Variational bounds on some bulk properties of a two-phase composite material

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A variational principle due to Hashin and Shtrikman is used to obtain theoretical upper and lower bounds on the effective bulk dielectric constant ϵ_e (or an analogous property such as magnetic permeability, electrical or thermal conductivity, or a diffusivity) of a two-phase macroscopically homogeneous composite material from information about another similar effective bulk property. For the case of a composite whose macroscopic symmetry under rotations is either isotropic or cubic, we obtain a new and rather simple pair of bounds that are usually considerably better than any of those that are presently obtainable under these conditions.

I. INTRODUCTION

The problem of finding absolute bounds on the effective bulk dielectric constant ϵ_e (or the magnetic permeability, or the electrical or thermal conductivity, or the diffusivity of some agent) of a macroscopically homogeneous composite material has been approached by several different methods. The simplest of these bounds is the well-established result[1]

$$\langle 1/\epsilon \rangle < \epsilon_e < \langle \epsilon \rangle \ . \tag{1}$$

The averages introduced here are simple arithmetic averages over the distribution of the pure phases in the composite

$$\langle \epsilon \rangle \equiv \sum_i p_i \epsilon_i \ , \tag{2}$$

where p_i is the volume fraction of the phase i and ϵ_i is its dielectric constant.

By assuming that the composite is macroscopically isotropic, in addition to being homogeneous, Hashin and Shtrikman[2] obtained greatly improved bounds on ϵ_e. For a two-phase medium, these bounds are given by

$$\epsilon_1 + \frac{p_2}{1/(\epsilon_2 - \epsilon_1) + p_1/3\epsilon_1} < \epsilon_e < \epsilon_2 + \frac{p_1}{1/(\epsilon_1 - \epsilon_2) + p_2/3\epsilon_2} \tag{3}$$

for $\epsilon_1 < \epsilon_2$. These bounds were obtained by using a variational principle. The authors were able to show that, for the two-phase system, these are also the best obtainable bounds if one assumes only homogeneity and isotropy.

In order to obtain better bounds on ϵ_e, one must have more information about the microscopic geometry of the mixture. If such additional information is available in the form of correlation functions of $\epsilon(r)$, the local dielectric constant, then one can construct improved trial functions for use in various variational principles and thus derive improved bounds. Several calculations of this kind have been made in recent years.[3-5]

In a different approach, Prager[6] used the inequalities of Dirichlet and Thomson to incorporate information from measurements of other effective bulk properties of the *same* two-phase material in order to improve the bounds on ϵ_e. This could be done both for systems with macroscopic isotropy and for systems without it. The reason why such measured values can lead to improved bounds on ϵ_e is that they provide implicit information about the microscopic geometry of the material under investigation that goes beyond the information included in the volume fractions and in the macroscopic rotational symmetry.

In yet another approach, an analysis of the convexity properties of the function $\epsilon_e(\epsilon_1, \epsilon_2, \ldots)$ enabled the present author[7] to obtain improved bounds for both two-phase and multiphase materials by again using known values of other effective bulk properties of the same material, as well as the bounds of Hashin and Shtrikman or of Eq. (1).

In this paper, we will show that the variational principle of Hashin and Shtrikman can also be applied to handle information about other bulk properties of the same two-phase composite. For cases where there is just a single bulk property whose value is known, we have been able to derive explicit upper and lower bounds on ϵ_e which are given analytically by simple rational expressions involving the various ϵ's of the problem. For the particular case of a two-phase composite whose macroscopic rotational symmetry is either isotropic or cubic, these bounds were apparently never obtained before. Moreover, they are always better than the bounds provided by the methods of either Ref. 6 or Ref. 7, and in most situations the improvement is quite considerable.

The outline of this article is as follows. In Sec. II we review the variational principle of Hashin and Shtrikman in its two forms. In Secs. III A–III E we apply this principle to get bounds for ϵ_e in a

series of situations by choosing in each case an appropriate trial function to be used in the variational calculation. The bounds obtained in these subsections are mostly either not new, or not interesting in themselves (note, however, the simplified and symmetric form that we have obtained for some previously established bounds in Sec. III E). They are discussed partly for didactic reasons—in preparation for the last subsection. In Sec. III F we use the methods and the strategy developed previously in order to construct bounds on ϵ_e for a cubic or isotropic composite with one known piece of information on some other bulk property. We obtain a greatly improved set of one upper and one lower bound on ϵ_e for this case [see Eqs. (69) and (76)], and that is the main practical result of this paper. In Sec. IV we discuss some of the limitations of this paper—mainly our having to rely so much on numerical experimentation in the derivation of some of the analytical results. We point out that if a better method of analyzing the variational expressions can be found, then the scope of our results might very well be considerably expanded. In the Appendix we present a detailed calculation of one of the terms in the variational integral, using the trial function of Hashin and Shtrikman. We show that this term, which was already evaluated in Ref. 2 for an isotropic system, can be evaluated also for a cubic system, leading to the same result. We also show that this result, which is crucial for obtaining the bounds of that reference, is only valid when the trial function of Hashin and Shtrikman is used. When other trial functions are used, the above-mentioned term must be evaluated by a different method.

II. REVIEW OF THE VARIATIONAL PRINCIPLE

The variational principle of Hashin and Shtrikman[2,3] states that the following integral over the entire volume V of the system (throughout this paper, r denotes a three-dimensional vector, and dr is the appropriate volume element)

$$U_T \equiv \frac{1}{8\pi}\int dr\left(\epsilon_0 E_0^2 - \frac{T^2}{\epsilon-\epsilon_0} + 2\vec{T}\cdot\vec{E}_0 + \vec{T}\cdot\vec{E}'\right) , \quad (4)$$

subject to the subsidiary conditions

$$\vec{E}' = -\nabla\psi' , \quad \epsilon_0 \mathrm{div}\vec{E}' = -\mathrm{div}\vec{T}, \quad (5)$$

and the boundary condition

$$\psi' = 0 \quad \text{on all surfaces}, \quad (6)$$

is stationary with respect to arbitrary variations of $\vec{T}$ for

$$\vec{T} = (\epsilon-\epsilon_0)\vec{E} = \vec{D} - \epsilon_0\vec{E} , \quad (7)$$

where

$$\vec{E} \equiv \vec{E}_0 + \vec{E}' . \quad (8)$$

In these equations, $\vec{E}(r)$ and $\vec{D}(r)$ are the local electric field and displacement vector in the system, respectively, $\epsilon(r)$ is the local dielectric constant, which varies from phase to phase in the composite material, and ϵ_0 is an arbitrary constant. Assuming that $\vec{E}(r)$ is produced by fixing the potential at the surface of the system, then $\vec{E}_0(r)$ is the field that would result from the same surface potential if the system were homogeneous rather than composite. The stationary value of U_T for unrestricted variations of $\vec{T}$, denoted by U_S, is equal to the electrostatic energy stored in the volume V. Furthermore, U_T is always an upper (lower) bound on U_S if $\epsilon_0 > \epsilon(r)$ [$0 < \epsilon_0 < \epsilon(r)$].

The effective bulk dielectric constant of the composite ϵ_e is defined most conveniently by considering a situation where $\vec{E}_0$ is a constant (e.g., the composite material fills a parallel-plate condenser whose plates extend to infinity and are held at a fixed potential difference). In that case we can write

$$\vec{E}_0 = \frac{1}{V}\int \vec{E}(r)dr , \quad (9)$$

$$\epsilon_e\vec{E}_0 = \frac{1}{V}\int \epsilon(r)\vec{E}(r)dr , \quad (10)$$

$$\epsilon_e\vec{E}_0^2 = \frac{1}{V}\int \epsilon(r)\vec{E}^2(r)dr = \frac{8\pi U_S}{V} . \quad (11)$$

A similar variational principle exists[2] for the function

$$\vec{R} = -(1/\epsilon_0)\vec{T} \equiv -\tilde{\epsilon}_0\vec{T} , \quad (12)$$

where here and henceforth we denote reciprocal dielectric constants by a tilde

$$\tilde{\epsilon} \equiv 1/\epsilon . \quad (12')$$

The following integral,

$$U_R \equiv \frac{1}{8\pi}\int dr\left(\tilde{\epsilon}_0 D_0^2 - \frac{R^2}{\tilde{\epsilon}-\tilde{\epsilon}_0} + 2\vec{R}\cdot\vec{D}_0 + \vec{R}\cdot\vec{D}'\right) , \quad (13)$$

subject to the subsidiary conditions

$$\mathrm{div}\vec{D}' = 0 , \quad \tilde{\epsilon}_0\,\mathrm{curl}\vec{D}' = -\mathrm{curl}\vec{R} , \quad (14)$$

and to the following boundary condition on the normal component of $\vec{D}'$,

$$D_n' = 0 \quad \text{on all surfaces}, \quad (15)$$

is stationary with respect to arbitrary variations of $\vec{R}$ for

$$\vec{R} = (\tilde{\epsilon}-\tilde{\epsilon}_0)\vec{D} , \quad (16)$$

where

$$\vec{D} \equiv \vec{D}_0 + \vec{D}' . \quad (16')$$

If we assume that the local electric displacement vector $\vec{D}(r)$ is produced by a system of fixed charges at the surface of the system, then $\vec{D}_0(r)$ is the displacement vector that would result from the same charges if the system were homogeneous. Again, the stationary value of U_R for unrestricted variations of $\vec{R}$ is equal to the electrostatic energy U_S stored in V, and U_R is always an upper (lower) bound on U_S if $\vec{\epsilon}_0 > \vec{\epsilon}(r)[0 < \vec{\epsilon}_0 < \vec{\epsilon}(r)]$.

