23) can then be shown[32] to reduce to

$$\tilde{W}(\overline{\mathbf{E}})=\sum_{r=1}^{N}c^{(r)}\left[w^{(r)}(\overline{\mathbf{E}}^{(r)})+\frac{1}{2}\frac{\partial w^{(r)}}{\partial\mathbf{E}}(\overline{\mathbf{E}}^{(r)})\cdot(\overline{\mathbf{E}}-\overline{\mathbf{E}}^{(r)})\right],\quad(26)$$

which is precisely the original version of the ''second-order'' estimate.[19,20] However, the above choice for the variables $\hat{\mathbf{E}}^{(r)}$ has the disadvantage[25] that the stationarity condition with respect to the variables $\boldsymbol{\varepsilon}_0^{(s)}$:

$$\langle(\mathbf{E}-\mathbf{E}^{(r)})\otimes(\mathbf{E}-\mathbf{E}^{(r)})\rangle^{(r)}=\mathbf{0},\quad(27)$$

cannot be satisfied in general (i.e., unless the electric field is constant in each phase). Because of this, the alternative, physically motivated prescription

$$\boldsymbol{\varepsilon}_0^{(r)}=\boldsymbol{\varepsilon}_t^{(r)}(\overline{\mathbf{E}}^{(r)})\quad(28)$$

was made to close the system of equations defining the effective behavior of the nonlinear composite in terms of that of the linear comparison composite. Note that this ''tangent'' condition (refer to Fig. 3) is fully consistent with expression (15) in the sense that it corresponds to taking the limit as $\hat{\mathbf{E}}^{(r)}\rightarrow\mathbf{E}^{(r)}$ in that expression.

C. Improved second-order estimates

As already mentioned in the context of Fig. 2, in addition to the trivial stationary point (i.e., $\hat{\mathbf{E}}^{(r)}=\mathbf{E}^{(r)}$), and the stationary point leading to the minimum (or maximum), there are other possible stationary points in the definition (14) of the functions $V^{(r)}$, which will be exploited in this subsection. Thus, use will be made of the ''generalized secant'' condition (15) depicted schematically in Fig. 3. Such a generalized condition can be seen to be somewhere intermediate between the ''secant'' condition, defined by Eq. (20) and used in the context of the ''variational'' bound (18), and the ''tangent'' condition defined by Eq. (28) and used in the ''second-order'' estimates (26).

Then, generalizing the procedure followed in the context of expression (18) for the bound, optimization with respect to the variables $\boldsymbol{\varepsilon}_0^{(s)}$ in the general estimate (16) for $\tilde{W}$ leads to

$$\widetilde{W}(\overline{\mathbf{E}}) = \operatorname*{stat}_{\boldsymbol{\varepsilon}_0^{(s)}} \left\{ \widetilde{W}_T(\overline{\mathbf{E}}; \mathbf{E}^{(s)}, \boldsymbol{\varepsilon}_0^{(s)}) + \sum_{r=1}^{N} c^{(r)} V^{(r)}(\mathbf{E}^{(r)}, \boldsymbol{\varepsilon}_0^{(r)}) \right\}, \tag{29}$$

where the variables $\mathbf{E}^{(s)}$ still remain to be specified. In principle, the optimization in this expression should be carried out over all possible anisotropic tensors $\boldsymbol{\varepsilon}_0^{(s)}$ $(s=1,\ldots,N)$. However, noting that condition (15) suggests (refer to Fig. 3) that the tensors $\boldsymbol{\varepsilon}_0^{(r)}$ are somewhat intermediate between the secant and tangent dielectric tensor of the nonlinear phases, and recalling that the phases are isotropic, the proposal is made here to restrict attention to tensors $\boldsymbol{\varepsilon}_0^{(r)}$ whose principal axes are aligned with the reference field $\mathbf{E}^{(r)}$ in phase r, in such a way that

$$\boldsymbol{\varepsilon}_0^{(r)} = \varepsilon_{\parallel}^{(r)} \mathbf{n}^{(r)} \otimes \mathbf{n}^{(r)} + \varepsilon_{\perp}^{(r)} (\mathbf{I} - \mathbf{n}^{(r)} \otimes \mathbf{n}^{(r)}), \tag{30}$$

where $\mathbf{n}^{(r)} = (1/E^{(r)})\mathbf{E}^{(r)}$ is a unit vector aligned with the reference electric field in phase r. This vector defines two directions: a ''parallel'' one, which is aligned with $\mathbf{n}^{(r)}$, and a ''perpendicular'' one, orthogonal to it.

With the choice (30) for the dielectric tensors $\boldsymbol{\varepsilon}_0^{(r)}$ in expression (29) for $\widetilde{W}$, optimization with respect to the variables $\varepsilon_{\parallel}^{(r)}$ and $\varepsilon_{\perp}^{(r)}$ leads to the conditions

$$(\hat{E}_{\parallel}^{(r)} - E_{\parallel}^{(r)})^2 = \langle (E_{\parallel} - E_{\parallel}^{(r)})^2 \rangle^{(r)}$$

and (31)

$$(\hat{E}_{\perp}^{(r)} - E_{\perp}^{(r)})^2 = \langle (E_{\perp} - E_{\perp}^{(r)})^2 \rangle^{(r)},$$

which can be seen to be a set of conditions on the second moments of the electric field in the phases relative to the reference electric fields $\mathbf{E}^{(r)}$. In these relations, use has been made of the notations $\hat{E}_{\parallel}$, $E_{\parallel}^{(r)}$, $E_{\parallel}$ and $\hat{E}_{\perp}$, $E_{\perp}^{(r)}$, $E_{\perp}$ for the ''parallel'' and ''perpendicular'' components of the variables $\hat{\mathbf{E}}^{(r)}$, $\mathbf{E}^{(r)}$, and $\mathbf{E}$, respectively, relative to the unit vector $n^{(r)}$.

Motivated by the choice made for the variables $\mathbf{E}^{(r)}$ in the context of the earlier second-order estimates (23), the same choice is proposed here for the new second-order estimates (29), that is, the condition (25), or $\mathbf{E}^{(r)} = \overline{\mathbf{E}}^{(r)}$, so that $E_{\parallel}^{(r)} = \overline{E}^{(r)}$ and $E_{\perp}^{(r)} = 0$. Then, defining the covariance tensor of the electric field fluctuations in phase r by[39,40]

$$\mathbf{C}_{\mathbf{E}}^{(r)} \doteq \langle (\mathbf{E} - \overline{\mathbf{E}}^{(r)}) \otimes (\mathbf{E} - \overline{\mathbf{E}}^{(r)}) \rangle^{(r)}, \tag{32}$$

and combining conditions (25) for the $\mathbf{E}^{(r)}$ with the conditions (31) for the $\hat{\mathbf{E}}^{(r)}$, leads to the result

$$\hat{E}_{\parallel}^{(r)} = \overline{E}^{(r)} + \sqrt{C_{\parallel}^{(r)}}, \quad \hat{E}_{\perp}^{(r)} = \sqrt{C_{\perp}^{(r)}}, \tag{33}$$

where $C_{\parallel}^{(r)}$ and $C_{\perp}^{(r)}$ are the parallel and perpendicular components of $\mathbf{C}_{\mathbf{E}}^{(r)}$. Note that the roots leading to positive values of $\hat{E}_{\parallel}^{(r)}$ and $\hat{E}_{\perp}^{(r)}$ have been selected in these relations, for consistency with the special case of homogeneous behavior, which should be reproduced exactly by the final expression below for $\widetilde{W}$. Note also that the vector $\hat{\mathbf{E}}^{(r)}$ need *not* be aligned with $\overline{\mathbf{E}}^{(r)}$.

In addition, the secant-type condition (15) then specializes to

$$\frac{\partial w^{(r)}}{\partial \mathbf{E}}(\hat{\mathbf{E}}^{(r)}) - \frac{\partial w^{(r)}}{\partial \mathbf{E}}(\overline{\mathbf{E}}^{(r)}) = \boldsymbol{\varepsilon}_0^{(r)}(\hat{\mathbf{E}}^{(r)} - \overline{\mathbf{E}}^{(r)}), \tag{34}$$

where $\hat{\mathbf{E}}^{(r)}$ must be chosen to be a suitable saddle point of the function $w^{(r)} - w_T^{(r)}$, for consistency with conditions (33).

