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Bounds on transport coefficients of porous media

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ABSTRACT

Transport coefficients such as electrical conductivity, thermal conductivity, fluid permeability, etc., can all be treated in mathematically equivalent terms. So an analytical formulation of conductivity bounds by Bergman and Milton can be used in a different way to obtain rigorous bounds on, for example, the real thermal conductivity (which is the particular transport coefficient chosen for the present study) of a fluid-saturated porous material. 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. The results are then applicable to other physical properties such as fluid permeability. In particular, the formation factors are measures of the microstructure (actually of the tortuosities) of the porous medium, and are therefore the same dimensionless numbers for all these transport processes within the same porous material.

INTRODUCTION

Bounds on various transport coefficients in heterogeneous media have been heavily studied now for over forty years (Hashin and Shtrikman, 1962; Milton, 2002; Torquato, 2002). One of the more interesting 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 (Bergman, 1978, 1980; Milton, 1980, 1981; Bergman, 1982; Korringa and LaTorraca, 1986; Stroud *et al.*, 1986). 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 some simpler and perhaps more robust methods and results were available.

In this short paper I 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. I will limit discussion here to real coefficients, taking thermal conductivity as our main example, but the results apply equally well to other transport coefficients including electrical conductivity and fluid permeability (Berryman, 1992). Furthermore, the resulting bounds depend only on commonly measured quantities in porous media called formation factors (Archie, 1942; Korringa and LaTorraca, 1986), and they show no unusual sensitivity to measurement errors

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or any need for careful checking of consistency relations among the measurements.

THE ANALTYICAL FORMULATION

The Bergman-Milton (Bergman, 1978, 1980; Milton, 1980, 1981; Bergman, 1982; Korringa and LaTorraca, 1986; Stroud *et al.*, 1986; Berryman, 1992) analytical approach to understanding some generic effective conductivity g^* of two-component inhomogeneous media shows that

$$g^* = G(g_1,g_2) = g_1 G(1,0) + g_2 G(0,1) + \int_0^\infty \frac{dx\mathcal{G}(x)}{\frac{1}{g_1}+\frac{x}{g_2}}, \tag{1}$$

where $G(1,0)$ and $G(0,1)$ are constants depending only on the geometry and $\mathcal{G}(x) \geq 0$ is a resonance density also depending only on the geometry. The integral in (1) is known as a Stieltjes integral (Baker, 1975). Although the representation (1) has usually been employed to study the behavior of g^* in the complex plane when g_1 and g_2 are themselves complex (corresponding to mixtures of conductors and dielectrics), I will restrict consideration here – as Bergman did in his early work (Bergman, 1978) – to pure conductors so that g_1, g_2, and g^* are all real and nonnegative.

In the limit that one or the other of the two constituents is a perfect insulator ($g_i = 0$), or in the more common case when one of the constituents is much more strongly conducting than the other, I can define two quantities called formation factors (Archie, 1942) by

$$\lim_{g_1\to\infty} \frac{g^*}{g_1} = \lim_{g_1\to\infty} G(1,g_2/g_1) = G(1,0) = \frac{1}{F_1}, \tag{2}$$

and, similarly, by

$$\lim_{g_2\to\infty} \frac{g^*}{g_2} = \lim_{g_2\to\infty} G(g_1/g_2,1) = G(0,1) = \frac{1}{F_2}. \tag{3}$$

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 (Johnson *et al.*, 1986; Wildenschild *et al.*, 2000), 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. Since the formation factor is strictly a measure of the microgeometry of the heterogeneous medium, it is the same number [except for those possible complications already mentioned of surface electrical conduction (Johnson *et al.*, 1986; Wildenschild *et al.*, 2000), which can be eliminated whenever necessary by known experimental methods] for all mathematically equivalent conductivities. For this presentation, I 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 I 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, I again consider the form of (1)

$$G(g_1,g_2) = \frac{g_1}{F_1} + \frac{g_2}{F_2} + \int_0^\infty \frac{dx\mathcal{G}(x)}{\frac{1}{g_1}+\frac{x}{g_2}}. \tag{4}$$