Assuming that $\vec{D}_0$ is a constant (e.g., the composite is inside an infinite parallel-plate condenser with a fixed charge on each plate), the effective reciprocal dielectric constant $\vec{\epsilon}_e$ now satisfies

$$\vec{D}_0 = \frac{1}{V}\int \vec{D}(r)\,dr \ , \tag{17}$$

$$\vec{\epsilon}_e \vec{D}_0 = \frac{1}{V}\int \vec{\epsilon}(r)\vec{D}(r)\,dr \ , \tag{18}$$

$$\vec{\epsilon}_e \vec{D}_0^2 = \frac{1}{V}\int \vec{\epsilon}(r)\vec{D}^2(r)dr = \frac{8\pi U_S}{V} \ . \tag{19}$$

III. VARIATIONAL BOUNDS ON ϵ_e FROM VARIOUS TRIAL FUNCTIONS

A. $\vec{T}$ = const (or $\vec{R}$ = const)

Taking a constant value as a trial function for $\vec{T}$,

$$\vec{T} \equiv T_0 \vec{E}_0 \ , \tag{20}$$

and using this in (4), we find the following trial value for ϵ_e:

$$\epsilon^* = \epsilon_0 - T_0^2 \langle 1/(\epsilon - \epsilon_0)\rangle + 2T_0 \ . \tag{21}$$

The stationary value of this expression with respect to variations of the parameter T_0 is

$$\epsilon^* = \epsilon_0 + \langle 1/(\epsilon - \epsilon_0)\rangle^{-1} \ . \tag{22}$$

Differentiation with respect to ϵ_0 shows that this stationary ϵ^* is a monotonic decreasing function of ϵ_0. Hence we obtain the best upper and lower bounds from (22) by choosing $\epsilon_0 = \infty$ and $\epsilon_0 = 0$, respectively. In this way we regain the bounds of Eq. (1).

If we choose a constant trial function $\vec{R}$,

$$\vec{R} \equiv T_0 \vec{D}_0 \ , \tag{23}$$

and use this in (13), we reproduce Eqs. (21) and (22) with all the ϵ's replaced by the appropriate $\vec{\epsilon}$'s. The discussion is identical, and the bounds of (1) are again produced.

B. Hashin and Shtrikman's trial function (Ref. 2)

Hashin and Shtrikman chose a trial function $\vec{T}(r)$ that had a constant value $T_i \vec{E}_0$ in each of the pure phases i. In order to evaluate the last term in (4) it was necessary to assume that the system is macroscopically isotropic. As we show in the Appendix, their evaluation of that term is in fact valid even when the macroscopic rotational symmetry of the system is only cubic. On the other hand, we show that their result is not valid in general unless $\vec{T}(r)$ has a fixed value in each phase.

A stationary value of U_T, found by varying the parameters T_i, leads to an approximation $\epsilon^*(\epsilon_0)$ for ϵ_e. Noting that ϵ^* is a monotonic increasing function of ϵ_0, the authors obtained the best upper (lower) bound on ϵ_e by choosing ϵ_0 equal to the largest (smallest) of the pure-phase ϵ_i's. For a two-phase system these bounds are given by (3).

If the same kind of trial function is chosen for $\vec{R}$ and the same procedure is followed, one again produces these same bounds.

C. Trial function based on another measurement

A conceptually different kind of trial function is obtained by taking

$$\vec{T}(r) = a\vec{T}_+(r) = a[\epsilon_+(r) - \epsilon_0^+]\vec{E}_+(r) \ , \tag{24}$$

where a is a variational parameter and $\vec{T}_+(r)$ is an exact solution of the variational principle for the same system (i.e., a phase mixture with the same microscopic geometry) but with a different local dielectric constant $\epsilon_+(r)$. In practice this usually means that one is considering some other physical property (e.g., the electrical or thermal conductivity or the magnetic permeability or a diffusion coefficient) for which the problem of finding the effective bulk value in the composite system is identical mathematically to the problem of finding the effective dielectric constant.[6,7] We assume that in addition to knowing the value ϵ_i^+ of ϵ_+ in each of the pure phases that make up the composite, we also know the exact effective bulk value ϵ_e^+ from a measurement or a calculation. Note, however, that we do not presume to know the exact form of the local fields $\vec{E}_+(r)$ or $\vec{T}_+(r)$ (this is certainly the case when ϵ_e^+ is known from a measurement). All we know about $\vec{T}_+$ and $\vec{E}_+$ is some information about their integrals

$$\begin{aligned} \epsilon_e^+ \vec{E}_0^2 &= \frac{8\pi U_{T^+}}{V} = \frac{1}{V}\int \epsilon_+(r)\vec{E}_+^2(r)\,dr \ , \\ \epsilon_e^+ \vec{E}_0 &= \frac{1}{V}\int \epsilon_+(r)\vec{E}_+(r)\,dr \ . \end{aligned} \tag{25}$$

We must therefore try to express the trial value of U_T that follows from (24) in terms of the known quantities ϵ_0^+, ϵ_i^+, ϵ_e^+.

To this end, we consider the equation for $\vec{E}'$,

$$\epsilon_0 \operatorname{div}\vec{E}' = -a \operatorname{div}\vec{T}_+ \ . \tag{26}$$

Since $\vec{E}_+'$ satisfies a similar equation,

$$\epsilon_0^+ \operatorname{div}\vec{E}_+' = -\operatorname{div}\vec{T}_+ \ , \tag{27}$$

as well as the same boundary conditions as $\vec{\mathrm{E}}'$, we can write

$$\vec{\mathrm{E}}' = a(\epsilon_0^+/\epsilon_0)\vec{\mathrm{E}}_+' = (a\epsilon_0^+/\epsilon_0)(\vec{\mathrm{E}}_+ - \vec{\mathrm{E}}_0) \ . \tag{28}$$

We also note that

$$\frac{1}{V}\int \vec{\mathrm{T}}_+ dr = \frac{1}{V}\int (\epsilon_+ - \epsilon_0^+)\vec{\mathrm{E}}_+ dr$$

$$= (\epsilon_e^+ - \epsilon_0^+)\vec{\mathrm{E}}_0 \ . \tag{29}$$

Using (24) and (28) to substitute for $\vec{\mathrm{T}}$ and $\vec{\mathrm{E}}'$ in (4), and (29) to calculate the integral of $\vec{\mathrm{T}}_+$, we get the following trial value for ϵ_e

$$\epsilon^* = \epsilon_0 - \frac{a^2}{V}\int \left(\frac{(\epsilon_+ - \epsilon_0^+)^2}{\epsilon - \epsilon_0} + \frac{(\epsilon_0^+)^2}{\epsilon_0}\right) \times \left(\frac{E_+}{E_0}\right)^2 dr + a^2\frac{(\epsilon_0^+)^2}{\epsilon_0} + 2a(\epsilon_e^+ - \epsilon_0^+). \tag{30}$$

Since we do not know the exact form of $\vec{\mathrm{E}}_+(r)$, we cannot in general evaluate the integral in this equation. But if we can choose ϵ_0^+ and a new parameter b so as to satisfy

$$(\epsilon_+ - \epsilon_0^+)^2/(\epsilon - \epsilon_0) + (\epsilon_0^+)^2/\epsilon_0 = b\epsilon_+ \tag{31}$$

in every one of the pure phases, then the integral reduces to ϵ_e^+, and we get

$$\epsilon^* = \epsilon_0 - a^2[\, b\epsilon_e^+ - (\epsilon_0^+)^2/\epsilon_0\,] + 2a(\epsilon_e^+ - \epsilon_0^+) \ . \tag{32}$$

Making this stationary with respect to the variational parameter a, we find

$$\epsilon^* = \epsilon_0 + \frac{(\epsilon_e^+ - \epsilon_0^+)^2}{b\epsilon_e^+ - (\epsilon_0^+)^2/\epsilon_0} \ . \tag{33}$$

