Stanford Exploration Project, Report 120, May 3, 2005, pages 1–437

Using knowledge of microstructure to improve estimates and bounds on elastic constants and transport coefficients in heterogeneous media

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ABSTRACT

The most commonly discussed measures of microstructure in composite materials are the spatial correlation functions, which in a porous medium measure either the grain-to-grain correlations, or the pore-to-pore correlations in space. Improved bounds based on this information such as the Beran-Molyneux bounds for bulk modulus and the Beran bounds for conductivity are well-known. It is first shown how to make direct use of bounds and spatial correlation information to provide estimates that always lie between these upper and lower bounds for any microstructure whenever the microgeometry parameters are known. Then comparisons are made between these estimates, the bounds, and two new types of estimates. One new estimate for elastic constants makes use of the Peselnick-Meister bounds (based on Hashin-Shtrikman methods) for random polycrystals of laminates to generate self-consistent values that always lie between the bounds. A second new type of estimate for conductivity assumes that measurements of formation factors (of which there are at least two distinct types in porous media, associated respectively with pores and grains for either electrical and thermal conductivity) are available, and computes new bounds based on this information. The paper compares and contrasts these various methods in order to clarify just what microstructural information — and how accurately that information — needs to be known in order to be useful for estimating material constants in random and heterogeneous media.

INTRODUCTION

A wide array of results is available for practical studies of the linear elastic constants of composite solid and/or granular materials, fluid suspensions, and emulsions. These results range from rigorous bounds such as the Voigt (1928), Reuss (1929), Hill (1952), and Hashin-Shtrikman (1962; 1963) bounds to the fairly popular and mostly well-justified [for sufficiently small concentrations of inclusions (Berryman and Berge, 1996)] approximate methods such as the explicit approximations of Kuster and Toksöz (1974) and Mori and Tanaka (Benveniste, 1987; Ferrari and Filiponni, 1991) and the implicit methods such as the differential effective medium (DEM) method (Cleary *et al.*, 1980; Norris, 1985) and the self-consistent (Hill, 1965;

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Budiansky, 1965) or the coherent potential approximation for elastic composites (Gubernatis and Krumhansl, 1975; Korringa *et al.*, 1979; Berryman, 1980; 1982). Older reviews (Watt *et al.*, 1976) and both early (Beran, 1968; Christensen, 1979) and more recent textbooks and research monographs (Nemat-Nasser and Hori, 1993; Cherkaev, 2000; Milton, 2002; Torquato, 2002) survey the state of the art. So it might seem that there is little left to be done in this area of research. However, continuing problems with applications of these methods have included lack of sufficient information [such as the required spatial correlation functions (Torquato, 1980; Torquato and Stell, 1982; Berryman, 1985a)] needed to compute the most accurate bounds known and the failure of some of the explicit methods to satisfy the rigorous bounds in some limiting cases such as three or more constituents (Norris, 1989) or extreme geometries such as disk-like inclusions (Berryman, 1980). The best implicit schemes, even though they are known to be realizable and therefore cannot ever violate the bounds, are often criticized by some workers (Christensen, 1990) because the microgeometry generated implicitly by these methods does not represent the true microgeometry with any obvious fidelity. Nevertheless, it has been shown (Berge *et al.*, 1993; 1995) that knowing general features of the microgeometry such as whether one constituent can be classified as the host medium and others the inclusions, or whether in fact there is no one constituent that serves as the host can be sufficient information to decide on a model that can then be used successfully to study a class of appropriate composites (Berge *et al.*, 1993; 1995; Garboczi and Berryman, 2000; 2001). Some critics also point out that the iteration or integration schemes required to compute the estimates for implicit schemes are sufficiently more difficult to implement than those of the explicit methods that workers are often discouraged from trying these approaches for this reason alone.

Virtually all of the improved bounds (*i.e.*, improved beyond the bounds of Hashin and Shtrikman, which do not make direct use of microstructural information except for the volume fractions) require some information about the microstructure. But it has not been very clear just how precisely this information needs to be known in order for it to be useful. The present work will show for several examples how some general knowledge of microstructure can be used in more than one way to generate estimates. And since the predicted properties (at least in some cases) do not seem to depend too strongly on details beyond those readily incorporated, it gives some confidence that the methods can be successfully applied to real materials. One comparison we can make is between predictions and bounds on elastic constants for random polycrystals of laminates and the predictions of improved bounds based on spatial correlation functions for disks. It is clear that these models should both apply at least approximately to the same types of random composites, yet the microstructure is assumed to be organized rather differently. The random polycrystal is an aggegrate of grains, each of which is a laminate material. These laminated grains are then jumbled together with random orientations so the overall composite is isotropic, even though the individual grains act like crystals having hexagonal symmetry. The improved bounds for composites with disk-shaped inclusions must have a microstructure that is at least crudely the same as the random polycrystal, since each layer of an individual grain could be seen as approximately disk-like. So one quantitative question we can ask is: How closely do these two models agree with each other, and if they are indeed close in value, what do we learn about the sensitivity of elastic constants to microstructure? Also, how does this information affect engineering efforts to design (Cherkaev, 2000; Torquato, 2002) new materials? Or, how does general knowledge of

the geology of a given region help us to choose good models of the rocks when we need to interpret our seismic data?

CANONICAL FUNCTIONS AND THE Y-TRANSFORM IN ELASTICITY

Canonical functions

To make progress towards our present goals, it will prove helpful to take advantage of some observations made earlier about both rigorous bounds and many of the known estimates for moduli of elastic composites (Berryman, 1982; 1995; Milton, 1987; 2002). In particular, it is known (Berryman, 1982) that if we introduce certain functionals — similar in analytical structure to Hill's formula for the overall bulk modulus K^*, which is

$$K^* = \left[\sum_{i=1}^{J} \frac{v_i}{K_i + 4\mu/3}\right]^{-1} - 4\mu/3, \tag{1}$$

valid when the shear modulus μ is a uniform constant throughout the medium. Here K_i is the bulk modulus of the ith constituent out of J constituents, and v_i is the corresponding volume fraction, with the constraint that $\sum_{i=1}^{J} v_i = 1$. This form is also similar to the form of the Hashin-Shtrikman bounds (Hashin and Shtrikman, 1962; 1963) for both bulk and shear moduli — many of the known formulas for composites can be expressed simply in terms of these functionals. Specifically, for analysis of effective bulk modulus K^*, we introduce

$$\Lambda(\beta) \equiv \left[\sum_{i=1}^{J} \frac{v_i}{K_i + \beta}\right]^{-1} - \beta, \tag{2}$$

while, for the effective shear modulus μ^*, we have

$$\Gamma(\theta) \equiv \left[\sum_{i=1}^{J} \frac{v_i}{\mu_i + \theta}\right]^{-1} - \theta. \tag{3}$$

Here μ_i is the shear modulus of the ith constituent out of J isotropic constituents. The arguments β and θ have dimensions of GPa, and are always nonnegative. Both functions increase monotonically as their arguments increase. Furthermore, when the argument of each functional vanishes, the result is the volume weighted *harmonic mean* (or Reuss average) of the corresponding physical property. Similarly, an analysis of the series expansion for each functional at large arguments shows that, in the limit when the arguments go to infinity, the functionals approach the volume weighted *mean* (or Voigt average) of the corresponding physical property. We call these expressions the "canonical functions" for elasticity, as results expressible in these terms appear repeatedly in the literature — although published results are not necessarily manipulated into these canonical forms by all authors. The arguments β and θ are called the "transform parameters."

TABLE 1. Various bounds on bulk and shear modulus can be expressed in terms of the canonical functions $\Lambda(\beta)$ and $\Gamma(\theta)$. Subscripts $\pm$ for β and θ are for upper/lower $(+/-)$ bounds. Subscripts $\pm$ for the elastic constants imply the highest/lowest $(+/-)$ values of the quantity present in the composite. Θ, X, Ξ, and the averages $\langle\cdot\rangle$ and $\langle\cdot\rangle_\zeta$ are all defined in the text. $K_R = \left\langle K^{-1}\right\rangle^{-1}$, $\mu_R = \left\langle\mu^{-1}\right\rangle^{-1}$, $K_V = \langle K\rangle$, and $\mu_V = \langle\mu\rangle$ are the Reuss and Voigt averages of the respective moduli.

