



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Bounds on Transport Coefficients of Porous Media

J. G. Berryman

March 21, 2005

ASME/ASCE/SES Conference on Mechanics and Materials
Baton Rouge, LA, United States
June 1, 2005 through June 3, 2005

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

McMat2005/TPC125-6

BOUNDS ON TRANSPORT COEFFICIENTS OF POROUS MEDIA

James G. Berryman

University of California, Lawrence Livermore National Laboratory
P.O. Box 808, L-200
Livermore, CA 94551-9900
Email: berryman1@llnl.gov

ABSTRACT

An analytical formulation of conductivity bounds by Bergman and Milton is used in a different way to obtain rigorous bounds on the real transport coefficients (electrical conductivity, thermal conductivity, and/or fluid permeability) of a fluid-saturated porous medium. These bounds do not depend explicitly on the porosity, but rather on two formation factors — one associated with the pore space and the other with the solid frame. Hashin-Shtrikman bounds for transport in random polycrystals of porous-material laminates will also be discussed.

INTRODUCTION

Bounds on various transport coefficients in heterogeneous media have been heavily studied now for over forty years [1–3]. One of the more unusual developments in this area has been the introduction of rigorous methods for developing bounds on complex constants (closed curves in the complex plane), especially the dielectric constant and conductivity of heterogeneous media [4–10]. These methods represent a great technical achievement in this field, but they nevertheless can sometimes be difficult to apply to real data since they require high precision and strong consistency among the data used in computing the bounds. In some cases it would be helpful for applications if simpler and more robust methods and results were available.

In this work we consider the question of whether it is possible to make use of the analytical methods in a different way to find bounds on transport coefficients. We limit discussion to real coefficients, taking thermal conductivity as our main example, but the results apply equally well to other transport co-

efficients including electrical conductivity and fluid permeability [11]. Furthermore, the resulting bounds depend only on commonly measured quantities in porous media called formation factors [9, 12], and they show no unusual sensitivity to measurement errors or any need for careful checking of consistency relations among the measurements.

THE ANALYTICAL FORMULATION

The Bergman-Milton [4–11] analytical approach to understanding some generic transport coefficient κ^* of two-component inhomogeneous media shows that

$$\kappa^* = k(\kappa_1, \kappa_2) = \kappa_1 k(1, 0) + \kappa_2 k(0, 1) + \int_0^\infty \frac{dx \mathcal{X}(x)}{\frac{1}{\kappa_1} + \frac{x}{\kappa_2}}, \quad (1)$$

where $k(1, 0)$ and $k(0, 1)$ are constants depending only on the geometry and $\mathcal{X}(x) \geq 0$ is a resonance density also depending only on the geometry. The integral in (1) is known as a Stieltjes integral [13]. Although the representation (1) has most often been employed to study the behavior of κ^* in the complex plane when κ_1 and κ_2 are themselves complex (corresponding in the electrical case to mixtures of conductors and dielectrics), we restrict consideration here – as Bergman did in his early work [4] – to pure conductors so that κ_1 , κ_2 , and κ^* are real and nonnegative.

In the limit that one or the other of the two constituents is a perfect insulator ($\kappa_i = 0$), or in the more common case when one of the constituents is much more strongly conducting than the other, we can define two quantities called formation factors [12]

by

$$\lim_{\kappa_1 \rightarrow \infty} \frac{\kappa^*}{\kappa_1} = \lim_{\kappa_1 \rightarrow \infty} k(1, \kappa_2/\kappa_1) = k(1, 0) = \frac{1}{F_1}, \quad (2)$$

and, similarly, by

$$\lim_{\kappa_2 \rightarrow \infty} \frac{\kappa^*}{\kappa_2} = \lim_{\kappa_2 \rightarrow \infty} k(\kappa_1/\kappa_2, 1) = k(0, 1) = \frac{1}{F_2}. \quad (3)$$

In a porous material, where solid and pore fluid are each continuously connected throughout the material, both formation factors are finite, and both satisfy $F \geq 1$. The more commonly measured quantity of this type is the electrical formation factor for the continuous fluid component. This measurement has some possible complications due to surface conductance [14, 15], but it is usually not contaminated by conductance through the bulk solid material because most rock grains can be correctly assumed to be electrically insulating to a very good approximation [16]. Since the formation factor is strictly a measure of the micro-geometry of the heterogeneous medium, it is the same number (except for those possible complications already mentioned of surface electrical conduction [14, 15], which can be eliminated whenever necessary using known experimental methods) for all mathematically equivalent conductivities. For this presentation, we will use F_1 to represent this formation factor associated with the pore space. On the other hand, for thermal conduction the rock grains are the most highly conducting component and the pore fluids tend to be much more poorly conducting – especially so in the case of saturating air. So we will take F_2 to be this formation factor associated with the solid frame of the porous material.