For a two-phase system we can write

$$\epsilon(r) = \epsilon_1\theta_1(r) + \epsilon_2\theta_2(r) \ , \tag{34}$$

$$\epsilon_+(r) = \epsilon_1^+\theta_1(r) + \epsilon_2^+\theta_2(r) \ , \tag{35}$$

where $\theta_i(r)$ is equal to 1 if r is in the phase i, and zero otherwise. For that case, (31) represents two coupled equations for ϵ_0^+ and b. By eliminating b, we get a single quadratic equation for ϵ_0^+

$$(\epsilon_0^+)^2\left(\frac{\epsilon_1}{\epsilon_1^+\epsilon_0(\epsilon_1 - \epsilon_0)} - \frac{\epsilon_2}{\epsilon_2^+\epsilon_0(\epsilon_2 - \epsilon_0)}\right) - 2\epsilon_0^+\frac{\epsilon_2 - \epsilon_1}{(\epsilon_1 - \epsilon_0)(\epsilon_2 - \epsilon_0)} + \frac{\epsilon_1^+}{\epsilon_1 - \epsilon_0} - \frac{\epsilon_2^+}{\epsilon_2 - \epsilon_0} = 0 \ , \tag{36}$$

whose discriminant is

$$\Delta = \frac{\epsilon_1^+ - \epsilon_2^+}{\epsilon_0(\epsilon_1 - \epsilon_0)(\epsilon_2 - \epsilon_0)}\left(\frac{\epsilon_2}{\epsilon_2^+} - \frac{\epsilon_1}{\epsilon_1^+}\right). \tag{37}$$

Therefore, if

$$\left(\epsilon_1^+ - \epsilon_2^+\right)\left(\frac{\epsilon_2}{\epsilon_2^+} - \frac{\epsilon_1}{\epsilon_1^+}\right) \geq 0 \ , \tag{38}$$

then we can solve (36) and (31) for any ϵ_0 that is either greater or smaller than both ϵ_1 and ϵ_2. From (33) we then get upper and lower bounds on ϵ_e that depend on ϵ_0, and we can look for the best bounds by varying ϵ_0. We have not been able to do this analytically, since the expressions for ϵ_0^+ and for b are quite complicated.

By contrast, it is very easy to make numerical experiments by evaluating the bounds from (33) for many different choices of ϵ_0. The results of these experiments indicate that the best bounds are obtained when ϵ_0^+ is either 0 or ∞, corresponding to $\vec{\mathrm{T}} \propto \vec{\mathrm{D}}_+$ and $\vec{\mathrm{T}} \propto \vec{\mathrm{E}}_+$, respectively. In those cases, both ϵ_0 and b are uniquely determined, and therefore also ϵ^* of (33). For $\epsilon_0^+ = 0$, we find

$$\epsilon_0 = (\epsilon_1^+\epsilon_2 - \epsilon_2^+\epsilon_1)/(\epsilon_1^+ - \epsilon_2^+) \ , \tag{39}$$

$$\frac{\epsilon^*}{\epsilon_1 - \epsilon_2} - \frac{\epsilon_e^+}{\epsilon_1^+ - \epsilon_2^+} = \frac{\epsilon_1^+\epsilon_2 - \epsilon_2^+\epsilon_1}{(\epsilon_1^+ - \epsilon_2^+)(\epsilon_1 - \epsilon_2)} \ , \tag{40}$$

whereas for $\epsilon_0^+ = \infty$ (i.e., $\tilde{\epsilon}_0^+ = 0$), we find

$$\tilde{\epsilon}_0 = (\tilde{\epsilon}_1^+\tilde{\epsilon}_2 - \tilde{\epsilon}_2^+\tilde{\epsilon}_1)/(\tilde{\epsilon}_1^+ - \tilde{\epsilon}_2^+) \ , \tag{41}$$

$$\frac{\tilde{\epsilon}^*}{\tilde{\epsilon}_1 - \tilde{\epsilon}_2} - \frac{\tilde{\epsilon}_0^+}{\tilde{\epsilon}_1^+ - \tilde{\epsilon}_2^+} = \frac{\tilde{\epsilon}_1^+\tilde{\epsilon}_2 - \tilde{\epsilon}_2^+\tilde{\epsilon}_1}{(\tilde{\epsilon}_1^+ - \tilde{\epsilon}_2^+)(\tilde{\epsilon}_1 - \tilde{\epsilon}_2)} \ . \tag{42}$$

Note that (41) and (42) are exactly the same as (39) and (40) with all ϵ's replaced by the appropriate $\tilde{\epsilon}$'s. Noting that (39) can be rewritten

$$\epsilon_0 = \epsilon_1 - \epsilon_1^+(\epsilon_1 - \epsilon_2)/(\epsilon_1^+ - \epsilon_2^+) = \epsilon_2 - \epsilon_2^+(\epsilon_1 - \epsilon_2)/(\epsilon_1^+ - \epsilon_2^+) \ , \tag{43}$$

we see that $\epsilon_0 - \epsilon_1$ and $\epsilon_0 - \epsilon_2$ always have the same sign. Therefore, if ϵ_0 of (39) is positive, and hence $\Delta > 0$, then ϵ^* of (40) gives an upper or lower bound on ϵ_e depending on whether ϵ_0 is greater or smaller than ϵ_1 and ϵ_2. The same is then true of $\tilde{\epsilon}_0$ of (41) and $\tilde{\epsilon}^*$ of (42), which now gives a bound on the other side of ϵ_e.

However, if (39) leads to a negative value for ϵ_0, the above procedure breaks down. In that case, we switch the roles of ϵ, ϵ_0, ϵ_e with those of ϵ_+, ϵ_0^+, ϵ_e^+, acting as if we know ϵ_e and are trying to calculate bounds on ϵ_e^+. It is easy to see that the transformed version of (39) must now lead to a positive value for ϵ_0^+. On the other hand, the transformed version of (40) is identical with the original form. Under the assumption that ϵ_e is known, we are thus led to an upper (lower) bound on ϵ_e^+. But since we really know ϵ_e^+, this result can obviously be turned around to yield a lower (upper) bound on ϵ_e, given again by ϵ^*—the solution of (40). Some careful consideration leads to the final conclusion that this ϵ^* is an upper (lower) bound on ϵ_e when the ratio

$$(\epsilon_1^+\epsilon_2 - \epsilon_2^+\epsilon_1)/(\epsilon_1 - \epsilon_2) \tag{44}$$

is negative (positive), and that one can forget about having to satisfy $\Delta > 0$ or $\epsilon_0 > 0$. A similar conclusion holds regarding the role of $\tilde{\epsilon}^*$ of (42) as a bound on $\tilde{\epsilon}_e$: One finds that $\tilde{\epsilon}^*$ is an upper (lower) bound on $\tilde{\epsilon}_e$ if the sign of (44) or of

$$(\tilde{\epsilon}_1^* \tilde{\epsilon}_2 - \tilde{\epsilon}_2^* \tilde{\epsilon}_1)/(\tilde{\epsilon}_1 - \tilde{\epsilon}_2) \tag{45}$$

is negative (positive). Between them, Eqs. (40) and (42) thus always yield one upper and one lower bound on ϵ_e.

As before, if we apply the above procedure to the other variational integral U_R, we arrive again at the same bounds. Note also that all the equations from (36) to (45) are invariant under a permutation of the two phases, so that no new bounds can be obtained in this way.

In practice, the bounds of (40) and (42), although they are apparently new, are not very useful, since they are not very stringent. This is due to the fact that they include no explicit information about the geometry of the mixture—not even the volume fractions. Since at least that much is usually known, and in many cases the mixture is also isotropic, we may expect that much better bounds can be obtained by incorporating that geometrical information too. The main reason why we elaborated on the derivation of these bounds was in order to show how experimental information about ϵ_e^* could be included when using the variational principles of Sec. II. In Secs. III D–III F, we will use combinations of the trial functions discussed up to now to obtain better bounds on ϵ_e.

D. Trial function based on more than one measurement

When there is more than one known value of a bulk property, we shall denote the appropriate ϵ's and other quantities by a Greek index: ϵ_α, $\epsilon_e^{(\alpha)}$, $\epsilon_0^{(\alpha)}$, $\vec{\mathrm{E}}_\alpha$, $\alpha = 1, \ldots, n$, instead of ϵ_+, ϵ_e^*, ϵ_0^*, $\vec{\mathrm{E}}_+$. The trial function of (24) is then generalized to

$$\vec{\mathrm{T}}(r) = \sum_\alpha a_\alpha \vec{\mathrm{T}}_\alpha(r) = \sum a_\alpha [\, \epsilon_\alpha(r) - \epsilon_0^{(\alpha)}]\, \vec{\mathrm{E}}_\alpha(r) \ . \tag{46}$$

The trial value ϵ^* is now a quadratic form in a_α. The diagonal terms of this form can be evaluated in the case of a two-phase system, as in (32), by solving a pair of equations, represented by

$$(\epsilon - \epsilon_0^{(\alpha)})^2/(\epsilon - \epsilon_0) + (\epsilon_0^{(\alpha)})^2/\epsilon_0 = b_\alpha \epsilon_\alpha \tag{47}$$

to get b_α and $\epsilon_0^{(\alpha)}$ for each of the known properties α.

