# MICROGEOMETRY OF RANDOM COMPOSITES AND POROUS MEDIA

James G. Berryman
Lawrence Livermore National Laboratory
P. O. Box 808 L-156
Livermore, CA 94550

Graeme W. Milton
Courant Institute of Mathematical Sciences
New York University
New York, NY 10012

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## ABSTRACT

For practical applications of variational bounds to the effective properties of composite materials, the information available is often not that required by the formulas for the optimal bounds. It is therefore important to determine what can be said rigorously about various unknown material properties when some other properties are known. The key quantities to be analyzed are the parameters $\zeta$ and $\eta$ depending on the microgeometry through integrals of the three-point correlation functions. The physical significance of these parameters for two-phase composites and porous media is elucidated here by examining the various relationships between them and material properties. The bounds on conductivity due to Beran and the bounds on elastic constants due to Beran and Molyneux and to McCoy, as well as those of Milton and Phan-Thien, are considered. For the special case of porous media, the formulas simplify greatly and the resulting analytical relationships between transport properties and geometrical parameters are easily interpreted. In particular, it is shown that the microgeometry parameter $\zeta$ places limits on the pore space connectivity. Examples of bounds on one effective material property from measurements of another are also derived. These include bounds correlating the effective electrical or thermal conductivities and the effective shear modulus with the effective bulk modulus. These bounds are somewhat more restrictive than the well-known bounds of Hashin and Shtrikman. For porous materials, measurements of bulk modulus provide bounds on electrical formation factor and vice versa.

## 1. INTRODUCTION

Practical application of variational bounds to the effective properties of composite materials often requires information that is not available. The tightest bounds currently known typically depend on knowledge of constituent properties, relative volume fractions, and one or more parameters characterizing the microgeometry. While material properties of the constituents may generally be assumed to be known, common examples of incomplete or inappropriate information include: (*i*) knowledge of the volume fractions, but not the microgeometry parameters, (*ii*) knowledge of the volume fractions and only one microgeometry parameter when two are required, (*iii*) knowledge of the value of some effective transport property of the composite – but not the one of most interest. It is therefore important to determine what can be said rigorously about various unknown geometrical and effective material properties when some of the other properties are known. A similar idea was apparently first proposed by Prager [1] who obtained bounds by correlating measurements of the magnetic permeability at different temperatures. Various other ideas for using available information to improve bounds have been proposed subsequently for applications to electrical and thermal conductivities [2-4] and to elastic constants [5,6]. For example, Kantor and Bergman [6] suggest using knowledge of the effective elastic constants of one composite to improve the bounds on the elastic constants of another composite with the same microgeometry.

The strategy employed in this paper differs from these earlier approaches in that the key quantities we analyze are the parameters of the microgeometry. Our purpose is to derive some of the more important relationships which exist among the geometrical parameters and the material properties. Section 2 defines the parameters of the microgeometry. Sections 3 and 4 derive relationships between the parameters and material properties. Section 5 presents some new bounds on bulk modulus, shear modulus, and electrical conductivity that improve on the Hashin-Shtrikman bounds when a measurement of another physical property has been made. For porous materials, these bounds have particularly simple analytical forms. Such cross-property bounds may prove to be quite useful when one material property is easy to measure, but the other is not.

The present results are restricted to isotropic two-phase materials such as porous media with easily distinguished solid and void phases. Generalization to anisotropic and multiphase materials would require a substantial amount of additional effort.

## 2. PARAMETERS OF MICROGEOMETRY

Let $p(\vec{x})$ be the value of some scalar property of a two-phase random composite material (e.g., electrical or thermal conductivity, dielectric constant, bulk or shear modulus, etc.) which assumes one of two values $p_0$ or $p_1$ depending on whether $\vec{x}$ is located in a grain of material $0$ or material $1$. Define the indicator or characteristic function

$$f(\vec{x}) = \frac{p(\vec{x}) - p_0}{p_1 - p_0}. \tag{1}$$

Then $f(\vec{x}) = 0$ in material $0$ and $f(\vec{x}) = 1$ in material $1$. For example, in a porous medium we may (arbitrarily) label all solid regions as material $0$ and all void regions as material $1$. Since complete knowledge of the stochastic variable $f$ is seldom available, our interest in the characteristic function is generally limited to a few of its statistical properties. If chosen properly, these quantities are often sufficient to provide the data needed for variational bounds on the macroscopic average of the property being studied [7].