Finally, using the result (31), together with the expression (14) for the functions $V^{(r)}$, the general estimate (16) for $\widetilde{W}$ can then be shown to reduce to

$$\widetilde{W}(\overline{\mathbf{E}}) = \sum_{r=1}^{N} c^{(r)} \left[w^{(r)}(\hat{\mathbf{E}}^{(r)}) - \frac{\partial w^{(r)}}{\partial \mathbf{E}}(\overline{\mathbf{E}}^{(r)}) \cdot (\hat{\mathbf{E}}^{(r)} - \overline{\mathbf{E}}^{(r)}) \right]. \tag{35}$$

In summary, the estimate (35) for the effective energy function of the nonlinear composite has been generated. Similar to the earlier second-order estimate,[19] it depends on the phase averages $\overline{\mathbf{E}}^{(r)}$ of the electric field in the linear comparison composite defined by relations (17), (8), and (9), subject to the self-consistent prescription (25) on the reference electric fields $\mathbf{E}^{(r)}$. However, the prescription (34) for the comparison dielectric tensors $\boldsymbol{\varepsilon}_0^{(r)}$ is different from the *ad hoc* choice (28) made earlier, being somewhat intermediate between the ''secant'' condition used in the context of the ''variational'' bounds and the ''tangent'' condition used in the context of the earlier ''second-order'' estimates. In addition, the estimate (35) depends directly on the variables $\hat{\mathbf{E}}^{(r)}$, which are related to the second moments of the fluctuations, or covariance tensors of the electric field in the phases of the linear comparison composite, as specified by the prescriptions (33). Thus, the new estimates—as with the variational bounds—also incorporate a dependence on the second moments of the electric field in the phases. Furthermore, as with the earlier ''second order'' estimates, they are exact to second order in the heterogeneity contrast. This can be easily verified by noticing that the variables $\overline{\mathbf{E}}^{(r)}$ and $\hat{\mathbf{E}}^{(r)}$ reduce to the average electric field $\overline{\mathbf{E}}$ to zeroth order in the contrast, in such a way that the new estimate becomes indistinguishable to second-order in the contrast from the second-order estimate (23), which is already known to be exact to second-order in the heterogeneity contrast. [Note that the functions $V^{(r)}$ in expression (16) are of higher order in the contrast, and therefore do not enter the calculation.] Finally, it is noted that completely analogous expressions may be developed starting from the dual formulation for the complementary energy function of the composite, as shown in the Appendix. However, the resulting approximation (A7) for the complementary energy function $\widetilde{U}$ is not exactly dual to the approximation (35) for $\widetilde{W}$, as will be seen in more detail in the following section.

The improved second-order estimates (35) require the computation of the phase averages $\overline{\mathbf{E}}^{(r)}$ and the covariance tensors $\mathbf{C}_{\mathbf{E}}^{(r)}$ of the electric field in the linear comparison composite with spontaneous polarizations defined by the ex-

pression (17) for $\tilde{W}_T$. In this connection, it is useful to remark that, given an estimate for $\tilde{W}_T$, $\overline{\mathbf{E}}^{(r)}$, and $\mathbf{C}_{\mathbf{E}}^{(r)}$ may be easily computed[39,40,24] from the expressions

$$\overline{\mathbf{E}}^{(r)}=\frac{1}{c^{(r)}}\frac{\partial(\tilde{W}_T-\overline{f})}{\partial\mathbf{P}^{(r)}} \quad \text{and} \quad \mathbf{C}_{\mathbf{E}}^{(r)}=\frac{2}{c^{(r)}}\frac{\partial\tilde{W}_T}{\partial\boldsymbol{\varepsilon}_0^{(r)}}, \tag{36}$$

where $f^{(r)}=w^{(r)}(\mathbf{E}^{(r)})-\mathbf{P}^{(r)}\cdot\mathbf{E}^{(r)}-\frac{1}{2}\mathbf{E}^{(r)}\cdot\boldsymbol{\varepsilon}_0^{(r)}\mathbf{E}^{(r)}$ (recall that $\mathbf{P}^{(r)}=\partial w^{(r)}/\partial\mathbf{E}^{(r)}-\boldsymbol{\varepsilon}_0^{(r)}\mathbf{E}^{(r)}$). In the first of these expressions, the quantity $(\tilde{W}_T-\overline{f})$ is expressed as a function of the $\mathbf{P}^{(r)}$ and $\boldsymbol{\varepsilon}_0^{(r)}$, and the derivative is taken with respect to $\mathbf{P}^{(r)}$, with $\boldsymbol{\varepsilon}_0^{(r)}$ being held fixed. In the second, $\tilde{W}_T$ is expressed in terms of the reference electric fields $\mathbf{E}^{(r)}$ and the dielectric tensors $\boldsymbol{\varepsilon}_0^{(r)}$, and the derivative is taken with respect to $\boldsymbol{\varepsilon}_0^{(r)}$, with the $\mathbf{E}^{(r)}$ held fixed.

IV. APPLICATION TO TWO-PHASE SYSTEMS

Effective medium estimates, as well as other types of estimates are available for $\tilde{W}_T$, as defined by Eq. (17), for *N*-phase composites. However, for the special case of two-phase composites, great simplification[41,20] is possible. In fact, in this case, the effective energy function of the linear comparison composite (17) with spontaneous polarizations is determined solely in terms of the effective dielectric tensor $\tilde{\boldsymbol{\varepsilon}}_0$ of a linear two-phase composite with phase dielectric tensors $\boldsymbol{\varepsilon}_0^{(1)}$ and $\boldsymbol{\varepsilon}_0^{(2)}$, with the same microstructure as the original composite and zero polarizations. Thus, the result for $\tilde{W}_T$ may be written in the form[20]

$$\tilde{W}_T(\overline{\mathbf{E}})=\overline{f}+\overline{\mathbf{P}}\cdot\overline{\mathbf{E}}+\frac{1}{2}\overline{\mathbf{E}}\cdot\overline{\boldsymbol{\varepsilon}_0\mathbf{E}}+\frac{1}{2}[\overline{\mathbf{E}}+(\Delta\boldsymbol{\varepsilon}_0)^{-1}(\Delta\mathbf{P})]\cdot(\tilde{\boldsymbol{\varepsilon}}_0-\overline{\boldsymbol{\varepsilon}_0})[\overline{\mathbf{E}}+(\Delta\boldsymbol{\varepsilon}_0)^{-1}(\Delta\mathbf{P})], \tag{37}$$

where $\Delta\boldsymbol{\varepsilon}_0=\boldsymbol{\varepsilon}_0^{(1)}-\boldsymbol{\varepsilon}_0^{(2)}$ and $\Delta\mathbf{P}=\mathbf{P}^{(1)}-\mathbf{P}^{(2)}$. From expression (37) for $\tilde{W}_T$, the phase averages $\overline{\mathbf{E}}^{(r)}$ and the corresponding phase covariance tensors $\mathbf{C}_{\mathbf{E}}^{(r)}$, which are needed in the above expressions to estimate the behavior of the nonlinear composites, may be computed using relations (36).

In particular, MGA and EMA estimates for $\tilde{W}_T$ may be obtained by making use of the corresponding estimates for $\tilde{\boldsymbol{\varepsilon}}_0$. A sufficiently general form[42] for the MGA and EMA estimates for $\tilde{\boldsymbol{\varepsilon}}_0$ is given by the expression

$$\tilde{\boldsymbol{\varepsilon}}_0=\sum_{r=1}^{2}c^{(r)}\boldsymbol{\varepsilon}_0^{(r)}[\mathbf{I}+\mathbf{T}^{(0)}(\boldsymbol{\varepsilon}_0^{(r)}-\boldsymbol{\varepsilon}^{(0)})]^{-1}\times\left\{\sum_{s=1}^{2}c^{(s)}[\mathbf{I}+\mathbf{T}^{(0)}(\boldsymbol{\varepsilon}_0^{(s)}-\boldsymbol{\varepsilon}^{(0)})]^{-1}\right\}^{-1}, \tag{38}$$

where $\boldsymbol{\varepsilon}^{(0)}$ denotes the dielectric tensor of a uniform reference material and $\mathbf{T}^{(0)}$ is an associated tensor depending on the microstructure of the composite. More explicitly, $\mathbf{T}^{(0)}$ has components

$$T_{ij}^{(0)}=\frac{1}{4\pi\det\mathbf{Z}}\int_{|\boldsymbol{\xi}|=1}\frac{\xi_i\xi_j}{\xi_k\varepsilon_{kl}^{(0)}\xi_l}|\mathbf{Z}^{-1}\boldsymbol{\xi}|^{-3}dS(\boldsymbol{\xi}), \tag{39}$$

where the second-order tensor $\mathbf{Z}$ serves to characterize the "shape" of the assumed "ellipsoidal" two-point correlation functions, such that the special case $\mathbf{Z}=\mathbf{I}$ corresponds to statistical isotropy.