For reasons that will become apparent I want to compare the values of $G(g_1+2g_0, g_2+2g_0)$ and $G(g_1,g_2)+2g_0$, where g_0 can take any positive value, but g_0 is limited in the negative range by the limitations that both g_1+2g_0 and g_2+2g_0 must always be nonnegative. A straightforward, but somewhat tedious calculation shows that

$$\begin{aligned} G(g_1+2g_0, g_2+2g_0) - G(g_1,g_2) - 2g_0 = \\ 2g_0(g_2-g_1)^2 \int_0^\infty \tfrac{dxx\mathcal{G}(x)}{(1+x)(g_2+xg_1)[g_2+xg_1+2(1+x)g_0]}. \end{aligned} \tag{5}$$

The right hand side of this equation is always positive whenever $g_0 > 0$ and $g_1 \neq g_2$. It vanishes when $g_0 = 0$ or $g_1 = g_2$. If $g_1 < g_2$, then for negative values of the parameter g_0, allowed values of g_0 lie in the range $0 > 2g_0 \geq -g_1$. For such values of g_0, the right hand side of (5) is strictly negative.

The limiting case obtained by taking $2g_0 \to -g_1$ is most useful because, in this limit, $G(g_1+2g_0, g_2+2g_0) \to (g_2-g_1)/F_2$ — thus eliminating the unknown functional $\mathcal{G}(x)$ from this part of the expression. Then, (5) shows that

$$G(g_1,g_2) \geq g_1 + \frac{g_2-g_1}{F_2} \equiv S_2(g_1,g_2), \tag{6}$$

which is a general lower bound on $G(g_1,g_2)$ without any further restrictions on the measurable quantities $g_1 \leq g_2$, and F_2.

A second bound can be obtained (again in the limit $2g_0 = -g_1$) by noting that

$$\int_0^\infty \frac{dxx\mathcal{G}(x)}{(1+x)(g_2+xg_1)} \leq \int_0^\infty \frac{dx\mathcal{G}(x)}{g_2+xg_1}, \tag{7}$$

and then recalling that

$$\int_0^\infty \frac{dx\mathcal{G}(x)}{g_2+xg_1} = \frac{1}{g_1g_2}\left[G(g_1,g_2) - \frac{g_1}{F_1} - \frac{g_2}{F_2}\right]. \tag{8}$$

Substituting (7) into (5) produces an upper bound on $G(g_1,g_2)$. By subsequently substituting (8) and then rearranging the result, the final bound is

$$G(g_1,g_2) \leq g_2 + \frac{g_1-g_2}{F_1} \equiv S_1(g_1,g_2). \tag{9}$$

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

$$g_1 + \frac{g_2-g_1}{F_2} \leq g_2 + \frac{g_1-g_2}{F_1} \tag{10}$$

must be true. Rearranging this expression gives the condition

$$0 \le (g_2 - g_1)\left(1 - \frac{1}{F_1} - \frac{1}{F_2}\right), \tag{11}$$

the validity of which I need to check. In the limit $g_1 = g_2 = 1$, a sum rule follows from (4), and from this I have:

$$1 - \frac{1}{F_1} - \frac{1}{F_2} = \int_0^\infty \frac{dx\mathcal{G}(x)}{1+x} \ge 0. \tag{12}$$

This shows explicitly that (11) is always satisfied as long as $g_2 \ge g_1$. If this inequality $g_2 \ge g_1$ does not hold, then the sense of the bounding inequalities is changed, so the expressions for the upper and lower bounds trade places.

When $g_2 =$ const and g_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 $g_1 = g_2$. The general bounds are therefore

$$\min(S_1, S_2) \le G(g_1, g_2) \le \max(S_1, S_2), \tag{13}$$

where S_1 and S_2 were defined in (6) and (9).

SECOND DERIVATION

Another derivation of the same bounds may provide additional insight into their significance.