The off-diagonal terms of the quadratic form include the integral

$$\int \epsilon_{\alpha\beta} \vec{\mathrm{E}}_\alpha \cdot \vec{\mathrm{E}}_\beta \, dr, \quad \alpha \neq \beta \ , \tag{48}$$

where

$$\epsilon_{\alpha\beta}(r) \equiv \frac{(\epsilon_\alpha - \epsilon_0^{(\alpha)})(\epsilon_\beta - \epsilon_0^{(\beta)})}{\epsilon - \epsilon_0} + \frac{\epsilon_0^{(\alpha)} \epsilon_0^{(\beta)}}{\epsilon_0} \ . \tag{49}$$

For two-phase systems, this can be evaluated by using a trick due to Prager[6]: we write

$$\epsilon_{\alpha\beta}(r) = A_{\alpha\beta} \epsilon_\beta(r) + A_{\beta\alpha} \epsilon_\alpha(r) \quad \text{for } \alpha \neq \beta \ , \tag{50}$$

where

$$A_{\alpha\beta} \equiv \frac{\epsilon_1^{(\alpha\beta)} \epsilon_2^{(\alpha)} - \epsilon_2^{(\alpha\beta)} \epsilon_1^{(\alpha)}}{\epsilon_1^{(\beta)} \epsilon_2^{(\alpha)} - \epsilon_1^{(\alpha)} \epsilon_2^{(\beta)}} \ , \tag{51}$$

and the subscripts 1, 2 refer, as before, to the two phases. Consequently, we find that

$$\frac{1}{V} \int \epsilon_{\alpha\beta} \vec{\mathrm{E}}_\alpha \cdot \vec{\mathrm{E}}_\beta \, dr = (A_{\alpha\beta} \epsilon_e^{(\beta)} + A_{\beta\alpha} \epsilon_e^{(\alpha)}) E_0^2 \ , \tag{52}$$

and the trial value for ϵ_e can be written

$$\begin{aligned} \epsilon^* = \epsilon_0 &- \sum_\alpha a_\alpha^2 \left(b_\alpha \epsilon_e^{(\alpha)} - \frac{(\epsilon_0^{(\alpha)})^2}{\epsilon_0} \right) \\ &- \sum_{\alpha \neq \beta} \sum a_\alpha a_\beta \left(A_{\alpha\beta} \epsilon_e^{(\beta)} + A_{\beta\alpha} \epsilon_e^{(\alpha)} - \frac{\epsilon_0^{(\alpha)} \epsilon_0^{(\beta)}}{\epsilon_0} \right) \\ &+ 2 \sum_\alpha a_\alpha (\epsilon_e^{(\alpha)} - \epsilon_0^{(\alpha)}) \ . \end{aligned} \tag{53}$$

The stationary value of this quadratic form, which still depends on ϵ_0, provides an upper (lower) bound on ϵ_e when $\epsilon_0 > \epsilon$ ($0 < \epsilon_0 < \epsilon$). Numerical experiments indicate that when ϵ_0 is chosen to give the lowest upper bound or the highest lower bound, the results for ϵ_0, $\epsilon_0^{(\alpha)}$, b_α, and ϵ^* are all rational functions of the various ϵ's entering the problem. Moreover, the optimum values of ϵ_0, $\epsilon_0^{(\alpha)}$, and b_α are independent of $\epsilon_e^{(\alpha)}$. We have been unable, however, to determine the analytical expression for any of these quantities, and this remains an open problem. In the following subsections we will therefore restrict our discussion to cases where there is information about only one bulk property ϵ_e^*.

E. Combination of A- and C-type trial functions

A trial function which takes advantage of the known volume fractions of a two-phase system, as well as the information about another effective bulk coefficient ϵ_e^*, is a combination of the func-

tions from Secs. III A and III C

$$\vec{\mathrm{T}}(r) = a\vec{\mathrm{T}}_+(r) + T_0\vec{\mathrm{E}}_0 \ , \tag{54}$$

where a and T_0 are now variational parameters. When this form is substituted in (4), we get some integrals that were already encountered in Secs. III A–III D, as well as a couple of new ones, namely,

$$T_0\vec{\mathrm{E}}_0 \cdot \int \vec{\mathrm{E}}' dr = 0 \ , \tag{55}$$

where the integral vanishes because of (6), and

$$\int \frac{\vec{\mathrm{T}}_+(r)\,dr}{\epsilon(r) - \epsilon_0} = \frac{1}{\epsilon_1 - \epsilon_0}\int \vec{\mathrm{T}}_+(r)\,\theta_1(r)\,dr + \frac{1}{\epsilon_2 - \epsilon_0}\int \vec{\mathrm{T}}_+(r)\,\theta_2(r)\,dr \ . \tag{56}$$

Even though we do not know the function $\vec{\mathrm{T}}_+(r)$, we can determine the last two integrals in (56) exactly. To that end we note that $\vec{\mathrm{T}}_+$ satisfies

$$\frac{1}{V}\int \vec{\mathrm{T}}_+(r)\,dr = \frac{1}{V}\int (\epsilon_+ - \epsilon_0^+)\vec{\mathrm{E}}_+ dr = (\epsilon_e^+ - \epsilon_0^+)\vec{\mathrm{E}}_0 \ , \tag{57}$$

$$\frac{1}{V}\int \vec{\mathrm{E}}_+(r)\,dr = \frac{1}{V}\int \frac{\vec{\mathrm{T}}_+\,dr}{\epsilon_+ - \epsilon_0^+} = \vec{\mathrm{E}}_0 \ . \tag{58}$$

Expressing the $\vec{\mathrm{T}}_+$ integrals in these equations as linear combinations of

$$\int \vec{\mathrm{T}}_+\theta_1\,dr \quad \text{and} \quad \int \vec{\mathrm{T}}_+\theta_2\,dr \ , \tag{59}$$

we can solve the resulting equations to get

$$\begin{aligned} \frac{1}{V}\int \vec{\mathrm{T}}_+\theta_1\,dr &= \vec{\mathrm{E}}_0\,\frac{(\epsilon_e^+ - \epsilon_2^+)(\epsilon_1^+ - \epsilon_0^+)}{\epsilon_2^+ - \epsilon_1^+} \ , \\ \frac{1}{V}\int \vec{\mathrm{T}}_+\theta_2\,dr &= \vec{\mathrm{E}}_0\,\frac{(\epsilon_e^+ - \epsilon_1^+)(\epsilon_2^+ - \epsilon_0^+)}{\epsilon_1^+ - \epsilon_2^+} \ . \end{aligned} \tag{60}$$

Besides using these expressions, we must also choose ϵ_0^+ and b so as to satisfy (31) and (36) in order that we may express U_T in terms of known quantites. In this way we get a trial value for ϵ_e that is a quadratic function of the variational parameters a, T_0. The stationary value of this function still depends on ϵ_0, which must be varied within certain limits [i.e., $0 < \epsilon_0 < \min(\epsilon_1, \epsilon_2)$ or $\epsilon_0 > \max(\epsilon_1, \epsilon_2)$] in order to find the best lower or upper bound on ϵ_e.

Carrying out this program by numerical experimentation and using both variational principles of Sec. II, we have found that the best upper bound is obtained when ϵ_0^+ assumes some finite, nonzero value, and likewise for the best lower bound. While we have not been able to characterize these optimum values analytically, we have found experimentally that the bounds are then identical with Prager's bounds for this case—Eqs. (27a)–(28b) of Ref. 6. These bounds can be characterized in the following way. We define an approximation ϵ^* to ϵ_e by the following equation:

$$\frac{\epsilon_2}{\epsilon^* - \epsilon_2} - \frac{\epsilon_2^+}{\epsilon_e^+ - \epsilon_2^+} = \frac{1}{p_1}\,\frac{\epsilon_1^+\epsilon_2 - \epsilon_2^+\epsilon_1}{(\epsilon_1 - \epsilon_2)(\epsilon_1^+ - \epsilon_2^+)} \ . \tag{61}$$

The solution of (61) for ϵ^* provides an upper (lower) bound on ϵ_e if

$$\epsilon_1^+\epsilon_2 - \epsilon_2^+\epsilon_1 \tag{62}$$

is positive (negative). Note that if all the ϵ's in (61) and (62) are replaced by $\tilde{\epsilon}$'s, one gets exactly the same bound on ϵ_e. These equations are not invariant, however, under a permutation of the two phases. In fact, if (61) and (62) lead to a lower (upper) bound, then the permuted equations lead to an upper (lower) bound. We are thus always led to one upper and one lower bound in every case.