For later reference, explicit expressions are given next for the tensor $\mathbf{T}^{(0)}$ for the case when $\boldsymbol{\varepsilon}^{(0)}$ is assumed to have the symmetry $\boldsymbol{\varepsilon}^{(0)}=\varepsilon_{\parallel}^{(0)}\mathbf{n}\otimes\mathbf{n}+\varepsilon_{\perp}^{(0)}(\mathbf{I}-\mathbf{n}\otimes\mathbf{n})$, where $\mathbf{n}$ is a unit vector. Then, for isotropic microstructures, the tensor $\mathbf{T}^{(0)}$ exhibits the same symmetry as the $\boldsymbol{\varepsilon}^{(0)}$ tensor, with "parallel" and "perpendicular" components given by

$$T_{\parallel}^{(0)}=\frac{1}{(k+\sqrt{k})\varepsilon_{\perp}^{(0)}}, \quad T_{\perp}^{(0)}=\frac{1}{(1+\sqrt{k})\varepsilon_{\perp}^{(0)}}, \tag{40}$$

and

$$T_{\parallel}^{(0)}=\frac{1}{(k-1)\varepsilon_{\perp}^{(0)}}\left[1-\frac{1}{\sqrt{k-1}}\arcsin\sqrt{\frac{k-1}{k}}\right],$$
$$T_{\perp}^{(0)}=\frac{1}{2(1-k)\varepsilon_{\perp}^{(0)}}\left[1-\frac{k}{\sqrt{k-1}}\arcsin\sqrt{\frac{k-1}{k}}\right], \tag{41}$$

in 2 and 3 dimensions, respectively, where $k=\varepsilon_{\parallel}^{(0)}/\varepsilon_{\perp}^{(0)}$ is the anisotropy factor associated with the tensor $\boldsymbol{\varepsilon}^{(0)}$.

Thus, MGA estimates are obtained formally by setting $\boldsymbol{\varepsilon}^{(0)}$ equal to $\boldsymbol{\varepsilon}_0^{(1)}$ (or $\boldsymbol{\varepsilon}_0^{(2)}$). This type of estimate is known to be appropriate for random systems with "particulate" microstructures, where phase 1 (2) corresponds to the "matrix" phase and 2 (1) to the "inclusion" phase. These estimates are exact to first order in the volume fraction of the inclusions, remaining fairly accurate up to moderate concentrations of inclusions (but far from percolation). In addition, the MGA estimate is known to be a lower (upper) bound[43] for $\tilde{\boldsymbol{\varepsilon}}_0$ when $\boldsymbol{\varepsilon}_0^{(1)}<\boldsymbol{\varepsilon}_0^{(2)}$ ($\boldsymbol{\varepsilon}_0^{(1)}>\boldsymbol{\varepsilon}_0^{(2)}$), in the sense of quadratic forms. The EMA estimate is correspondingly generated by setting $\boldsymbol{\varepsilon}^{(0)}$ equal to $\tilde{\boldsymbol{\varepsilon}}_0$, which gives an implicit relation for $\tilde{\boldsymbol{\varepsilon}}_0$. The EMA estimate is known to be more appropriate for systems with "granular" microstructures, at least in 2 dimensions. For example, a two-phase system with isotropic dielectric constants $\varepsilon^{(1)}$ and $\varepsilon^{(2)}$ distributed in a checkerboard pattern (an example of a microstructure with phase interchangeability) is known[44] to be isotropic with effective conductivity given by $\tilde{\varepsilon}=\sqrt{\varepsilon^{(1)}\varepsilon^{(2)}}$, in precise agreement with the corresponding prediction of the self-consistent estimate in two dimensions and for equal proportions of the phases. More generally, the EMA having been shown[45] to correspond exactly to certain rather special types of hierarchical microstructures (there is also a recent generalization[46] of checkerboard-type microstructures also attaining the EMA estimate). Of course, both the standard MGA and EMA estimates for linear composites are known to be exact to second order in the contrast.

A. Infinite contrast: The case of a conducting second phase

It has already been noted that the "new" second-order estimates (35) for nonlinear composites are exact to second order in the contrast and, therefore, very accurate at low contrast. It remains to consider large-contrast situations. In this sense, the special case where one phase is taken to be a conductor is the most extreme situation, since it corresponds to infinite contrast. In this section, this case will be considered in detail, as it lends itself to almost fully analytical treatment. As discussed in more detail later, the resulting expressions for two-phase systems with a conducting phase are found to also apply, with appropriate reinterpretations, to two-phase conductors with ideally conducting and insulating second phases.

Thus, in this section, two-phase materials are considered, where one of the phases, labeled phase 2, with volume fraction $c^{(2)}=p$, is a conductor ($\chi^{(2)}\to\infty$), so that $w^{(2)}$ will be taken to be infinite, unless the electric field in the phase is exactly zero, in which case $w^{(2)}=0$. The other phase, labeled 1, with volume fraction $c^{(1)}=1-p$, will be taken to be of the power-law type (4). In this case, the linear comparison composite is also taken to have a conducting phase 2, so that the function $V^{(2)}$ vanishes identically. In addition, the estimate (37) for the effective energy function $\tilde{W}_T$ of the linear comparison composite simplifies further, and the result $\overline{\mathbf{E}}^{(1)}=\overline{\mathbf{E}}/(1-p)$ is generated for the average electric field in the nonconducting phase, since the electric field in the conducting phase is identically zero. Using these results, the estimate (29) for the effective energy function $\tilde{W}$ of this composite material may be written in the form

$$\tilde{W}(\overline{\mathbf{E}})=\operatorname*{stat}_{\boldsymbol{\varepsilon}_0^{(1)}}\left\{\frac{1}{2}\overline{\mathbf{E}}\cdot\tilde{\boldsymbol{\varepsilon}}_0\overline{\mathbf{E}}+(1-p)\left[\mathbf{P}^{(1)}(\overline{\mathbf{E}}^{(1)})\cdot(\overline{\mathbf{E}}^{(1)}-\hat{\mathbf{E}}^{(1)})+w^{(1)}(\hat{\mathbf{E}}^{(1)})-\frac{1}{2}\hat{\mathbf{E}}^{(1)}\cdot\boldsymbol{\varepsilon}_0^{(1)}\hat{\mathbf{E}}^{(1)}\right]\right\},\tag{42}$$

where it is recalled that $\mathbf{P}^{(1)}(\overline{\mathbf{E}}^{(1)})=\partial w^{(1)}/\partial E(\overline{\mathbf{E}}^{(1)})-\boldsymbol{\varepsilon}_0^{(1)}\overline{\mathbf{E}}^{(1)}$.