Again starting from (4), this time I will go directly to the integral term and start making approximations to it. First, consider

$$\int_0^\infty \frac{dx\mathcal{G}(x)}{\frac{1}{g_1} + \frac{x}{g_2}} = g_1 \int_0^\infty \frac{dx\mathcal{G}(x)}{1 + \frac{xg_1}{g_2}} \ge g_1 \int_0^\infty \frac{dx\mathcal{G}(x)}{1+x}, \tag{14}$$

where the inequality holds whenever $g_1 \le g_2$. Then, similarly, I have

$$\int_0^\infty \frac{dx\mathcal{G}(x)}{\frac{1}{g_1} + \frac{x}{g_2}} = g_2 \int_0^\infty \frac{dx\mathcal{G}(x)}{\frac{g_2}{g_1} + x} \le g_2 \int_0^\infty \frac{dx\mathcal{G}(x)}{1+x}, \tag{15}$$

again whenever $g_1 \le g_2$. I can then make use of the identity in sumrule (12) to replace the integral on the far right in both of these expressions. And, finally, applying (14) to (4) gives exactly the lower bound (6), while applying (15) to (4) gives exactly the upper bound (9). All the same comments about reversal of the sense of the inequalities applies here if instead $g_1 \ge g_2$. So, the final result is again (13).

This derivation has the advantage that it is clear from the inequalities (14) and (15) exactly what approximations have been made in each case to arrive at the bounds on $G(g_1, g_2)$.

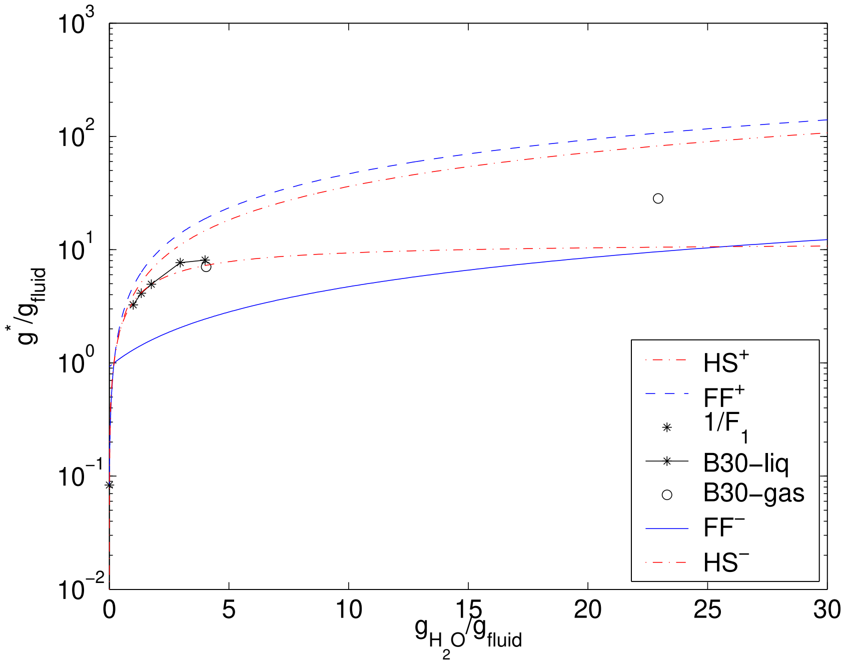

Figure 1: Comparison of the formation factor bounds (FF$^{\pm}$), the Hashin-Shtrikman bounds (HS$^{\pm}$), and thermal conductivity data from Asaad (1955). Data are for sandstone sample B. jim1-gBasaadsmlgwg [NR]