One such statistical property is the three-point spatial correlation function defined by

$$\hat{S}_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) = < f(\vec{x} + \vec{r}_1) f(\vec{x} + \vec{r}_2) f(\vec{x} + \vec{r}_3) > . \tag{2}$$

The brackets $< \cdot >$ indicate a volume average over the spatial coordinate $\vec{x}$. The volume fraction of constituent $1$ is given by $\phi_1$. The three-point correlations may be measured by processing digital images of material cross sections[8-10], or for certain special choices of microgeometry they may be calculated[11,12]. In general, we assume that the composite medium of interest is statistically homogeneous so that on average only the differences in the coordinate values are significant (translational invariance). Furthermore, we often assume that the material is statistically isotropic so that the averages do not depend on orientation of the arguments. The resulting simplified functional form for the three-point correlation is given by

$$\hat{S}_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \tilde{S}_3(\vec{r}_{12}, \vec{r}_{13}) = S_3(r_{12}, r_{13}, \mu_{12,13}), \tag{3}$$

where

$$\vec{r}_{ij} = \vec{r}_j - \vec{r}_i, \quad r_{ij} = \mid \vec{r}_{ij} \mid,$$

and

$$\mu_{ij,ik} = cos\,\theta = \vec{r}_{ij} \cdot \vec{r}_{ik} / r_{ij} r_{ik}.$$

The formulas which follow may be simplified greatly by introducing two parameters[13,14] depending on the microgeometry of a composite through the three-point correlation function $S_3$. For studies of magnetic permeability, electrical or thermal conductivities, and elastic constants, the two geometric parameters of interest are

$$\zeta_1 = \lim_{\Delta\to 0} \lim_{\Delta'\to\infty} \frac{9}{2\phi_0\phi_1} \int_\Delta^{\Delta'} dr \int_\Delta^{\Delta'} ds \int_{-1}^{+1} d\mu \frac{S_3(r,s,\mu)}{rs} P_2(\mu) \tag{4}$$

and

$$\eta_1 = \frac{5\zeta_1}{21} + \lim_{\Delta\to 0} \lim_{\Delta'\to\infty} \frac{150}{7\phi_0\phi_1} \int_\Delta^{\Delta'} dr \int_\Delta^{\Delta'} ds \int_{-1}^{+1} d\mu \frac{S_3(r,s,\mu)}{rs} P_4(\mu), \tag{5}$$

where $\phi_1$ is the volume fraction of material 1, $\phi_0 = 1 - \phi_1$, and $P_2(\mu)$ and $P_4(\mu)$ are the Legendre polynomials of order 2 and 4 given respectively by

$$P_2(\mu) = \frac{1}{2}(3\mu^2 - 1)$$

and

$$P_4(\mu) = \frac{1}{8}(35\mu^4 - 30\mu^2 + 3).$$

To obtain the values of $\zeta_1$ and $\eta_1$ for real materials, we first measure $S_3$ using image processing methods[9]. Then, we interpolate and integrate the values $S_3$ known on a square lattice using methods developed recently[15].

Various facts about $\zeta_1$ and $\eta_1$ are known[13,14]. For example, $0 \le \zeta_1 \le 1$ and $0 \le \eta_1 \le 1$. Furthermore, Milton and Phan-Thien[5] have shown that $5\zeta_1/21 \le \eta_1$.

Once $\zeta_1$ and $\eta_1$ are known, we also know the complementary microgeometry parameters $\zeta_0 = 1 - \zeta_1$ and $\eta_0 = 1 - \eta_1$. Using all these parameters together with the corresponding volume fractions $\phi_1$ and $\phi_0 = 1 - \phi_1$, Milton[13,14] defines three averages of any physical property $\Pi$ of a two-phase composite by

$$\langle \Pi \rangle = \Pi_0 + (\Pi_1 - \Pi_0)\phi_1, \tag{6}$$

$$\langle \Pi \rangle_\zeta = \Pi_0 + (\Pi_1 - \Pi_0)\zeta_1, \tag{7}$$

and

$$\langle \Pi \rangle_\eta = \Pi_0 + (\Pi_1 - \Pi_0)\eta_1. \tag{8}$$

Many of the variational bounds on electrical or thermal conductivity [16] and elastic constants [17,18,5] of random composites can be written compactly in terms of these averages. The parameters of the microgeometry therefore play a central role in the analysis. The purpose of this paper is to elucidate the physical significance of these parameters by showing their various relationships to well-defined physical properties.