FORMATION FACTOR BOUNDS

To obtain some useful bounds, we again consider the form of (1) using (2) and (3)

$$k(\kappa_1, \kappa_2) = \frac{\kappa_1}{F_1} + \frac{\kappa_2}{F_2} + \int_0^\infty \frac{dx \mathcal{X}(x)}{\frac{1}{\kappa_1} + \frac{x}{\kappa_2}}. \quad (4)$$

For reasons that will become apparent we want to compare the values of $k(\kappa_1 + 2\kappa_0, \kappa_2 + 2\kappa_0)$ and $k(\kappa_1, \kappa_2) + 2\kappa_0$, where κ_0 can take any positive value, but κ_0 is limited in the negative range by the limitations that both $\kappa_1 + 2\kappa_0$ and $\kappa_2 + 2\kappa_0$ must always be nonnegative. A straightforward, but somewhat tedious calculation shows that

$$k(\kappa_1 + 2\kappa_0, \kappa_2 + 2\kappa_0) - k(\kappa_1, \kappa_2) - 2\kappa_0 = \frac{2\kappa_0(\kappa_2 - \kappa_1)^2 \int_0^\infty \frac{dx \mathcal{X}(x)}{(1+x)(\kappa_2 + x\kappa_1)[\kappa_2 + x\kappa_1 + 2(1+x)\kappa_0]}}{2\kappa_0(\kappa_2 - \kappa_1)^2 \int_0^\infty \frac{dx \mathcal{X}(x)}{(1+x)(\kappa_2 + x\kappa_1)[\kappa_2 + x\kappa_1 + 2(1+x)\kappa_0]}}. \quad (5)$$

The right hand side of this equation is always positive whenever $\kappa_0 > 0$ and $\kappa_1 \neq \kappa_2$. It vanishes when $\kappa_0 = 0$ or $\kappa_1 = \kappa_2$. If $\kappa_1 < \kappa_2$, then for negative values of the parameter κ_0 , allowed values of κ_0 lie in the range $0 > 2\kappa_0 \geq -\kappa_1$. For such values of κ_0 , the right hand side of (5) is strictly negative.

The limiting case obtained by taking $2\kappa_0 \rightarrow -\kappa_1$ is most useful because, in this limit, $k(\kappa_1 + 2\kappa_0, \kappa_2 + 2\kappa_0) \rightarrow (\kappa_2 - \kappa_1)/F_2$ — thus eliminating the unknown functional $\mathcal{X}(x)$ from this part of the expression. Then, (5) shows that

$$k(\kappa_1, \kappa_2) \geq \kappa_1 + \frac{\kappa_2 - \kappa_1}{F_2} \equiv Q_2(\kappa_1, \kappa_2), \quad (6)$$

which is a general lower bound on $k(\kappa_1, \kappa_2)$ without any further restrictions on the measurable quantities $\kappa_1 \leq \kappa_2$, and F_2 .

A second bound can be obtained (again in the limit $2\kappa_0 = -\kappa_1$) by noting that

$$\int_0^\infty \frac{dx \mathcal{X}(x)}{(1+x)(\kappa_2 + x\kappa_1)} \leq \int_0^\infty \frac{dx \mathcal{X}(x)}{\kappa_2 + x\kappa_1}, \quad (7)$$

and then recalling that

$$\int_0^\infty \frac{dx \mathcal{X}(x)}{\kappa_2 + x\kappa_1} = \frac{1}{\kappa_1 \kappa_2} \left[k(\kappa_1, \kappa_2) - \frac{\kappa_1}{F_1} - \frac{\kappa_2}{F_2} \right]. \quad (8)$$