The relation between (61) and (62) and Prager's formulation of these bounds is as follows: Eqs. (28a) and (27a) of Ref. 6 are equivalent to our Eq. (61) with a positive and a negative sign, respectively, for (62). Similarly, Eqs. (27b) and (28b) of Ref. 6 are equivalent to the $\tilde{\epsilon}$ version of (61) with a positive and a negative sign, respectively, for the $\tilde{\epsilon}$ version of (62).

Prager's derivation of these bounds is of course much more satisfactory than ours, since it does not rely on any "numerical experimentation" but is a true analytical proof. The main value of our less rigorous derivation is to give us confidence in our partly empirical approach for deriving bounds. This approach becomes important for the case discussed in the following subsection, since at present it is the only method by which we have been able to arrive at any results.

F. Combination of B- and C-type trial functions

The trial function we shall be discussing here, for an isotropic or a cubic two-phase system, is a linear combination of the Hashin-Shtrikman function from Sec. III B and the function used in (24) of Sec. III C:

$$\vec{\mathrm{T}}(r) = a\vec{\mathrm{T}}_+(r) + [T_1\theta_1(r) + T_2\theta_2(r)]\vec{\mathrm{E}}_0 \ . \tag{63}$$

This form will enable us to take advantage of the information about the known quantity ϵ_e^+, as well as

the explicit geometric information about the volume fractions and the macroscopic rotational symmetry. We will now describe in detail the derivation of bounds on ϵ_e from the trial function of (63).

In order to evaluate the variational integral U_T of (4), we must use all the tricks of Hashin and Shtrikman[2] as well as the tricks developed in Sec. III C and E. In particular, we must use (60), (A22), (36), and (31). In this way we get the following trial value for ϵ_e:

$$\epsilon^* = \epsilon_0 - a^2\left(\epsilon_e^+ b - \frac{(\epsilon_0^+)^2}{\epsilon_0}\right) - T_1^2\left(\frac{p_1}{\epsilon_1-\epsilon_0}+\frac{p_1p_2}{3\epsilon_0}\right)$$
$$- T_2^2\left(\frac{p_2}{\epsilon_2-\epsilon_0}+\frac{p_1p_2}{3\epsilon_0}\right) + 2T_1T_2\frac{p_1p_2}{3\epsilon_0}$$
$$- 2aT_1\left[p_1\frac{\epsilon_0^+}{\epsilon_0}+\frac{\epsilon_e^+-\epsilon_2^+}{\epsilon_1^+-\epsilon_2^+}\left(\frac{\epsilon_1^+-\epsilon_0^+}{\epsilon_1-\epsilon_0}-\frac{\epsilon_0^+}{\epsilon_0}\right)\right]$$
$$- 2aT_2\left[p_2\frac{\epsilon_0^+}{\epsilon_0}+\frac{\epsilon_e^+-\epsilon_1^+}{\epsilon_2^+-\epsilon_1^+}\left(\frac{\epsilon_2^+-\epsilon_0^+}{\epsilon_2-\epsilon_0}-\frac{\epsilon_0^+}{\epsilon_0}\right)\right]$$
$$+ 2a(\epsilon_e^+-\epsilon_0^+)+2(p_1T_1+p_2T_2)\,. \qquad (64)$$

This is a quadratic form in a, T_1, T_2 whose stationary value can be found explicitly without any difficulty. The stationary value of ϵ^* depends on ϵ_0 in a very complicated way, partly through b and ϵ_0^+, which are determined by (36) and (31) and which turn out to be nonrational functions of ϵ_0. Since we were not able to analyze this dependence analytically, we have resorted to numerical experimentation, as in some previous subsections of Sec. III. We have thus concluded that the stationary value of ϵ^* is not a monotonic function of ϵ_0 even when ϵ_0 is restricted to be in one of the two regions $0<\epsilon_0<\min(\epsilon_1,\epsilon_2)$, $\epsilon_0>\max(\epsilon_1,\epsilon_2)$. But these experiments have also shown that the best bounds on ϵ_e are obtained from the stationary value $\epsilon^*(\epsilon_0)$ when ϵ_0 is chosen so that $\epsilon_0^+=0$ or $\epsilon_0^+=\infty$, as we also found in Sec. III C.

Using this hindsight, we can now assume $\epsilon_0^+=0$ from the outset. As a result of this our equations simplify considerably, and we now get the following explicit expressions for both ϵ_0 and b from (36) and (31):

$$\epsilon_0 = (\epsilon_2^+\epsilon_1 - \epsilon_1^+\epsilon_2)/(\epsilon_2^+-\epsilon_1^+)\,, \qquad (65)$$

$$b = (\epsilon_2^+-\epsilon_1^+)/(\epsilon_2-\epsilon_1)\,. \qquad (66)$$

We substitute these results, as well as $\epsilon_0^+=0$, into (64), and determine analytically the stationary value of ϵ^* with respect to variations of T_1, T_2, a. A tedious but straightforward calculation leads to the following expression for that stationary value

$$\epsilon^* = [A'(\epsilon_e^+)^2 + B'\epsilon_e^+ + C']/[A(\epsilon_e^+)^2 + B\epsilon_e^+ + C]\,, \qquad (67)$$

where

$$A = -[(\epsilon_2^+-\epsilon_1^+)/(\epsilon_2-\epsilon_1)^3]\langle 1/\epsilon_+\rangle\,,$$
$$B = \frac{\epsilon_2^+-\epsilon_1^+}{(\epsilon_2-\epsilon_1)^3}\left(2+\frac{p_1p_2}{\epsilon_1^+\epsilon_2^+}(\epsilon_2^+-\epsilon_1^+)^2\right)$$
$$+\frac{p_1p_2}{3}\frac{(\epsilon_2^+-\epsilon_1^+)^3}{\epsilon_2^+\epsilon_1-\epsilon_1^+\epsilon_2}\left\langle\frac{1}{\epsilon_+}\right\rangle,$$
$$C = -\frac{\epsilon_2^+-\epsilon_1^+}{(\epsilon_2-\epsilon_1)^3}\langle\epsilon_+\rangle$$
$$-\frac{p_1p_2}{3}\frac{(\epsilon_2^+-\epsilon_1^+)^3}{(\epsilon_2-\epsilon_1)^2(\epsilon_2^+\epsilon_1-\epsilon_1^+\epsilon_2)}, \qquad (68)$$
$$A' = -\frac{1}{(\epsilon_2-\epsilon_1)^2}\left(1+\frac{p_1p_2}{\epsilon_1^+\epsilon_2^+}(\epsilon_2^+-\epsilon_1^+)^2\right)$$
$$+\frac{p_1p_2}{3}\frac{(\epsilon_2^+-\epsilon_1^+)^2}{(\epsilon_2-\epsilon_1)(\epsilon_2^+\epsilon_1-\epsilon_1^+\epsilon_2)}\left\langle\frac{1}{\epsilon_+}\right\rangle,$$
$$B' = \frac{\langle\epsilon_+\rangle}{(\epsilon_2-\epsilon_1)^2}\left(2+\frac{p_1p_2}{\epsilon_1^+\epsilon_2^+}(\epsilon_2^+-\epsilon_1^+)^2\right)$$
$$-\frac{p_1p_2}{3}\frac{(\epsilon_2^+-\epsilon_1^+)^2}{(\epsilon_2-\epsilon_1)(\epsilon_2^+\epsilon_1-\epsilon_1^+\epsilon_2)},$$
$$C' = -\langle\epsilon_+\rangle^2/(\epsilon_2-\epsilon_1)^2\,.$$

Further numerical experiments, using these expressions, indicated that the numerator and the denominator of (67) have a common factor—a fact which is not at all obvious from (68). Subsequently, this factor was identified as $\epsilon_e^+ - 1/\langle\tilde{\epsilon}_+\rangle$. When it was cancelled out we obtained, after tedious manipulations, the following equation that is equivalent to (67)

$$\frac{\epsilon_2^+-\epsilon_1^+}{\epsilon_e^+-\langle\epsilon_+\rangle}-\frac{\epsilon_2-\epsilon_1}{\epsilon^*-\langle\epsilon\rangle}=\frac{3}{p_1p_2}\frac{\epsilon_2^+\epsilon_1-\epsilon_1^+\epsilon_2}{(\epsilon_2^+-\epsilon_1^+)(\epsilon_2-\epsilon_1)}\,. \qquad (69)$$

