Bounds on Elastic Properties Involving Two-Point Statistics: the Question of Equiaxiality in Polycrystals

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Abstract

An explicit formula is given for computing bounds on macroscopic constants of linearly elastic polycrystals based on measurements of one- and two-point statistics. Various existing methods for bounding elastic constants, with their inherent assumptions and limitations, are also discussed.

1 Introduction

The question of effective moduli of microscopically heterogeneous materials has been the subject of much research over the last 40 years. A number of models have been developed in order to obtain bounds or approximations for the overall behavior of such materials. Descriptions of these efforts can be found in references [1] through [6].

With recent progress in developing automated experimental capabilities to determine 2-point statistics of the lattice orientation distribution in polycrystals ([7] – [10]), there has been a resurgence of interest in bounding theories which incorporate 2-point statistics.

In this paper we concentrate on the formulation of such bounds and applications to polycrystalline materials, with an eye to clarifying the physical meaning of some mathematical assumptions made in the work of Hashin & Shtrikman [11]. We suggest bounds which do not depend on assumptions of this type.

In their landmark 1962 paper [12], Hashin & Shtrikman develop a pair of variational principles which can be used to obtain bounds on macroscopic elastic moduli of composites obeying a Hooke's law. They applied these principles to mixtures of isotropic constituent materials [13, 14] as well as to macroscopically isotropic polycrystals [11] to obtain bounds depending only upon the volume fractions of the phases. In obtaining an explicit form for a Greens function operator, however, they make some unspecified mathematical assumptions about their "polarization field." Hashin recognized this fact and noted that, in the bounds for an *isotropic* mixture of two phases, "The original derivation of the bounds ...included some mathematical liberties ...[which were] removed by application of Fourier transform methods" [2].

In the case of polycrystals, however, the physical meaning of the assumptions was still unclear. Bounds similar to those of Hashin & Shtrikman have been derived by Walpole [15]. In applying these to polycrystals, Walpole makes it clear that his bounds involving one-point statistics included assumptions about many-point statistics by considering a material in which "each distinct phase was assumed to be distributed homogeneously and isotropically in a statistical sense" [16].

One advantage of Hashin & Shtrikman's bounds is that they are usually narrower than the Hill-Paul bounds (also known as the "Voigt-Reuss bounds")[17, 18]. Surprisingly, however, the work of Avellaneda and Milton shows that *the Hill-Paul bounds for the bulk modulus of polycrystals are the tightest possible based on volume fraction information <u>alone</u>*[19]. This clearly shows that Hashin & Shtrikman have assumed more than just given volume-fractions (one-point statistics) in the derivation of their bounds.

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In deriving their expressions in the context of isotropic constituent phases, Hashin & Shtrikman [14] assume their polarization field is isotropic within each grain and then that this polarization field satisfies certain equations dependent upon the moduli of the grain. This is incompatible with anisotropic moduli, unless the moduli can be considered to be averaged over rotations in some sense. For instance, one could consider a statistical ensemble of polycrystals where orientations are distributed randomly throughout the grains in each realization. Such an ensemble is called "equiaxed". Assuming the ergodic hypothesis, one may average over realizations to obtain locally isotropic behavior before calculating the desired polarization field and spatial averages.

Other bounds depending on correlation functions up to a certain order n have been derived via the classical variational principles. The first were derived for odd n, by Beran and Molyneux [20](isotropic phases) and Zeller and Dederichs [21](polycrystals). These were later generalized to include bounds for even n by Kröner [5](for general composites) and Willemse and Caspers [22](applied to polycrystals). Kröner's paper brings up the notion of "graded disorder" which quantifies the extent to which a material may be considered random. A material is said to be "disordered of grade m" when all correlation functions up to order m are disordered. He shows that the Hashin-Shtrikman polycrystal bounds may be derived under the assumption that the heterogeneous material has moduli and topology which is disordered of grade 2, which is logical since the Hashin-Shtrikman bounds only contain correlation information up to order two.

Still other estimates and bounds on the effective properties have employed special models of "random" composites, deriving bounds that depend on higher-order statistics through some averaged parameter: Miller's bounds [23] depend on a "shape factor" G, while Avellaneda and Bruno [24] calculate bounds based upon a quantity they term the "polarizability."

After a brief introduction to the notion of effective moduli, we begin our discussion by stating the Hashin-Shtrikman variational principles in full generality for linearly elastic composites in section 3.1. We discuss bounds proposed by Walpole and Willis, and the problems inherent in implementing these with actual polycrystal data.

To formulate an alternative bound which is amenable to computation, we make use of Hashin & Shtrikman's variational principle, choosing a trial polarization field which gives us explicit bounds as functions of arbitrary one- and two-point statistics. When neither the grain-shape nor the ODF have a preferred direction, our model recaptures the Hashin-Shtrikman polycrystal bounds for crystallites with cubic symmetry. The final section (4) contains details necessary for calculation of bounds.

2 Notation and the Definition of Effective Moduli

2.1 Notation

We shall generally use bold upper-case letters for eighth-order tensors. Non-bold upper-case letters denote fourth-order tensors and lower-case letters denote second-order tensors (matrices). Variables with an arrow above indicate vectors. Finally, scalar quantities will be denoted by Greek letters. Some obvious exceptions to these rules include sub- and super-scripts.