Substituting (7) into (5) produces an upper bound on $k(\kappa_1, \kappa_2)$. By subsequently substituting (8) and then rearranging the result, the final bound is

$$k(\kappa_1, \kappa_2) \leq \kappa_2 + \frac{\kappa_1 - \kappa_2}{F_1} \equiv Q_1(\kappa_1, \kappa_2). \quad (9)$$

Comparing (6) and (9), we see consistency requires that

$$\kappa_1 + \frac{\kappa_2 - \kappa_1}{F_2} \leq \kappa_2 + \frac{\kappa_1 - \kappa_2}{F_1} \quad (10)$$

must be true. Rearranging this expression gives the condition

$$0 \leq (\kappa_2 - \kappa_1) \left(1 - \frac{1}{F_1} - \frac{1}{F_2} \right), \quad (11)$$

the validity of which must be checked. In the limit $\kappa_1 = \kappa_2 = 1$, a sum rule follows from (4), and from this we have:

$$1 - \frac{1}{F_1} - \frac{1}{F_2} = \int_0^\infty \frac{dx \mathcal{X}(x)}{1+x} \geq 0. \quad (12)$$

This shows explicitly that (11) is always satisfied as long as $\kappa_2 \geq \kappa_1$. If the inequality $\kappa_2 \geq \kappa_1$ does not hold, then the sense of the bounding inequalities is changed, so the expressions for the upper and lower bounds trade places.

When $\kappa_2 = \text{const}$ and κ_1 varies (as would be expected in a series of thermal conductivity experiments with different fluids in the same porous medium), then (6) and (9) are both straight lines that cross at $\kappa_1 = \kappa_2$. The general bounds are therefore

$$\min(Q_1, Q_2) \leq k(\kappa_1, \kappa_2) \leq \max(Q_1, Q_2), \quad (13)$$

where Q_1 and Q_2 were defined in (6) and (9). [Note that there is also another rather obvious lower bound on $k(\kappa_1, \kappa_2)$ obtainable from (4) by simply dropping the term involving $\chi(x)$. Although this bound has the same asymptotic behavior as $\min(Q_1, Q_2)$, it is easy to see (using the same arguments already presented) that this lower bound is always inferior to $\min(Q_1, Q_2)$, so we need not consider it further.]

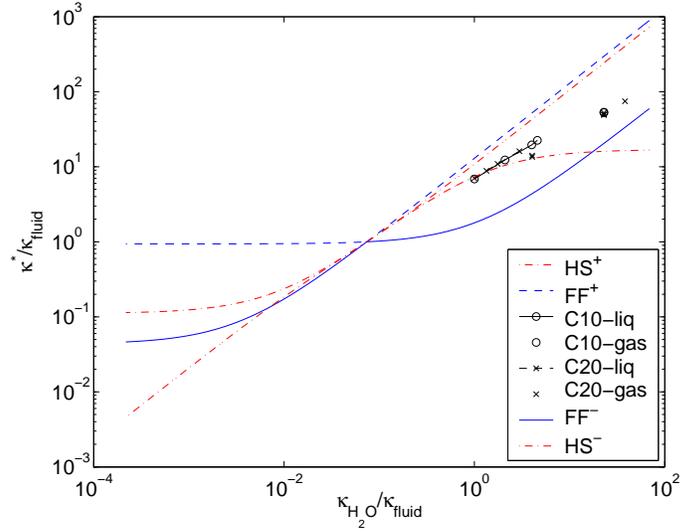


Figure 2. Same as Figure 1 for sandstone sample C, including two distinct data sets.

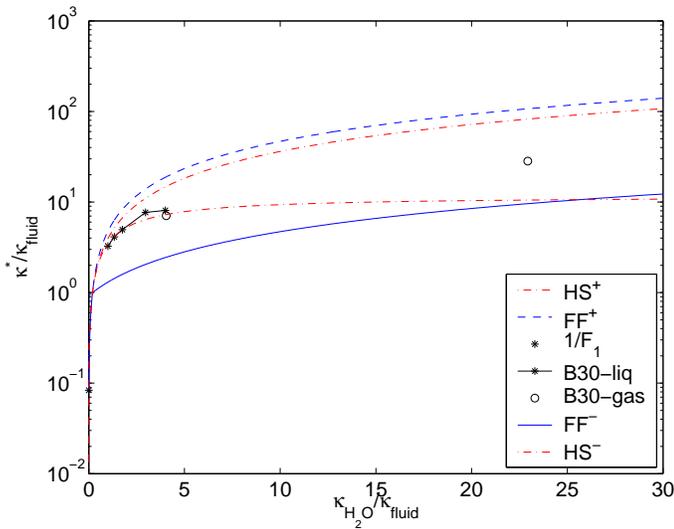


Figure 1. Comparison of the formation factor bounds (FF^\pm), the Hashin-Shtrikman bounds (HS^\pm), and thermal conductivity data from Asaad [17]. Data are for sandstone sample B.