From the properties of the variational integral U_T, one can expect that the approximation ϵ^* derived for ϵ_e from this equation is an upper or a lower bound on ϵ_e if ϵ_0 of (65) satisfies

$$\epsilon_0 > \max(\epsilon_1,\epsilon_2) \qquad (70)$$

or

$$0<\epsilon_0<\min(\epsilon_1,\epsilon_2)\,, \qquad (71)$$

respectively. Using (43), we can write [note that (65) and (39) are identical expressions for ϵ_0]

$$\epsilon_i-\epsilon_0=\epsilon_i^+(\epsilon_2-\epsilon_1)/(\epsilon_2^+-\epsilon_1^+)\,,\quad i=1,2\,. \qquad (72)$$

Therefore, $\epsilon_0-\epsilon_1$ and $\epsilon_0-\epsilon_2$ always have the same sign, equal to the sign of

$$-(\epsilon_2-\epsilon_1)/(\epsilon_2^+-\epsilon_1^+)\,. \qquad (73)$$

However, if $\epsilon_0<0$, we cannot use this argument to show that ϵ^* provides a bound because (71) is violated. In that case, it is easy to see from (72) that $\epsilon_2-\epsilon_1$ and $\epsilon_2^+-\epsilon_1^+$ must have the same sign. Consequently, if we switch the roles of ϵ and ϵ_+ we find that the transformed version of (65) satis-

fies

$$\frac{\epsilon_2\epsilon_1^+ - \epsilon_1\epsilon_2^+}{\epsilon_2 - \epsilon_1} = -\frac{\epsilon_2^+\epsilon_1 - \epsilon_1^+\epsilon_2}{\epsilon_2^+ - \epsilon_1^+}\,\frac{\epsilon_2^+ - \epsilon_1^+}{\epsilon_2 - \epsilon_1} > 0\,. \tag{74}$$

Since (69) is invariant under the permutation of ϵ and ϵ_+, we can look upon it as an equation for ϵ_e^+ given ϵ^*, and use the transformed versions of (70) and (71) to decide whether ϵ_e^+ is an upper or a lower bound on ϵ^*.

Similarly to what we found earlier in Sec. III C, the approximation ϵ^* obtained from (69) thus always provides a bound on ϵ_e. This bound is an upper (lower) bound on ϵ_e if

$$(\epsilon_2^+\epsilon_1 - \epsilon_1^+\epsilon_2)/(\epsilon_1 - \epsilon_2) \tag{75}$$

is positive (negative). This result, as well as (69), is invariant under a permutation of the two phases, and we thus get a single upper or lower bound.

In order to obtain the other bound we have to go to the other extreme in ϵ_0^+, namely, $\epsilon_0^+ = \infty$, and make our way through a similarly tedious calculation. Alternatively, we can use the other variational principle of Sec. II—the one built around U_R of (13)—with a form for the trial function R that is similar to (63). This leads to similar calculations and to bounds which are identical to the ones obtained from U_T. The bound we are looking for is now obtained by assuming $\tilde{\epsilon}_0^+ = 0$ from the outset. The whole procedure for U_R then exactly reproduces *all* of the equations of this subsection, except that T is replaced by R, every ϵ is replaced by $\tilde{\epsilon} \equiv 1/\epsilon$, and every factor $\frac{1}{3}$ is replaced by $\frac{2}{3}$ [this is explained in the Appendix following Eq. (A23)]. This symmetry thus allows us to get the other bound on ϵ_e from a simple transformation of (69) and (75)

$$\frac{\tilde{\epsilon}_2^+ - \tilde{\epsilon}_1^+}{\tilde{\epsilon}_e^+ - \langle\tilde{\epsilon}_+\rangle} - \frac{\tilde{\epsilon}_2 - \tilde{\epsilon}_1}{\tilde{\epsilon}^* - \langle\tilde{\epsilon}\rangle} = \frac{3}{2p_1p_2}\,\frac{\tilde{\epsilon}_2^+\tilde{\epsilon}_1 - \tilde{\epsilon}_1^+\tilde{\epsilon}_2}{(\tilde{\epsilon}_2^+ - \tilde{\epsilon}_1^+)(\tilde{\epsilon}_2 - \tilde{\epsilon}_1)}, \tag{76}$$

$$(\tilde{\epsilon}_2^+\tilde{\epsilon}_1 - \tilde{\epsilon}_1^+\tilde{\epsilon}_2)/(\tilde{\epsilon}_1 - \tilde{\epsilon}_2)\,. \tag{77}$$

The solution of (76) for $\tilde{\epsilon}^*$ yields an upper (lower) bound on $\tilde{\epsilon}_e$ when (77) or (75) is positive (negative).

In order to demonstrate the quality of the bounds produced by (69) and (76), we have computed them for a series of examples characterized by

$$p_1 = p_2 = \tfrac{1}{2}\,,\quad \epsilon_1^+ = \epsilon_1 = 1\,,\quad \epsilon_2^+ = \tfrac{1}{3}\,,\quad \epsilon_e^+ = \tfrac{3}{5}\,, \tag{78}$$

and values of ϵ_2 ranging between 0 and 10. These bounds are listed in Table I, along with the bounds produced for the same examples by three other methods:

(a) the Hashin and Shtrikman bounds,[2,3] described in Sec. III B and given explicitly in Eq.

TABLE I. Upper and lower bounds (ϵ_u and ϵ_l, respectively) on ϵ_e produced by various methods for the following example: $p_1 = p_2 = \frac{1}{2}$, $\epsilon_1^+ = \epsilon_1 = 1$, $\epsilon_2^+ = \frac{1}{3}$, $\epsilon_e^+ = \frac{3}{5}$, $\epsilon_2 =$ as shown in the left-hand column. $\Delta\epsilon$ denotes the difference between a pair of upper and lower bounds $\Delta\epsilon \equiv \epsilon_u - \epsilon_l$; HS refers to the Hashin-Shtrikman bounds [Eqs. (4.7) and (4.8) of Ref. 2, Eq. (3) of this paper]; P refers to Prager's best bounds [Eqs. (51), (52a), and (52b) of Ref. 3]; I refers to the polynomial bounds described in Ref. 7 [Eqs. (48)–(51) of that reference]; II refers to the bounds of this paper [Eqs. (69) and (76)]. All of these methods assume that the macroscopic rotational symmetry of the composite material is either isotropic or cubic. All the methods except HS also use the information about ϵ_e^+.

ϵ_2	HS			P			I			II		
	ϵ_l	ϵ_u	$\Delta\epsilon$	ϵ_l	ϵ_u	$\Delta\epsilon$	ϵ_l	ϵ_u	$\Delta\epsilon$	ϵ_l	ϵ_u	$\Delta\epsilon$
0	0	0.4000	0.40	0	0.3182	0.32	0	0.3014	0.30	0	0.2500	0.25
0.1	0.2800	0.4706	0.191	0.3149	0.4130	0.098	0.3088	0.4018	0.093	0.3284	0.3813	0.053
0.2	0.4400	0.5385	0.099	0.4676	0.4982	0.031	0.4658	0.4923	0.027	0.4737	0.4857	0.012
0.4	0.6400	0.6667	0.0267	0.6480	0.6524	0.0043	0.6491	0.6525	0.0035	0.6500	0.6512	0.0012
0.6	0.7800	0.7857	57×10^{-4}	0.7808	0.7836	28×10^{-4}	0.7810	0.7840	28×10^{-4}	0.7818	0.7826	8×10^{-4}
0.8	0.8960	0.8966	55×10^{-5}	0.8960	0.8964	41×10^{-5}	0.8960	0.8965	48×10^{-5}	0.8962	0.8963	11×10^{-5}
1.5	1.2308	1.2353	45×10^{-4}	1.2310	1.2352	42×10^{-4}	1.2305	1.2352	47×10^{-4}	1.2329	1.2344	15×10^{-4}
3	1.7500	1.8750	0.125	1.7586	1.8718	0.113	1.7399	1.8741	0.134	1.8000	1.8571	0.057
6	2.3636	3.0968	0.29	2.4053	3.0814	0.26	2.3143	3.0949	0.31	2.5979	3.0192	0.14
10	2.8000	4.7059	1.91	2.8832	4.6712	1.79	2.7031	4.7035	2.00	3.2836	4.5357	1.25

(3) (recall that these bounds do not include information about ϵ_e^+);

(b) the best bounds of Ref. 6 [Eqs. (51), (52a), and (52b) of that reference]. These bounds include information about the known value ϵ_e^+, as well as about the volume fractions and the rotational symmetry. Note that these bounds are different (i.e., more stringent) from the other bounds obtained in that reference, which were described in Sec. III E and which do not assume any rotational symmetry;

(c) the best bounds of Ref. 7 [Eqs. (48)–(51) of that reference]. These bounds also include information about ϵ_e^+, as well as about volume fractions and rotational symmetry.