Noting that the average electric field in the nonconducting phase is aligned with the applied macroscopic electric field $\overline{\mathbf{E}}$, the choice $\boldsymbol{\varepsilon}_0^{(1)}=\varepsilon_{\parallel}\mathbf{n}\otimes\mathbf{n}+\varepsilon_{\perp}(\mathbf{I}-\mathbf{n}\otimes\mathbf{n})$ is made for the comparison dielectric tensor, where $\mathbf{n}=(1/\overline{E})\overline{\mathbf{E}}$ is the unit vector aligned with the average electric field. As before, this vector defines two directions: a "parallel" one, aligned with $\mathbf{n}$, and a "perpendicular" one, orthogonal to it. Then, use of this relation for $\boldsymbol{\varepsilon}_0^{(1)}$ in expression (42) for $\tilde{W}$, and optimizing with respect to the variables $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ leads to the following expressions determining the "parallel" and "perpendicular" components of $\hat{\mathbf{E}}^{(1)}$:

$$\hat{E}_{\parallel}=\frac{\overline{E}}{(1-p)}+\frac{1}{\sqrt{1-p}}\left[\frac{\partial}{\partial\varepsilon_{\parallel}}(\overline{\mathbf{E}}\cdot\Delta\tilde{\boldsymbol{\varepsilon}}_0\overline{\mathbf{E}})\right]^{1/2},\tag{43}$$

$$\hat{E}_{\perp}=\frac{1}{\sqrt{1-p}}\left[\frac{\partial}{\partial\varepsilon_{\perp}}(\overline{\mathbf{E}}\cdot\Delta\tilde{\boldsymbol{\varepsilon}}_0\overline{\mathbf{E}})\right]^{1/2},$$

where use has been made of the notation $\Delta\tilde{\boldsymbol{\varepsilon}}_0=\tilde{\boldsymbol{\varepsilon}}_0-\boldsymbol{\varepsilon}_0^{(1)}/(1-p)$.

These expressions for the components of $\hat{\mathbf{E}}^{(1)}$, together with the generalized secant condition (34) for the tensor $\boldsymbol{\varepsilon}_0^{(1)}$, and appropriate estimates for the effective dielectric tensor $\tilde{\boldsymbol{\varepsilon}}_0$ of the linear comparison composite, can be used in expression (42) to generate corresponding estimates for $\tilde{W}$. Here, use will be made of the following estimates[42] of the MGA and EMA types:

$$\tilde{\boldsymbol{\varepsilon}}_0^{\mathrm{MGA}}=\boldsymbol{\varepsilon}_0^{(1)}+\frac{p}{1-p}(\mathbf{T}^{(1)})^{-1},\qquad\tilde{\boldsymbol{\varepsilon}}_0^{\mathrm{EMA}}=\frac{1}{1-p}\boldsymbol{\varepsilon}_0^{(1)}+\frac{p}{1-p}(\tilde{\mathbf{T}})^{-1}.\tag{44}$$

In these relations, the microstructural tensors $\mathbf{T}^{(1)}$ and $\tilde{\mathbf{T}}$ are defined by the choices $\boldsymbol{\varepsilon}_0^{(1)}$ and $\tilde{\boldsymbol{\varepsilon}}_0$, respectively, for the reference dielectric tensor $\boldsymbol{\varepsilon}^{(0)}$ in relation (39).

An analogous procedure could be followed to generate a corresponding estimate for $\tilde{U}$. However, the analysis is complicated by the fact that the average electric displacement in phase 1 is not known explicitly (since the average electric displacement in phase 2 is not zero). Because of this, and for conciseness, the details of the calculations, which involve the general expressions given in the Appendix, will not be given here. Only the results will be quoted below for one special case, with the objective of estimating the possible size of the duality gap (relative to the estimates arising from $\tilde{W}$).

Results for specific classes of microstructures may now be generated by specifying the geometric tensor $\mathbf{Z}$ in the expression (39) for the $\mathbf{T}$ tensor. Fairly explicit results may be generated for power-law composites with isotropic microstructures in 2 and 3 dimensions, taking advantage of the explicit forms (40) and (41) for the tensors $\mathbf{T}$, respectively. Here, for simplicity, only the two-dimensional case will be considered in detail, leaving the qualitatively similar, but algebraically more complicated three-dimensional case for future work. Thus, two-dimensional MGA and EMA estimates for the effective nonlinear susceptibility $\tilde{\chi}$ are listed below. In these expressions, $\tilde{\chi}$ is defined by the same relation (4) used to define the nonlinear susceptibility χ of the matrix phase.

Energy-density MGA estimates in two dimensions. Use of the 2-dimensional MGA estimate for the effective dielectric tensor $\tilde{\boldsymbol{\varepsilon}}_0$ of the relevant linear comparison composite in the simplified expression (42) for $\tilde{W}$ leads to the estimate:

$$\frac{\tilde{\chi}}{\chi}=\left(\frac{1}{1-p}\right)^m\left\{\left[\left(\frac{\hat{E}_{\parallel}}{\overline{E}^{(1)}}\right)^2+\left(\frac{\hat{E}_{\perp}}{\overline{E}^{(1)}}\right)^2\right]^{(m+1)/2}+(m+1)\left(1-\frac{\hat{E}_{\parallel}}{\overline{E}^{(1)}}\right)\right\}\tag{45}$$

for the effective susceptibility of the power-law composite. Here, $\overline{E^{(1)}}=\overline{E}/(1-p)$, and $\hat{E}_{\|}$ and $\hat{E}_{\perp}$ are given by

$$\frac{\hat{E}_{\|}}{\overline{E^{(1)}}}=\left(1+\sqrt{\frac{p}{2}}k^{1/4}\right) \quad \text{and} \quad \frac{\hat{E}_{\perp}}{\overline{E^{(1)}}}=\sqrt{\frac{p}{2}}\frac{1}{k^{1/4}}, \tag{46}$$

which follow by specializing relations (43). In turn, k is determined as a function of m and p from

$$1-m=\frac{\ln\left[\frac{1}{k}+\left(1-\frac{1}{k}\right)\left(1+\sqrt{\frac{p}{2}}k^{1/4}\right)\right]^2}{\ln\left[\left(1+\sqrt{\frac{p}{2}}k^{1/4}\right)^2+\left(\sqrt{\frac{p}{2}}\frac{1}{k^{1/4}}\right)^2\right]}, \tag{47}$$

which follows by solving for the anisotropy ratio $k=\varepsilon_{\|}^{(1)}/\varepsilon_{\perp}^{(1)}$ in the generalized secant condition (34) associated with phase 1.

It is easy to verify that $k\to 1$ as $m\to 1$ in expression (47). It then follows trivially that the above estimate (45) reduces exactly to the linear MGA estimate in this limit, as expected. It turns out that the limits as m tends to 0 and ∞, corresponding to thresholds in the electric displacement and electric fields, respectively, can be simplified further. Thus, it can be verified that $k\to\infty$ as $m\to 0$, so that the effective threshold in the electric displacement field reduces to $\tilde{D}_0=D_0$, where D_0 has been used to denote the electric displacement threshold in the nonconducting phase (see Fig. 1). On the other hand, k satisfies the expression $k^{-3/4}-k^{1/4}=\sqrt{2/p}$ in the limit as $m\to\infty$, which can be solved for k as a function to p to estimate the effective threshold in the electric field via the expression $\tilde{E}_0=(1-p)(1-k)(1+k)^{-1/2}E_0$, where E_0 has been used to denote the threshold electric field in the nonconducting phase in this limit (see Fig. 1).

It is also possible in this case to work out the dilute expansion

$$\frac{\tilde{\chi}}{\chi}=1+m[1+(m+1)/(2m^{1/2})]p, \tag{48}$$

which is valid for general values of the nonlinearity, provided that m is not too large (i.e., $m\ll p^{-2/3}$). It is remarked that this result is in perfect agreement with the corresponding expression derived in Ref. 20 [refer to Eq. (4.5) in that reference] for the ''old'' second order theory. Recalling that it was shown in that reference that the above expression for the dilute limit is a very good approximation to the numerical results of Lee and Mear[36] in the analogous mechanical case, it follows that the ''new'' theory also does a good job in this particular limit (for values of m between 1/10 and 1). However, it is emphasized that the dilute expansion (48) does not hold in the limit as m tends to ∞, where a different nonanalytic prediction is generated (as will be seen later). Unfortunately, there are no numerical results available in the limit as m tends to ∞ and comparisons are therefore not possible in this case at the present time.