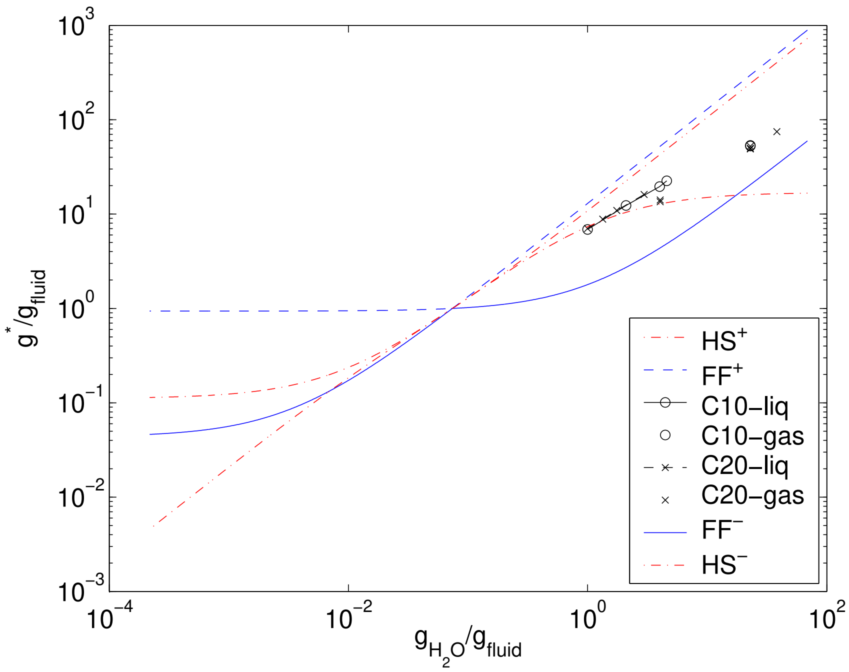

Figure 2: Comparison of the formation factor bounds (FF$^{\pm}$), the Hashin-Shtrikman bounds (HS$^{\pm}$), and thermal conductivity data from Asaad (1955). Data are for sandstone sample C, including two distinct data sets. jim1-gCasaadlglgwg [NR]

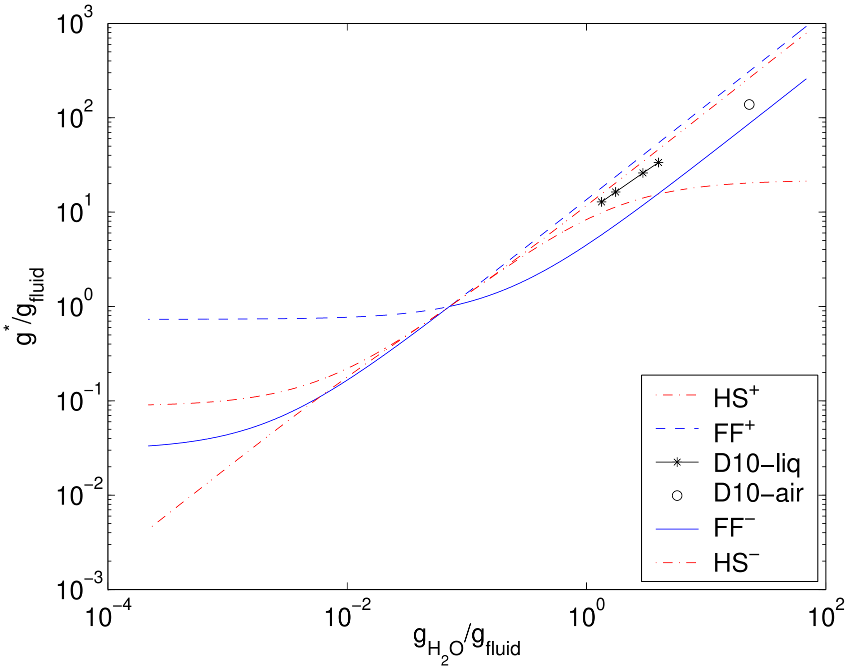

Figure 3: Comparison of the formation factor bounds (FF$^{\pm}$), the Hashin-Shtrikman bounds (HS$^{\pm}$), and thermal conductivity data from Asaad (1955). Data are for sandstone sample D. jim1-gDasaadlglgwg [NR]

NUMERICAL EXAMPLES

Examples shown in Figures 1–3 make use of thermal conductivity and electrical formation factor data from Asaad (1955). 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. I plot both the new formation factor bounds (FF) 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 be found. Asaad (1955) 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 $G(g_1 = g_2^{\rm eff}, g_2) \simeq g_2^{\rm eff}$. Results displayed as they are here on the log-log plots in Figs. 2 and 3 show that Asaad's method is in fact quite accurate for all these data. Then, $F_2^{\rm eff} \simeq g_2^{\rm eff}/G(0, g_2)$, and I find $F_2^B = 13.5$, $F_2^C = 15.9$, $F_2^D = 3.72$. Measured porosity values were $\phi^B = 0.220$, $\phi^C = 0.158$, $\phi^D = 0.126$.

CONCLUSIONS

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

g_{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 g_{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 I reach 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.

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 $\mathcal{G}$ and its integral moments.

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