Bound	β_-	β_+	θ_-	θ_+
HS (HS, 1962; Walpole, 1969)	$\frac{4}{3}\mu_-$	$\frac{4}{3}\mu_+$	$\Theta(K_-,\mu_-)$	$\Theta(K_+,\mu_+)$
BM (Beran and Molyneux, 1966)	$\frac{4}{3}\left\langle\mu^{-1}\right\rangle_\zeta^{-1}$	$\frac{4}{3}\langle\mu\rangle_\zeta$		
MS (McCoy, 1970)			$\frac{1}{6}X$	$\frac{1}{6}\Xi^{-1}$
MPT (Milton and Phan-Thien, 1982)			$\frac{1}{6}\hat{X}$	$\frac{1}{6}\hat{\Xi}^{-1}$

Rigorous bounds

Some of the rigorous bounds that are expressible in terms of the canonical functions for $J = 2$ are listed in TABLE 1. Functions and averages required as definitions for some of the more complex terms in TABLE 1 are:

$$\Theta(K,\mu) = \frac{\mu}{6}\left(\frac{9K+8\mu}{K+2\mu}\right), \tag{4}$$

and the expressions needed for the McCoy-Silnutzer (MS) bounds (McCoy, 1970; Silnutzer, 1972), which are

$$\begin{aligned} X &= \left[10\mu_V^2\langle K\rangle_\zeta + 5\mu_V(2K_V+3\mu_V)\langle\mu\rangle_\zeta\right. \\ &\quad \left. + (3K_V+\mu_V)^2\langle\mu\rangle_\eta\right]/(K_V+2\mu_V)^2, \end{aligned} \tag{5}$$

$$\begin{aligned} \Xi &= \left[10K_V^2\left\langle K^{-1}\right\rangle_\zeta + 5\mu_V(2K_V+3\mu_V)\left\langle\mu^{-1}\right\rangle_\zeta\right. \\ &\quad \left. + (3K_V+\mu_V)^2\left\langle\mu^{-1}\right\rangle_\eta\right]/(9K_V+8\mu_V)^2. \end{aligned} \tag{6}$$

The averages $\langle M\rangle = v_1M_1 + v_2M_2$, $\langle M\rangle_\eta = \eta_1M_1 + \eta_2M_2$, and $\langle M\rangle_\zeta = \zeta_1M_1 + \zeta_2M_2$ are defined for any modulus M. The volume fractions are v_1, v_2, while ζ_1, ζ_2 and η_1, η_2 are the microgeometry parameters or Milton numbers (Milton, 1981; 1982), related to spatial correlation functions of the composite microstructure. The Voigt averages of the moduli are $K_V = \langle K\rangle$ and $\mu_V = \langle\mu\rangle$. For symmetric cell materials: $\zeta_1 = \eta_1 = v_1$ for spherical cells, $\zeta_1 = \eta_1 = v_2$ for disks, while $\zeta_1 = (v_2+3v_1)/4$ and $\eta_1 = (v_2+5v_1)/6$ for needles.

Alternative bounds that are at least as tight as the McCoy-Silnutzer (MS) bounds for any choice of microstructure were given by Milton and Phan-Thien (1982) as

$$\hat{X} = \frac{<3\mu>_\eta <6K+7\mu>_\zeta -5<\mu>_\zeta^2}{<2K-\mu>_\zeta + <5\mu>_\eta} \tag{7}$$

and

$$\hat{\Xi} = \frac{N}{< 128/K + 99/\mu >_\zeta + < 45/\mu >_\eta}, \tag{8}$$

where

$$\begin{aligned} N = &< 5/\mu >_\zeta < 6/K - 1/\mu >_\zeta + \\ &< 1/\mu >_\eta < 2/K + 21/\mu >_\zeta . \end{aligned} \tag{9}$$

It has been shown numerically that the two sets of bounds (MS and MPT) using the transform parameters X, Ξ and $\hat{X}, \hat{\Xi}$ are nearly indistiguishable for the penetrable sphere model (Berryman, 1985).

Note that "improved bounds" are not necessarily improved for every choice of volume fraction, constituent moduli, and microgeometry. It is possible in some cases that "improved bounds" will actually be less restrictive, than say the Hashin-Shtrikman bounds, for some range of the parameters. In such cases we obviously prefer to use the more restrictive bounds when our parameters happen to fall in this range.

Milton (1987; 2002) has shown that, for the commonly discussed case of two-component composites, the canonical functionals can be viewed as fractional linear transforms with the arguments β and θ of the canonical functionals as the transform variables. In light of the monotonicity properties of the functionals, this point of view is very useful because the problem of determining estimates of the moduli can then be reduced to that of finding estimates of the parameters β and θ. Furthermore, properties of the canonical functions also imply that excellent estimates of the moduli can be obtained from fairly crude estimates of the transformation parameters β and θ. (Recall, for example, that estimates of zero and infinity for these parameters result in Reuss and Voigt bounds on the moduli.) Milton calls this transformation procedure the Y-transform, where Y stands for one of these transform parameters (*i.e.*, β and θ in elasticity, or another combination when electrical conductivity and/or other mathematically analogous properties are being considered).

Estimation schemes based on bounds for elasticity

One very famous approximation scheme for elastic composites is due to Hill (1952). The idea is to take the known Voigt and Reuss averages of the elastic system stiffnesses or compliances, and then make direct use of this information by computing either the arithmetic or geometric mean of these two limiting values. These formulas have been found to be very effective for fitting real data in a wide variety of circumstances (Simmons and Wang, 1971; Thomsen, 1972; Watt and Peselnick 1980). Clearly the same basic idea can be applied to any pairs of bounds for scalars, such as the Hashin-Shtrikman bounds; or, for complex constants, a similar idea based on finding the center-of-mass of a bounded region in the complex plane could be pursued (but to date apparently has not been). The advantage of such approaches is that they can provide the user with just one estimate per choice of volume fraction, while at the same time requiring no additional information over that contained in the bounds themselves.

Hill's concept clearly works just as well, and possibly somewhat better, if we apply it instead — whenever we have an analytical function at our disposal as we do here in the canonical functions — to the transform variables β and θ rather than to the moduli K and μ directly. So one set of estimates we might test in our examples takes the form

$$\beta_H \equiv \frac{1}{2}(\beta_- + \beta_+) \quad \text{and} \quad \theta_H \equiv \frac{1}{2}(\theta_- + \theta_+), \tag{10}$$

where the bounds on β and θ were already given in TABLE 1, and the averages are just the arithmetic means. The subscript H is intended to reference Hill's contribution to this idea.

Another rather different approach (although still expected to give quite similar results) is to examine the forms of the β and θ transform variables in order to determine if some other estimate that lies between the bounds might suggest itself. One useful tool we can introduce here is the weighted geometric mean. For example, if we define

$$\mu_G^{\zeta} \equiv \mu_1^{\zeta_1}\mu_2^{\zeta_2}, \tag{11}$$

it is well-known (Hardy *et al.*, 1952) that this is a geometric mean and it always lies between (or on) the corresponding mean $\langle\mu\rangle_\zeta$ and harmonic mean $\left\langle\mu^{-1}\right\rangle_\zeta^{-1}$:

$$\left\langle\mu^{-1}\right\rangle_\zeta^{-1} \le \mu_1^{\zeta_1}\mu_2^{\zeta_2} \le \langle\mu\rangle_\zeta\,. \tag{12}$$

So $\beta_G = \frac{4}{3}\mu_G^{\zeta}$ is one natural choice we could make for the bulk modulus transform parameter estimate. This approach has one clear advantage over the usual self-consistent estimates in that the microstructural information can easily be incorporated this way, whereas the means of doing so for self-consistent methods usually involves more complicated calculations via scattering theory (Gubernatis and Krumhansl, 1975; Berryman, 1980). This approach also provides a formula, rather than an implicit equation requiring an iteration procedure for its solution, thus eliminating another common criticism of implicit estimators.

Similar results are not as easy to find for the shear modulus bounds. The reason is that there are either two or three averages that come into play for shear, always including $\langle\cdot\rangle_\zeta$ and $\langle\cdot\rangle_\eta$, while the formulas (5) and (6) also depend on the usual volume averages $\langle\cdot\rangle$. Since it is known that the McCoy-Silnutzer bounds are never tighter than those of Milton and Phan-Thien (1982), we will consider only the Milton and Phan-Thien bounds from here on, since they have only two types of averages present.

In general ζ_i and η_i differ. But in some cases (spheres and disks, for example) they are the same. Furthermore, it is easy to show that for any modulus M, we have the result (relevant in particular to needles) that

$$\begin{aligned}\langle M\rangle_\eta - \langle M\rangle_\zeta &= \tfrac{1}{12}\left[\langle M\rangle - \left\langle\tilde{M}\right\rangle\right] \\ &= \tfrac{1}{12}(v_1 - v_2)(M_1 - M_2).\end{aligned} \tag{13}$$

Thus, the differences always vanish for $50-50$ concentrations, and furthermore the factor of $\frac{1}{12}$ reduces the difference further by an order of magnitude. If we make the approximation that

$\langle\cdot\rangle_\eta \simeq \langle\cdot\rangle_\zeta$, this is often a quite reasonable compromise. When this is so, we can then choose to make the further approximations that

$$\langle M\rangle_\zeta \simeq M_G^\zeta = M_1^{\zeta_1} M_2^{\zeta_2}, \tag{14}$$

and also that

$$\left\langle M^{-1}\right\rangle_\zeta \simeq M_G^{-\zeta}. \tag{15}$$

Substituting these approximations into the Milton and Phan-Thien bounds (7) and (8), we find that both transform parameters for the upper and lower bounds are replaced by the same effective transform parameter:

$$\theta_G^\zeta \equiv \Theta(K_G^\zeta, \mu_G^\zeta). \tag{16}$$

This result provides a unique estimate that will always lie between these bounds.

