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Calculation of bounds for some average bulk properties of composite materials

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The problem of calculating the effective bulk dielectric constant ϵ_e (or magnetic permeability or conductivity) of a macroscopically homogeneous composite material is shown to require the evaluation of a single characteristic function which includes all the relevant information about the microscopic geometry of the composite. This function is found to have some remarkable convexity properties that allow the construction of various new and improved bounds on ϵ_e for two-phase as well as for multiphase systems by incorporating information on other similar effective bulk properties of the same system.

I. INTRODUCTION

Calculations of the magnetic permeability or of the dielectric constant or of the thermal or electrical conductivity of a composite material (i.e., a material made by mixing two or more phases which remain distinct and segregated into mutally exclusive regions) from the known properties of the pure phases are all similar problems. Mathemetically they all reduce to a boundary-value problem in a straight cylinder along the x axis involving a second-order partial differential equation for the potential Φ or for the temperature:

$$\begin{aligned}
&\nabla\cdot(\epsilon\nabla\Phi)=0\,,\\
&\Phi(r)=\Phi_0, \quad \text{at } x=0\\
&\Phi(r)=\Phi_0+LE_0, \quad \text{at } x=L\\
&\frac{\partial\Phi}{\partial n}=0 \quad \text{at the other boundaries.}
\end{aligned} \tag{1}$$

Here $\epsilon(r)$ denotes the local dielectric constant, which has a different value in each phase, E_0 is a constant imposed electric field along the cylinder axis, and L is the length of the cylinder (see Fig. 1). The effective dielectric constant ϵ_e of the composite material, which can be used to describe phenomena on a length scale over which the material can be considered as homogeneous, is given by

$$\epsilon_e E_0^2 \equiv \frac{1}{V}\int \epsilon(r)(\nabla\Phi)^2\,dr\,. \tag{2}$$

The problem of solving (1) and calculating ϵ_e is usually a formidable one even when the microscopic geometry of the composite is fairly regular. But when the multiphase mixture is random, this problem becomes totally intractable because $\epsilon(r)$ is then a very complicated function of position. Indeed, Brown[1] has shown explicitly that it is not enough merely to know the volume fractions of the various phases that comprise the random mixture, and that one must have detailed statistical information about the geometry of the mixture in order to evaluate ϵ_e. Since that information is usually not available, one can try to set bounds on ϵ_e by using the available information on volume fractions and the macroscopic isotropy of the mixture. This has been done by Hashin and Shtrikman.[2] One can also assume a simplified model for the statistical properties of the mixture, as was done by Weissberg.[3] Following these early efforts, various articles have appeared in which improved bounds on ϵ_e were sought by incorporating additional statistical information about the mixture in the construction of trial functions for use with a variational principle. Many of these calculations are described, together with the appropriate references, in the chapter on heterogeneous materials in Beran's book.[4] A more recent discussion of such bounds can be found in the articles by Miller[5] and Hori.[6] Finally, one can utilize measurements of one property in a certain material to set bounds on other properties of the same material, as was done by Prager[7] for the case of two-phase systems. The latter approach is especially appealing, since it affords us almost the only way of incorporating some measured statistical information in our evaluations. Moreover, we do not need to worry about getting a detailed statistical description—the measurements effectively extract only that information which is relevant for determining bulk properties. One can thus use measurements of bulk thermal conduction to get information about

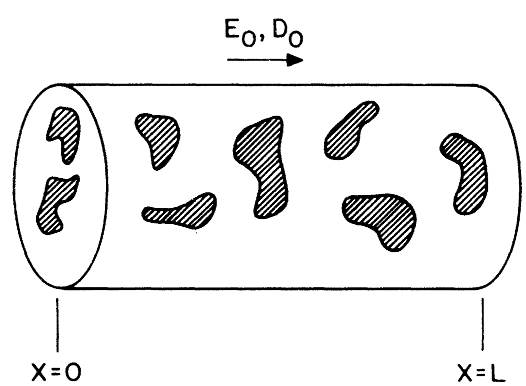

FIG. 1. Schematic drawing of a two-phase system on which the boundary value problem (1) is defined.

the bulk dielectric constant, and one can even use a measurement of ϵ_e at one temperature or frequency to get information about ϵ_e at a different temperature or frequency.

The main contribution of this paper is to point out that while the detailed calculation of ϵ_e is quite impossible, one can readily obtain a great deal of qualitative information about the function $\epsilon_e(\epsilon_1, \epsilon_2, \ldots)$, where ϵ_i are the dielectric constants of the various pure phases. This information is in the form of rigorous statements about the sign of ϵ_e and all its differentials, and results in a whole set of convexity properties for $\epsilon_e(\epsilon_i)$. From a practical point of view, these properties allow us to generate bounds on ϵ_e for two-phase systems in a simple and intuitively obvious manner from a single measured bulk property plus information about volume fractions and isotropy. These bounds offer somewhat greater flexibility than the ones derived earlier by Prager[7]: They are easy to obtain and can easily be extended to include information from any number of measured values. They are also sometimes better than Prager's bounds. More importantly, however, these convexity properties allow us for the first time to generate bounds on ϵ_e from measured values when the composite is made of more than two phases.