EXAMPLE: THERMAL CONDUCTIVITY

Examples shown in Figures 1–3 make use of thermal conductivity and electrical formation factor data from Asaad [17]. Three different sandstones (labelled B, C, D) were studied by Asaad, and several different sets of experiments were performed on each. The Figures show data from experiments B30, C10, C20, and D10. We plot both the formation factor bounds (FF

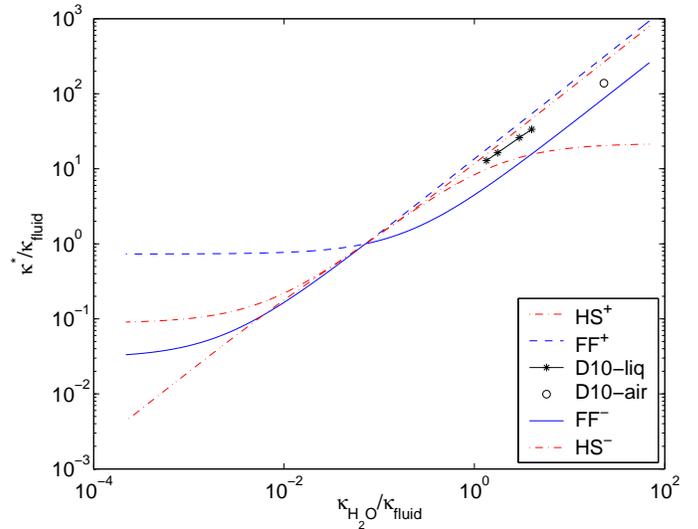


Figure 3. Same as Figure 1 for sandstone sample D.

and the Hashin-Shtrikman bounds (HS) based on volume fraction information. A selection of the data is displayed in all three cases. Electrical formation factor measurements were made on all three samples ($F_1^B = 12.0$, $F_1^C = 23.0$, $F_1^D = 33.0$). Frame formation factor can be determined from measurements of thermal conductivity when the pores are evacuated. But a value of effective grain thermal conductivity must also be found. Asaad [17] solved this problem — using an extrapolation method — assuming that a certain geometric mean approximation (which is just a straight line on a log-log plot) when fit to the data

would then give an accurate estimate of the point at which $k(\kappa_1 = \kappa_2^{\text{eff}}, \kappa_2) \simeq \kappa_2^{\text{eff}}$. Results displayed as they are here on the log-log plots in Figs. 2 and 3 show that Asaad’s method is very accurate for all these data. Then, $F_2^{\text{eff}} \simeq \kappa_2^{\text{eff}}/k(0, \kappa_2)$, and we find $F_2^B = 13.5$, $F_2^C = 15.9$, $F_2^D = 3.72$. Measured porosity values were $\phi^B = 0.220$, $\phi^C = 0.158$, $\phi^D = 0.126$.

The results show an interesting common pattern in all three examples. The Hashin-Shtrikman upper bound is always smaller, and therefore a better/tighter bound, than the upper FF bound. But the situation is more complicated for the lower bounds. Near the point where all the bounds cross, the lower Hashin-Shtrikman bounds are just slightly better for higher values of κ_{fluid} , but significantly better for the lower values. On the other hand, far from this convergence point the lower FF bound is clearly superior to Hashin-Shtrikman, both at quite high and quite low values of κ_{fluid} . In fact this is not surprising, since it is in these asymptotic regimes that the FF bounds tend to become exact estimates. So a reasonable conclusion obtained from these observations is that the combination of the two Hashin-Shtrikman bounds and the lower FF bound provides quite accurate estimates of overall conductivity for the entire range of pore-fluid conductivities.