Complementary-energy MGA estimates in two dimensions. Use of the two-dimensional MGA estimates in the corresponding expression for $\tilde{U}$ in this case leads to the estimate

$$\frac{\tilde{\chi}}{\chi}=\left(\frac{1}{1-p}\right)^m\left\{\left[\left(\frac{\hat{D}_{\|}}{\overline{D}}\right)^2+\left(\frac{\hat{D}_{\perp}}{\overline{D}}\right)^2\right]^{(m+1)/2m}+\frac{m+1}{m}\left(\frac{\overline{D^{(1)}}}{\overline{D}}\right)^{1/m}\left(\frac{\overline{D^{(1)}}}{\overline{D}}-\frac{\hat{D}_{\|}}{\overline{D}}\right)\right\}^{-m}, \tag{49}$$

where

$$\frac{\overline{D^{(1)}}}{\overline{D}}=\frac{\sqrt{2}k^{3/4}+(k-1)\sqrt{p}}{\Delta}, \quad \frac{\hat{D}_{\|}}{\overline{D}}=\frac{\sqrt{2}k^{3/4}+k\sqrt{p}}{\Delta}, \quad \frac{\hat{D}_{\perp}}{\overline{D}}=\frac{\sqrt{k}\sqrt{p}}{\Delta}. \tag{50}$$

In these relations, k is determined as a function of m and p from the same relation (47) above, and $\Delta=\sqrt{2}k^{3/4}+(k-1)\sqrt{p}+\sqrt{2}pk^{1/4}$. It can be checked again that this estimate for $\tilde{\chi}$ is consistent with the standard MGA estimate in the limit of linear behavior, and also that it reproduces exactly the above energy-density estimates for the threshold fields in the limits as m tends to zero and infinity.

Energy-density EMA estimates in two dimensions. Use of the corresponding two-dimensional EMA estimates in the simplified expressions for $\tilde{W}$ leads to the same expression (45) for $\tilde{\chi}$, with $\overline{E^{(1)}}=\overline{E}/(1-p)$, but where now

$$\frac{\hat{E}_{\|}}{\overline{E^{(1)}}}=1+\sqrt{\frac{\frac{p}{2}\sqrt{k}}{1-\frac{p}{2}\left(\sqrt{k}+2+\frac{1}{\sqrt{k}}\right)}}, \quad \frac{\hat{E}_{\perp}}{\overline{E^{(1)}}}=\sqrt{\frac{\frac{p}{2}\frac{1}{\sqrt{k}}}{1-\frac{p}{2}\left(\sqrt{k}+2+\frac{1}{\sqrt{k}}\right)}}, \tag{51}$$

with k determined as a function of m and p from the relation

$$1-m=\frac{\ln\left[\left[(1-p)\left(\sqrt{k}-\frac{1}{\sqrt{k}}\right)\left(\frac{\hat{E}_{\|}}{\overline{E^{(1)}}}\right)+(1-p)\frac{1}{\sqrt{k}}-p\right]\Big/\left[(1-p)\sqrt{k}-p\right]\right]^2}{\ln\left[\left(\frac{\hat{E}_{\|}}{\overline{E^{(1)}}}\right)^2+\left(\frac{\hat{E}_{\perp}}{\overline{E^{(1)}}}\right)^2\right]}. \tag{52}$$

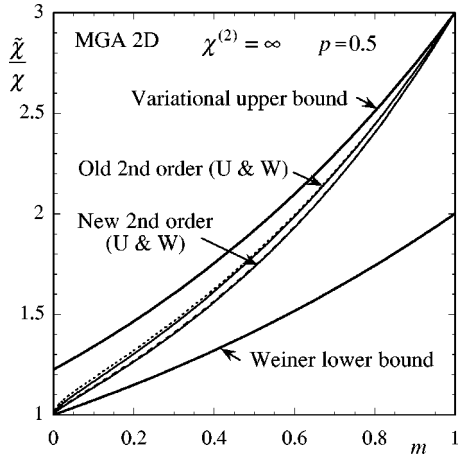

FIG. 4. MGA estimates for the effective nonlinear susceptibility $\tilde{\chi}$ of an isotropic, two-dimensional, two-phase, power-law composite dielectric with 50% of a conducting second phase, plotted as a function of the nonlinearity m ($m<1$). The ''new'' second-order are compared with the earlier ''old'' second-order estimates, as well as the ''variational'' upper bounds. The energy (W) and complementary-energy (U) versions of the estimates are shown as continuous and dashed or dotted lines, respectively, for the ''new'' and ''old'' second-order estimates.

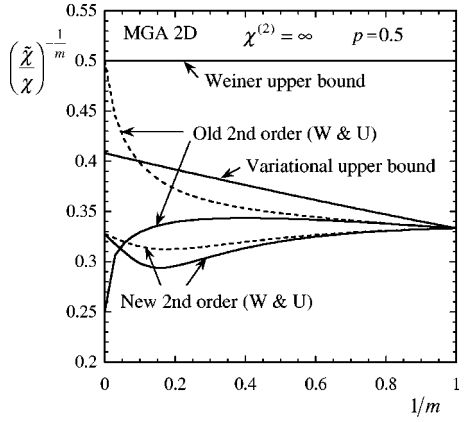

FIG. 5. MGA estimates for the effective nonlinear susceptibility $\tilde{\chi}$ of an isotropic, two-dimensional, two-phase, power-law composite dielectric with 50% of a conducting second phase, plotted as a function of the nonlinearity m ($m>1$). The ''new'' second-order are compared with the earlier ''old'' second-order estimates, as well as the ''variational'' upper bounds. The energy (W) and complementary-energy (U) versions of the estimates are shown as dashed or continuous lines, respectively, for the ''new'' and ''old'' second-order estimates.

Once again it can be verified that $k\to 1$ as $m\to 1$ in expression (52). It then follows that this nonlinear EMA estimate reproduces exactly the linear EMA estimate. Also, k can be shown to tend to a finite value, greater than 1 (for $p<1/2$), in the limit as $m\to 0$. In this case, $\tilde{D}_0/D_0$ reaches some given finite value, depending on the value of p, in such a way that it equals 1 for p equal to zero and blows up as p approaches 1/2 (which is the percolation threshold in this case). Similarly, k tends to a finite value, less than 1 (for $p<1/2$), in the limit as $m\to\infty$, yielding also finite values, less than 1, for $\tilde{E}_0/E_0$, except in the limit as p tends to 1/2, when it vanishes.

It should be noted here that the above MGA and EMA expressions are obviously also valid for nonlinear conductors involving metal/superconductor mixtures. In addition, it can be shown that the above two-dimensional expressions also hold in the ''opposite'' infinite-contrast case involving metal/insulator mixtures, provided that the following replacements are made: $\tilde{\chi}/\chi$ should be changed to $(\tilde{\chi}/\chi)^{-1/m}$ and m to $1/m$. (This is a generalization[23] of a well-known duality result in the linear case.)

B. Discussion and comparisons

Figures 4 and 5 present comparisons of the ''new'' MGA second-order estimates, given in the preceding subsection for two-dimensional, infinite-contrast, power-law composites, with earlier bounds and estimates of various types for this special class of systems. Results are shown for the effective nonlinear susceptibility $\tilde{\chi}$, normalized by the nonlinear susceptibility χ of the power-law phase, as a function of the nonlinearity exponent m, for 50% volume fraction of the conducting phase ($p=0.5$).

In Fig. 4, the ''new'' energy (continuous line) and complementary-energy (dashed line) MGA estimates (45) and (49) are compared with the ''variational'' MGA estimate,[9,10] as well as with the corresponding energy (continuous line) and complementary-energy (dotted line) ''old'' second-order estimates,[20] for values of $m<1$. The variational MGA estimate in this case is defined[9] by the relation $\tilde{\chi}/\chi=(1+p)^{(m+1)/2}(1-p)^{-m}$, and the corresponding old second-order estimates may be found in Ref. 20. It should be noted that the ''variational'' MGA estimate is in fact a bound for all other MGA estimates. This follows from the fact[9,25] that the MGA estimate is an exact result for statistically isotropic linear composites with extreme values of the Milton-Torquato[47,48] three-point parameters. The following observations may then be made in the context of this figure. First, the two types of estimates (arising from the energy versus complementary-energy formulations) are slightly different from each other, for the ''new,'' as well as the ''old'' second-order estimates. This confirms the existence of a duality gap, anticipated earlier; however, it appears that the gap is quite small, for both the ''new'' and ''old'' estimates, in this case. Second, it can be seen that both the ''new,'' as well as the ''old'' second-order estimates lie well below the variational bound for all values of m less than 1. They also lie well above the Wiener[49] lower bound, except in the limit as m tends to 0, where the ''new'' and ''old'' second-order estimates both tend to the Wiener bound.