The outline of the rest of this paper is as follows: In Sec. II we discuss the general features of ϵ_e for a multiphase system in terms of two geometric functions which are characteristic of the material under discussion. In Sec. III we discuss the principles which enable us to generate bounds on ϵ_e of a two-phase system based on one other measurement. As an example, we obtain improved bounds for a hypothetical case of a two-phase system. We indicate how these results may be extended to incorporate results from additional measurements. In Sec. IV we extend the discussion to indicate how bounds on ϵ_e which include information from other measurements can sometimes be generated for systems consisting of more than two phases. As an example, we obtain such improved bounds for a three-phase system where the value of one average bulk property has been measured and is assumed to be known precisely. In the Appendix we give a detailed mathematical derivation of the properties of the geometric functions introduced in Sec. II.

II. CHARACTERISTIC GEOMETRIC FUNCTION FOR A COMPOSITE SYSTEM

Consider a composite material made by mixing m homogeneous phases whose dielectric constants are $\epsilon_1 \cdots \epsilon_m$. The local dielectric constant appearing in (1) can be written as

$$\epsilon(r) = \sum_1^m \epsilon_i \theta_i(r) , \tag{3}$$

where $\theta_i(r)$ is 1 or 0 when r is, respectively, inside or outside the phase i. We obviously have $\sum_1^m \theta_i = 1$. We now recast the boundary-value problem (1) into the following more convenient form

$$\begin{aligned} &\nabla \cdot [(1-\theta_u)\nabla\psi] = 0 , \\ &\psi(r) = 0, \quad \text{at } x = 0 \\ &\psi(r) = L, \quad \text{at } x = L \\ &\frac{\partial\psi}{\partial n} = 0, \quad \text{at the other boundaries} \end{aligned} \tag{4}$$

where

$$\begin{aligned} &\theta_u(r) \equiv \sum_1^{m-1} u_i \theta_i(r) , \\ &u_i \equiv 1 - \epsilon_i/\epsilon_m, \quad i = 1, \ldots, m-1 \\ &u_m \equiv 0 , \\ &\psi(r) \equiv [\Phi(r) - \Phi_0]/E_0 . \end{aligned} \tag{5}$$

Clearly, u_i and θ_u satisfy the following inequalities:

$$u_i \le 1, \quad \theta_u(r) \le 1 . \tag{6}$$

The effective (or average) dielectric constant, defined by (2), satisfies

$$1 - \frac{\epsilon_e(\epsilon_1, \ldots, \epsilon_m)}{\epsilon_m} = 1 - \frac{1}{V}\int (1-\theta_u)(\nabla\psi)^2\, dr \equiv f(u) , \qquad u \equiv (u_1, \ldots, u_m) , \tag{7}$$

where we have now defined the characteristic geometric function $f(u)$. This function, which depends only on the $m-1$ variables $u_1, \ldots, u_{m-1}$, depends in general on the detailed geometry of the composite, but is independent of the specific physical property we are considering. Once it is known for a particular material or configuration, it can be used to obtain the effective magnetic permeability or thermal conductivity from their values for the pure phases by using a formula similar to (7).

While it is usually impossible to calculate $f(u)$ with any accuracy, we can readily determine some of its remarkable qualitative features. For that purpose, we consider the first differential of ψ with respect to u:

$$\delta\psi(r, u) \equiv \sum_1^{m-1} \frac{\partial\psi}{\partial u_i}\, du_i . \tag{8}$$

This expression, which defines the δ operator, is to be understood as a linear form in the independent variables du_i, the coefficients $\partial\psi/\partial u_i$ being functions of u and r.[8] By similarly differentiating (4) and (7), we find that $\delta\psi$ satisfies the following boundary value problem

$$\nabla\cdot[(1-\theta_u)\nabla\delta\psi]=\nabla\cdot(\delta\theta_u\nabla\psi)\,,$$
$$\delta\psi=0,\quad \text{at } x=0 \text{ and } x=L\,, \tag{9}$$
$$\frac{\partial\delta\psi}{\partial n}=0,\quad \text{at the other boundaries}$$

where

$$\delta\theta_u\equiv\sum_1^{m-1}du_i\,\theta_i(r)\,, \tag{10}$$

while the differential of $f(u)$ satisfies

$$\delta f(u)\equiv\sum_1^{m-1}\frac{\partial f}{\partial u_i}du_i =\frac{1}{V}\int\delta\theta_u(\nabla\psi)^2\,dr-\frac{2}{V}\int(1-\theta_u)\nabla\psi\cdot\nabla\delta\psi\,dr\,. \tag{11}$$

Using integration by parts, the second integral transforms into

$$\int\nabla\cdot[\delta\psi(1-\theta_u)\nabla\psi]\,dr-\int\delta\psi\nabla\cdot[(1-\theta_u)\nabla\psi]\,dr\,. \tag{12}$$

Both of these terms vanish—the second by the differential equation of (4), and the first by transforming to a surface integral and using the boundary conditions of (4) and (9). We thus get

$$\delta f(u)=\frac{1}{V}\int\delta\theta_u(\nabla\psi)^2\,dr\,. \tag{13}$$

By (10) this is positive if all the du_i are positive.