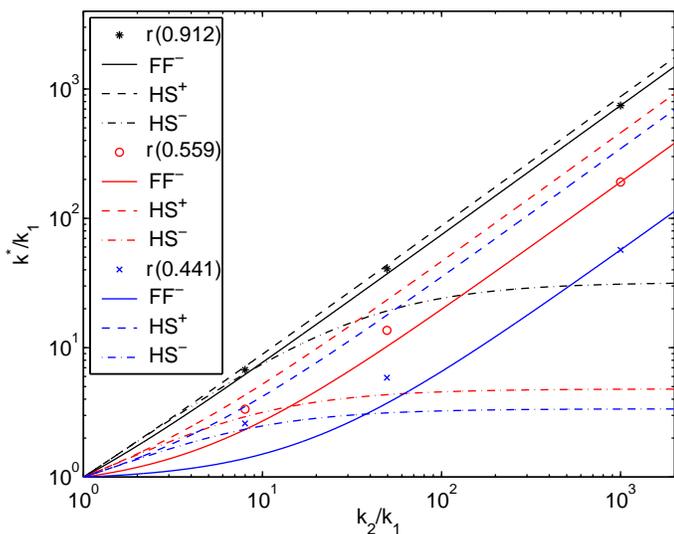


Figure 4. Rigorous bounds on fluid permeability numerical simulation data of Warren and Price [18] obtained using just the lower formation factor bounds (FF^-) from this work, and the upper and lower Hashin-Shtrikman bounds (HS^\pm) [1]. The Warren and Price data sets are for three types of binary (X/Y) composites. Y always has the lowest permeability k_1 ; k_2 is the permeability value for the other constituent present; and $f_1 + f_2 = 1$. For X_1 data, $k_2/k_1 \simeq 1000.0$; for X_2 data, $k_2/k_1 \simeq 50.0$; for X_3 data, $k_2/k_1 \simeq 8.0$. The examples presented here are for volume fractions $v_2 = 0.912$, $v_2 = 0.559$, and $v_2 = 0.441$, where in all cases $r(v_2) \equiv k^*/k_1$ is then a functional of k_2/k_1 .

EXAMPLE: FLUID PERMEABILITY

Warren and Price [18] presented a sophisticated numerical simulation data set that is pertinent to our problem and that can be analyzed quite easily using the formation factor bounds. The physical model treated numerically was composed of a $9 \times 9 \times 9$ cube, containing $9^3 = 729$ porous blocks. Each of these blocks had a well-defined permeability, being approximately one of the four values: 1, 8, 50, 1000 (using normalized units). The smallest permeability (k_1) was always one constituent of the random porous composite, but the remaining volume filler was always chosen from just one of the other three types. So there were three distinct types of binary (X/Y) composites studied: 8/1, 50/1, and 1000/1. Furthermore, there were only four distinct volume fractions used, and these came in pairs: one pair being $f_1 = 0.088$ and $f_1 = 0.912$ and the other pair being $f_1 = 0.441$ and $f_1 = 0.559$. Since these pairs sum to unity, this means that to a very good approximation the two relevant formation factors were effectively interchanged within each of these types of data sets, each porous component being occupied in an X/Y composite once by X and once by Y . This means that phase interchange relationships [2, 19–22] could also be tested within the context of this numerical experiment, but we do not pursue this issue here.

Bounds obtained by first estimating the F_1 and F_2 formation factors from the Warren and Price numerical simulation data are illustrated in Figure 4 along with the upper and lower Hashin-Shtrikman bounds for comparison. The FF^+ upper bounds are never as good (low) as the HS^+ (although usually quite close to them [23]), so they are not discussed further or shown in these Figures. The Hashin-Shtrikman bounds depend only on known volume fractions and constituent conductivities. Figure 4 clearly shows that the Hashin-Shtrikman bounds provide fairly tight upper bounds all the time. The HS^- lower bounds are best at low values of the permeability ratio k_2/k_1 . They diverge from the data at higher values, as they must since they do not incorporate the fact that the formation factors of both components are finite. The formation factor bounds on the other hand give excellent results for the lower bounds at all values of k_2/k_1 . In fact they agree exactly in this case with the simulated values for the highest value of k_2/k_1 , which is clearly unrealistic, but nevertheless a natural result of the way the formation factors were themselves estimated from this data set. The true formation factor F_2 is actually just slightly larger than the lower bound we have estimated directly from the data. But, since $k_2/k_1 \simeq 1000.0$, we assume that this error is small, and also of the same order as the numerical errors in these simulations.