Fourth-order tensors act on second-order tensors in a manner analogous to the action of matrices on vectors:

$$\begin{array}{rclcrcl} (Ce)_{ij} & = & C_{ijkl}e_{kl} & \qquad & (e\vec{r})_i & = & e_{ij}\vec{r}_j \\ (CC')_{ijkl} & = & C_{ijmn}C'_{mnkl} & \qquad & (es)_{ij} & = & e_{in}s_{nj} \end{array} \tag{1}$$

where summation on repeated indices is implied here and throughout. We also define an analogous scalar "dot product" on the set of matrices

$$e : s \stackrel{\text{def}}{=} e_{ij}s_{ij}. \tag{2}$$

The action of an eighth-order tensor on a fourth-order tensor will be indicated by four dots:

$$(\mathbf{H} \mathbin{\vdots} C)_{ijkl} \stackrel{\text{def}}{=} \mathbf{H}_{ijklmnpq}C_{mnpq}. \tag{3}$$

Inequalities between tensors of the same order should be interpreted in terms of positive definiteness:

$$\{A > B\} \stackrel{\text{def}}{=} \{\ A - B \text{ is positive definite.}\} \tag{4}$$

We shall use the symbol " $\tilde{\times}$ " to denote the following product of fourth-order tensors:

$$(C \,\tilde{\times}\, C')_{ijklabcd} \stackrel{\text{def}}{=} C_{ijab}C'_{cdkl}. \tag{5}$$

The reader should note the permutation of the indices.

2.2 Effective moduli

We consider a macroscopic volume V of inhomogeneous material with fixed boundary conditions; for simplicity we assume these are uniform boundary conditions of the form

$$u_i(\vec{r}) = e^0_{ij} r_j \qquad\qquad \vec{r} \in \partial V \tag{6}$$

where u represents the displacement vector, e is the elastic strain, and ∂V is the boundary of V. Under such boundary conditions, a *homogeneous* material would experience a uniform deformation, with stress s^0 a linear function of the strain e^0:

$$s^0 = C^0 e^0. \tag{7}$$

Here the superscripts "o" indicate quantities which are constant in space.

In an inhomogeneous material, the deformation will depend upon the spatially-varying elastic moduli $C(\vec{r})$. Our model assumes that these moduli are well-defined, although in a real material they might not be defined in certain regions (for example, at grain boundaries) and in practice the moduli cannot be determined at every point. In order to formulate our theory, we must assume that the regions where the moduli an not known are small relative to the size of the sample and that boundary effects between grains are also small.

Now the local stress-strain relations are

$$\begin{aligned} \nabla \cdot s(\vec{r}) &= 0 & (8)\\ s(\vec{r}) &= C(\vec{r})e(\vec{r}) & (9)\\ e(\vec{r}) &= \frac{1}{2}(\nabla\vec{u}(\vec{r}) + \nabla\vec{u}(\vec{r})^T). & (10) \end{aligned}$$

In describing the macroscopically homogeneous behavior of the material, we define the effective tensor C^* so that the heterogeneous material satisfies a relationship analogous to (7) for the "average" stress and strain fields, averaging denoted by angular brackets:

$$< f > \stackrel{\text{def}}{=} \frac{1}{vol(V)} \int_V f(\vec{r}) d\vec{r}. \tag{11}$$

Thus the tensor of effective moduli is defined by

$$\begin{aligned} < s > &= C^* < e > & (12)\\ &= C^* e^0 & (13) \end{aligned}$$

where $s(\vec{r})$ and $e(\vec{r})$ satisfy (6,8-10).

2.3 Polycrystals and Correlation Functions

The polycrystal model we shall use is composed of many microscopic regions ("grains") each containing the same anisotropic crystalline material, the orientation of which may vary from one grain to the next. This model is completely general; it may be applied to multi-phase materials (isotropic or not) by simply replacing the notion of "orientation" with that of "phase" thoughout.

One-point statistics of a polycrystal are generally encoded in the "orientation distribution function" (ODF) $f_1(g)dg$, which is the probability density of the orientation g occurring in the polycrystal [25]. For example, one can calculate the volume fraction of crystallites falling within 5^o of a particular orientation g by integrating the ODF over all orientations within 5^o of g.

Note that f_1 gives no information about the shapes of the grains or about two-grain interactions. For this we need the two-point correlation function $f_2(g, g'; \vec{r})$. Given that two points in the material are separated by a vector $\vec{r}$, $f_2(g, g'; \vec{r})dgdg'$ is the probability that the first point lies in a crystallite with orientation g while the second lies in one with orientation g'. Clearly, this two-point function depends in part on the one-point function f_1; for example, $f_2(g, g'; \vec{0}) = f_1(g)\delta(g-g')$, where $\delta(g-g')$ is the Dirac mass.

In the model we consider, it is assumed that the grains are small relative to the macroscopic medium and have fixed boundaries. Thus our discussion does not include that of a matrix material containing inclusions.