The second differential of $f(u)$, which is a quadratic form in du_i and is denoted by $\delta^2 f(u)$, is obtained by applying the δ operator to this last equation.[9] Noting that $\delta\theta_u$ is independent of u, and integrating by parts over r, we get the following expression for $\delta^2 f$:

$$\delta^2 f(u)=\frac{2}{V}\int\delta\theta_u\nabla\psi\cdot\nabla\delta\psi\,dr =\frac{2}{V}\int\nabla\cdot(\delta\psi\delta\theta_u\nabla\psi)\,dr -\frac{2}{V}\int\delta\psi\nabla\cdot(\delta\theta_u\nabla\psi)\,dr\,. \tag{14}$$

Again, the first of these integrals transforms to a surface integral which vanishes. The second integral is transformed by the differential equation of (9), a partial integration, and subsequent use of the boundary conditions of (9) to make the resulting surface integral vanish. We thus get[9]

$$\tfrac{1}{2}\delta^2 f(u)=\frac{1}{V}\int(1-\theta_u)(\nabla\delta\psi)^2\,dr\,. \tag{15}$$

In the Appendix these calculations are extended to obtain differentials of arbitrary order $\delta^n f(u)$. The conclusion is that the even-order differentials are always positive, like $\delta^2 f$, while the odd-order differentials are, like δf, positive if all the du_i are positive.

For $u_i=0$, the boundary-value problem of (4) is solved by $\psi(r,0)=x$, and hence we find

$$f(0)=0\,. \tag{16}$$

From (7) we may also conclude

$$f(u)\le 1\,. \tag{17}$$

Finally, if one of the u_i tends to $-\infty$, then it can be shown that $f(u)$ is asymptotically linear, tending either to $-\infty$ or to a finite negative constant (the exact result depends on a percolation property of the medium and is discussed in the Appendix).

A function closely related to $f(u)$ is obtained by considering an alternative definition of ϵ_e. Instead of imposing E_0 as in (1), we impose a boundary value D_0 for the normal component of the electric displacement vector $D\equiv\epsilon E$. Since $\operatorname{div}D=0$, we may define

$$D\equiv|D_0|\,\mathrm{curl}A\,, \tag{18}$$

and get the following boundary-value problem instead of (1):

$$\mathrm{curl}((1/\epsilon)\mathrm{curl}A)=0\,,$$
$$(\mathrm{curl}A)_n=1,\quad \text{at } x=0 \text{ and } x=L \tag{19}$$
$$(\mathrm{curl}A)_n=0,\quad \text{at the other boundaries.}$$

The effective dielectric constant satisfies

$$\frac{D_0^2}{\epsilon_e}=\frac{1}{V}\int\frac{1}{\epsilon(r)}D^2(r)\,dr\,. \tag{20}$$

Denoting reciprocal ϵ's by $\tilde\epsilon$

$$\tilde\epsilon\equiv1/\epsilon\,, \tag{21}$$

we write

$$\tilde\epsilon(r)=\sum_1^m\tilde\epsilon_i\theta_i(r)$$
$$v_i\equiv1-\tilde\epsilon_i/\tilde\epsilon_m,\quad i=1,\ldots,m-1 \tag{22}$$
$$v_m\equiv0\,.$$

The differential equation of (19) then takes the form

$$\mathrm{curl}[(1-\theta_v)\mathrm{curl}A]=0\,, \tag{23}$$

and we can define a new characteristic geometric function

$$\varphi(v)\equiv1-\frac{\tilde\epsilon_e}{\tilde\epsilon_m}=1-\frac{1}{V}\int(1-\theta_v)(\mathrm{curl}A)^2\,dr\,. \tag{24}$$

To calculate the differential $\delta\varphi(v)$, we again first write the boundary-value problem for δA:

$$\mathrm{curl}[(1-\theta_v)\mathrm{curl}\,\delta A] = \mathrm{curl}(\delta\theta_v \mathrm{curl} A), \tag{25a}$$

$$(\mathrm{curl}\,\delta A)_n = 0, \quad \text{at all boundaries.} \tag{25b}$$

The expression for $\delta\varphi(v)$ is

$$\delta\varphi(v) = \frac{1}{V}\int \delta\theta_v(\mathrm{curl}A)^2\,dr - \frac{2}{V}\int (1-\theta_v)\mathrm{curl}A\cdot\mathrm{curl}\,\delta A\,dr. \tag{26}$$

The second integral can be transformed by noting that because of (23), we can write $(1-\theta_v)\mathrm{curl}A$ as the gradient of a scalar α. Therefore that integral becomes

$$\int \nabla\boldsymbol{\alpha}\cdot\mathrm{curl}\,\delta A\,dr = \int \nabla\cdot(\alpha\,\mathrm{curl}\,\delta A)\,dr. \tag{27}$$

This vanishes by transforming to a surface integral and using (25b). We thus get

$$\delta\varphi(v) = \frac{1}{V}\int \delta\theta_v(\mathrm{curl}A)^2\,dr. \tag{28}$$

Differentiating this once again we get

$$\delta^2\varphi(v) = \frac{2}{V}\int \delta\theta_v \mathrm{curl}A\cdot\mathrm{curl}\,\delta A\,dr. \tag{29}$$

We now use (25a) to define another gradient of a scalar α

$$\delta\theta_v\mathrm{curl}A = (1-\theta_v)\mathrm{curl}\,\delta A + \nabla\alpha. \tag{30}$$

Using this in (29) we find

$$\delta^2\varphi = \frac{2}{V}\int (1-\theta_v)(\mathrm{curl}\,\delta A)^2\,dr + \frac{2}{V}\int \nabla\alpha\cdot\mathrm{curl}\,\delta A\,dr.$$