## 3. ELECTRICAL CONDUCTIVITY AND FORMATION FACTOR

The variational bound of Beran [16] on the conductivity $\sigma$ may be written very concisely in terms of the following function:

$$\Sigma(x) = \langle\frac{1}{\sigma + 2x}\rangle^{-1} - 2x, \tag{9}$$

where $x$,the independent variable of the function $\Sigma$, is always non-negative. It is easy to show that $\Sigma$ is a monotonically increasing function with its non-negative argument. With this definition, the upper (+) and lower (–) bounds on the conductivity are respectively

$$\sigma^{+} = \Sigma(\langle\sigma\rangle_{\zeta}) \tag{10}$$

and

$$\sigma^{-} = \Sigma(\langle\frac{1}{\sigma}\rangle_{\zeta}^{-1}). \tag{11}$$

If a porous insulator ($\sigma_0 = 0$) is filled with a conducting fluid of conductivity $\sigma_1$ and the effective conductivity of the resulting fluid-filled composite is $\sigma^*$, then we define the electrical formation factor to be $F^* = \sigma_1/\sigma^*$. It is not difficult to show that the nontrivial Beran bound is given by

$$F^* \geq 1 + (1 + \frac{1}{2\zeta_1})\frac{\phi_0}{\phi_1}. \tag{12}$$

For comparison, the Hashin-Shtrikman bound [19] is given by

$$F^* \geq 1 + \frac{3}{2}\frac{\phi_0}{\phi_1}. \tag{13}$$

It follows that, if we have a measurement of the formation factor $F^*$, Eq. (12) can be rearranged to provide a useful bound on the geometric parameter $\zeta_1$. This bound is

$$\frac{1}{2}\phi_0/(\phi_1 F^* - 1) \leq \zeta_1. \tag{14}$$

Tighter bounds on $\zeta_1$ have also been obtained by Korringa and LaTorraca [4,20] from experimental measurements of the complex dielectric constant at various frequencies.

Now define the tortuosity $\tau$ by $\tau^2 = \phi_1 F^*$. Then (14) may be rewritten as

$$\tau^2 - 1 \geq \frac{\phi_0}{2\zeta_1}. \tag{15}$$

When $\zeta_1 = 1$, we have the Hashin-Shtrikman bound on tortuosity. When $\zeta_1 \to 0$, (15) rapidly improves this bound. To provide a physical interpretation, note that as the tortuosity increases the average connectivity of the pore space decreases. Thus, (15) shows that $\zeta_1$ places limits on the pore space connectivity. As $\zeta_1 \to 0$, so does the connectivity.

## 4. ELASTIC CONSTANTS

The variational bounds of Beran and Molyneux [17] and McCoy [18] on the bulk $K$ and shear $G$ moduli may be written very concisely in terms of the following functions:

$$\Lambda(y) = \left\langle \frac{1}{K + \frac{4}{3}y} \right\rangle^{-1} - \frac{4}{3}y \tag{16}$$

and

$$\Gamma(z) = \left\langle \frac{1}{G + z} \right\rangle^{-1} - z, \tag{17}$$

where $y$ and $z$, the independent variables of the functions $\Lambda$ and $\Gamma$, are always non-negative. It is easy to show that $\Lambda$ and $\Gamma$ are again both monotonically increasing functions of these non-negative arguments. With these definitions, the upper (+) and lower (−) bounds on the bulk modulus are respectively

$$K^+ = \Lambda(\langle G \rangle_\zeta) \tag{18}$$

and

$$K^- = \Lambda(\langle \frac{1}{G} \rangle_\zeta^{-1}). \tag{19}$$

The bounds on the shear modulus are respectively

$$G^+ = \Gamma(\Theta/6) \tag{20}$$

and

$$G^- = \Gamma(1/6\Xi) \tag{21}$$

where

$$\begin{aligned} \Theta = [10\langle G \rangle^2 \langle K \rangle_\zeta + 5\langle G \rangle \langle 2K + 3G \rangle \langle G \rangle_\zeta \\ + \langle 3K + G \rangle^2 \langle G \rangle_\eta]/\langle K + 2G \rangle^2 \end{aligned} \tag{22}$$