A somewhat better (*i.e.*, more balanced) approximation is achieved for $\zeta_i \neq \eta_i$ by defining $\epsilon_i \equiv \frac{1}{2}(\zeta_i + \eta_i)$. Then, all occurrences of $\langle\mu\rangle_\zeta$, $\langle\mu\rangle_\eta$, $\langle\mu^{-1}\rangle_\zeta^{-1}$, and $\langle\mu^{-1}\rangle_\eta^{-1}$ are replaced by μ_G^ϵ. The errors introduced now through differences $\eta_i - \epsilon_i$ are half those in (13). But new errors are introduced through the differences $\zeta_i - \epsilon_i$. The resulting geometric approximation turns out to be

$$\theta_G^* = \Theta(K_G^\zeta, \mu_G^\epsilon), \tag{17}$$

which still reduces to (16) whenever $\eta_i = \zeta_i$. Also note that, if $\eta_i + \zeta_i = 1$, then $\mu_G^\epsilon = \sqrt{\mu_1\mu_2}$.

[Note: If ζ_i is known but η_i is not known (either experimentally or theoretically), Berryman and Milton (1988) discuss how to use knowledge of ζ_i to constrain estimates of η_i. However, we will not pursue this option here.]

To maintain internal consistency of the approximation, we can choose to set

$$\beta_G^* = \frac{4}{3}\mu_G^\zeta, \tag{18}$$

or we could choose instead to use β_H from (10). However, we do not expect that these choices will differ by very much for the bulk modulus estimates.

Elasticity for random polycrystals of laminates

In order to have a more precise model for comparison purposes, and to get a better feeling for just how much difference it makes whether we model the microstructure very accurately or not, we will now consider a model material called a "random polycrystal of laminates." Suppose we construct a random polycrystal by packing small bits of a laminate material (*i.e.*, a composite layered along a symmetry axis) into a large container in a way so that the axis of symmetry of the grains appears randomly over all possible orientations and also such that no misfit of surfaces (and therefore porosity) is left in the resulting composite. If the ratio

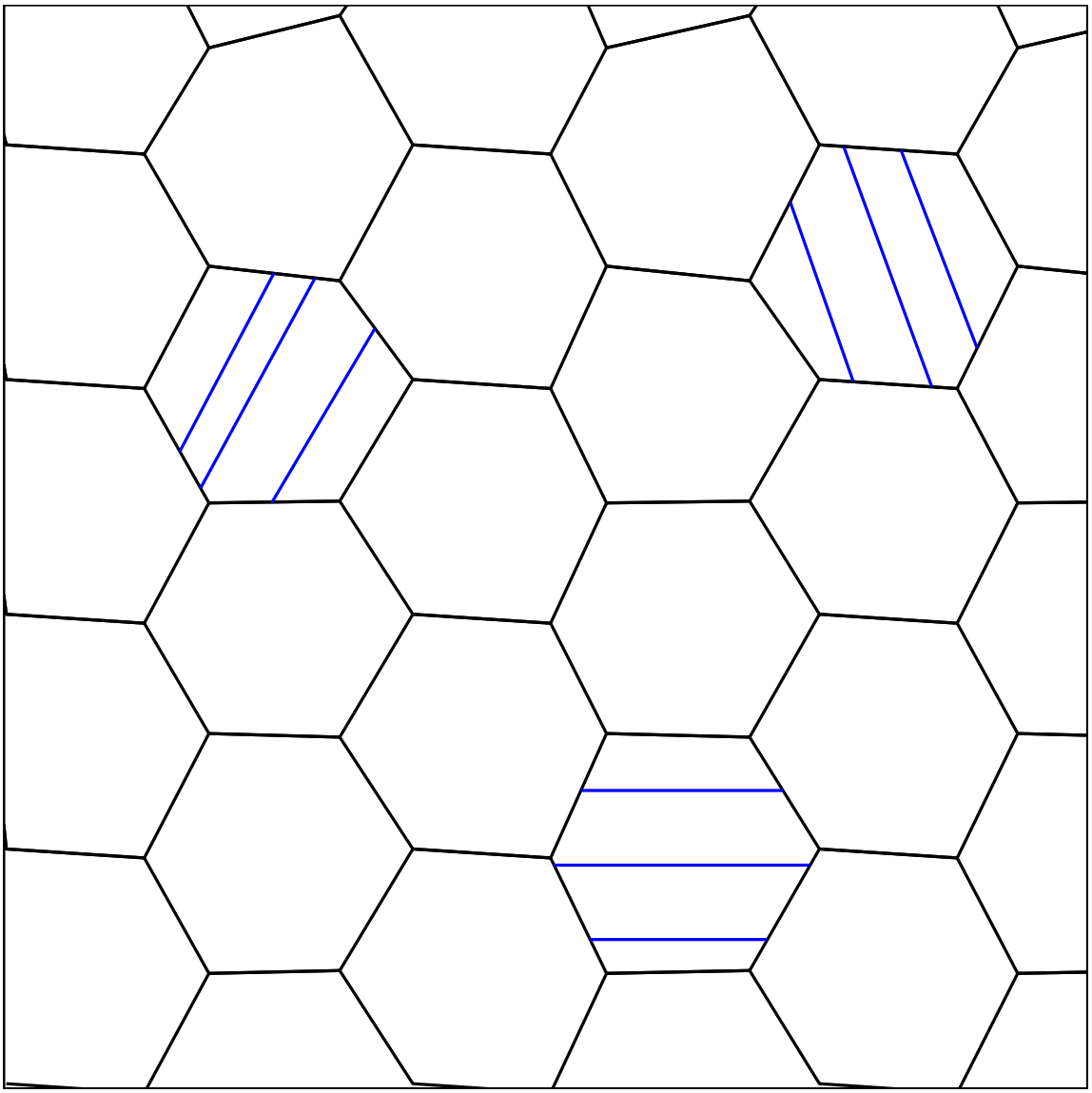

Figure 1: Schematic illustrating the model of random polycrystals of laminates. Grains are assumed to fit tightly so there is no misfit porosity. But the shapes of the grains are not necessarily the same, and the symmetry axes of the grains (three examples are shown here) are randomly oriented so the overall polycrystal is equiaxed (statistically isotropic). jim1-laminated_poly_l12 [NR]

of laminate grain size to overall composite is small enough so the usual implicit assumption of scale separation applies to the composite — but not so small that we are violating the continuum hypothesis — then we have an example of a random polycrystal of laminates. See schematic in Figure 1.

The analytical advantage of this model is that the layers can be composed of the two elastic constituents in the composites discussed here previously. Furthermore, the elastic behavior of the laminate material itself can be predicted using well-known exact methods (Backus, 1962). We will not dwell on these details here, but just make use of the results to be found in many publications (Berryman, 2004b). The only results needed in the following are the Reuss and Voigt averages for the grains, which are $1/K_R = 2s_{11} + 2s_{12} + 4s_{13} + s_{33}$ for Reuss in terms of compliances, or

$$\frac{1}{K_R - c_{13}} = \frac{1}{c_{11} - c_{66} - c_{13}} + \frac{1}{c_{33} - c_{13}}, \tag{19}$$

in terms of stiffness, and

$$K_V = [2(c_{11} + c_{12}) + 4c_{13} + c_{33}]/9 \tag{20}$$

for the Voigt average of bulk modulus. Similarly, the Voigt average for shear of the stiffness matrix may be written as

$$\mu_V = \frac{1}{5}\left(G^v_{\rm eff} + 2c_{44} + 2c_{66}\right). \tag{21}$$

This expression can be taken as the definition of $G^v_{\rm eff}$. Eq. (21) implies that $G^v_{\rm eff} = (c_{11} + c_{33} - 2c_{13} - c_{66})/3$. In fact, $G^v_{\rm eff}$ is the energy per unit volume in a grain when a pure uniaxial shear strain of unit magnitude is applied to the grain along its axis of symmetry (Berryman, 2004a,b). Then, the Reuss average for shear is

$$\mu_R = \left[\frac{1}{5}\left(\frac{1}{G^r_{\rm eff}} + \frac{2}{c_{44}} + \frac{2}{c_{66}}\right)\right]^{-1}, \tag{22}$$

which is also a rigorous lower bound on the overall shear modulus of the polycrystal (Hill, 1952). Each laminated grain thus has hexagonal symmetry, so the product formulas $3K_R G^v_{\rm eff} = 3K_V G^r_{\rm eff} = \omega_+\omega_-/2 = c_{33}(c_{11} - c_{66}) - c_{13}^2$ are valid (Berryman, 2004a). The symbols $\omega_\pm$ stand for the quasi-compressional and quasi-uniaxial shear eigenvalues for all the grains.