The second integral vanishes just as in (27), and we finally get

$$\tfrac{1}{2}\delta^2\varphi(v) = \frac{1}{V}\int (1-\theta_v)(\mathrm{curl}\,\delta A)^2\,dr. \tag{31}$$

In the Appendix we extend these calculations to differentials of arbitrary order $\delta^n\varphi$, and we find that they have the same qualitative behavior regarding their sign as do the differentials $\delta^n f$. Likewise, we find that

$$\varphi(0)=0, \quad \varphi(u)\le 1. \tag{32}$$

From their definitions, it is clear that $f(u)$ and $\varphi(v)$, as well as u and v, are closely related:

$$v_i = u_i/(u_i-1) \tag{33}$$

$$\varphi(v) = f(u)/[f(u)-1]. \tag{34}$$

This connection, however, does not obviate the need for a separate demonstration of the positivity properties of $\delta^n\varphi$, since these properties do not follow merely from (33) and (34).

Further properties of $f(u)$ and $\varphi(v)$ are found from various, previously established, bounds on ϵ_e. We first consider the well-known and universally valid inequalities (i.e., macroscopic isotropy is not required for them to hold)

$$\langle\tilde{\epsilon}\rangle^{-1} < \epsilon_e < \langle\epsilon\rangle, \tag{35}$$

where

$$\langle\epsilon\rangle \equiv \sum_1^m p_i\epsilon_i, \tag{36}$$

and p_i is the volume fraction of the phase i. From this we get

$$\langle u\rangle < f(u) < \frac{\langle v\rangle}{\langle v\rangle - 1} = -(\langle v\rangle + \langle v\rangle^2 + \cdots). \tag{37}$$

Expanding v_i in powers of u_i we get

$$\langle v\rangle = -(\langle u\rangle + \langle u^2\rangle + \cdots), \tag{38}$$

and thus

$$\langle u\rangle < f(u) < \langle u\rangle + (\langle u^2\rangle - \langle u\rangle^2) + O(u^3). \tag{39}$$

These inequalities provide us with quantitative information about the differentials of $f(u)$ at $u=0$:

$$\delta f(0) = \sum_1^{m-1} p_i\,du_i$$

$$0 < \tfrac{1}{2}\delta^2 f(0) < \sum_1^{m-1} p_i\,du_i^2 - \Big(\sum_1^{m-1} p_i\,du_i\Big)^2. \tag{40}$$

The same relationships continue to hold if we replace f and u by φ and v.

More stringent bounds were obtained for ϵ_e by Hashin and Shtrikman[2] under the assumption that the composite system is macroscopically isotropic as well as homogeneous. Those bounds lead to inequalities for f and φ

$$f_<(u) < f(u) < f_>(u), \tag{41}$$

$$\varphi_<(v) < \varphi(v) < \varphi_>(v), \tag{42}$$

where $f_{\gtrless}$ and $\varphi_{\gtrless}$ can be obtained explicitly from the results of Ref. 2. Expanding these functions in powers of u and v we find

$$f_{\lessgtr}(u) = \langle u\rangle + \tfrac{1}{3}\langle(u-\langle u\rangle)^2\rangle + \frac{1}{3^2}[\langle(u-\langle u\rangle)^3\rangle + \langle(u-\langle u\rangle)^2\rangle(\langle u\rangle + 2u_{\lessgtr})] + O(u^4), \tag{43}$$

$$\varphi_{\lessgtr}(v) = \langle v\rangle + \tfrac{2}{3}\langle(v-\langle v\rangle)^2\rangle + (\tfrac{2}{3})^2[\langle(v-\langle v\rangle)^3\rangle + \langle(v-\langle v\rangle)^2\rangle(\langle v\rangle + 2v_{\lessgtr})] + O(v^4), \tag{44}$$

where $u_{\lessgtr}$ is the smallest (largest) among u_i, and similarly for $v_{\lessgtr}$. In this case we find that both the first and the second differentials of f and φ at the origin are determined uniquely, and there are bounds on the third-order differential. Note that the only difference between $f_{\lessgtr}$ and $\varphi_{\lessgtr}$ is in the factor $\frac{1}{3}$, which gets replaced by $\frac{2}{3}$ everywhere in the expression for $\varphi_{\lessgtr}$.

For a two-phase system, f and φ depend on only one variable each

$$u = 1 - \epsilon_1/\epsilon_2, \quad f(u) = 1 - \epsilon_e/\epsilon_2,$$
$$v = 1 - \tilde{\epsilon}_1/\tilde{\epsilon}_2, \quad \varphi(v) = 1 - \tilde{\epsilon}_e/\tilde{\epsilon}_2. \tag{45}$$

We can therefore write the expansions of f and φ as follows for the case of an isotropic system

$$f(u) = p_1 u + \tfrac{1}{3} p_1 p_2 u^2 + \tfrac{1}{9}(p_1 p_2^2 + a)u^3 + O(u^4),$$
$$\varphi(v) = p_1 v + \tfrac{2}{3} p_1 p_2 v^2 + \tfrac{4}{9}(p_1 p_2^2 + a)v^3 + O(v^4), \tag{46}$$

where

$$0 < a < 2p_1 p_2. \tag{47}$$

For further information about the values of $f(u)$ and $\varphi(v)$ one needs either additional information about the statistics of the composite, or else some measurements of bulk properties whose values are related to f and φ as ϵ_e is by (7) and (24). In Sec. III we will show how such experimental information about one or more values of f or φ can lead to improved bounds on these functions, and consequently on ϵ_e, over whole ranges of u and v.