3 Bounds

3.1 Hashin & Shtrikman's Variational Principles

Before stating the result of Hashin & Shtrikman, we introduce an integral operator Γ^r, which solves a related homogeneous problem.

Consider a homogeneous body with moduli C^r of the same shape as our composite which is subject to body forces $-\nabla \cdot p$ and boundary displacements with average zero. The equilibrium strain is given by a convolution of the body forces with a "generalized Green's function" (see, for example, [26]) which we shall write symbolically as

$$\Gamma^r p. \tag{14}$$

The equations of equilibrium which define $\Gamma^r p$ are

$$\begin{aligned} <\Gamma^r p> &= 0 && (15)\\ \Gamma^r p &= 1/2(\nabla\vec{u} + \nabla\vec{u}^t) \qquad \text{for some } \vec{u}(\vec{r}) && (16)\\ \nabla\cdot(C^r\Gamma^r p) - \nabla\cdot p &= 0. && (17)\end{aligned}$$

The reader should keep in mind that some authors (e.g., McCoy [1]) define their Green's operator Γ in terms of non-zero boundary displacements and so their "Γp" may not have average zero.

Using this notation, the variational principles of Hashin & Shtrikman may be stated in the following form:

$$\begin{aligned} <e>:(C^* - C^r)<e> &\geq 2<p>:<e> - <p:\delta C^{-1}p> - <p:\Gamma^r p> && (18)\\ \text{when } \delta C &> 0 && (19)\end{aligned}$$

and

$$\begin{aligned} <e>:(C^* - C^r)<e> &\leq 2<p>:<e> - <p:\delta C^{-1}p> - <p:\Gamma^r p> && (20)\\ \text{when } \delta C &< 0, && (21)\end{aligned}$$

for any choice of $p(\vec{r})$, $<e>$, and any set of spatially constant reference moduli C^r, where

$$\delta C(\vec{r}) \stackrel{\text{def}}{=} C(\vec{r}) - C^r. \tag{22}$$

Note that equality is achieved by the actual polarization stress $p(\vec{r}) = \delta C(\vec{r})e(\vec{r})$, when $e(\vec{r})$ satisfies (6,8-10).

3.2 The Work of Walpole and Willis

Hashin & Shtrikman obtain bounds by choosing appropriate piecewise-constant fields "p" and reference moduli "C^r", and inserting them into the variational principles (18,20). The last term on the right is evaluated in Fourier-transform space, making use of an assumption about the Fourier transform of the polarization field. These assumptions are made clear in the works of Walpole [15, 16], who derives similar bounds under explicit assumptions, and Willis [3], who derives similar bounds without any such assumptions.

Walpole's Bounds

Walpole's bounds are derived directly from the classical variational principles, using a trial strain field derived from a piecewise-constant polarization [15, 16]. The bounds are equivalent to those of Hashin & Shtrikman (except that Walpole allows the reference material to be anisotropic). In order to evaluate the term involving the Green's function, Walpole assumes that the two-point statistics of the material are isotropic. Walpole's results may be summarized as

> If the two-point correlation may be written as
>
> $$f_2(g, g'; \vec{r}) = f(g, g'; |r|^2) \tag{23}$$
>
> then
>
> $$C^* \overset{(>)}{<} C^r + (B^{-1} - I)E^{-1} \qquad C \overset{(>)}{<} C^r \tag{24}$$
>
> $$B \overset{\text{def}}{=} < (I + \delta C E)^{-1} > \tag{25}$$
>
> where E is a constant fourth-order tensor depending only on the reference medium (specifically, $E =< \Gamma^r >$; see [15, 26] and section 4.2 for more details). [1]

Willis's Bounds

The bounds of Willis are obtained from the Hashin-Shtrikman variational principles using a piecewise-constant trial polarization field

$$p(\vec{r}) = \tau(g(\vec{r})) \tag{26}$$

and optimizing the choice of τ. To write the bounds in a compact form, we suppose that the polycrystal contains crystallites with N distinct orientations and let $f_1(g)$ represent the volume fraction of crystallites with orientation g. The resulting bound may be written as

$$<e>: (C^* - C^r) <e> \overset{(>)}{<} <e>: \sum_g f_1(g)\tau(g) \qquad \delta C \overset{(>)}{<} 0 \tag{27}$$

where $\tau(g)$ solves

$$(\delta C(g))^{-1}\tau(g) + \sum_{g'} H(g, g')\tau(g') \ = <e> \tag{28}$$

and $H(g, g')$ is obtained from two-point statistics

$$H(g, g') = \frac{1}{f_1(g)} \int \Gamma^r(\vec{r}) f_2(g, g'; \vec{r}) d\vec{r}. \tag{29}$$

When the two-point statistics are isotropic (i.e., equation (23) holds), these bounds reduce to those of Walpole and Hashin & Shtrikman.

[1] "E" is Kröner's notation [26]. Kröner's "E" is the same as Walpole's "P" [15] and Willis's "P_0" [27] or "P" for spheres [3].

3.3 A Compromise: Explicit Bounds Incorporating 1- and 2-point Statistics

Both of the bounds described above have some drawbacks when it comes to practical applications to polycrystals.