and

$$\begin{aligned} \Xi = [10\langle K \rangle^2 \langle 1/K \rangle_\zeta + 5\langle G \rangle \langle 2K + 3G \rangle \langle 1/G \rangle_\zeta \\ + \langle 3K + G \rangle^2 \langle 1/G \rangle_\eta]/\langle 9K + 8G \rangle^2 \end{aligned}. \tag{23}$$

Variational bounds on the bulk $K$ and shear $G$ moduli have also been derived by Milton and Phan-Thien[5]. The bounds on the bulk modulus are the same as those of Beran and Molyneux [17]. The bounds on the shear modulus are different and take the form:

$$\hat{G}^{+} = \Gamma(\hat{\Theta}/6) \tag{24}$$

and

$$\hat{G}^{-} = \Gamma(1/6\hat{\Xi}) \tag{25}$$

where

$$\hat{\Theta} = \frac{3\langle G\rangle_\eta \langle 6K + 7G\rangle_\zeta - 5\langle G\rangle_\zeta^2}{\langle 2K - G\rangle_\zeta + 5\langle G\rangle_\eta} \tag{26}$$

and

$$\hat{\Xi} = \frac{5\langle 1/G\rangle_\zeta \langle 6/K - 1/G\rangle_\zeta + \langle 1/G\rangle_\eta \langle 2/K + 21/G\rangle_\zeta}{\langle 128/K + 99/G\rangle_\zeta + \langle 45/G\rangle_\eta}. \tag{27}$$

Milton and Phan-Thien[5] show that their bounds are at least as tight as the McCoy bounds [18] for any choice of microstructure. Berryman[21] has shown that the two sets of bounds are nearly indistinguishable for the penetrable sphere model[11,22].

It has been discovered recently[15] that, while it is relatively straightforward to calculate $\zeta_1$, it may be significantly more difficult to obtain accurate estimates of the microgeometry parameter $\eta_1$ from digital measurements of $S_3$. This fact provides a motivation to obtain bounds on the elastic constants that have no dependence on the parameter $\eta_1$. This goal can be attained by studying the monotonicity properties of $\Lambda$ and $\Gamma$ and of the arguments $\Theta$, $\Xi$, $\hat{\Theta}$, and $\hat{\Xi}$. We already know that $\Lambda$ and $\Gamma$ are monotonically increasing functions. If we view the arguments as functions of their $\eta$ averages according to

$$\Theta = Q(\langle G\rangle_\eta), \tag{28}$$

$$\Xi = X(\langle 1/G\rangle_\eta), \tag{29}$$

$$\hat{\Theta} = \hat{Q}(\langle G\rangle_\eta), \tag{30}$$

and

$$\hat{\Xi} = \hat{X}(\langle 1/G\rangle_\eta), \tag{31}$$

then it is easy to show that the functions defined by

$$\begin{aligned} Q(\alpha) = [10\langle G\rangle^2 \langle K\rangle_\zeta + 5\langle G\rangle\langle 2K + 3G\rangle\langle G\rangle_\zeta \\ + \langle 3K + G\rangle^2 \alpha]/\langle K + 2G\rangle^2 \end{aligned}, \tag{32}$$

$$X(\beta) = [10\langle K\rangle^2\langle 1/K\rangle_\zeta + 5\langle G\rangle\langle 2K+3G\rangle\langle 1/G\rangle_\zeta + \langle 3K+G\rangle^2\beta]/\langle 9K+8G\rangle^2, \quad (33)$$

$$\hat{Q}(\alpha) = \frac{3\alpha\langle 6K+7G\rangle_\zeta - 5\langle G\rangle_\zeta^2}{\langle 2K-G\rangle_\zeta + 5\alpha}, \quad (34)$$

and

$$\hat{X}(\beta) = \frac{5\langle 1/G\rangle_\zeta\langle 6/K - 1/G\rangle_\zeta + \beta\langle 2/K + 21/G\rangle_\zeta}{\langle 128/K + 99/G\rangle_\zeta + 45\beta} \quad (35)$$