III. IMPROVED BOUNDS ON ϵ_e FROM MEASUREMENTS: TWO-PHASE SYSTEMS

The bounds we shall describe in this section are not optimum bounds, nor do they exhaust the possibilities for constructing bounds from similar information.[10] They should rather be viewed as illustrations of some of the principles that can be used to derive such bounds.

We start with the simplest case—an isotropic two-phase system where one value of $f(u=u_+)$ [and consequently also the value of $\varphi(v=v_+)$, where $v_+ = u_+/(u_+ - 1)$] is known, say, from a measurement of another bulk property. Consider the following polynomial approximations to $f(u)$

$$\begin{aligned}
f_1 &= f_0 + \tfrac{1}{9} p_1 p_2^2 u^3 + a_1 u^4 + b_1 u^5, \\
f_2 &= f_0 + \tfrac{1}{9} p_1 p_2 (p_2 + 2) u^3 + a_2 u^4 + b_2 u^5, \\
f_3 &= f_0 + \tfrac{1}{9} p_1 p_2 (p_2 + 2) u^3 + a_3 u^4, \\
f_4 &= f_0 + \tfrac{1}{9} p_1 p_2^2 u^3 + a_4 u^4, \\
f_5 &= f_0 + a_5 u^3 + b_5 u^4, \\
f_6 &= f_0 + a_6 u^3,
\end{aligned} \tag{48}$$

where

$$f_0(u) \equiv p_1 u + \tfrac{1}{3} p_1 p_2 u^2. \tag{49}$$

The unknown parameters a_i and b_i on which these functions depend are determined by requiring that the functions satisfy

$$f_i(u_+) = f(u_+), \quad \text{for } i = 1, \ldots, 6 \tag{50}$$

$$f_i(1) = 1, \quad \text{for } i = 1, 2, 4. \tag{51}$$

We note that each of these functions can intersect with $f(u)$ only a limited number of times. For example, since

$$\frac{d^6 f_1}{du^6} = 0 \quad \text{and} \quad \frac{d^6 f}{du^6} > 0, \tag{52}$$

the difference $f(u) - f_1(u)$ can have at most six zeros. Three of those occur at the origin, which is clearly a zero of third order, while two more are accounted for by (50) and (51) [since 1 is an absolute upper bound for the physically meaningful values of u as well as for $f(1)$, we can always imagine that right at $u=1$ $f(u)$ jumps up to the value 1, with all of its derivatives jumping to $+\infty$]. Some further consideration shows that there is one more spurious intersection at u_s, and that the qualitative relationship of f_1 and f is as shown in Fig. 2(a) when $u_+ > 0$ and in Fig. 2(b) when $u_+ < 0$. While the exact location of u_s is not known, it must occur in the region shown in Fig. 2 (one of the regions marked I, II, III). In the other regions of u, $f_1(u)$ thus provides absolute bounds on the values of $f(u)$. Similar considerations applied to the other f_i lead to the result that all of them provide useful upper or lower bounds for some or all values of u. These results are summarized in Tables I(a) and I(b) which list the functions that lead to absolute bounds on f in each of the three regions shown in Figs. 2(a) and 2(b) for $u_+ > 0$ and $u_+ < 0$, respectively. Note that whereas in $f - f_1$ the spurious zero u_s could be identified as occurring in region I for $u_+ > 0$ and in region III for $u_+ < 0$, and therefore f_1 fails to provide a bound only in those regions, a more complicated situation can occur with other functions. For example, $f - f_2$, which has the same first five zeros as $f - f_1$, has a sixth spurious zero that can occur in either region II or III for $u_+ > 0$, and in either region I or II for $u_+ < 0$. Therefore f_2 only provides a bound in one region for each sign of u_+. From Tables I(a) and I(b) it is clear that altogether we get two upper and two lower bounds in each region of u. This leads to a similar number of bounds for ϵ_e. We can get another similar number of bounds on ϵ_e by looking for bounds on $\varphi(v)$. The discussion and results are qualitatively the same as for the bounds on $f(u)$, including Figs. 2(a) and 2(b), and Tables I(a) and I(b). Even Eqs. (48)–(52) remain almost unchanged except for the factors $\frac{1}{3}$ and $\frac{1}{9}$ which are replaced