In Walpole's bound, the problem lies in knowing to what extent the assumption holds, and how deviations from this assumption are likely to affect the resulting bounds. Of course, when the assumption doesn't hold, this is not a rigorous bound. Furthermore, this bound has no hope of capturing the effects of any interesting microstructure.

Willis's bound, on the other hand, is completely rigorous and is capable of incorporating aribitrary two-point statistics. However, its implicit nature makes it computationally unwieldy in cases where there may be an enormous number of orientations present.

In this section, we propose an alternative bound. Although this bound is not optimal, it is explicit and reasonably computable[2], even for a large set of orienations. In addition, it provides a rigorous bound without additional assumptions about two-point correlations. When the two-point statistics are isotropic, our model recaptures the Hashin-Shtrikman polycrystal bounds for crystallites with cubic symmetry.

In order to obtain bounds which depend explicitly on the statistics of the polycrystal, we use the Hashin-Shtrikman variational principles with a trial polarization field $p(\vec{r})$ which is itself a function of the statistics. Noting that the actual polarization stress would be $\delta C(\vec{r})e(\vec{r})$, we choose a trial polarization stress with similar dependence on δC:

$$p(\vec{r}) = \delta C(\vec{r})t \qquad \text{for constant } t. \tag{30}$$

Plugging this ansatz into the variational principles and optimizing over t, we obtain

$$C^* \overset{(>)}{<} C^r + A_1(A_1 + A_2)^{-1}A_1 \tag{31}$$

$$\text{when } C(\vec{r}) - C^r \overset{(>)}{<} 0 \tag{32}$$

The fourth-order tensors

$$A_1 \overset{\text{def}}{=} < C > - C^r \tag{33}$$

$$A_2 \overset{\text{def}}{=} < \delta C \Gamma^r \delta C > \tag{34}$$

are functions of one- and two- point statistics, respectively.

4 Implementation for Polycrystalline Materials

Although this section deals explicitly with evaluating the bound in equation (31), many of the comments which follow are also useful in computation of the Walpole and Willis bounds

4.1 Choosing a Reference Medium

The form of the bounds indicates that they will be tighter when reference moduli for the upper and lower bounds are chosen closer together. This means that generally the best choice of reference moduli will be as close as possible to the actual moduli without violating the positivity (for the lower bound) or negativity (for the upper bound) conditions on δC. For example, for the lower bound we should choose C^r as large as allowed by (19).

The reader should note that this does not prescribe precisely the optimal choice of reference medium in most cases, since tensors are not well-ordered in terms of positivity. It may be possible to increase one

[2] For a definition of "reasonably", ask Tom Mason.

eigenvalue in the reference medium only by decreasing another in order to satisfy $\delta C \overset{(>)}{<} 0$. In general, such cases will yield different bounds depending on which reference medium is used.

When we are describing polycrystals whose anisotropic moduli may conceivably take any orientation, the reference moduli are constrained by an inequality (19 or 21) which must be satisfied for any orientation of the crystal moduli. Equivalently, these inequalities must hold for a fixed orientation of the crystal moduli and *any* orientation of the reference material. Due to this condition and the fact that we want to choose an extremal C^r, for polycrystals it will suffice to use isotropic reference media.

4.2 The Integral Operator Γ^r

Because the Green's function operator can not be calculated for a body of arbitrary shape, we must make some simplifying assumptions. Two common assumptions, that our sample is repeated periodically throughout space or that the size of our material sample is effectively infinite, are discussed in this section. Green's functions corresponding to other geometries (e.g., a sphere-shaped body) could also be used.

"Periodic Box" Model

In order to write an explicit formula for Γ^r, we assume here that the statistics of our polycrystal are contained in a representative volume element of the material. Experimentally, for example, we might interpret this as the region over which measurements can be taken and we assume that the crystal statistics would be the same in any other region of the same size. It is generally assumed that the representative volume element is much larger than the typical grain size so that reliable statistics may be deduced. Since we are interested in two-point statistics, the representative volume element should also be much larger than the natural correlation length.

For ease in computing the necessary Green's functions, we can assume that the representative volume element is a box which is repeated periodically throughout space. Again this may be explained physically by noting that, if our box is truly representative, the physical characteristics of the actual material should not be changed when it is replaced by a material made of such boxes. Provided that the microstructure is small compared to the size of the sample (which we assume holds in order to have a macroscopically homogeneous material), the approximation of periodicity has little effect on the results of our theory.