Once this notation has been established, then it is straightforward to express the Peselnick-Meister bounds (Peselnick and Meister, 1965) for hexagonal symmetry as

$$K^\pm_{PM} = \frac{K_V(G^r_{\rm eff} + Y_\pm)}{(G^v_{\rm eff} + Y_\pm)}. \tag{23}$$

for effective bulk modulus K^* of the polycrystal, where

$$Y_\pm = \frac{G_\pm}{6}\left(\frac{9K_\pm + 8G_\pm}{K_\pm + 2G_\pm}\right). \tag{24}$$

The precise values of the parameters $G_\pm$ and $K_\pm$ (being shear and bulk moduli of the HS isotropic comparison material) were given algorithmically by Watt and Peselnick (1980.) Similarly,

$$\frac{1}{\mu^{\pm}_{PM}+Y_\pm} = \frac{1}{5}\Big[\frac{1-A_\pm(K_V-K_\pm)}{R_\pm(K_V-K_\pm)+G^{v}_{\rm eff}+Y_\pm}+\frac{2}{c_{44}+Y_\pm}+\frac{2}{c_{66}+Y_\pm}\Big], \tag{25}$$

for the effective shear modulus μ^* of the polycrystal. The meaning of $Y_\pm$ is the same in (23) and (25). Here $A_\pm = \frac{-1}{K_\pm+4G_\pm/3}$, $B_\pm = \frac{2A_\pm}{15} - \frac{1}{5G_\pm}$, and $R_\pm = A_\pm/2B_\pm$. These bounds are of Hashin-Shtrikman type, but were first obtained for hexagonal symmetry by Peselnick and Meister (1965) with some corrections supplied later by Watt and Peselnick (1980).

Since we now have analytical forms for the bounds in (23)-(25), it seems it should be possible to arrive at self-consistent formulas (estimates related to the bounds) by making substitutions $K_\pm \to K^*$ and $\mu_\pm \to \mu^*$, as well as $K^{\pm}_{PM} \to K^*$ and $\mu^{\pm}_{PM} \to \mu^*$. This procedure can be followed without difficulty for the bulk modulus bounds in (23). However, for the shear modulus estimator, we need to take into account a step in the derivation of (25) that restricted its applicability to a certain curve in the $(G_\pm, K_\pm)$-plane. Since the self-consistent estimate will not normally lie on this curve, we need to back up in the analysis presented by Watt and Peselnick (1980) and take into account a correction term that vanishes along the curve in question but not in general. When we do this, and also make use of the self-consistent formula for the bulk modulus K^*, which is

$$K^* = \frac{K_V(G^{r}_{\rm eff}+Y^*)}{(G^{v}_{\rm eff}+Y^*)}, \tag{26}$$

we find that the self-consistent estimator for the shear modulus μ^* is

$$\frac{1}{\mu^*+Y^*} = \frac{1}{5}\left[\frac{1-A^*(K_V-K^*)}{G^{v}_{\rm eff}+Y^*}+\frac{2}{c_{44}+Y^*}+\frac{2}{c_{66}+Y^*}\right]. \tag{27}$$

The transform variable for these two formulas is just $Y^* = \Theta(K^*, \mu^*)$, with Θ defined as in (4).

From the derivation, it is expected that these self-consistent estimates based on the polycrystal bounds will always lie between the bounds. In fact, this feature is observed in all the results from calculations done using these formulas. It can also be shown that the self-consistent estimator obtained this way is the same as that found by Willis (1981) using different arguments. Furthermore, the results are also in agreement with the self-consistent formulas of Olson and Avellaneda (1992) for polycrystals composed of spherical grains when their results for orthorhombic symmetry are specialized to hexagonal symmetry.

Examples

We will now provide some examples of elastic constant bounds and estimates.

Figures 2 and 3 provide some examples of elastic constant bounds and estimates for a system having two constituents with $K_1 = 20$, $K_2 = 50$, $\mu_1 = 4$, $\mu_2 = 40$, all constants measured in GPa.

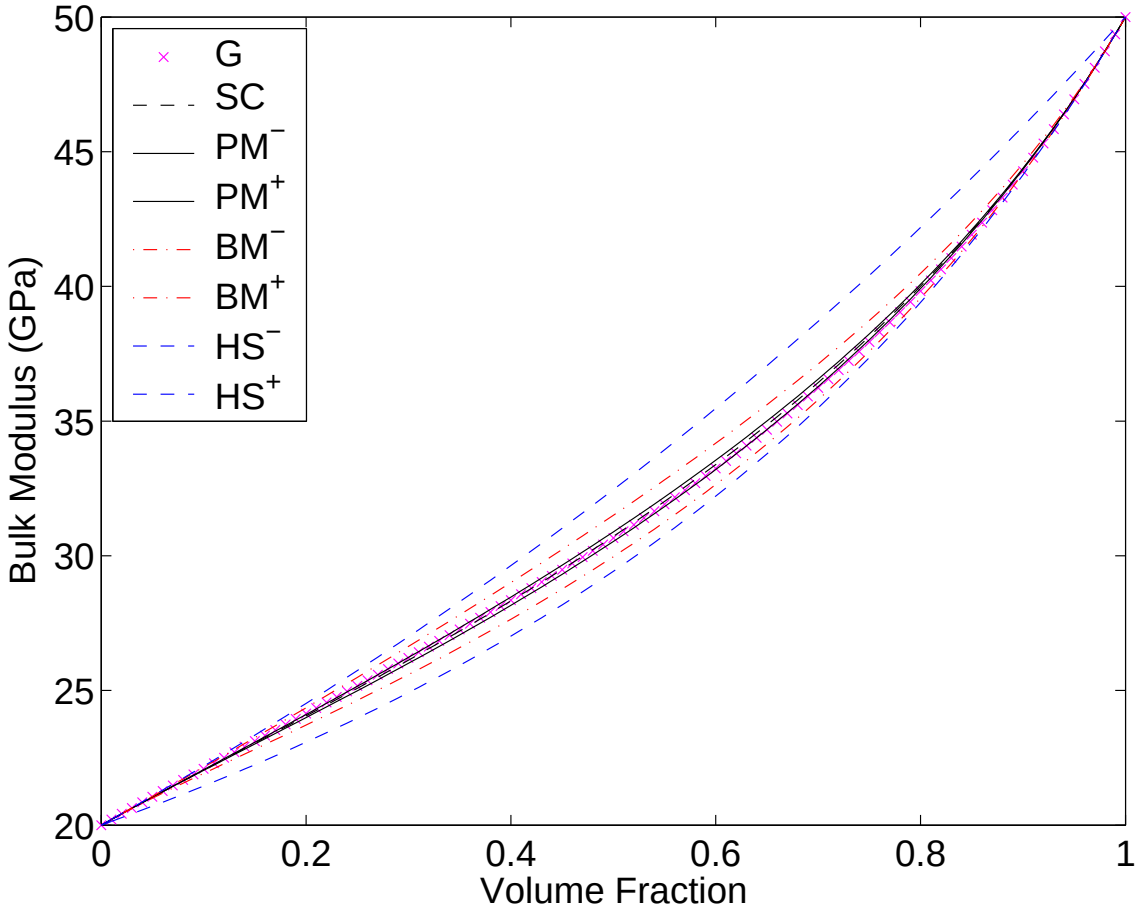

Figure 2: Comparison of (a) the (uncorrelated) bounds of Hashin and Shtrikman (HS$^{\pm}$), (b) the microstructure-based bounds (assuming disk inclusions) of Beran and Molyneaux (BM$^{\pm}$) for bulk modulus, and (c) the random polycrystal bounds of Peselnick and Meister (PM$^{\pm}$) assuming that the composite is an aggregate of randomly oriented laminated (hexagonal symmetry) grains. A self-consistent (SC) estimate based on the Peselnick-Meister bounds lies between the PM$^{\pm}$ bounds for both bulk and shear moduli. A new estimator (G) is based on the BM and MPT bounds and uses a geometric mean approximation in order to incorporate information contained in the microstructure constants ζ_i and η_i. jim1-GSCblkmd [NR]