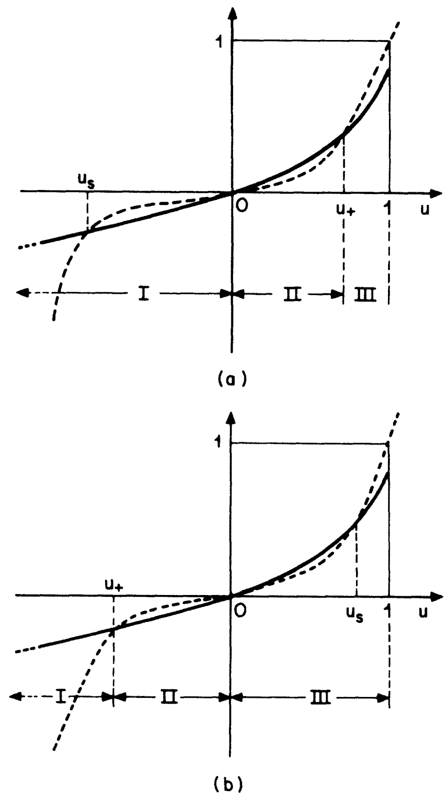

FIG. 2. Schematic graphs of $f(u)$ (full line) and the approximating polynomial $f_1(u)$ (dashed line) vs u. Note that, according to results from the Appendix, $f(u)$ is asymptotically linear as $u \to -\infty$. Note also that f_1 is made to pass through the upper right-hand corner of the positive unit square, and to intersect f at u_+. It is also made to intersect f at the origin and to have first and second derivatives that coincide with those of f at that point. The point u_s is a spurious intersection point whose region of occurrence can be determined as I, II, or III but whose exact location is unknown. (a) For $u_+ > 0$ f_1 bounds f in regions II and III. (b) For $u_+ < 0$ f_1 bounds f in regions I and II. These graphs also describe the function $\varphi(v)$ and its approximating polynomial $\varphi_1(v)$.

TABLE I. A list of polynomial approximations that give absolute upper or lower bounds on $f(u)$ in the various regions defined in Fig. 2: (a) for $u_+ > 0$; (b) for $u_+ < 0$. The numbers in the table refer to the index i from f_i of (48). The same table applies also to $\varphi_i(v)$ for $v_+ \gtrless 0$, respectively.

	Region of u [Fig. 2(a)]		
(a): $u_+ > 0$	I	II	III
upper bound	4, 5	3, 6	1, 5
lower bound	2, 6	1, 5	3, 6
	Region of u [Fig. 2(b)]		
(b): $u_+ < 0$	I	II	III
upper bound	3, 5	1, 6	2, 5
lower bound	1, 6	3, 5	4, 6

by $\frac{2}{3}$ and $\frac{4}{9}$, as explained in the comments following (44).

The bounds on ϵ_e obtained from these bounds on $\varphi(v)$ are in general different from the bounds obtained by use of $f(u)$. Furthermore, we can redefine the variables u, v and the functions f, φ by permuting the two phases, i.e., we replace (45) by

$$u \equiv 1 - \epsilon_2/\epsilon_1, \quad f(u) \equiv 1 - \epsilon_e/\epsilon_1, \qquad v \equiv 1 - \tilde{\epsilon}_2/\tilde{\epsilon}_1, \quad \varphi(v) \equiv 1 - \tilde{\epsilon}_e/\tilde{\epsilon}_1. \tag{53}$$

This leads to a whole new set of bounds on ϵ_e. Altogether we get eight upper and eight lower bounds in this way. In the absence of a criterion that definitely favors one pair of these over all the others we must evaluate them all and choose the best bounds in each case separately.

As an illustration, we apply this procedure to an example studied by Prager[7]:

$$p_1 = p_2 = \tfrac{1}{2}, \quad \epsilon_1 = \epsilon_1^+ = 1, \quad \epsilon_2 = \tfrac{1}{5}, \quad \epsilon_2^+ = \tfrac{1}{3}, \quad \epsilon_e^+ = \tfrac{3}{5}, \tag{54}$$

where the symbols ϵ_1^+, ϵ_2^+ stand for the pure-phase values of some other property whose bulk average value for the same system is known and represented by ϵ_e^+. Our best bounds for this case are

$$0.4658 < \epsilon_e < 0.4923. \tag{55}$$

For comparison, we reproduce Prager's bounds for this example, which, like our bounds, also make use of the information on ϵ_e^+ as well as the assumed macroscopic isotropy:

$$0.4676 < \epsilon_e < 0.4980. \tag{56}$$

We see that while our upper bound is slightly better, our lower bound is slightly worse.

Our method for obtaining bounds on ϵ_e can be extended in two directions: (a) If more than one measured value ϵ_e^+ exists for the system, the additional information can easily be incorporated in the calculation of bounds: We merely add more terms of successively higher order in u to each of the approximating polynomials f_i of (48), and require that f_i pass through all the additional determined points. Consideration of the possible intersections of f and f_i leads, as before, to a number of absolute upper and lower bounds for f. A similar incorporation of additional bits of experimental information is also possible using Prager's method, but it requires a tedious algebraic calculation rather than the simple curve fitting that suffices in our approach. (b) The procedures that we have used until now to get bounds for two-phase systems can sometimes be extended to get improved bounds even when the number of phases is greater than two, as we will now show.

IV. IMPROVED BOUNDS ON ϵ_e FROM MEASUREMENTS: MULTIPHASE SYSTEMS

The main step in extending the discussion of Sec. III to composites consisting of more than two phases is to choose an appropriate trajectory in the space of u. In order to take advantage of the special properties of f, we must restrict our choice to trajectories $u(t)$ that pass through the origin and all of whose derivatives $d^n u_i(t)/dt^n$ are non-negative at least over the regions of interest. This will ensure that along the trajectory, all the derivatives of the function $f(u(t))$ will be positive, as was the case with $f(u)$ in the two-phase system. In order to be useful, the trajectory should also pass through the points at which we have information on $f(u)$, as well as through the point at which we need to know the bounds on f. We can then define approximating polynomials $f_i(t)$, as in (48), which have the correct behavior at the origin [i.e., $f(u(t)) - f_i(t)$ must have a zero of order three at $t=0$] and also satisfy the analogs of (50) and (51), i.e.,