The convenience of periodicity allows us to express the operator Γ^r in terms of a discrete Fourier series. In Fourier space, Γ^r becomes a local operator acting by multiplication:

$$(\widehat{\Gamma^r p})_{ij}(\vec{k}) = \hat{\Gamma}^r{}_{ijmn}(\vec{k})\, \hat{p}_{mn}(\vec{k}) \tag{35}$$

where hats indicate Fourier transforms over the periodic box. The equation for Γ^r can be found explicitly by solving the equations for $\Gamma^r p$ (15,16,17) in Fourier space using periodic boundary conditions. For an isotropic reference medium with bulk and shear moduli κ_r and μ_r:

$$\hat{\Gamma}^r{}_{ijml}(\vec{k}) = \frac{1}{4\mu_r |k|^2}(k_i k_m \delta_{jl} + k_i k_l \delta_{jm} + k_j k_m \delta_{il} + k_j k_l \delta_{im}) \tag{36}$$

$$+\frac{-3\kappa_r - \mu_r}{\mu_r(3\kappa_r + 4\mu_r)} \frac{k_i k_j k_m k_l}{|k|^4} \tag{37}$$

for $\vec{k} \neq \vec{0}$, with $\hat{\Gamma}^r(\vec{0}) = 0$. This form of the operator Γ^r is particularly useful when dealing with rotational invariants, since the traces

$$\sum_{ij} \hat{\Gamma}^r{}_{iijj} \qquad \text{and} \qquad \sum_{ij} \hat{\Gamma}^r{}_{ijij} \tag{38}$$

are independent of k.

Infinite-Body Green's Functions

Several authors have suggested using the Green's function for an infinite body as an approximation to Γ^r (e.g., [3], [26], [28]). In using such an approximation, one must be sure that the integrals in the convolution extend over the full range where the kernel is signigicantly different from zero. It is also important to regularize the singularity in the kernel (see [29]), a problem which is avoided in the periodic model by excluding the $\vec{k}=\vec{0}$ mode. Furthermore, one must check that the "boundary conditions" for the Green's function match those required here. In the infinite-body case, this involves checking that the convolution has average zero (thereby satisfying equation (15)).

For example, Kröner [26] writes his generalized Green's function as convolution with the kernel

$$\Gamma^{(K)}_{ijkl}(\vec{r}) = \phi_{ijkl}(\vec{r}) + E_{ijkl}\,\delta(\vec{r}), \tag{39}$$

where the integral involving ϕ is to be taken as a principle value. To correct for the fact that boundary conditions are not considered in deriving this infinite-body Green's function, we subtract off the average value:

$$\Gamma^r p \;=\; \Gamma^{(K)} p - < \Gamma^{(K)} p > . \tag{40}$$

Then the A_2 term in the bound may be written in terms of Kröner's Green's function:

$$< \delta C \Gamma^r \delta C > \;=\; \frac{1}{vol(V)} \int_V \int_V \delta C(\vec{r})\,\phi(\vec{r}-\vec{r}\,')\,\delta C(\vec{r}\,')\,d\vec{r}\,d\vec{r}\,' \tag{41}$$

$$+\frac{1}{vol(V)} \int_V \delta C(\vec{r})\,E\,\delta C(\vec{r})\,d\vec{r} - \;< \delta C > E < \delta C > . \tag{42}$$

It should be noted that Kröner's Green's operator (39) is identical to our Green's operator *only when acting on fields with average value zero.*

4.3 Calculating $\mathbf{A_2}$

We can now proceed to evaluate the term A_2 which involves two-point statistics through the non-local action of the Γ^r operator. In the *periodic-box* model, we use the Fourier series representation of Γ^r (37) and Parseval's formula to write

$$A_2 = \sum_{\vec{k}\neq\vec{0}} \hat{\mathbf{F}}(\vec{k}) \,\vdots\, \hat{\Gamma}^r(\vec{k}) \tag{43}$$

where $\hat{\mathbf{F}}(\vec{k})$ is an eighth-order tensor defined by

$$\hat{\mathbf{F}}_{\alpha\beta cd\gamma\delta ab}(\vec{k}) = \frac{1}{vol(V)}\hat{C}_{\alpha\beta\gamma\delta}(-\vec{k})\hat{C}_{abcd}(\vec{k}) \qquad \text{i.e. -} \qquad \hat{\mathbf{F}}(\vec{k}) = \frac{1}{vol(V)}\hat{C}(-\vec{k}) \,\tilde{\times}\, \hat{C}(\vec{k}). \tag{44}$$

When using the *infinite-body operator*, one must evaluate

$$A_2 = \int_V \mathbf{F}(\vec{r}) \,\vdots\, \Gamma^r(\vec{r})\,d\vec{r} \tag{45}$$

with

$$\mathbf{F}(\vec{r}) = \frac{1}{vol(V)} \int_V C(\vec{r}\,') \,\tilde{\times}\, C(\vec{r}\,'+\vec{r})d\vec{r}\,'. \tag{46}$$

As the notation suggests, $\hat{\mathbf{F}}$ is the Fourier-series representation of $\mathbf{F}(\vec{r})$.