In Fig. 5, both the ''new'' energy (dashed lines), as well as the complementary-energy (continuous lines) estimates (45) and (49), respectively, are shown again, but this time for values of $m>1$. Here, the results are plotted for the quantity $(\chi/\tilde{\chi})^{-1/m}$, which is the physically meaningful variable, tending to $\tilde{E}_0/E_0$, in the limit as $m\to\infty$, as mentioned earlier. It can be seen that the two types of ''new'' second-order

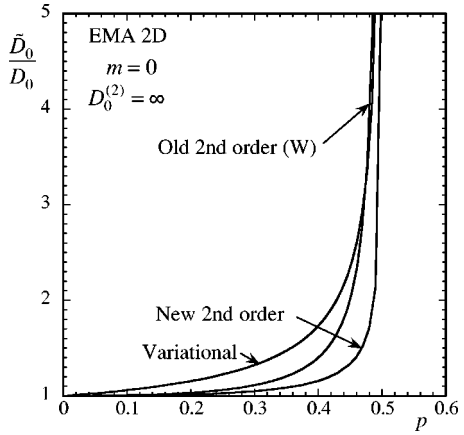

FIG. 6. EMA estimates for the effective nonlinear susceptibility $\tilde{\chi}$ of an isotropic, two-dimensional, two-phase, threshold-type ($m=0$) composite, plotted as a function of the concentration p of the conducting phase. The ''new'' second-order are compared with the earlier ''old'' second-order estimates, as well as the ''variational'' upper bounds. Here, the energy-density (W) and complementary-energy (U) versions of the ''new'' second-order estimates are identical. For the ''old'' estimates, only the energy-density (W) estimates are shown.

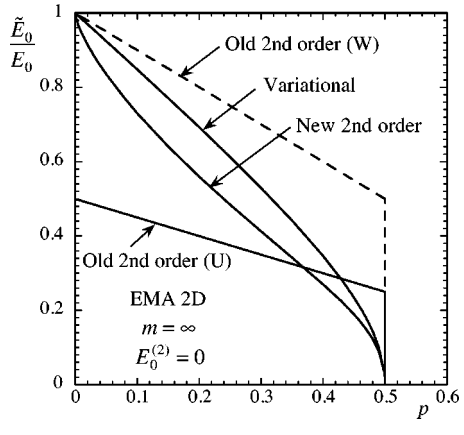

FIG. 7. EMA estimates for the effective nonlinear susceptibility $\tilde{\chi}$ of an isotropic, two-dimensional, two-phase, threshold-type ($m=\infty$) composite, plotted as a function of the concentration p of the conducting phase. The ''new'' second-order are compared with the earlier ''old'' second-order estimates, as well as the ''variational'' upper bounds. Here, the energy-density (W) and complementary-energy (U) estimates are identical for the ''new'' theory, but very different for the ''old'' theory.

estimates are somewhat different, demonstrating the existence of a duality gap, but note that the gap is zero not only for linear behavior ($m=1$), but also, much more interestingly, in the limit as $m\to\infty$. On the other hand, the ''old'' second-order estimates are seen to diverge from each other in this limit, which is clearly a deficiency in the earlier theory. Also, while both versions of the ''new'' second-order estimates satisfy the upper bound provided by the ''variational'' MGA estimate, only one (the complementary energy, or U) of the two ''old'' second-order estimates satisfies the variational upper bound, the other one (the energy, or W) tending to the higher Wiener upper bound in the limit as $m\to\infty$. Thus, these results demonstrate that the ''new'' second-order estimates are superior to the earlier version (''old'') of the estimates, especially in the limit of strongly nonlinear behavior with a threshold in the electric field.

In Figs. 6 and 7, plots are shown for the ''new'' EMA estimates for the effective nonlinear susceptibility of two-dimensional, infinite-contrast, power-law composites, as a function of the concentration of the conducting phase p. Two cases are considered: (a) a threshold in the electric displacement ($m=0$) and (b) a threshold in the electric field ($m=\infty$). Note that in these particular cases, the two versions (W and U) of the ''new'' theory provide identical predictions. The ''old'' second-order[20] and ''variational''[9,14] EMA estimates are included for comparison purposes. Here, the ''variational'' EMA estimates are given[9] by the expression $\tilde{\chi}/\chi=(1-p)^{(1-m)/2}/(1-2p)^{(m+1)/2}$, while the ''old'' second-order estimates are taken from the work of Ponte Castañeda and Kailasam.[20] Again, it is noted that the ''variational'' EMA estimate provides an upper bound for all other self-consistent estimates. This follows from the fact the EMA estimate is known to be exact for linear composites with a special class of hierarchical microstructures.[45]

In Fig. 6 ($m=0$), all the EMA estimates for the effective threshold electric displacement $\tilde{D}_0$ are seen to blow up at 50% volume fraction, which is the known value of the percolation threshold for these two-dimensional microstructures. However, it is interesting to note that the ''new'' estimates remain well below the variational EMA upper bounds (in the sense described in the above paragraph) for all values of p, while the ''old'' second-order estimates are seen to violate the bound at a volume fraction of about 47.5%. This observation demonstrates that the ''new'' estimates are superior to the ''old'' second-order estimates, which violate a rigorous bound. It is also observed that both the ''new'' and ''old'' estimates predict a vanishingly small effect [$\sim o(p)$] of the conducting phase on the effective response for dilute concentrations in this case ($m=0$). This is in contrast with the ''variational'' upper bound, which predicts a finite enhancement [$\sim O(p)$] in the effective susceptibility.

In Fig. 7 ($m=\infty$), all the EMA estimates for the effective threshold electric field $\tilde{E}_0$ are seen to vanish at 50% volume fraction. Here again, the ''new'' second-order EMA estimates (note that the W and U versions are identical) are seen to satisfy the bound provided by the ''variational'' method for all values of the concentration of the conducting phase, while the ''old'' second-order estimates are seen to violate the bound: the U version of the ''old'' theory for concentrations above approximately 43%, and the corresponding W version for all values of p up to percolation. Note also the hugely different behavior predicted by the two theories in the dilute limit. The ''old'' theory predicts widely inconsistent results, while the ''new'' theory yields a more reasonable, albeit *nonanalytic* prediction for small values of the concentration (i.e., an infinite, negative slope at $p=0$). Recalling the observations at the end of the previous subsection on the correspondences with metal/insulator mixtures, it is further remarked here that the results for the cases $m>1$ are plotted in

Figs. 5 and 7 in such a way that they would correspond directly as shown to the case of metal/insulator mixtures with $m<1$.

C. Critical exponents

Following up on the above discussion for the effective behavior near the percolation threshold ($p_c=1/d$), it is straightforward to compute the relevant critical exponents for the ''new'' second-order estimates. The result is that $t=s=(1+m)/2$, so that the ''new'' second-order estimates—unlike the ''old'' second-order estimates—satisfy the bounds (1) (they are in fact identical to them) provided by the ''variational'' method.[28] (It is recalled[14,27] also that both sets of critical exponents satisfy certain duality relations.[1,23]) Thus, for example, in Fig. 6, corresponding to $m=0$, the critical exponent associated with the ''old'' method is $s=1$, which is in violation of the upper bound provided by $s=1/2$ [recall that $m<1$, so the opposite sign applies for the inequalities in Eq. (1)]. On the other hand, the ''new'' estimates can be seen to exhibit the same critical exponent as the bound ($s=1/2$). Similarly, from Fig. 7, it is deduced that the value of t predicted by the ''old'' theory (namely, $t=0$ in this case corresponding to $m=0$) is in violation of the corresponding lower bound ($t=1/2$) in this case. Again the ''new'' theory is seen to yield the same exponent as the bound ($t=1/2$). In this connection, it is important to emphasize that the reason for the improvement provided by the new theory over the earlier second-order theory is directly related to the additional dependence on the second moments of the field fluctuations, as is the case with the variational bounds. This is especially significant near the percolation threshold where field fluctuations are known to become unbounded. The old theory, which does not incorporate dependence on the field fluctuations, is doomed to fail near the percolation threshold, even when it possesses several important advantages relative to the variational theory, which, on the other hand, does make use of the second-moments of the fields.