$$f_i(t_+) = f(u(t_+)) \quad \text{for } i = 1, \ldots, 6\,, \tag{57}$$

$$f_i(t_1) = 1 \quad \text{for } i = 1, 2, 4\,. \tag{58}$$

Here $u(t_+)$ is a value of u for which f is known, while t_1 is the point where $u(t)$ leaves the positive unit cube and the largest u_i becomes greater than 1, i.e.,

$$\mathrm{Max}_i u_i(t_1) = 1\,. \tag{59}$$

However, whereas in the two-phase system our procedure always led to bounds on $f(u)$ whatever the values of u and u_+, this is no longer true here: First of all, it may not be possible to find a trajectory that passes through the origin as well as through u_+ and u and has the required non-negative derivatives at least over the region of interest. Secondly, even if that is possible, it may be that one is forced to use a high-order polynomial for $u(t)$, in which case the approximating polynomials will also be of a correspondingly high order and we may not be able to identify any one of them as being an absolute upper or lower bound. Despite these qualifications, we can still sometimes obtain useful bounds in this way, as we will demonstrate in the specific example treated below. When attempting to find bounds on ϵ_e one should, as in Sec. III, attempt to permute the phases in the definition of u_i, since different permutations lead in general to different bounds (though sometimes to none at all). Also, since all of the above discussion applies equally well to $v(t)$ and $\varphi(v(t))$, one can get a whole new set of bounds on ϵ_e by considering φ.

We have carried out the above procedure for a three-phase system with one known value for a bulk property in cases where we could find a simple parabola $u_2(u_1)$ that satisfied all the requirements for being an acceptable trajectory. For the specific example defined by [we use the same notation as in (54)]

$$\begin{aligned} &p_1 = \tfrac{5}{18}\,,\; p_2 = \tfrac{6}{18}\,,\; p_3 = \tfrac{7}{18}\,, \\ &\epsilon_1^+ = 1,\;\; \epsilon_2^+ = 6,\;\; \epsilon_3^+ = 9,\;\; \epsilon_e^+ = 4.5\,, \\ &\epsilon_1 = 1,\;\; \epsilon_2 = 11.5,\;\; \epsilon_3 = 18, \end{aligned} \tag{60}$$

we found the following best bounds

$$6.694 < \epsilon_e < 8.014\,. \tag{61}$$

Comparing these with the Hashin-Shtrikman bounds for this example

$$5.314 < \epsilon_e < 10.026\,, \tag{62}$$

we find a considerable improvement. This should not come as a surprise since the bounds of (62) do not incorporate the information on ϵ_e^+ but only the information on the volume fractions and the macroscopic isotropy.

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APPENDIX: DERIVATION OF SOME MATHEMATICAL PROPERTIES OF $f(u)$ AND $\phi(v)$

In order to derive explicit expressions for all the differentials of $f(u)$, we first write a boundary-value problem that the nth differential of $\psi(r, u)$ with respect to u satisfies:

$$\begin{aligned} &\nabla \cdot [(1-\theta_u)\nabla \delta^n \psi] = n \nabla \cdot (\delta\theta_u \nabla \delta^{n-1}\psi)\,, \\ &\delta^n \psi = 0, \quad \text{at } x = 0 \text{ and } x = L \\ &\frac{\partial \delta^n \psi}{\partial n} = 0, \quad \text{at the other boundaries.} \end{aligned} \tag{A1}$$

This is easily proved by induction, starting from (9). Using these equations and the techniques described in Sec. II, it is straightforward to show that

$$\begin{aligned} \delta \int (1-\theta_u)(\nabla\delta^n\psi)^2\, dr &= -\int \delta\theta_u (\nabla\delta^n\psi)^2\, dr \\ &\quad - 2\int \delta^n\psi \nabla \cdot [(1-\theta_u)\nabla\delta^{n+1}\psi]\, dr \\ &= (2n+1)\int \delta\theta_u (\nabla\delta^n\psi)^2\, dr\,, \end{aligned} \tag{A2}$$

and that

$$\delta \int \delta\theta_u(\nabla\delta^n\psi)^2\,dr = -2\int \delta^{n+1}\psi\nabla\cdot(\delta\theta_u\nabla\delta^n\psi)\,dr$$

$$= \frac{2}{n+1}\int(1-\theta_u)(\nabla\delta^{n+1}\psi)^2\,dr. \quad \text{(A3)}$$

Using these results together with (13) and (15), it is easy to show by induction that the differentials of $f(u)$ are given by

$$\frac{(n!)^2}{(2n)!}\delta^{2n}f(u) = \frac{1}{V}\int(1-\theta_u)(\nabla\delta^n\psi)^2\,dr, \quad \text{(A4)}$$

$$\frac{(n!)^2}{(2n+1)!}\delta^{2n+1}f(u) = \frac{1}{V}\int\delta\theta_u(\nabla\delta^n\psi)^2\,dr. \quad \text{(A5)}$$

Clearly, the even differentials are always positive while the odd differentials are positive if all the du_i are positive.