EXAMPLE: RANDOM POLYCRYSTAL OF LAMINATES

Finally, suppose that at the macroscale we have an isotropic composite that is a random polycrystal, *i.e.*, an aggregate of randomly oriented crystalline grains, each of which has the same anisotropic effective transport coefficients (thermal conductivity,

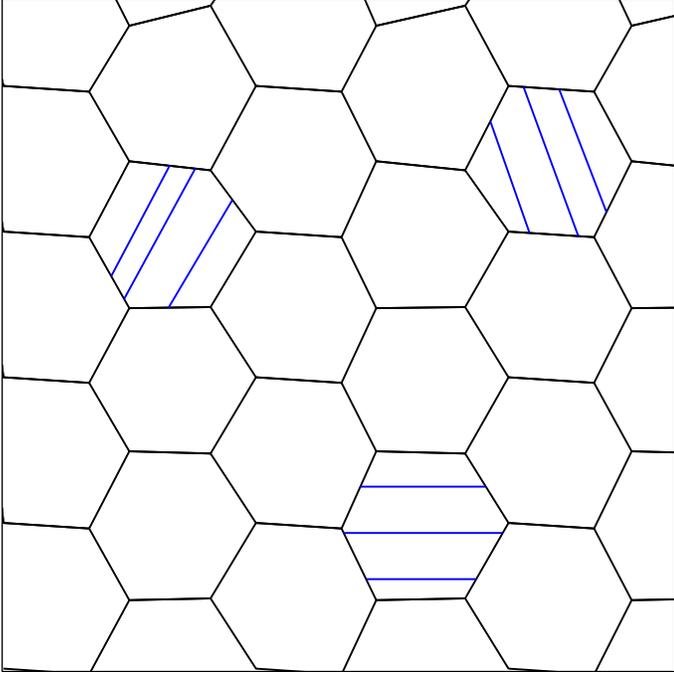


Figure 5. Schematic illustrating the random polycrystals of laminates model. Grains are assumed to fit tightly so there is no misfit. But the shapes of the grains are not necessarily the same, and the symmetry axes of the grains (three examples are shown here) are randomly oriented so the overall polycrystal is equiaxed (statistically isotropic).

electrical conductivity, or fluid permeability). We assume (for purposes of model studies only, as we have no reason to think this model represents any real physical system, unless it has been specifically engineered to be so) that the crystals themselves are composed of layers of isotropic materials (see Figure 5). These crystals can come in any size, and, furthermore, they may not be layered identically at the microscale. But the model assumption is that each crystalline grain has the same overall anisotropic constants. When considering transport coefficients, it is well-known that *it does not matter* exactly what order the layers are grouped in, or exactly how thick each layer is, etc. But *it does matter* that, for each crystalline grain of the polycrystal, the corresponding volume fractions are the same. Furthermore, these crystalline aggregates at the mesoscale are assumed to be layered at a small enough microscale so that “sufficient scale separation” is a good assumption. The main consequence of this assumption when true is simply that edge (or boundary) effects at interfaces between contiguous grains can be safely neglected.

If we choose to do so, we can continue this hierarchy by supposing that each of the isotropic layers is itself composed of a very much finer microstructure. This next level of hierarchy is important for some of the modeling we plan to pursue in the future. In particular for porous media, our aggregates composed

of layers can have layer constituents that are porous and have fluids saturating the pores.

Estimates and bounds on transport coefficients make use of the standard mean and harmonic mean (based on layer volume fractions v_1, \dots, v_N and conductivities $\kappa_1, \dots, \kappa_N$):

$$\kappa_M = \sum_{n=1}^N v_n \kappa_n \quad \text{and} \quad \kappa_H = \left[\sum_{n=1}^N \frac{v_n}{\kappa_n} \right]^{-1}. \quad (14)$$

These quantities are, respectively, the true conductivities normal and parallel to the symmetry axis (*i.e.*, the layering direction) of each laminated grain.