V. CONCLUDING REMARKS

An improved version of the second-order theory[19,20] for strongly nonlinear composites has been proposed. As with the earlier version of the theory, it produces MGA and EMA estimates that are exact to second-order in the contrast. It has also been found to satisfy all known bounds, including some recent bounds on the critical exponents associated with the EMA, which had been found to be violated by the previous version of the theory. (Both versions of the theory produce nonlinearity-independent percolation thresholds). In addition, the new version of the theory appears to give reasonable predictions, even for the extreme cases of threshold-type nonlinearities. Thus, the new second-order theory appears to satisfy most, if not all of the desirability criteria identified in the introduction. There is an alternative improved version of the second-order theory, recently proposed by Pellegrini,[29] that may also satisfy all these criteria, although this remains to be checked, at least for threshold-type nonlinearities. However, our theory may be a little easier to implement than the theory of Pellegrini, even if in principle it uses the same information, namely, the averages and covariance tensors of the field fluctuations in the phases of similarly chosen (but not identical) linear comparison composites.

One limitation of the theory, which is shared with the alternative theory of Pellegrini, is that it exhibits a duality gap (the energy and complementary energy formulations of the theories do not yield identical predictions). However, our theory has been shown to have vanishingly small duality gaps, not only in the special case of linear behavior ($m=1$), but also in the limiting cases of threshold-type nonlinearities ($m\to 0$ and ∞). This suggests that it may indeed be possible to find further improvements of the theory leading to complete closure of the duality gap.

Referring to the two-dimensional results, the critical exponents of the new EMA theory have been found to satisfy the duality relation.[23] However, the two critical exponents (s and t) associated with the new EMA theory were also found to have identical values. This is in disagreement with simulation results[50,51] for nonlinear random resistor networks which suggest that the critical exponents may in fact be different in value. While this is probably the case for real systems, it is perhaps not too surprising that the nonlinear version of the EMA theory that has been developed in this work inherits the feature of equal critical exponents from the corresponding linear theory which it uses to generate an estimate for the relevant linear comparison composite. It stands to reason that if a better estimate—one with perhaps different critical exponents—were used to characterize the linear comparison composite, the resulting nonlinear estimate would also be likely to exhibit more realistic exponents, which would be expected to be different in value. In this connection, it should be emphasized that more definitive conclusions may be extracted by full consideration of results of duality theory, including its implications for the relevant scaling functions.

Another issue that probably merits further investigation is the behavior of these nonlinear systems in the dilute limit. While the predictions of the theory in the dilute limit were found to be in good agreement with numerical results for the few cases for which numerical results are available, the predictions of the theory were also found to be nonstandard in at least one special case involving a threshold-type nonlinearity, where the dependence of the effective threshold coefficients on the concentration p of the dilute phase was found to be *nonanalytic*. This observation may have implications for earlier EMA schemes which implicitly assume analytic dependence on p. Could this shed some light, for example, on the fact that some such schemes appear to give nonlinearity-dependent percolation thresholds?

ACKNOWLEDGMENTS

This research was supported by NSF Grant No. DMS-99-71958. The article was completed while the author was visiting the L.M.S. at the Ecole Polytechnique. The author is grateful to Dr. Y.-P. Pellegrini of the C.E.A. at Bruyères-le-

Châtel for stimulating discussions and for insightful comments on the manuscript.

APPENDIX: DUAL FORMULATION

There an exactly dual formulation[31] which makes use of the local complementary energy-density function u, such that $\mathbf{E}=\partial u/\partial \mathbf{D}$. The function u is defined in terms of w via the Legendre transformation

$$u(\mathbf{x},\mathbf{D})=\underset{\mathbf{E}}{\text{stat}}\{\mathbf{D}\cdot\mathbf{E}-w(\mathbf{x},\mathbf{E})\}, \tag{A1}$$

where the ''stat'' (stationary) operation means taking the derivative of the terms inside the curly brackets with respect to $\mathbf{E}$, solving for $\mathbf{E}$ as a function of $\mathbf{D}$, and substituting the result back inside the brackets to obtain a function of $\mathbf{D}$. Note that the requisite smoothness hypotheses have been made about the function w, and that, because of the convexity hypothesis on the $w^{(r)}$, there is no ambiguity in the above definition—and the function u is also convex.

In terms of the complementary energy function u, the effective constitutive relation for the nonlinear composite may then be alternatively written as

$$\overline{\mathbf{E}}=\frac{\tilde{\partial} U}{\partial \overline{\mathbf{D}}}, \tag{A2}$$

where $\tilde{U}$ is the effective complementary energy function for the composite, defined by

$$\tilde{U}(\overline{\mathbf{D}})=\min_{\mathbf{D}\in\mathcal{S}}\langle u(\mathbf{x},\mathbf{D})\rangle=\min_{\mathbf{D}\in\mathcal{S}}\sum_{r=1}^{N} c^{(r)}\langle u^{(r)}(\mathbf{D})\rangle^{(r)}. \tag{A3}$$

In this relation, $\mathcal{S}=\{\mathbf{D},\ \text{div}\mathbf{D}=0\ \text{in}\ \Omega,\ \mathbf{D}\mathbf{n}=\overline{\mathbf{D}}\mathbf{n}\ \text{on}\ \partial\Omega\}$ denotes the set of trial electric displacement fields. Again, under the above-mentioned hypotheses on the $w^{(r)}$, the two formulations are exactly equivalent in the sense of Legendre duality: $\tilde{U}=\tilde{W}^{*}$.

Following the development in Sec. III, an analogous estimate for the effective complementary energy function of the nonlinear composite may also be generated such that

$$\tilde{U}(\overline{\mathbf{D}})=\underset{\boldsymbol{\sigma}_0^{(s)}}{\text{stat}}\left\{\tilde{U}_T(\overline{\mathbf{D}};\mathbf{D}^{(s)},\boldsymbol{\sigma}_0^{(s)})-\sum_{r=1}^{N} c^{(r)}V^{(r)}(\mathbf{D}^{(r)},\boldsymbol{\sigma}_0^{(r)})\right\}, \tag{A4}$$

where $\tilde{U}_T$ is the effective complementary energy function associated with a linear comparison composite with local phase energy functions defined by

$$u_T^{(r)}(\mathbf{D})=u^{(r)}(\mathbf{D}^{(r)})+\frac{\partial u^{(r)}}{\partial \mathbf{D}}(\mathbf{D}^{(r)})\cdot(\mathbf{D}-\mathbf{D}^{(r)})$$

$$+\frac{1}{2}(\mathbf{D}-\mathbf{D}^{(r)})\cdot\boldsymbol{\sigma}_0^{(r)}(\mathbf{D}-\mathbf{D}^{(r)}), \tag{A5}$$

and where the functions $V^{(r)}$ are now given by

$$V^{(r)}(\mathbf{D}^{(r)},\boldsymbol{\sigma}_0^{(r)})=\underset{\hat{\mathbf{D}}^{(r)}}{\text{stat}}[u_T^{(r)}(\hat{\mathbf{D}}^{(r)})-u^{(r)}(\hat{\mathbf{D}}^{(r)})]. \tag{A6}$$

The result (A4) for $\tilde{U}$ can be shown to further simplify to

$$\tilde{U}(\overline{\mathbf{D}})=\sum_{r=1}^{N} c^{(r)}\left[u^{(r)}(\hat{\mathbf{D}}^{(r)})-\frac{\partial u^{(r)}}{\partial \mathbf{D}}(\overline{\mathbf{D}}^{(r)})\cdot(\hat{\mathbf{D}}^{(r)}-\overline{\mathbf{D}}^{(r)})\right]. \tag{A7}$$