From this table, and in particular from the columns that give the difference $\Delta\epsilon$ between the upper and lower bounds obtained with each method, it is clear that (69) and (76) always lead to better bounds than any of the other methods, and that in most cases the improvement is a major one.

IV. CONCLUDING REMARKS

We have shown that the variational principle of Hashin and Shtrikman[2] can be used effectively for a two-phase system with trial functions that include information on one other effective bulk coefficient of the same material. This necessitates an evaluation of some terms in the variational integral by methods that are different from those that were used for the trial function of Ref. 2. In this way, various bounds on ϵ_e were obtained which depend on the variational parameters of the trial function and on ϵ_0, the free parameter of the variational integral. All of these parameters were then adjusted in order to obtain the highest lower bound and the lowest upper bound in each case.

The results we got were always in the form of absolute bounds on ϵ_e—this follows rigorously from the variational principle. However, we do not know whether these bounds are optimum bounds, namely, whether with the given information it is possible to have a system whose ϵ_e is equal to one of the bounds. (This property was demonstrated for the Hashin-Shtrikman bounds in the case of a two-phase system.[2])

Moreover, we were not even able to prove rigorously (i.e., analytically) that our choice for ϵ_0 was the best choice in any of the cases discussed in Secs. III C, III E, and III F. We made our choice in these cases purely on the basis of the empirical evidence provided by numerical experimentation. Even when we made this "best choice," our analytical derivations did not lead in any natural way to the highly symmetric form of the expressions for the various bounds that we eventually managed to obtain by laborious manipulations.

These difficulties, when contrasted with the beautiful symmetry and simplicity of the final results, lead us to suspect that there must exist a different, perhaps more sophisticated, mathematical approach to this problem. Such an approach might be expected to lead to the same results but in a more natural way, and also be able to provide rigorous proofs for those points that we had to establish empirically.

As we showed in Sec. III D, our methods can be applied also to two-phase systems where more than one bulk property is known. However, we were unable to characterize the resulting best bounds analytically. The main difficulty here is our inability to obtain an analytical expression for the best choice of ϵ_0. Once we know the correct choice of ϵ_0, then the best bound may be calculated by simply finding the stationary value of a quadratic form [Eq. (53) of Sec. III D, or an appropriate generalization of (64)]. But even though numerical experiments have indicated that the best bound is a rational function of all the ϵ's in the problem, and that the best value for ϵ_0 is a similar kind of rational function but is independent of any of the ϵ_e's, we have not been able to determine the analytical form of either the bound itself or of the appropriate ϵ_0. It seems that progress in these matters too will require a more powerful analytical approach to the discussion of the variational principle.

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APPENDIX: EVALUATION OF U_T AND U_R FOR HASHIN AND SHTRIKMAN'S TRIAL FUNCTION

The crucial step in evaluating U_T or U_R with the Hashin-Shtrikman trial function is to calculate the last term in (4) or (13), i.e.,

$$\frac{1}{V}\int \vec{T}\cdot\vec{E}'\,dr \tag{A1}$$

and

$$\frac{1}{V}\int \vec{R}\cdot\vec{D}'\,dr\,. \tag{A2}$$

The evaluation of both of these integrals involves similar calculations, and we will therefore continue to discuss them in parallel: We will often list side by side a pair of corresponding equations arising from the two discussions.

We represent the trial function by imagining each phase of the composite to be made up of a large number of finite, bounded portions, which we will call grains. We will assume that these grains are

distributed over the total volume in such a way that, on the average, the system is not only homogeneous but possesses a high degree of rotational symmetry as well: either complete isotropy or at least cubic symmetry. Obviously, this kind of description in terms of bounded grains can always be applied, even if some of the phases stretch continuously over the system from end to end. If $\theta_i(\vec{r})$ denotes a function equal to 1 for $\vec{r}$ inside the grain i and equal to 0 for $\vec{r}$ outside that grain, then the trial functions $\vec{T}$ and $\vec{R}$ can be written

$$\vec{T}(\vec{r}) = \sum_i \vec{T}_i \theta_i(\vec{r}), \quad \vec{R}(\vec{r}) = \sum_i \vec{R}_i \theta_i(\vec{r}), \tag{A3}$$

where all the $\vec{T}_i$ or $\vec{R}_i$ belonging to a single pure phase are equal.

We now represent the curl-free vector fields $\vec{E}'$ and $\vec{D}' + \vec{R}/\tilde{\epsilon}_0$ as gradients of scalar fields ψ and φ, where ψ and φ are each represented as a sum of contributions whose source is a single grain

$$\vec{E}' = -\nabla\psi, \quad \vec{D}' + \vec{R}/\tilde{\epsilon}_0 = \nabla\varphi, \tag{A4}$$

$$\psi = \sum_i \psi_i, \quad \varphi = \sum_i \varphi_i, \tag{A5}$$

$$\nabla^2\psi_i = 1/\epsilon_0 \vec{T}_i \cdot \nabla\theta_i, \quad \nabla^2\varphi_i = 1/\tilde{\epsilon}_0 \vec{R}_i \cdot \nabla\theta_i, \tag{A6}$$

$$\psi_i = 0 \text{ on the surface}$$
$$\tilde{\epsilon}_0 \frac{\partial\varphi_i}{\partial n} = R_{in}\theta_i \text{ on the surface}. \tag{A7}$$

Note that the boundary condition on φ_i is in fact usually $\partial\varphi_i/\partial n = 0$, except for cases where the grain i is at the surface. A solution to (A6) is given by

$$\psi_i(\vec{r}) = -\frac{\vec{T}_i}{4\pi\epsilon_0} \cdot \int \frac{\nabla\theta_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}',$$
$$\varphi_i(\vec{r}) = -\frac{\vec{R}_i}{4\pi\tilde{\epsilon}_0} \cdot \int \frac{\nabla\theta_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'. \tag{A8}$$

Although these solutions do not satisfy the boundary conditions of (A7), the correction we would have to add to each of them in order to repair that fault would be of order $O(1/V)$ if both $\vec{r}$ and $\vec{r}'$ are well away from the surface. We can therefore use (A8) to represent ψ_i and φ_i inside the grain i and also in its vicinity, but not over the entire system.

The total potential field ψ or φ inside the grain i is made up of three contributions: (a) the internal self-field of that grain, (b) the field produced by all other grains situated within a finite spherical region S_i centered around the grain i, and (c) the field produced by the rest of the system outside S_i. If S_i is large enough, the latter contribution can be taken as the field produced by a uniform electric polarization $\vec{P}_T$ (or $\vec{P}_R$) given by [see (A6)]

$$\vec{P}_T = \frac{1}{4\pi\epsilon_0}\frac{1}{V}\int \vec{T}(\vec{r})\, d\vec{r} = \frac{1}{4\pi\epsilon_0}\langle\vec{T}\rangle;$$
$$\vec{P}_R = \frac{1}{4\pi\tilde{\epsilon}_0}\langle\vec{R}\rangle. \tag{A9}$$

The average used here and elsewhere in this Appendix has the same meaning as the average defined in (2) since we are taking all of the $\vec{T}_i$ (or $\vec{R}_i$) belonging to a single phase to be equal.

Using (A3) to substitute in (A1) and (A2), we evaluate these integrals grain by grain. In each grain, we separate the fields $\vec{E}'$ and $\vec{D}'$ into a "near-field contribution," corresponding to (a) and (b), and a "far-field contribution," corresponding to (c).