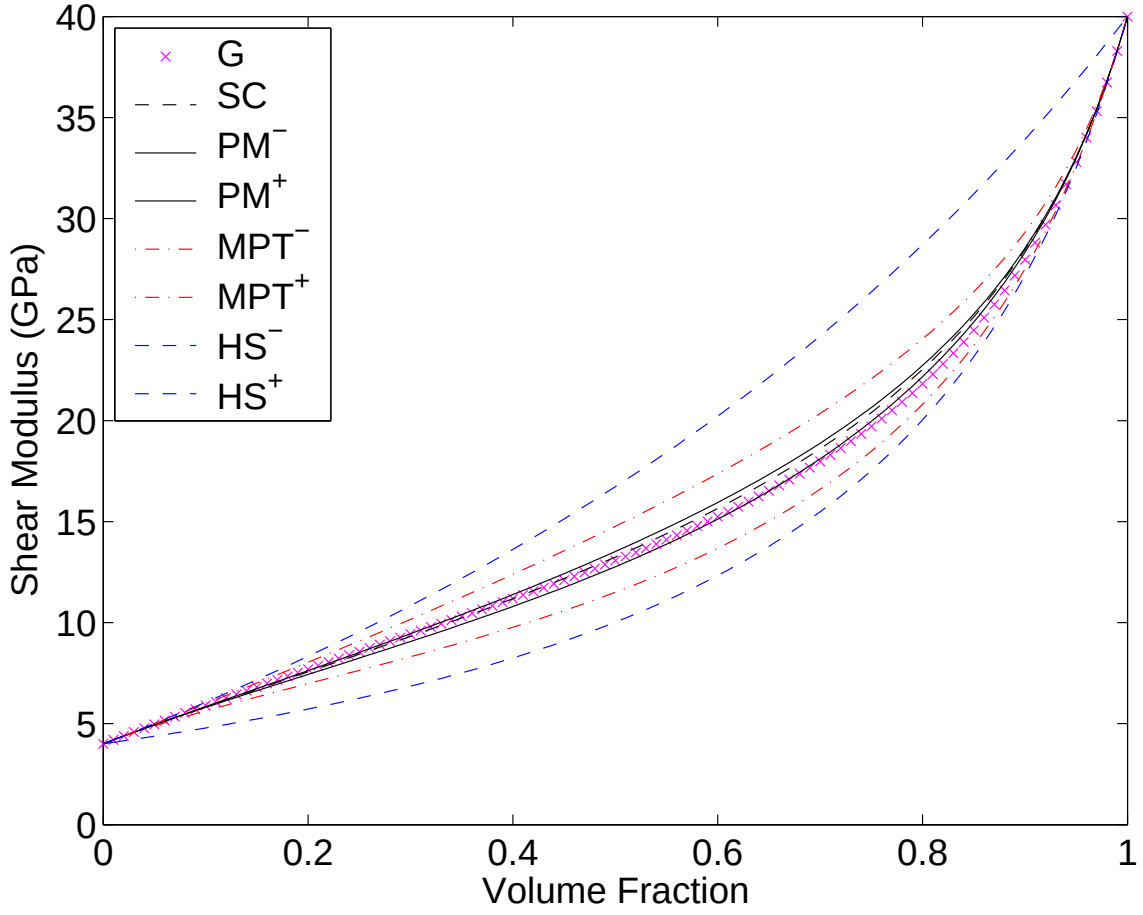

Figure 3: As in Figure 1, but the Milton and Phan-Thien ($MPT^{\pm}$) bounds are used instead for shear modulus. jim1-GSCshrmd [NR]

The Hashin-Shtrikman (uncorrelated) bounds ($HS^{\pm}$) are the outer most bounds for both bulk and shear modulus. The Beran-Molyneux ($BM^{\pm}$) bounds for bulk modulus and the Milton-Phan-Thien ($MPT^{\pm}$) bounds for shear modulus — in both cases the shapes of the inclusions are assumed to be disk-like — are the next bounds as we move inward. Then the Peselnick-Meister ($PM^{\pm}$) bounds for polycrystals of hexagonal grains are applied to grains laminated so that their volume fractions of type-1 and type-2 are always the same as that of the overall composite being considered here. These $PM^{\pm}$ bounds lie strictly inside the $BM^{\pm}$ and $MPT^{\pm}$ bounds. Then the inner most curve is the SC curve generated as described here by using the analytical forms of the $PM^{\pm}$ bounds to construct self-consistent estimates for the random polycrystal of laminates model. This SC curve is always inside the $PM^{\pm}$ bounds and therefore inside all the bounds considered here. Finally, we have the geometric mean estimates G, based on the improved bounds of $BM^{\pm}$ and $MPT^{\pm}$. These estimates always lie between these two bounds, but not always inside the $PM^{\pm}$ bounds. This result shows that the BM and MPT bounds are allowing for a wider range of microstructures than are the PM bounds, which is entirely reasonable under the circumstances. The main practical observation however is that the $PM^{\pm}$, SC, and G curves (both bounds and estimates) are in fact all very close to each other (differing by less than 2% maximum for this high contrast example). This fact suggests that any or all of these curves could be used when designing new composites having preassigned elastic properties, or for analysis of seismic wave data for interpretation purposes. The errors in these predictions would likely be close to the experimental errors in the construction of such composites and therefore negligible for many, though perhaps not all, practical purposes.

CONDUCTIVITY: CANONICAL FUNCTIONS AND ANALYTIC CONTINUATION

Canonical functions

Another topic of broad and continuing interest in the field of composite materials is the study of heterogeneous conductors, dielectrics, and — for porous media — fluid permeability (Beran, 1968; Milton, 2002; Torquato, 2002). Because of the wide range of applications, including both thermal and electrical conduction, and the theoretical interest in analysis of critical phenomena such as percolation thresholds in resistor networks and localization (Kirkpatrick, 1971; 1973), this topic has surely been studied as much or more than any other in the field of heterogeneous media.

Many results in this field of research can also be expressed in terms of canonical functions. First define

$$\Sigma(\sigma) \equiv \left[\sum_{i=1}^{J} \frac{v_i}{\sigma_i + 2\sigma} \right]^{-1} - 2\sigma, \tag{28}$$

where σ_i is the conductivity in the ith component, and v_i is the corresponding volume fraction, again having the space filling constraint that $\sum_{i=1}^{J} v_i = 1$. Hashin-Shtrikman bounds (Hashin and Shtirkman, 1962) on conductivity for a multicomponent composite material can then be

expressed as

$$\sigma_{HS}^{\pm} = \Sigma(\sigma_{\pm}), \tag{29}$$

where $\sigma_{\pm}$ are the largest and smallest values of the J isotropic conductivities present. These bounds are generally improvements on the mean and harmonic mean bounds:

$$\sigma_M = \sum_{i=1}^{J} v_i \sigma_i \qquad \text{and} \qquad \sigma_H = \left[\sum_{i=1}^{J} \frac{v_i}{\sigma_i} \right]^{-1}. \tag{30}$$

Beran (1965; 1968) used variational methods to arrive at improved bounds on conductivity for two-component media, again based on information in spatial correlation functions. His results are also expressible in terms of the canonical functions as

$$\sigma_B^{+} = \Sigma(\langle \sigma \rangle_{\zeta}) \tag{31}$$

and

$$\sigma_B^{-} = \Sigma(\langle 1/\sigma \rangle_{\zeta}^{-1}), \tag{32}$$

where σ_B^{+} (σ_B^{-}) is the upper (lower) bound and the ζ averages are the same ones we introduced here previously [following Eq. (6)]. Since some of the same measures of microstructure (in this case the ζ_i's) can be used to bound both conductivity and elastic constants, it has been noticed before that this fact and similar relations for other systems can be used to produce various cross-property bounds (Berryman and Milton, 1988; Gibiansky and Torquato, 1995), thereby measuring one physical property in order to bound another.

Estimation schemes based on bounds for conductivity

The fundamental ideas used earlier to obtain estimates of elastic constants by using the analytical structure of the bounds (by making informed approximations for the elastic constants) can again be used for effective conductivity. The ideas are virtually the same, but somewhat easier to apply since we have only one constant to estimate, not two. Since we are now dealing with the Beran bounds on two-component media that depend specifically on the average $\langle \cdot \rangle_{\zeta}$, we want to define again the geometric mean

$$\sigma_G^{\zeta} = \sigma_1^{\zeta_1} \sigma_2^{\zeta_2}. \tag{33}$$

Then we will have an estimator for a new transform variable that lies between the transform variables of the rigorous bounds according to

$$\left\langle \sigma^{-1} \right\rangle_{\zeta}^{-1} \le \sigma_G^{\zeta} \le \langle \sigma \rangle_{\zeta}. \tag{34}$$

The properties of the canonical function Σ guarantee that

$$\sigma_B^{-} \le \sigma_G^{*} \equiv \Sigma(\sigma_G^{\zeta}) \le \sigma_B^{+}. \tag{35}$$

Conductivity for random polycrystals of laminates

For random polycrystals (see the earlier discussion of the basic model in the second section), it is most convenient to define a new canonical function:

$$\Sigma_X(s) = \left[\frac{1}{3}\left(\frac{1}{\sigma_H + 2s} + \frac{2}{\sigma_M + 2s}\right)\right]^{-1} - 2s, \tag{36}$$

where the mean $\sigma_M = \sum_{i=1}^{J} v_i \sigma_i$ and harmonic mean $\sigma_H = \left[\sum_{i=1}^{J} \frac{v_i}{\sigma_i}\right]^{-1}$ of the layer constituents are the pertinent conductivities (off-axis and on-axis of symmetry, respectively) in each layered grain. Then, the Hashin-Shtrikman bounds for the conductivity of the random polycrystal are

$$\sigma_{HSX}^{\pm} = \Sigma_X(\sigma_{\pm}), \tag{37}$$

where $\sigma_+ = \sigma_M$ and $\sigma_- = \sigma_H$. These bounds are known not to be the most general ones since they rely on an implicit assumption that the grains are equiaxed. A more general lower bound that is known to be optimal is due to Schulgasser (1983) and Avellaneda *et al.* (1988):

$$\sigma_{ACLMX}^{-} = \Sigma_X(\sigma_{ACLMX}^{-}/4). \tag{38}$$

Helsing and Helte (1991) have reviewed the state of the art for conductivity bounds for polycrystals, and in particular have noted that the self-consistent [or CPA (*i.e.*, coherent potential approximation)] for the random polycrystal conductivity is given by

$$\sigma_{CPAX}^{*} = \Sigma_X(\sigma_{CPAX}^{*}). \tag{39}$$

It is easy to show (39) always lies between the two rigorous bounds σ_{ACLMX}^{-} and σ_{HSX}^{+}, and also between σ_{HSX}^{-} and σ_{HSX}^{+}. Note that σ_{ACLMX}^{-} and σ_{HSX}^{-} cross when $\sigma_m/\sigma_H = 10$, with σ_{ACLMX}^{-} becoming the superior lower bound for mean/harmonic-mean contrast ratios greater than 10.