To finish the discussion of A_2, we show how it can be written in terms of the two-point correlation function $f_2(g,g';\vec{r})$. Let us write the elastic moduli at each point $\vec{r}$ as

$$C(\vec{r}) = \int_{g\in SO(3)} \chi_g(\vec{r})C(g)\,dg \tag{47}$$

where χ_g is the indicator function of grains with orientation g:

$$\chi_g(\vec{r}) = \begin{cases} 1 & \text{grain at } \vec{r} \text{ has orientation } g \\ 0 & \text{otherwise .} \end{cases} \tag{48}$$

Then the function $\mathbf{F}(\vec{r})$ becomes

$$\mathbf{F}(\vec{r}) = \int_V \int_g \int_{g'} \chi_g(\vec{r}')\, C(g) \tilde{\times} C(g')\, \chi_{g'}(\vec{r}' + \vec{r})\, dg'\, dg\, d\vec{r}' \tag{49}$$

$$= \int_g \int_{g'} C(g) \tilde{\times} C(g') f_2(g, g'; \vec{r}) \tag{50}$$

by virtue of the fact that

$$f_2(g, g'; \vec{r}) = \int_V \chi_g(\vec{r}')\chi_{g'}(\vec{r}' + \vec{r})\, d\vec{r}'. \tag{51}$$

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APPENDIX

A Duality, Variational Principles, and Legendre Transforms

The standard variational principles of linear elasticity are commonly phrased in terms of minimizing the energy or the complementary energy. The variational principles of Hashin & Shtrikman can be better understood after examining the duality between these two energies. The following discussion will be phrased in terms of the boundary displacement problem with zero body forces and zero boundary tractions, but it can be generalized easily.

The role of strain e in the principle of minimum energy is dual to the role of stress s in the principle of minimum complementary energy. By use of the Legendre transformation, one can show that the principle of minimum energy implies the principle of complementary energy, and vice-versa. The principle of minimum energy states that the actual strain field in the material minimizes the potential energy

$$U = e^0 : C^* e^0 = \int e : Ce \tag{52}$$

where e is allowed to vary over all fields derived from a displacement field u satisfying the prescribed boundary conditions

$$u_i(\vec{r}) = e^0_{ij} r_j \qquad \vec{r} \in \partial V. \tag{53}$$

Making use of the Legendre transformation, we see that

$$\begin{aligned} U &= \min_{e'=e-e^0} \int (e^0 + e') : C(e^0 + e') &(54)\\ &= \min_{e'} \max_{s} \int 2s : (e^0 + e') - s : C^{-1} s &(55)\\ &= \max_{s} \min_{e'} \int 2s : (e^0 + e') - s : C^{-1} s &(56)\end{aligned}$$

where interchanging the min and max requires justification through a saddle-point principle of convex analysis (see, e.g., [30]). Because the minimum over e' will be $-\infty$ except when the integral of $s : e'$ is zero, we can restrict our choice of s to this case without changing the value of the maximum. Thus we have

$$U = \max_{\nabla\cdot s=0} \int 2s : e^0 - s : C^{-1} s. \tag{57}$$

Finally, noting that the extremal s satisfies $<s>= C^* e^0$ and rearranging terms, we obtain the dual variational principle:

$$U = \min_{\substack{\nabla\cdot s=0 \\ <s>=C^* e^0}} \int s : C^{-1} s. \tag{58}$$

The Hashin-Shtrikman variational principle is derived from the principle of minimum energy in a similar manner, using the Legendre transformation to find the dual principle involving the fictitious energy $e : \delta C e$.

B Derivation of Hashin & Shtrikman's Variational Principles

In this section we review the derivation of the Hashin-Shtrikman variational principles, following loosely the development of Kohn and Milton [31]. Mathematically, this derivation involves subtracting a spatially constant reference tensor C^r from the tensor of elastic moduli and using a Legendre transform in order to estimate fluctuations in the strain field separately from fluctuations in the moduli. Physically, this amounts to dealing with the "polarization stress field," the perturbation in the stress field caused by adding inhomogeneities to a homogeneous C^r. Unlike some approximation schemes and perturbation expansions, we do *not* choose C^r to be some average of the crystallite moduli and so what we call the polarization stress may differ slightly from the meaning familiar to the reader.

B.1 Elementary Bounds

The total strain energy of our composite, subject to boundary displacements (53) and zero body forces, is

$$U \stackrel{\text{def}}{=} < e : Ce > = < e >: C^* < e > . \tag{59}$$

The principle of minimum energy states that the heterogeneous body subject to given boundary conditions will undergo a deformation such that U is minimized, which is expressed by the "Dirichlet variational inequality"

$$< e >: C^* < e > = \min_{e' \in \mathcal{E}} < \ (< e > + e') : C(< e > + e') \ > \tag{60}$$

where $\mathcal{E}$ is the set of allowable "trial fields":

$$\text{" } e' \in \mathcal{E} \text{ "} \qquad \text{means} \qquad \left\{ \begin{array}{rcl} < e' > & = & 0 \\ e' & = & \frac{1}{2}(\nabla \vec{u} + \nabla \vec{u}^T) \text{ for some } \vec{u} \end{array} \right\}. \tag{61}$$

Plugging in the trial field $e' = 0$ into the right-hand-side of (60), we obtain the Hill-Paul upper bound on the effective elastic moduli C^*. An analogous lower bound can be found via the principle of complementary energy.

The Hashin-Shtrikman variational principles which we review next are analogous to the Dirichlet variational principle, with the addition that we compare the energy of the composite material with that of a homogeneous material and deal with the polarization stress field rather than the strain field. Bounds can be obtained by plugging in an appropriate trial polarization field.