Here the variables $\mathbf{D}^{(r)}$ in Eq. (A5) have been identified with the averages $\overline{\mathbf{D}}^{(r)}=\langle\mathbf{D}\rangle^{(r)}$ of the electric displacements in the various phases of the linear comparison composite with spontaneous polarizations defined by Eq. (A5). On the other hand, the second-moment variables $\hat{\mathbf{D}}^{(r)}$ are obtained from appropriate traces of the covariance matrix $\mathbf{C}_{\mathbf{D}}^{(r)}$ of the electric displacement fluctuations in phases. The variables $\boldsymbol{\sigma}_0^{(s)}$ in expression (A4) for $\tilde{U}$ are chosen to be of the form $\boldsymbol{\sigma}_0^{(r)}=(1/\varepsilon_{\parallel}^{(r)})\mathbf{m}^{(r)}\otimes\mathbf{m}^{(r)}+(1/\varepsilon_{\perp}^{(r)})(\mathbf{I}-\mathbf{m}^{(r)}\otimes\mathbf{m}^{(r)})$, where $\mathbf{m}^{(r)}=(1/\overline{D}^{(r)})\overline{\mathbf{D}}^{(r)}$ is a unit vector aligned with the average electric displacement field in phase r, defining two directions in a natural way: a ''parallel'' one, and a ''perpendicular'' one. The comparison permittivity tensors $\boldsymbol{\sigma}_0^{(r)}$ are determined, in turn, by the secant-type condition

$$\frac{\partial u^{(r)}}{\partial \mathbf{D}}(\hat{\mathbf{D}}^{(r)})-\frac{\partial u^{(r)}}{\partial \mathbf{D}}(\overline{\mathbf{D}}^{(r)})=\boldsymbol{\sigma}_0^{(r)}(\hat{\mathbf{D}}^{(r)}-\overline{\mathbf{D}}^{(r)}). \tag{A8}$$

It is emphasized that because of the existence of a duality gap, the constitutive relation resulting from these expressions are not exactly equivalent to the corresponding expressions derived in Sec. III for the energy density function of the composite. However, because of the restricted Legendre duality of the linear comparison problems involved, the following relations can be shown to hold among the variables that are used in these two formulations: $\overline{\mathbf{D}}^{(r)}=\partial w^{(r)}/\partial\overline{\mathbf{E}}^{(r)}$, $\overline{\mathbf{E}}^{(r)}=\partial u^{(r)}/\partial\overline{\mathbf{D}}^{(r)}$, $\hat{\mathbf{D}}^{(r)}=\partial w^{(r)}/\partial\hat{\mathbf{E}}^{(r)}$, $\hat{\mathbf{E}}^{(r)}=\partial u^{(r)}/\partial\hat{\mathbf{D}}^{(r)}$, and $\boldsymbol{\sigma}_0^{(r)}=(\boldsymbol{\varepsilon}_0^{(r)})^{-1}$. (But note that $\overline{\mathbf{D}}^{(r)}$ and $\overline{\mathbf{E}}^{(r)}$ do not correspond exactly to the average electric displacement and electric field in phase r of the nonlinear composite in the context of the energy and complementary-energy formulations, respectively.)

*Email address: ponte@seas.upenn.edu

[1] J. P. Straley and S. W. Kenkel, Phys. Rev. B **29**, 6299 (1984).
[2] D. R. S. Talbot and J. R. Willis, IMA J. Appl. Math. **35**, 39 (1985).
[3] D. Stroud and P. M. Hui, Phys. Rev. B **37**, 8719 (1988).
[4] X. C. Zeng, D. J. Bergman, P. M. Hui, and D. Stroud, Phys. Rev. B **38**, 10 970 (1988).
[5] D. Stroud and V. E. Wood, J. Opt. Soc. Am. B **6**, 778 (1989).
[6] D. J. Bergman, Phys. Rev. B **39**, 4598 (1989).
[7] R. Blumenfeld and D. J. Bergman, Phys. Rev. B **40**, 1987 (1989); **44**, 7378 (1991); D. J. Bergman and R. Blumenfeld, *ibid.* **54**, 9555 (1996).
[8] D. J. Bergman, in *Composite Media and Homogenization Theory*, edited by G. Dal Maso and G. F. Dell'Antonio (Birkhauser,

Boston, 1991), pp. 67–78.
[9] P. Ponte Castañeda, Philos. Trans. R. Soc. London **340**, 531 (1992).
[10] P. Ponte Castañeda, G. deBotton, and G. Li, Phys. Rev. B **46**, 4387 (1992).
[11] O. Levy and D. J. Bergman, Phys. Rev. B **46**, 7189 (1992).
[12] K. W. Yu and G. Q. Gu, Phys. Lett. A **193**, 311 (1994).
[13] H. C. Lee and K. W. Yu, Phys. Lett. A **197**, 341 (1995).
[14] W. M. V. Wan, H.-C. Lee, P. M. Hui, and K. W. Yu, Phys. Rev. B **54**, 3946 (1996).
[15] P. M. Hui and W. M. V. Wan, Appl. Phys. Lett. **69**, 1810 (1996).
[16] K. W. Yu, P. M. Hui, and H.-C. Lee, Phys. Lett. A **210**, 115 (1996).
[17] L. Gao and Z. Li, Phys. Lett. A **219**, 324 (1996).
[18] M. A. Palenberg and B. U. Felderhof, Phys. Rev. B **55**, 10 326 (1997).
[19] P. Ponte Castañeda, Phys. Lett. A **224**, 163 (1997).
[20] P. Ponte Castañeda and M. Kailasam, Proc. R. Soc. London, Ser. A **453**, 793 (1997); **453**, 1791(E) (1997).
[21] L. Sali and D. J. Bergman, J. Stat. Phys. **86**, 455 (1997).
[22] M. Barthélémy and H. Orland, Eur. Phys. J. B **6**, 537 (1998).
[23] O. Levy and R. V. Kohn, J. Stat. Phys. **90**, 159 (1998).
[24] P. Ponte Castañeda, Phys. Rev. B **57**, 12 077 (1998).
[25] P. Ponte Castañeda and J. R. Willis, Proc. R. Soc. London, Ser. A **455**, 1799 (1999).
[26] Y.-P. Pellegrini, Phys. Rev. B **61**, 9365 (2000).
[27] M. Barthélémy, Phys. Rev. B **62**, 8576 (2000).
[28] Y. Leroy and P. Ponte Castañeda, C. R. Acad. Sci., Ser. IIb: Mec., Phys., Chim., Astron. **329**, 571 (2001).
[29] Y.-P. Pellegrini, Phys. Rev. B **64**, 134211 (2001).
[30] Y.-P. Pellegrini (private communication).
[31] D. J. Bergman and D. Stroud, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1992), Vol. 46, p. 147.
[32] P. Ponte Castañeda and P. Suquet, Adv. Appl. Mech. **34**, 171 (1998).
[33] M. Sahimi, Phys. Rep. **306**, 213 (1998).
[34] J. C. M. Garnett, Philos. Trans. R. Soc. London **203**, 385 (1904).
[35] D. A. G. Bruggeman, Ann. Phys. (Leipzig) **24**, 636 (1935).
[36] B. J. Lee and M. E. Mear, Mech. Mater. **13**, 313 (1992).
[37] D. R. S. Talbot and J. R. Willis, Int. J. Solids Struct. **29**, 1981 (1992).
[38] P. Suquet, C. R. Acad. Sci., Ser. II: Mec., Phys., Chim., Sci. Terre Univers. **320**, 563 (1995).
[39] D. J. Bergman, Phys. Rep., Phys. Lett. **43C**, 377 (1978).
[40] M. Bobeth and G. Diener, J. Mech. Phys. Solids **34**, 1 (1986).
[41] V. M. Levin, Mekh. Tverd. Tela. **2**, 83 (1967).
[42] J. R. Willis, J. Mech. Phys. Solids **25**, 185 (1977).
[43] Z. Hashin and S. Shtrikman, J. Appl. Phys. **33**, 3125 (1962).
[44] J. B. Keller, J. Math. Phys. **5**, 548 (1964).
[45] G. W. Milton, Commun. Math. Phys. **99**, 463 (1985).
[46] S. Torquato and S. Hyun, J. Appl. Phys. **89**, 1725 (2001).
[47] G. W. Milton, Phys. Rev. Lett. **46**, 542 (1981).
[48] S. Torquato, Ph.D. thesis, State University of New York, Stony Brook, 1980.
[49] O. Wiener, Abh. Sächs. Akad. Wiss. Leipzig Math.-Naturwiss. Kl. **32**, 509 (1912).
[50] Y. Meir, R. Blumenfeld, A. Aharony, and A. B. Harris, Phys. Rev. B **34**, 3424 (1986).
[51] H.-C. Lee, W.-H. Siu, and K. W. Yu, Phys. Rev. B **52**, 4217 (1995).