Comparisons of conductivity bounds and estimates

We will now provide some comparisons like those presented in the previous section for elastic constant bounds and estimates.

Figure 4 shows a comparison of (a) the correlated bounds of Hashin and Shtrikman ($HSX^{\pm}$) based on the random polycrystal microgeometry, (b) the microstructure-based bounds (assuming disk inclusions) of Beran ($B^{\pm}$), (c) the random polycrystal lower bounds of Avellaneda *et al.* (1988) [$ACLMX^{-}$] laminated (hexagonal symmetry) grains. A self-consistent (CPAX) estimate is based on the random polycrystal microstructure. A new estimator (B^{G}) is based on the Beran bounds and uses a geometric mean approximation in order to incorporate information contained in the microstructure constants ζ_i.

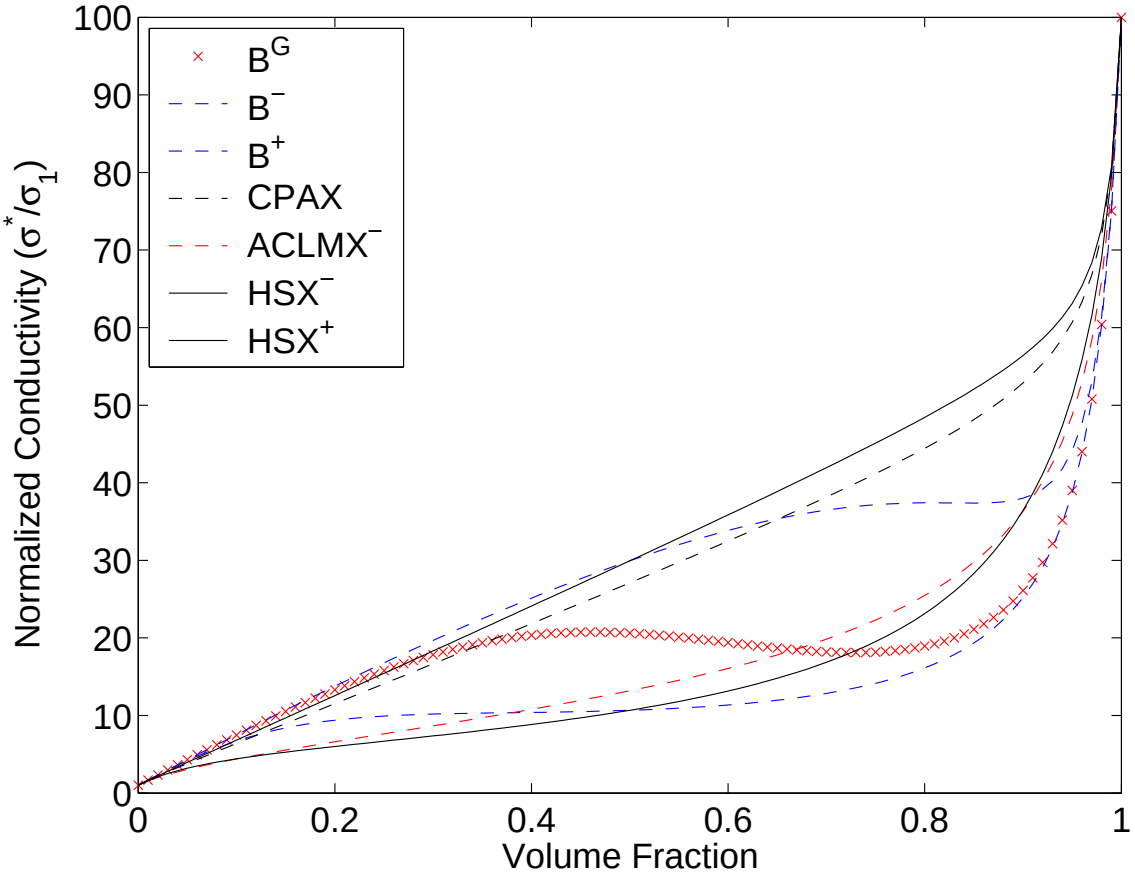

Figure 4: Conductivity comparisons. jim1-volsigmaall [NR]

Analytical continuation methods

There are other methods for conductivity/permittivity analysis. The Bergman-Milton (Bergman, 1978; 1980; 1982; Milton, 1980; 1981; Korringa and LaTorraca, 1986; Stroud *et al.*, 1986; Berryman, 1992) analytical approach to understanding some general effective transport coefficient or permittivity — which we take for example to be σ^* — of two-component inhomogeneous media shows that

$$\sigma^* = S(\sigma_1, \sigma_2) = \sigma_1 S(1,0) + \sigma_2 S(0,1) + \int_0^\infty \frac{dy\, \mathcal{S}(y)}{\frac{1}{\sigma_1} + \frac{y}{\sigma_2}}, \tag{40}$$

where $S(1,0)$ and $S(0,1)$ are constants depending only on the geometry and $\mathcal{S}(y) \geq 0$ is a resonance density functional also depending only on the geometry. The integral in (40) is known as a Stieltjes integral (Baker, 1975). This formula is typically derived and used for the case of complex constants: σ_1, σ_2, and σ^*. But we will restrict consideration here – as Bergman (1978) did in his early work – to pure conductors so that σ_1, σ_2, and σ^* are all real and nonnegative.

A short derivation of (40) is instructive, so we will present one now.

Following (for example) Korringa and LaTorraca (1986) we consider the defining equation for the function $Z(s)$

$$\sigma^* = \sigma_1 Z(s), \tag{41}$$

where

$$s \equiv \sigma_1/(\sigma_1 - \sigma_2). \tag{42}$$

Then, Milton (1981) shows [also see Korringa and LaTorraca, 1986] that

$$Z(s) = 1 - \sum_{n=0}^{N} A_n(1 - s_n)/(s - s_n), \tag{43}$$

where the s_n's are the locations of the poles, and are enumerated in increasing order. The A_n's are the residues. These real constants satisfy the following inequalties: $0 < A_n < 1$, $0 \leq s_n < 1$, and $\sum_n A_n \leq 1$. Note that N might be a very large number in practice, so that it may then be more convenient to think of turning this sum into an integral. Define a density functional

$$\mathcal{A}(s) \equiv \sum_{n=1}^{N} A_n \delta(s - s_n), \tag{44}$$

where δ is the Dirac delta function. Then, (43) can be rewitten as

$$Z(s) = 1 - A_0/s - \int_0^1 dx\, \mathcal{A}(x)(1 - x)/(s - x), \tag{45}$$

which is so far just a restatement of (43), assuming only that there exists a finite A_0 for which $s_0 \equiv 0$. Substituting (42) into (45) and rearranging, we find

$$Z(s) = 1 - A_0 + A_0\frac{\sigma_2}{\sigma_1} - \int_0^1 dx\, \mathcal{A}(x)\frac{(1-x)(\sigma_1-\sigma_2)}{(1-x)\sigma_1 + x\sigma_2}. \tag{46}$$

We can then symmetrize this expression by adding and subtracting the term $x\sigma_2$ in the numerator of the displayed ratio inside the integral. Then we can pull out another constant and finally have the form we want:

$$Z(s) = [1 - A_0 - \int_0^1 dx\, \mathcal{A}(x)] + A_0\frac{\sigma_2}{\sigma_1} + \int_0^1 dx\, \mathcal{A}(x)\frac{\sigma_2}{(1-x)\sigma_1 + x\sigma_2}. \tag{47}$$

Substituting this back into the original definition (41), we find the symmetrical result

$$\sigma^* = \frac{\sigma_1}{F_1} + \frac{\sigma_2}{F_2} + \int_0^1 dx\, \mathcal{A}(x)\frac{1}{(1-x)/\sigma_2 + x/\sigma_1}, \tag{48}$$

where $1 \geq 1/F_2 = A_0 > 0$ and $1 > 1/F_1 = 1 - A_0 - \int_0^1 dx\, \mathcal{A}(x) \geq 0$, since $\sum_{n=0}^{\infty} A_n = A_0 + \int_0^1 dx\, \mathcal{A}(x) \leq 1$. The F_i's are known as "formation factors" (Archie, 1942; Avellandea and Torquato, 1991).