Figure 6 shows comparisons to a number of the available estimates and bounds for this model. Five of these estimates and bounds can be expressed in terms of the canonical functional for polycrystal conductivity, which is defined by

$$\Sigma_X(P\kappa) = \left[\frac{1}{3} \left(\frac{1}{\kappa_H + P\kappa} + \frac{2}{\kappa_M + P\kappa} \right) \right]^{-1} - P\kappa. \quad (15)$$

The Hashin-Shtrikman bounds for polycrystals [24] are given by

$$\kappa_{HSX}^{\pm} = \Sigma_X(2\kappa_{\pm}), \quad (16)$$

where $\kappa_+ = \kappa_M$ and $\kappa_- = \kappa_H$, as defined previously. The estimates CPAX and ModelX are given respectively by $\kappa_{CPAX}^* \equiv \Sigma_X(2\kappa_{CPAX}^*)$ and $\kappa_{ModelX}^* \equiv \Sigma_X(\kappa_{ModelX}^*)$, so $P = 2$ for CPA and $P = 1$ for the model. This ModelX is intended to mimic the behavior of a system that has imperfect connectivity, similar to what would be expected in a simple cubic resistor network in 3D with some fraction of the nearest neighbors being disconnected due to network flaws.

CONCLUSIONS

Future work along these lines will be directed towards improving the estimates obtained from the analytical method by making more direct use of various known constraints on the resonance density \mathcal{X} and its integral moments. For applications to fluid permeability, some extra care is required in formulating the physical model due to lack of scale invariance for this parameter.

ACKNOWLEDGMENTS

Work performed by University of California, Lawrence Livermore Laboratory, under the auspices of the U.S. Department of Energy under contract No. W-7405-ENG-48 and supported specifically by the Geosciences Research Program of the DOE Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences.

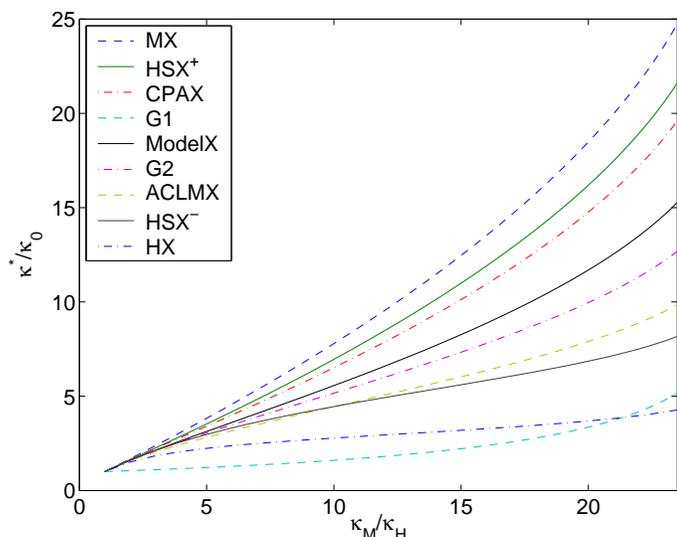


Figure 6. Correlated bounds and estimates based on formulas for random polycrystalline microstructure. Except for estimate G1, volume fractions of microstructural components may be assumed unknown. Conductivities parallel (κ_H) and perpendicular (κ_M) to the symmetry axis of a (laminated) grain are assumed known. The mean (MX) and harmonic mean (HX) bounds for polycrystals are $\kappa_{MX} = \frac{1}{3}(\kappa_H + 2\kappa_M)$ and $\kappa_{HX}^{-1} = \frac{1}{3}(\kappa_H^{-1} + 2\kappa_M^{-1})$, respectively. The two geometric means G1 and G2 displayed are, respectively, $\kappa_1^{v_1} \kappa_2^{v_2}$ and $(\kappa_H \kappa_M^2)^{1/3}$, where the layer volume fractions are v_1, v_2 , and satisfy $v_1 + v_2 = 1$. ACLMX is the lower bound of Avellaneda *et al.* [21], given by $\kappa_{ACLMX}^- \equiv \Sigma_X(\kappa_{ACLMX}^-/2)$. Other estimates are defined in the text. Also see Berryman [25].