The near-field contribution to (A1) is given by

$$\frac{1}{V}\int d\vec{r} \sum_i \vec{T}_i \theta_i(\vec{r}) \cdot [-\nabla\psi(\vec{r})]_{\text{near}}$$
$$= \frac{1}{4\pi\epsilon_0}\sum_i \sum_{j\in S_i} \sum_{\alpha,\beta} T_{i\alpha} T_{j\beta} \frac{1}{V} \int d\vec{r} \int d\vec{r}'\, \theta_i(\vec{r})\theta_j(\vec{r}') \times \nabla_\alpha \nabla_\beta \frac{1}{|\vec{r} - \vec{r}'|}, \tag{A10}$$

where we have used the near-field restriction $j \in S_i$ in performing a partial integration over $\vec{r}'$. If one restricts the sums on i and j to a particular phase or pair of phases I and J then, since $\vec{T}_i$ and $\vec{T}_j$ are constant, one can sum first over the product of θ functions

$$\sum_i \sum_{\substack{I,\, j\in J \\ j\in S_i}} \theta_i(\vec{r})\theta_j(\vec{r}') \equiv g_{IJ}(\vec{r}, \vec{r}'). \tag{A11}$$

The function $g_{IJ}(\vec{r}, \vec{r}')$ is a truncated correlation function which is equal to 0 for large separations $|\vec{r} - \vec{r}'|$. For separations somewhat below the radius of S_i, this correlation function tends to the probability for finding $\vec{r}$ in the phase I and $\vec{r}'$ in the phase J, and for $\vec{r} = \vec{r}'$ it satisfies

$$g_{IJ}(\vec{r}, \vec{r}) = p_I \delta_{IJ}, \tag{A12}$$

where p_I is the volume fraction of the phase I. Finally, for arbitrary $\vec{r}$ and $\vec{r}'$, g_{IJ} has the same rotational symmetry as the multiphase mixture. When that symmetry is either cubic or isotropic, then the double integral

$$\frac{1}{V}\int d\vec{r} \int d\vec{r}'\, g_{IJ}(\vec{r}, \vec{r}')\nabla_\alpha \nabla_\beta \frac{1}{|\vec{r} - \vec{r}'|}, \tag{A13}$$

which must yield a constant second rank tensor, must be proportional to $\delta_{\alpha\beta}$. Consequently, we can rewrite (A13) as

$$\frac{1}{3V}\int dr \int dr' g_{IJ}(r,r')\nabla^2\frac{1}{|r-r'|} = -\tfrac{4}{3}\pi p_I \delta_{IJ} \,. \tag{A14}$$

Using this result in (A10), and summing now over the phases I and J, we get the following result for the near-field contribution to (A1)

$$-\frac{1}{3\epsilon_0}\sum_I p_I T_I^2 = -(1/3\epsilon_0) - \frac{1}{3\epsilon_0}\langle T^2\rangle \,. \tag{A15}$$

Similar considerations lead to the following expression for the near-field contribution to (A2):

$$\frac{1}{V}\int dr \sum_i \vec{R}_i \theta_i(r)\cdot\left(\nabla\varphi(r) - \frac{\vec{R}(r)}{\tilde{\epsilon}_0}\right)_{\text{near}} = \frac{1}{3\tilde{\epsilon}_0}\langle R^2\rangle - \frac{1}{\tilde{\epsilon}_0}\langle R^2\rangle = -\frac{2}{3\tilde{\epsilon}_0}\langle R^2\rangle \,. \tag{A16}$$

In order to evaluate the far-field contribution to (A1), we note that the far field at the center of S_i is just the usual internal Lorentz field intensity $\vec{E}_{\text{ext}} + 4\pi\vec{P}_T/3$. Because of the boundary condition on ψ, the external field $\vec{E}_{\text{ext}}$ vanishes in this case, and we have

$$(\vec{E}')_{\text{far}} = \tfrac{1}{3}(4\pi\vec{P}_T) = \langle\vec{T}\rangle/3\epsilon_0 \,. \tag{A17}$$

Consequently, the far-field contribution to (A1) is

$$\frac{1}{V}\int \vec{T}(r)\cdot\frac{\langle\vec{T}\rangle}{3\epsilon_0} = \frac{\langle\vec{T}\rangle^2}{3\epsilon_0} \,. \tag{A18}$$

The far-field contribution to $\vec{D}'$ is due entirely to $\nabla\varphi$, since $\vec{R}(r)$ contributes only to the self-field in any grain. At the center of S_i, this is again an internal Lorentz field but now the external field does not vanish: Because of the boundary condition on φ, which merely reflects the existence of a uniform average polarization $\vec{P}_R$, there is a surface charge distribution which produces a uniform field far away in the interior whose magnitude is

$$(-\nabla\varphi)_{\text{ext}} = -4\pi\vec{P}_R = -\langle\vec{R}\rangle/\tilde{\epsilon}_0 \,. \tag{A19}$$

The Lorentz field is therefore given by

$$(-\nabla\varphi)_{\text{far}} = -4\pi\vec{P}_R + \tfrac{4}{3}\pi\vec{P}_R = -(2/3\tilde{\epsilon}_0)\langle\vec{R}\rangle \,. \tag{A20}$$

Consequently, the far-field contribution to (A2) is

$$\frac{1}{V}\int \vec{R}(r)\cdot\left(\frac{2}{3\tilde{\epsilon}_0}\langle\vec{R}\rangle\right) dr = \frac{2}{3\tilde{\epsilon}_0}\langle\vec{R}\rangle^2 \,. \tag{A21}$$

Combining the near- and far-field contributions to (A1) and (A2), we finally get

$$\frac{1}{V}\int \vec{T}\cdot\vec{E}'\,dr = -\frac{1}{3\epsilon_0}(\langle T^2\rangle - \langle T\rangle^2) \,, \tag{A22}$$

$$\frac{1}{V}\int \vec{R}\cdot\vec{D}'\,dr = -\frac{2}{3\tilde{\epsilon}_0}(\langle R^2\rangle - \langle R\rangle^2) \,. \tag{A23}$$

Note the close similarity of the two results—it leads to great simplifications in many equations of this article: An equation derived from the variational integral U_T can usually be transformed to the corresponding equation resulting from U_R by replacing all ϵ's by $\tilde{\epsilon}$'s (i.e., reciprocal ϵ's), and all factors of $\frac{1}{3}$ by factors of $\frac{2}{3}$.

Although (A22) was already obtained by Hashin and Shtrikman,[2] we have produced here a somewhat more detailed derivation, which also obtains the analogous result (A23) for the corresponding term in the other variational integral. We have also shown that these results hold not only for an isotropic system, but also for a system with a macroscopic cubic symmetry (in fact, the system can be ordered rather than random, such as a cubic lattice of identical, homogeneous spheres embedded in some other homogeneous material).

Finally, we wish to emphasize that it is important to have T equal to a constant in each of the phases in order for these results to hold. Although it should always be possible to partition any composite system into grains in such a way that $\vec{T}(r)$ is effectively constant over each grain, it is in general impossible to ensure that $\vec{T}(r)$ will remain effectively constant over an entire phase.

We will now demonstrate this caveat in the case $\vec{T}(r) = \vec{T}_+(r)$, where $\vec{T}_+$ is the exact solution of the variational equations with a given different set of dielectric constants $\epsilon_0^+, \epsilon_1^+, \epsilon_2^+, \epsilon_e^+$. This case is of practical importance since we have shown in Secs. III C–III F that this type of trial function can be used to incorporate the information about ϵ_e^+ in the generation of bounds on ϵ_e.

Consider the following portion from the variational integral U_T of (4):

$$\frac{1}{V}\int\left(-\frac{T^2}{\epsilon-\epsilon_0} + \vec{T}\cdot\vec{E}'\right) dr \,. \tag{A24}$$

By using the methods of Sec. III C [in particular, Eqs. (30)–(37)], (A24) is transformed into

$$-[b\epsilon_e^+ - (\epsilon_0^+)^2/\epsilon_0]E_0^2 \,. \tag{A25}$$

Alternatively, we could try to use (A22) to evaluate the second term in (A24). Using this method, as well as the fact that $\vec{T}_+ = (\epsilon_+ - \epsilon_0^+)\vec{E}_+$, we get the following form for (A24):

$$-\frac{1}{V}\int\frac{(2\epsilon_0+\epsilon)(\epsilon_+-\epsilon_0^+)^2}{\epsilon_0(\epsilon-\epsilon_0)}E_+^2\,dr + \frac{(\epsilon_e^+-\epsilon_0^+)^2}{3\epsilon_0}E_0^2 \,. \tag{A26}$$

In order to reduce this to an expression in terms of known quantities, we must choose ϵ_0^+ and a new parameter c so as to satisfy

$$(2\epsilon_0+\epsilon)(\epsilon_+-\epsilon_0^+)^2/\epsilon_0(\epsilon-\epsilon_0) = c\epsilon_+ \tag{A27}$$

in both phases. This leads to the following result,

supposedly equivalent to (A24) and hence to (A25):

$$-[c\epsilon_e^+ - (\epsilon_e^+ - \epsilon_0^+)^2/3\epsilon_0]E_0^2 . \quad \text{(A28)}$$

However, since both b and c are independent of ϵ_e^+, this result is clearly inconsistent with (A25), which is only linear in ϵ_e^+. Therefore, (A28) must be in error and the fault can only be in the unjustified use of (A22).

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[1]Although this result seems to be well established and widely known, we could not find a derivation in any textbook. Its first proof is ascribed in Ref. 2 to O. Wiener, Abh. Math. Phys. Kl. Sächs. Akad. Wiss. Leipz. 32, 509 (1912). A more recent derivation, cast in the language of thermal conductivity coefficients, can be found in W. Woodside and J. H. Messmer, J. Appl. Phys. 32, 1688 (1961). Other derivations can be found in Refs. 2 and 3.

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