This equation is not yet in the same form as (40), but it is nevertheless worthwhile to pause for a moment to consider this form on its own merits. In particular, the first two terms on the right hand side are exactly what is expected when conductors are connected in parallel inside a complex conducting medium. And the remaining integral looks like some sort of weighted average of conductors connected in series. The first physical analogy (conductors in parallel) is entirely appropriate. The second one is no doubt an oversimplification of what is happening in the medium, since the weights in the denominator (*i.e.*, x and $1-x$) are not really volume fractions (even though they do range from 0 to 1), and the density functional $\mathcal{A}$ in the numerator also contributes important numerical weights depending on the local shapes and interconnectedness of the microstructure of the conductors. This dependence on microstructure would correspond approximately to the network connectivity in a resistor network, but usually does not have a perfect analog for most 3D conducting composites.

To complete the derivation of (40), we now need only to make the further substitutions $x = 1/(1+y)$ where y ranges from 0 to ∞, and define $\mathcal{S}(y) \equiv \mathcal{A}(x)/(1+x)$. Then, we arrive finally at precisely (40), having found that $S(1,0) = 1/F_1$ and $S(0,1) = 1/F_2$. Furthermore, taking the limit $\sigma_1 = \sigma_2 = 1 = \sigma^*$, we find the useful sumrule

$$\frac{1}{F_1} + \frac{1}{F_2} + \int_0^{\infty} dy\frac{\mathcal{S}(y)}{1+y} = 1. \tag{49}$$

Clearly, other choices of the integral transform in (48) may also be useful. In particular, taking instead $x = 1/(1-y)$ is a good choice in preparation for analysis of the resonance density $\mathcal{S}(y)$ itself, as this transform places it most appropriately on the negative real axis. But for present purposes either (40) or (48) is a satisfactory choice for study.

Formation factor bounds

In a porous medium, when $\sigma_2 = \text{const}$ and σ_1 varies [as would be expected in a series of electrical conductivity experiments with different conducting fluids — such as brines (Wildenschild *et al.*, 2000) — in the same pores], then general bounds can be derived from the form of (40). These bounds [see Berryman (2005a) for the full derivation] are given by

$$\min(L_1, L_2) \le \sigma^*(\sigma_1, \sigma_2) \le \max(L_1, L_2), \tag{50}$$

where L_1 and L_2 are defined, respectively, by

$$L_1(\sigma_1, \sigma_2) \equiv \sigma_2 + \frac{\sigma_1 - \sigma_2}{F_1}, \tag{51}$$

and

$$L_2(\sigma_1, \sigma_2) \equiv \sigma_1 + \frac{\sigma_2 - \sigma_1}{F_2}. \tag{52}$$

If one of the σ_i's varies while the other remains constant, L_1 and L_2 are both straight lines, crossing when $\sigma_1 = \sigma_2$. We call (50) the formation factor bounds. One of them (always the lower bound for conductivities) often provides nontrivial improvements over the Hashin-Shtrikman and Beran bounds as we shall demonstrate by example.

The bounds obtained this way are in fact special cases of some earlier bounds by Prager (1969) and Bergman (1976), as discusssed recently by Milton (2002, pp. 580–581). The approach as described by Milton is based on Padé approximation methods (Torquato, 1985a; Milton, 2002), although the original papers did not couch the analysis in these terms. Besides the much simpler derivation permitted by direct analysis of the Bergman-Milton analytic formulas (Berryman, 2005a). the main technical difference between the results here and those of Prager and Bergman is that we have implicitly assumed that two distinct (possibly idealized) formation factors have actually been carefully measured. To do so in practice requires either extremely high or extremely low conductivities of one or the other conducting component, or it requires a careful extrapolation process based on multiple measurements (Berryman, 2005b). These assumed direct measurements (or an extrapolation process) are perfectly reasonable when one or the other component is actually (or nearly) an insulator (electrical or thermal) [see Guéguen and Palciauskas (1994) for a discussion]. On the other hand, Prager's approach differs from this by providing bounds directly from any and all measurements on the same system as the constituents or choices of physical constants to be measured are allowed to vary. Bergman's method is very similar in this regard to Prager's. In both cases, these methods were applied to real constants just as we have done, but generalization to complex constants is also possible (Milton, 2002).

In our present notation, Prager's bounds can also be written in terms of the canonical function Σ. Assuming that two measurements have been made of the formation factors, we have four bounds from Prager's results. Two of these are the same as the Wiener (1912) bounds, *i.e.*, the mean and harmonic mean based on volume fractions. The other two bounds are given by

$$\sigma_{P1}^* = \Sigma(x_1\sigma_1) \quad \text{and} \quad \sigma_{P2}^* = \Sigma(x_2\sigma_2), \tag{53}$$

where

$$x_1 = \frac{v_2}{2(v_1F_1 - 1)} \quad \text{and} \quad x_2 = \frac{v_1}{2(v_2F_2 - 1)}. \tag{54}$$

Using Hashin-Shtrikman bounds, it is not difficult to show that x_1 and x_2 are both nonnegative and bounded above by unity. Also, since $\sigma^{\pm}_{HS} = \Sigma(\sigma_{\pm})$, one of Prager's bounds is always lower than the lower HS bound, and therefore not an improved bound, so not of interest to us. Furthermore, the other Prager bound is always lower than the upper HS bound. We show in the examples that for the case considered here this bound is in fact a useful lower bound on σ^* that has the right asymptotic behavior — *i.e.*, approaching the formation factor bounds for large ratios of the constituent conductivities.

Similarly, two of the Bergman bounds can be written as

$$\sigma^*_{B1} = \Sigma(x_1\sigma_1 + (1 - x_1)\sigma_2) \quad \text{and} \quad \sigma^*_{B2} = \Sigma((1 - x_2)\sigma_1 + x_2\sigma_2), \tag{55}$$

where x_1 and x_2 were defined previously in (54). There are two other Bergman bounds, but these reduce exactly to the HS bounds for the case under consideration here. It is also clear from the monotonicity of the canonical function Σ and the facts $0 \le x_1, x_2 \le 1$ that the Bergman bounds given in (55) must always lie between or on the HS bounds. Furthermore, it is easy to see also that $\sigma^*_{P1} \le \sigma^*_{B1}$ and that $\sigma^*_{P2} \le \sigma^*_{B2}$, so Bergman's lower bound will always be superior to Prager's lower bound.

Asaad (1955) performed a series of thermal conductivity measurements on three different sandstones. He also measured the electrical formation factor of each sample. This data set is therefore most interesting to us for testing the theory. When the pores are filled with an electrically conducting fluid, current flows (in saturated sandstone) mostly through the pore fluid because sand grains are generally poor electrical conductors (Guéguen and Palciauskas, 1994). When the pores are filled instead with air, heat flows mostly through the sand grains because air is a poor thermal conductor. So the thermal conductivity properties of samples is quite different from those of electrical conductivity. But the microgeometry is still the same and, therefore, the structure of the equations for thermal conductivity is exactly the same as in (40). For Asaad's sandstone sample D, we find that $F_2^D = 3.72$ (from thermal conductivity measurements) and $F_1^D = 33.0$ (from electrical conductivity measurements). The porosity of this sample was $\phi^D = 0.126$, so $x_1 \simeq 0.138$ and $x_2 \simeq 0.028$. With these values known, we can make comparisons between and among the various theoretical results available to us. In particular note that since x_2 is quite small, σ^*_{B2} will clearly be very close to (nearly indistinguishable from) the Hashin-Shtrikman upper bound when $\sigma_1/\sigma_2 > 1$.

The uncorrelated Hashin-Shtrikman bounds (29) apply to this problem, as do the Beran bounds (31) and (32). To apply the Hashin-Shtrikman bounds we need only the volume fractions, but to apply the Beran bounds we also need some estimate of the microstructure parameters (the ζ_i's). Sandstones having a low porosity like 0.126 might have fairly round grains, but the pores themselves will surely not be well-approximated by spheres. So the common choice $\zeta_i = v_i$ is probably not adequate for this problem. A better choice is available however, since the values of ζ_i and η_i have been computed numerically for the penetrable sphere model (Berryman, 1985b; Torquato, 1985b; 2002). This model microstructure is very much like that

of a sandstone and, therefore, should prove adequate for our present comparisons. For porosity $v_1 = 0.126$, the penetrable sphere model has the value $\zeta_1 \simeq 0.472$. Since both formation factors are known for these experimental data, the formation factor (FF$\pm$) bounds can also be applied without difficulty. Figure 3 shows the results. (Note that the units of the conductivity have been normalized so all the curves cross at unity on this plot in order to make the Figure universal.)