are also monotonically increasing functions of their arguments. On the other hand, the sign of the monotonic variation of the $\eta$ averages depends on the sign of the difference in the constituent shear moduli:

$$\alpha = \langle G\rangle_\eta = G_0 + (G_1 - G_0)\eta_1 \quad (36)$$

and

$$\beta = \langle 1/G\rangle_\eta = 1/G_0 + (1/G_1 - 1/G_0)\eta_1. \quad (37)$$

Since the upper bounds must always be greater than or equal to the lower bounds, the arguments $\hat{\Theta}$ and $\hat{\Xi}^{-1}$ must satisfy $\hat{\Theta} \geq \hat{\Xi}^{-1}$. As Milton and Phan-Thien[5] have shown, it follows that $5\zeta_1/21 \leq \eta_1$ and that $5\zeta_0/21 \leq \eta_0$. Thus, if $\zeta_1$ has been measured accurately, the value of $\eta_1$ must fall in the range

$$\eta_1^- \equiv 5\zeta_1/21 \leq \eta_1 \leq (16 + 5\zeta_1)/21 \equiv \eta_1^+. \quad (38)$$

It follows that, if $(G_0 - G_1) \geq 0$, then

$$G^+ = \Gamma(\Theta/6) \leq \Gamma[Q(\langle G\rangle_{\eta^-})/6], \quad (39)$$

$$G^- = \Gamma(1/6\Xi) \geq \Gamma[1/6X(\langle 1/G\rangle_{\eta^+})], \quad (40)$$

$$\hat{G}^+ = \Gamma(\hat{\Theta}/6) \leq \Gamma[\hat{Q}(\langle G\rangle_{\eta^-})/6], \quad (41)$$

and

$$\hat{G}^- = \Gamma(1/6\hat{\Xi}) \geq \Gamma[1/6\hat{X}(\langle 1/G\rangle_{\eta^+})]. \quad (42)$$

In (39)-(42), the averages are found by replacing $\eta_1$ in (36) and (37) by $\eta_1^+$ or $\eta_1^-$ as indicated. Similarly, if $(G_0 - G_1) \leq 0$, then we obtain valid bounds interchanging the roles of $\eta_1^+$ and $\eta_1^-$ in the averages.

The bounds (41) and (42) were obtained previously by Milton and Phan-Thien[5], and are somewhat more restrictive than (39) and (40). However, the simpler functional form of (39) and (40) – through $Q$ and $X$ – has some advantages over that of (41) and (42) for our present purposes.

Now consider a porous medium with $K_1 = G_1 = 0$. Then, we find

$$\Lambda(y) = \frac{4y\phi_0 K_0}{3\phi_1 K_0 + 4y} \tag{43}$$

and

$$\Gamma(z) = \frac{z\phi_0 G_0}{\phi_1 G_0 + z}. \tag{44}$$

All the lower bounds vanish for porous media, so the nontrivial arguments (for the upper bounds) are given by

$$y = \langle G \rangle_\zeta = G_0\zeta_0, \tag{45}$$

and

$$z = Q(\alpha)/6 = [5G_0^2(4K_0 + 3G_0)\zeta_0 + (3K_0 + G_0)^2\alpha]/6(K_0 + 2G_0)^2 \tag{46}$$

or

$$z = \hat{Q}(\alpha)/6 = \left(\frac{\zeta_0}{6}\right)\frac{3\alpha(6K_0 + 7G_0) - 5G_0^2\zeta_0}{(2K_0 - G_0)\zeta_0 + 5\alpha} \tag{47}$$

where

$$\alpha = G_0\eta_0 \leq G_0(1 - \eta_1^-). \tag{48}$$

If $K^*$ and $G^*$ are measured values of the bulk and shear moduli, then we can use the facts that (43) and (44) are bounds to derive the inequalities

$$\frac{3\phi_1 K^*/4}{\phi_0 - K^*/K_0} \leq y \tag{49}$$

and

$$R^* \equiv \frac{\phi_1 G^*/G_0}{\phi_0 - G^*/G_0} \leq z. \tag{50}$$

Combining these results, we find that upper bounds on the microgeometry parameters are given by