A similar procedure is followed to derive explicit expressions for the differentials of $\varphi(v)$. We first show by induction, starting from (25), that the nth differential of $A(r,u)$ with respect to u satisfies the following boundary-value problem

$$\begin{aligned}&\text{curl}[(1-\theta_v)\,\text{curl}\,\delta^n A] = n\,\text{curl}(\delta\theta_v\,\text{curl}\,\delta^{n-1}A),\\ &\text{curl}\,\delta^n A = 0 \ \text{ at all boundaries.}\end{aligned} \quad \text{(A6)}$$

We then show that

$$\delta\int(1-\theta_v)(\text{curl}\,\delta^n A)^2\,dr = -\int\delta\theta_v(\text{curl}\,\delta^n A)^2\,dr$$

$$+\,2(n+1)\int\delta\theta_v(\text{curl}\,\delta^n A)^2\,dr$$

$$= (2n+1)\int\delta\theta_v(\text{curl}\,\delta^n A)^2\,dr, \quad \text{(A7)}$$

and that

$$\delta\int\delta\theta_v(\text{curl}\,\delta^n A)^2\,dr = \frac{2}{n+1}\int(1-\theta_v)(\text{curl}\,\delta^{n+1}A)^2\,dr. \quad \text{(A8)}$$

From these results together with (28) and (31) it is again easy to show by induction that

$$\frac{(n!)^2}{(2n)!}\delta^{2n}\varphi(v) = \frac{1}{V}\int(1-\theta_v)(\text{curl}\,\delta^n A)^2\,dr, \quad \text{(A9)}$$

$$\frac{(n!)^2}{(2n+1)!}\delta^{2n+1}\varphi(v) = \frac{1}{V}\int\delta\theta_v(\text{curl}\,\delta^n A)^2\,dr. \quad \text{(A10)}$$

Thus the differentials of φ have the same properties as the differentials of f: The even ones are always positive while the odd ones are positive if all the dv_i are positive.

In order to derive the asymptotic properties of $f(u)$ as one or more of the u_i tend to $-\infty$, we note first that one can in fact define m different functions $f_n(u_i^{(n)})$ by giving each of the ϵ_n in turn the role of ϵ_m in (5) and in (7):

$$\begin{aligned}&u_i^{(n)} \equiv 1-\epsilon_i/\epsilon_n, \quad i=1,\ldots,m\\ &f_n(u_i^{(n)}) \equiv 1-\epsilon_e/\epsilon_n,\end{aligned} \quad \text{(A11)}$$

where

$$n = 1,\ldots,m,$$

and obviously

$$u_n^{(n)} \equiv 0, \quad u_i^{(n)} \le 1 \ \text{ for } i\ne n, \quad f_n(u^{(n)}) \le 1. \quad \text{(A12)}$$

All of the functions f_n and sets of variables $u^{(n)}$ are connected to each other by

$$\begin{aligned}&u_i^{(n)} = (u_i^{(r)} - u_n^{(r)})/(1-u_n^{(r)}),\\ &f_n(u^{(n)}) = [f_r(u^{(r)}) - u_n^{(r)}]/[1-u_n^{(r)}].\end{aligned} \quad \text{(A13)}$$

Suppose now that some $u_n^{(r)} \to -\infty$. Using (A13) to express $f_r(u^{(r)})$ in terms of $u^{(r)}$ and $f_n(u^{(n)})$ we find

$$f_r(u^{(r)}) = u_n^{(r)}[1-f_n(u^{(n)})] + f_n(u^{(n)}). \quad \text{(A14)}$$

If no other $|u_i^{(r)}|$ increases faster than $|u_n^{(r)}|$, then all the $u_i^{(n)}$ remain bounded. Thus $f_r(u^{(r)})$ will tend linearly to $-\infty$ unless $f_n(u^{(n)})$ tends to 1, in which case f_r will tend to a finite negative value. We note that $f_n = 1$ can occur only when at least one of the $u_i^{(n)}$ is also equal to 1. In that case, the region of space occupied by the union of the phases i such that $u_i^{(n)} < 1$ is nonpercolating (i.e., it does not stretch continuously from end to end of the system). For a two-phase system, it is precisely the phase n that must be nonpercolating. If only $u_n^{(r)}$ diverges while the other $u_i^{(r)}$ remain finite we find the result

$$f_r(u^{(r)}) = u_n^{(r)}[1-f_n(1)] + f_n(1)$$

$$+\sum_{i\ne n}\frac{\partial f_n(1)}{\partial u_i^{(n)}}(u_i^{(r)}-1) + O(1/u_n^{(r)}). \quad \text{(A15)}$$

In the case of a two-phase system there are only two functions f_1 and f_2, each of them depending on only one variable. Equation (A15) then reduces to

$$f_2(u) = u[1-f_1(1)] + f_1(1) + O(1/u). \quad \text{(A16)}$$

Obviously, all of these results hold also for $\varphi(v)$.

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[8]In other words, $\delta\psi$ is just the first-order term in the Taylor expansion of $\psi(r,u')$ around $\psi(r,u)$ in powers of $du_i \equiv u_i' - u_i$. The entire expansion can, of course, be written as a sum of terms of the form $\delta^n\psi$

$$\psi(r,u') - \psi(r,u) = \delta\psi + \frac{1}{2!}\delta^2\psi + \frac{1}{3!}\delta^3\psi + \cdots .$$

[9]In other words

$$\delta^2 f(u) = \sum_{i,j} \frac{\partial^2 f(u)}{\partial u_i \partial u_j} du_i du_j .$$

Consequently, Eqs. (14) and (15) could also be written more explicitly as expressions for the second derivatives of $f(u)$.

[10]In particular, in the case of a macroscopically isotropic two-phase system with one known value of a bulk average property, it is possible to generate much better bounds on ϵ_e than either those presented here or in Ref. 4. These new and improved bounds, which apparently cannot be extended to multiphase systems, are described in D. J. Bergman, Phys. Rev. B (to be published).