We will limit this discussion to the region $\sigma_1/\sigma_2 \geq 1$. We find that the formation factor upper bound is well above the Hashin-Shtrikman upper bound, which is above the Beran bound as expected. All the bounds cross at $\sigma_1/\sigma_2 = 1$, as is necessary. The lower bounds have more complicated behavior. The Beran lower bound is always superior to the Hashin-Shtrikman lower bound, but they are both quite close together for all values of the ratio $\sigma_1/\sigma_2 > 1$. Both bounds are also superior to the lower formation factor bound for values of σ_1/σ_2 ratio close to unity. But, for higher values of contrast in the range $\sigma_1/\sigma_2 > 12$, these two bounds become inferior to the formation factor lower bound. This result is expected since it is for the asymptotic regimes (very high or very low ratios of the conductivities) that one of the FF bounds tends to become an exact estimate. Neither the Hashin-Shtrikman lower bounds nor the Beran lower bounds can compete in this regime because they must allow for the possibility that the more poorly conducting component plays host to the more strongly conducting component. Measured formation factor values provide new information that largely determines the status of this important long-range spatial correlation feature (due to the presence or absence of such a host/inclusion arrangement) throughout the microstructure.

Bergman lower bounds are best for moderate to high values of the contrast ratio, and they asymptote to the formation factor lower bounds (as do the Prager lower bounds) in the very high contrast regime. Note that Beran lower bounds can be superior to the Bergman lower bounds for small contrast ratios, since they use different measures of microstructure (ζ_i instead of F_i).

Figure 5 shows comparisons of (a) the uncorrelated bounds of Hashin and Shtrikman (HS$^{\pm}$), (b) the microstructure-based bounds (assuming penetrable spheres) of Beran (Beran$^{\pm}$), (c) the Padé approximant bounds of Bergman (B$^{\pm}$) and Prager (P^{-}), and (d) the new formation factor (FF$^{\pm}$) bounds. Beran upper bounds are always the best ones shown here. Bergman lower bounds are best for moderate to high values of the contrast ratio, and they asymptote to the formation factor lower bounds (as do the Prager lower bounds) in the very high contrast regime. Beran lower bounds can be superior to the Bergman lower bounds for small contrast ratios. For the sake of universality, units of conductivity have been normalized so the curves all cross at unity.

So at high contrast ($\sigma_1/\sigma_2 \gg 1$), the Beran upper bound and the Bergman lower bound are the best (tightest) bounds for this sample sandstone D. For contrast ratios up to 300, we obtain bounds confining the conductivity to variations less than about a factor of 2, which will often be quite satisfactory for such difficult, but nevertheless fairly typical, estimation problems. The use of the formation factor lower bounds together with some of the earlier bounds like the Hashin-Shtrikman and Beran bounds therefore seems to be one satisfactory solution to some of the problems of high contrast conductivity estimation noted in the previous section.

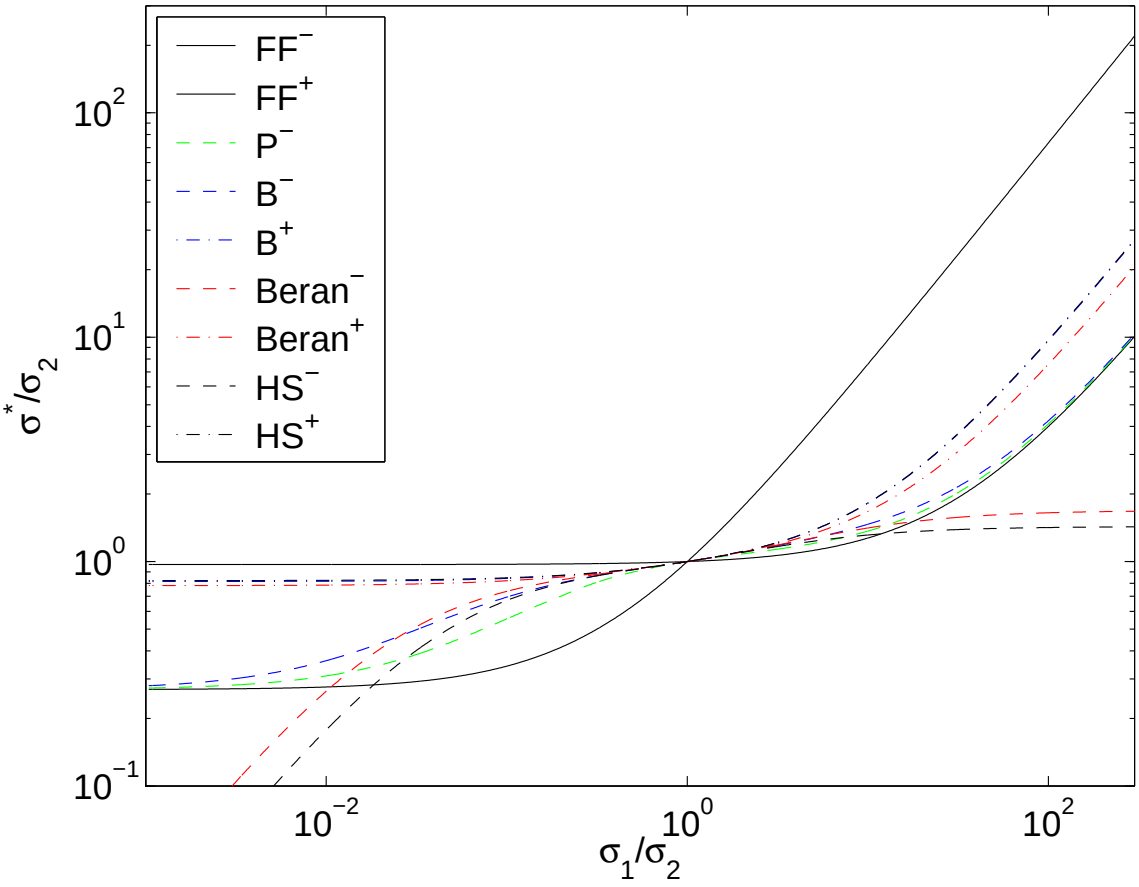

Figure 5: Conductivity comparisons including formation factor bounds. jim1-DNmixed [NR]

Otherwise, improvements can be made when desired using Prager, Bergman, and also Milton bounds (Milton, 1981b) [not discussed here]. Although the formation factor lower bounds are not the best known bounds, they are nevertheless very easy to use and give remarkably accurate estimates at very high contrasts.

ASSESSMENT AND CONCLUSIONS

The point of the paper has been to study how microstructure, and especially any special knowledge we may have of either quantitative measures or qualitative features of that microstructure, affects estimates of material constants.

For elasticity, we considered various improvements on the Hashin-Shtrikman bounds such as the Beran-Molyneux bounds, the McCoy-Silnutzer bounds, and the Milton-Phan-Thien bounds. We found that knowledge of microstructure can be used very effectively in these improved bounds. New estimates (not themselves rigorous bounds) can also be formulated based on the analytical structure of the bounds, and the microstructure parameters can then be incorporated directly into these estimates in a way so the resulting estimates always satisfy the bounds. When making comparisons between models based on disk-like inclusions in a host medium, and the random polycrystals of laminates model, we found that these models predict very similar results when there is a relatively small volume fraction of disks present. But when the volume fraction of disks is large, the bounds do not constrain the results as well, and so there is still more work to be done relating constants to microstructure in the mid-range of volume fractions, and generally for high contrast problems.

For electrical conductivity and other related physical constants such as thermal conductivity and dielectric constant (and in some cases fluid permeability), the microstructure can be introduced not only through the volume fractions and microstructural parameters as was done in the case of elasticity, but also through the use of more global measures of microstructure such as the formation factors. Global measures like the F_i's that determine the long-range spatial correlations and connectivity (within our material object of study) — by means of two fairly common and relatively simple measurements — are very advantageous and clearly more information of this type is desirable. The case of high contrast composites is always very important for all types of conductivity estimation and so formation factor bounds and Padé approximant schemes both provide convenient means of addressing this problem. The formation factor bounds are elementary in mathematical structure, but nevertheless provide very useful lower bounds on conductivity and permittivity for high contrast problems.

One general observation is that behavior of high contrast mixtures and composites remains poorly constrained by most of the methods presented, and more work in that direction is therefore still needed. A typical example that always generates high contrast situations is porous and/or granular media, where the pores may be filled with air; then, both the mechanical and the transport properties can have a very wide range of variation depending on the details of the microstructure. Some of the same types of information (such as formation factors) used here for studies of transport properties can also be applied to elasticity estimates in porous media as has been pointed out previously in studies of "cross-property" relationships and bounding

methods (Berryman and Milton, 1988; Gibiansky and Torquato, 1995) – *i.e.*, estimating one physical quantity after measuring another. So, one possibility for future progress that has yet to be explored in very great detail is how the formation factor bounds as well as other improved bounds on electrical or thermal conductivity may provide useful information about microstructure that can then be used to constrain further the elastic behavior of the same system.

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