$$\zeta_1 \leq 1 - \frac{3\phi_1 K^*/4G_0}{\phi_0 - K^*/K_0}, \tag{51}$$

$$\eta_1 \leq 1 - \left[6R^*\left(K_0 + 2G_0\right)^2 - 5G_0\zeta_0(4K_0 + 3G_0)\right]/(3K_0 + G_0)^2, \tag{52}$$

and

$$\eta_1 \leq 1 - (\zeta_0/3)\left[6R^*(2K_0/G_0 - 1) + 5\zeta_0\right]/\left[\zeta_0(6K_0/G_0 + 7) - 10R^*\right]. \tag{53}$$

Inequality (51) follows from (43) and (45). Inequality (52) follows from (44), (46), and (48), while (53) follows from (44), (47), and (48).

The inequalities (51)-(53) show that bounds on the microgeometry parameters may be obtained from measurements of the bulk and shear moduli. These formulas will not be useful if these bulk and shear moduli are the unknown quantities that we wish to bound. However, one example of a useful application of these expressions is the following experiment: Suppose we measure $K^*$ and $G^*$ for a porous material. Then (51)-(53) provide estimates of the microgeometry parameters for this particular geometry. Now, if we introduce some new substance into the pores, these parameters do not change; so they can be used to bound the properties of the new two-phase composite using (18), (40), and (42) or (19), (39), and (41) respectively – depending on the sign of the shear modulus difference $G_0 - G_1$. A similar strategy in a different analytical context has been proposed by Kantor and Bergman [6] for obtaining bounds on elastic constants.

## 5. CROSS-PROPERTY BOUNDS

One very useful extension of the ideas presented so far involves comparing the bounds on the parameters of the microgeometry obtained from measurements of one material property with those of another. The idea of correlating measurements of electrical or thermal conductivity [1-4] or measurements of elastic constants [6] to produce bounds on the same material property under somewhat different physical circumstances has been proposed previously. However, our result will be bounds on one material property from measurements on another. Again, Prager [1] proposed a similar idea by suggesting that bounds on magnetic permeability could be found by making measurements on thermal conductivity. We will concentrate on examples for porous media since the final formulas are then relatively simple, but these ideas apply to any two-phase composite.

Combining (14) and (51), we find that

$$\frac{1}{2}\phi_0/(\phi_1 F^* - 1) \leq \zeta_1 \leq 1 - \frac{3\phi_1 K^*/4G_0}{\phi_0 - K^*/K_0}. \tag{54}$$

Thus, measurements of $K^*$ provide bounds on $F^*$, and vice versa.

Now, if we recall the definition of the tortuosity $\tau$ as $\tau^2 = \phi_1 F^*$, it follows easily from (54) that

$$\tau^2 \geq 1 + \frac{\frac{1}{2}\phi_0(\phi_0 - K^*/K_0)}{\phi_0 - K^*(1/K_0 + 3\phi_1/4G_0)}. \tag{55}$$

Recall from (13) that the Hashin-Shtrikman bound on the tortuosity is $\tau^2 \geq 1 + \frac{1}{2}\phi_0$; this value is achieved by (55) with $K^* = 0$. Since the right hand side of (55) is easily shown to be a monotonically increasing function of $K^*$, we see that (55) is an improvement on the Hashin-Shtrikman bound whenever $K^* > 0$. The nontrivial Hashin-Shtrikman bound on the bulk modulus [23] is

$$K^* \leq \frac{\frac{4}{3}\phi_0 G_0 K_0}{\phi_1 K_0 + \frac{4}{3}G_0} \equiv K_{HS}^+. \tag{56}$$

It is known that (56) is an optimum bound (when no geometrical information is available) and that the equality is satisfied for the coated sphere geometry [24]. When the equality in (56) is satisfied, the right hand side of (55) is infinite – which is physically correct since the void phase is unconnected for this geometry and, therefore, the tortuosity is infinite. No other value of $K^*$ will make the right hand side of (55) infinite. Nevertheless, the fact that this choice of $K^*$ pushes (55) to its limiting value suggests that this bound will sometimes be a significant improvement on the Hashin-Shtrikman bound.