B.2 HS for Lower Bound

Interpreting the inhomogeneities in our material as perturbations from a homogeneous reference material with moduli C^r, we express the spatially-varying moduli as

$$C(\vec{r}) = C^r + \delta C(\vec{r}) \tag{62}$$

In deriving bounds based on a comparison between the composite and the reference, we need to know how the moduli are affected by the perturbations δC, and so we choose δC to have a definite sign. For example, for a lower bound we should ensure that the reference material is everywhere more compliant than the composite, and we choose

$$\delta C(\vec{r}) > 0 \qquad\qquad \vec{r} \in V. \tag{63}$$

Now we substitute (62) into the Dirichlet variational principle. Because we have chosen δC to be positive definite, we can take the Legendre transformation[3] of the term involving δC. At each point $\vec{r}$, the strain field is written as

$$e : \delta C e = \max_p \left[\ 2p : e - p : \delta C^{-1} p \ \right] \qquad \text{when } \delta C > 0 \tag{64}$$

where the maximum is over matrices p. A brief discussion of the Legendre transformation can be found in appendix A.

Writing our inequality in terms of the transformed variables, we have

$$\begin{aligned} < e >: C^* < e > \ &= \ \min_{e' \in \mathcal{E}} \Big\{ < \ (< e > + e') : C^r(< e > + e') \ > && (65) \\ &\qquad + \max_p \left[2 < p : (< e > + e') > - < p : \delta C^{-1} p > \right] \Big\}. && (66) \end{aligned}$$

Notice that the maximum in p is achieved when $p = \delta C e$ for the actual strain field e.

[3]This inequality comes from the fact that δC is positive definite and symmetric, so it can be written as the square of fourth-order tensor, $\delta C = A^T A$. Expanding the elementary inequality $|Ae - A^{-1}p|^2 = (Ae - A^{-1}p) : (Ae - A^{-1}p) \geq 0$, we obtain (64), with equality holding when $p = A^T Ae$.

Taking advantage of the fact that every field can be split into its average plus something with average zero,we write $p = <p> + p'$ and further simplify the inequality. Thus **for any $\mathbf{p}(\vec{\mathbf{r}})$**

$$
\begin{aligned}
&<e>: (C^* - C^r) <e> \;\geq \\
&\quad 2 <p>:<e> - <p : \delta C^{-1} p> + \min_{e' \in \mathcal{E}} \; <e' : C^r e'> + 2 <p' : e'> . \qquad (67)
\end{aligned}
$$

To perform the minimization over e', we shall examine the related

* * * * * * *

Homogeneous Reference Problem

Consider a homogeneous body with moduli C^r of the same shape as our composite which is subject to body forces $-\nabla \cdot p$ and zero boundary displacements. The equilibrium strain e_v (corresponding to the equilibrium displacement $\vec{v}$) is given by a convolution of the body forces with a "generalized Green's function" (see, for example, [26]) which we shall write symbolically as

$$e_v = \Gamma^r p. \qquad (68)$$

The equations of equilibrium which define e_v are

$$
\begin{aligned}
e_v &\in \mathcal{E} &\qquad (69)\\
\nabla \cdot (C^r e_v) - \nabla \cdot p &= 0. &\qquad (70)
\end{aligned}
$$

We shall later discuss solutions to these equations, which define Γ^r, in the context of our specific model. For now we note that Γ^r is a self-adjoint integral operator which depends on the reference moduli. Although written as a function of p, $\Gamma^r p$ actually depends only on the fluctuations in p ($p' = p - <p>$) and annihilates constants. One final property of the solution to (69, 70) which is worth noting is that

$$\Gamma^r C^r \Gamma^r p = \Gamma^r p, \qquad (71)$$

i.e., if e_v solves (69, 70), then it also solves those equations with p replaced by $C^r \Gamma^r p$ (this is clear since then $C^r \Gamma^r p = C^r e_v$). The reader should keep in mind that many authors (e.g., McCoy [1]) define Γ^r in terms of non-zero boundary displacements and so their "Γp" may not have average zero.

Now the theorem of minimum potential energy for this configuration tells us that $\tilde{e} = e_v$ minimizes

$$
\begin{aligned}
&\int_V \tilde{e} : C^r \tilde{e} + 2 \int_V (\nabla \cdot p) \cdot \tilde{v} \\
&\quad = \int_V \tilde{e} : C^r \tilde{e} + 2 \int_{\partial V} (p \cdot \tilde{v}) \cdot n - 2 \int_V p : \nabla \tilde{v} \\
&\quad = <\tilde{e} : C^r \tilde{e}> - 2 <p : \tilde{e}>
\end{aligned}
$$

over all fields with $<\tilde{e}> = 0$ and $\tilde{e} = 1/2(\nabla \tilde{v} + \nabla \tilde{v}^T)$ for some $\tilde{v}(\vec{r})$. In other words,

$$\tilde{e} = \Gamma^r p \qquad \text{achieves} \qquad \min_{\tilde{e} \in \mathcal{E}} <\tilde{e} : C^r \tilde{e}> - 2 <p : \tilde{e}> . \qquad (72)$$

* * * * * * *

We return now to the minimization over e' in (67). Comparing (72) with (67) and keeping in mind that the integral of $<p>: e'$ is zero, we see that the minimizer we seek is $e' = -\Gamma^r p$ and therefore

$$
\begin{aligned}
\min_{e' \in \mathcal{E}} <e' : C e'> + 2 <p' : e'> &= <(\Gamma^r p') : C^r \Gamma^r p'> - 2 <p' : \Gamma^r p'> &\qquad (73)\\
&= - <p' : \Gamma^r p'> . &\qquad (74)
\end{aligned}
$$

The second equality comes from equation (71) and the self-adjointness of Γ^r.