REFERENCES

- [1] Hashin, Z., and Shtrikman, S., 1962. “A variational approach to the theory of the effective magnetic permeability of multiphase materials”. *J. Appl. Phys.*, **33**, pp. 3125–3131.
- [2] Milton, G. W., 2002. *The Theory of Composites*. Cambridge University Press, Cambridge, UK.
- [3] Torquato, S., 2002. *Random Heterogeneous Materials: Microstructure and Macroscopic Properties*. Springer, NY.
- [4] Bergman, D. J., 1978. “The dielectric constant of a composite material — a problem of classical physics”. *Phys. Repts.*, **43**, pp. 378–407.
- [5] Bergman, D. J., 1980. “Exactly solvable microscopic geometries and rigorous bounds for the complex dielectric constant of a two-component composite material”. *Phys. Rev. Lett.*, **44**, pp. 1285–1287.
- [6] Milton, G. W., 1980. “Bounds on the complex dielectric constant of a composite material”. *Appl. Phys. Lett.*, **37**, pp. 300–303.
- [7] Milton, G. W., 1981. “Bounds on the complex permittivity of a two-component composite material”. *J. Appl. Phys.*,

52, pp. 5286–5293.

- [8] Bergman, D. J., 1982. “Rigorous bounds for the complex dielectric constant of a two-component composite”. *Ann. Phys.*, **138**, pp. 78–114.
- [9] Korringa, J., and LaTorraca, G. A., 1986. “Application of the Bergman-Milton theory of bounds to the permittivity of rocks”. *J. Appl. Phys.*, **60**, pp. 2966–2976.
- [10] Stroud, D., Milton, G. W., and De, B. R., 1986. “Analytical model for the dielectric response of brine-saturated rocks”. *Phys. Rev. B*, **34**, pp. 5145–5153.
- [11] Berryman, J. G., 1992. “Effective stress for transport properties of inhomogeneous porous rock”. *J. Geophys. Res.*, **97**, pp. 17409–17424.
- [12] Archie, G. E., 1942. “The electrical resistivity log as an aid in determining some reservoir characteristics”. *Trans. AIME*, **146**, pp. 54–62.
- [13] Baker, Jr., G. A., 1975. *Essentials of Padé Approximants*. Academic, San Diego, California.
- [14] Johnson, D. L., Koplik, J., and Schwartz, L. M., 1986. “New pore-size parameter characterizing transport in porous media”. *Phys. Rev. Lett.*, **57**, pp. 2564–2567.
- [15] Wildenschild, D., Roberts, J. J., and Carlberg, E. D., 2000. “On the relationship between microstructure and electrical and hydraulic properties of sand-clay mixtures”. *Geophys. Res. Lett.*, **27**, pp. 3065–3068.
- [16] Guéguen, Y., and Palciauskas, V., 1994. *Introduction to the Physics of Rocks*. Princeton University Press, Princeton, NJ.
- [17] Asaad, Y., 1955. “A study of the thermal conductivity of fluid-bearing porous rocks”. PhD thesis, University of California – Berkeley, Berkeley, CA.
- [18] Warren, J. E., and Price, H. S., 1961. “Flow in heterogeneous porous media”. *Soc. Petrol. Eng. J.*, **1**, pp. 153–169.
- [19] Keller, J. B., 1964. “A theorem on the conductivity of a composite medium”. *J. Math. Phys.*, **5**, pp. 548–549.
- [20] Schulgasser, K., 1976. “On the phase interchange relationship for composite materials”. *J. Math. Phys.*, **17**, pp. 378–381.
- [21] Avellaneda, M., Cherkaev, A. V., Lurie, K. A., and Milton, G. W., 1988. “On the effective conductivity of polycrystals and a three-dimensional phase-interchange inequality”. *J. Appl. Phys.*, **63**, pp. 4989–5003.
- [22] Nesi, V., 1991. “Multiphase interchange inequalities”. *J. Math. Phys.*, **32**, pp. 2263–2275.
- [23] Berryman, J. G., 2005. “Thermal conductivity of porous media”. *Appl. Phys. Lett.*, **86**, pp. 032905–1–032905–3.
- [24] Hashin, Z., and Shtrikman, S., 1962. “A variational approach to the theory of the elastic behaviour of polycrystals”. *J. Mech. Phys. Solids*, **10**, pp. 343–352.
- [25] Berryman, J. G., 2005. “Bounds and estimates for transport coefficients of random and porous media with high contrasts”. *J. Appl. Phys.*, **97**, pp. 063504–1–063504–11.