We can also obtain an improved bound on the bulk modulus by making a measurement of the formation factor or, equivalently, the tortuosity so that

$$K^* \leq \frac{4}{3}\phi_0 G_0 K_0 \frac{\tau^2 - 1 - \frac{1}{2}\phi_0}{(\tau^2 - 1)\phi_1 K_0 + (\tau^2 - 1 - \frac{1}{2}\phi_0)\frac{4}{3}G_0}. \tag{57}$$

Inequality (57) is an improvement over (56) for any value of $\tau$ such that $\infty > \tau$. To illustrate the behaviour of Eq. (57), consider a porous material with $\phi_1 = 0.2$ and $G_0/K_0 = 3/4$. Then, the Hashin-Shtrikman upper bound on the bulk modulus obtained from (56) is $K_{HS}^+/K_0 = 2/3$. In Figure 1, the upper bound $K^+/K_0$ is plotted as a function of $\tau^2$. We see that, for values of $\tau^2$ toward the low end of the range $1.4 \leq \tau^2 \leq 3.0$, the new bound can be a substantial improvement on the Hashin-Shtrikman bound. The new bound may be expected to find some use, since values of $\tau^2$ are quite commonly found to lie in this range for real materials [25].

To provide an analytical example, consider the three approximations to the tortuosity given by

$$\tau^2 \simeq \frac{1}{2}(1 + \phi_1^{-1}), \tag{58}$$

$$\tau^2 \simeq \phi_1^{-\frac{1}{2}}, \tag{59}$$

$$\tau^2 \simeq \frac{2}{1+\phi_1}. \tag{60}$$

These expressions have been derived by Berryman [26], Sen *et al.* [27], and Berryman [28] respectively. All three expressions have the property that they approach the Hashin-Shtrikman bound as $\phi_1 \to 1$, and all three are expected to apply to porous media consisting of sphere packs or approximations to sphere packs. Evaluating these expressions at $\phi_1 = 0.2$, we find that $\tau^2 \simeq 3, 2.24$, and $1.67$ respectively. Thus, all three expressions give estimates of $\tau^2$ in the range where the new rigorous bound is expected to provide some improvement over the Hashin-Shtrikman bound.

Figures 2 and 3 show how a measurement of effective conductivity leads first to bounds on the microgeometry parameter $\zeta_1$ and then to bounds on the bulk modulus $K^*$. Figure 2 illustrates the process for the porous material treated in Figure 1: $\phi_1 = 0.2$ and $G_0/K_0 = 3/4$. We see that tight bounds are possible even for a porous medium when the measured conductivity is close to its maximum allowed value, since $\zeta_1$ is constrained to lie between $\zeta_1 = 1$ and the intercept value which is then very close to unity. Figure 3 illustrates the process for a composite with $\phi_0 = \phi_1 = 1/2$, $\sigma_1/\sigma_0 = 5$, $K_1/K_0 = 10$, $G_0/K_0 = 3/4$, and $G_1/G_0 = 2/3$. If $\sigma^*$ is measured and found to be $\sigma^* = 0.52\sigma_1$, then the bounds on $K^*$ can be narrowed from the range $2.21 \le K^*/K_0 \le 2.39$ for the Hashin-Shtrikman bounds to the range $2.22 \le K^*/K_0 \le 2.28$ for the bounds depending on the parameters of the microgeometry. Even though the ratios $\sigma_1/\sigma_0$ and $K_0/K_1$ are both rather large, the bounds on $K^*$ are quite tight in this example because the ratio $G_1/G_0$ controlling the spread in the bounds is of order unity. Recall that the upper and lower bounds are identical if the shear moduli of the constituents are the same [29].

Another application of these ideas is to obtain bounds correlating $K^*$ and $G^*$ that improve upon the Hashin-Shtrikman bounds [23] without incorporating additional geometric information about the composite directly. In the $(K, G)$ plane, the Hashin-Shtrikman bounds define a rectangle (see Figure 4). Now, to any composite we can associate a triplet of values $(K, G, \zeta_1)$ with the exact value of $\zeta_1$ unknown. Let us suppose $G_0 \ge G_1$. Then the Beran-Molyneux bounds [17] given by (18) and (19) imply

$$\frac{1/\Lambda^{-1}(K^*) - 1/G_0}{1/G_1 - 1/G_0} \le \zeta_1 \le \frac{G_0 - \Lambda^{-1}(K^*)}{G_0 - G_1} \tag{61}$$

where

$$\Lambda^{-1}(k) = \frac{3K_0K_1(k < 1/K > -1)}{4(< K > -k)} \tag{62}$$

is the inverse of the function $\Lambda(y)$ defined by (16). By letting $\zeta_1$ range over the interval (61) and calculating the maximum value of $\hat{G}^+$ and the minimum value of $\hat{G}^-$ within this interval, we obtain bounds correlating measured values $G^*$ and $K^*$ that are more restrictive than the rectangular Hashin-Shtrikman bounds. These bounds are illustrated in Figure 4 for a composite with $\phi_0 = \phi_1 = 1/2$, $K_0/K_1 = 30$, and $G_0/G_1 = 20$. When $G_1 \geq G_0$, the inequalities in (61) are reversed, and the same method may still be used to generate bounds correlating $G^*$ with $K^*$.

## 6. SUMMARY AND DISCUSSION

When the information available is not the same as the information required by the optimum variational bounds, it is important to know what can be said rigorously about various unknown material properties with the information at hand. An exhaustive listing of all the possible combinations of approximations has not been attempted. However, since many results are listed and others are easily derived from these, it may be helpful to summarize our main conclusions: (*i*) If $\zeta_1$ has been measured using image processing methods[15], then bounds on $\eta_1$ are given by (38) and bounds on elastic constants are given by (39)-(42). (*ii*) For porous media, we have shown that lower and upper bounds on the parameter $\zeta_1$ are given by measurements of formation factor (14) and bulk modulus (51). These bounds on $\zeta_1$ can then be used to provide lower and upper bounds on the parameter $\eta_1$ using (38). The lower bounds on $\zeta_1$ and $\eta_1$ may then be used with (45), (46), and (48) to provide arguments for the upper bounds (43) and (44) on the bulk and shear moduli. (*iii*) If we have measurements of formation factor (or tortuosity), we may use these directly in (57) to find bounds on the bulk modulus; similarly, if we have measurements of the bulk modulus of a porous material, we can use (55) directly to bound the tortuosity, or, equivalently, the formation factor. (*iv*) If we have measurements of the bulk modulus, then we can use them to find bounds on the shear modulus; similarly, measurements on the shear modulus imply bounds on the bulk modulus.

We conclude that useful bounds on physical properties can be obtained even when our knowledge of the microstructure is imperfect or incomplete. Any information we do have can be used to place limits on the range of variation of the microgeometry parameters, and these limits can then be used to provide bounds on the material properties of interest. When these material properties are either difficult or expensive to determine by other means, the bounds generated this way provide an important alternative.

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## Figure Captions

Figure 1. Plot of the upper bound on bulk modulus $K^+$ of a porous material given by (57) as a function of the squared tortuosity $\tau^2$. The parameters are given by $\phi_1 = 0.2$ and $G_0/K_0 = 3/4$.

Figure 2. Illustrating the process through which a measurement of effective conductivity of a porous insulating material filled with a conducting fluid leads to an upper bound on the bulk modulus of the porous frame. The material parameters are the same as in Figure 1.

Figure 3. Illustrating the process through which a measurement of effective conductivity of a composite material leads to improved upper and lower bounds on the bulk modulus of the composite. The material parameters are given by $\phi_0 = \phi_1 = 1/2$, $\sigma_1/\sigma_0 = 5$, $K_1/K_0 = 10$, $G_0/K_0 = 3/4$, and $G_1/G_0 = 2/3$. A measured value of $\sigma^* = 0.52\sigma_1$ implies that $0.62 \le \zeta_1 \le 0.90$ which in turn means that $2.22 \le K^*/K_0 \le 2.28$.

Figure 4. Illustrating bounds (solid lines) correlating measured shear modulus $G^*$ with measured bulk modulus $K^*$. These bounds are more restrictive than the Hashin-Shtrikman bounds (dashed lines). The material parameters in the example are $\phi_0 = \phi_1 = 1/2$, $K_0 = 30$, $K_1 = 1$, $G_0 = 10$, and $G_1 = 1/2$. Each dot indicates the location of a change in the analytic behavior of the bounds.