Incorporating this solution in our inequality we obtain the Hashin-Shtrikman variational principle for the lower bound:

$$
\begin{aligned}
<e>:(C^*-C^r)<e> \quad &\geq \quad 2<p>:<e> - <p:\delta C^{-1}p> - <p:\Gamma^r p> && (75)\\
\delta C \quad &> \quad 0. && (76)
\end{aligned}
$$

B.3 HS for upper bound

Choosing $\delta C < 0$ and performing manipulations parallel to those for the lower bound, we obtain

$$
\begin{aligned}
<e>:(C^*-C^r)<e> \quad &\leq \quad 2<p>:<e> - <p:\delta C^{-1}p> - <p:\Gamma^r p> && (77)\\
\delta C \quad &< \quad 0. && (78)
\end{aligned}
$$

Remark

The Hashin-Shtrikman upper bound can also be derived by plugging a trial field

$$e = e^0 + \Gamma^r \delta C t$$

into the principle of minimum energy (60) and optimizing over matrix-fields t (as done, for example, by [5] for the general theory or [32] for application to polycrystals), and then using the Cauchy-Schwartz inequality

$$< \delta C \Gamma^r \delta C \Gamma^r \delta C > \quad \leq \quad - < -\delta C >^{-1} < \delta C \Gamma^r \delta C >^2 \qquad \text{when } \delta C < 0. \qquad (79)$$

References

[1] John J. McCoy. Macroscopic response of continua with random microstructures. In S. Nemat-Nasser, editor, *Mechanics Today, Vol. 6*, pages 1–40. Pergamon Press, 1981.

[2] Z. Hashin. Analysis of composite materials – a survey. *J. Appl. Mech.*, 50:481–503, Sept. 1983.

[3] J.R. Willis. Variational and related methods for the overall properties of composite materials. In C.S. Yih, editor, *Advances in Applied Mechanics*, pages 2–77. Academic Press, New York, 1981.

[4] Graeme W. Milton. On characterizing the set of possible effective tensors of composites: the variational method and the translation method. *Comm. Pure and Appl. Math.*, XLIII:63–125, 1990.

[5] E. Kröner. Bounds for effective elastic moduli of disordered materials. *J. Mech. Phys. Solids*, 25:137–155, 1977.

[6] Mark J. Beran. *Statistical Continuum Theories*, volume 9 of *Monographs in Statistical Physics*. John Wiley and Sons, Inc., Providence, 1968.

[7] B.L. Adams et al. Description of orientation coherence in polycrystalline materials. *Acta metall.*, 35(12):2935 –2946, 1987.

[8] Stuart I. Wright and Brent L. Adams. Automatic analysis of electron backscatter diffraction patterns. *Metallurgical Trans. A*, 23A:759 – 767, March 1992.

[9] K. Kunze, S.I. Wright, B.L. Adams, and D.J. Dingley. Advances in automatic EBSP single orientation measurements. Submitted to *Textures and Microstructures*, Jan. 1992.

[10] B.L. Adams, S.I. Wright, and K. Kunze. Orientation imaging: The emergence of a new microscopy. *Metallurgical Trans.*, 1993. To appear.

[11] Z. Hashin and S. Shtrikman. A variational approach to the theory of the elastic behavior of polycrystals. *J. Mech. Phys. Solids*, 10:343–352, 1962.

[12] Z. Hashin and S. Shtrikman. On some variational principles in anisotropic and nonhomogeneous elasticity. *J. Mech. Phys. Solids*, 10:335–342, 1962.

[13] Z. Hashin and S. Shtrikman. A variational approach to the theory of the effective magnetic permeability of multiphase materials. *J. Appl. Phys.*, 33:3125–3131, 1962.

[14] Z. Hashin and S. Shtrikman. A variational approach to the theory of the elastic behavior of multiphase materials. *J. Mech. Phys. Solids*, 11:127–140, 1963.

[15] L.J. Walpole. On bounds for the overall elastic moduli of inhomogeneous systems — i. *J. Mech. Phys. Solids*, 14:151–162, 1966.

[16] L.J. Walpole. On bounds for the overall elastic moduli of inhomogeneous systems — ii. *J. Mech. Phys. Solids*, 14:289–301, 1966.

[17] R. Hill. The elastic behavior of a crystalline aggregate. *Proc. Phys. Soc. A*, 65:349–354, 1952.

[18] B. Paul. Prediction of elastic constants of multiphase materials. *Trans. of the Metallurgical Society of the AIME*, 218:36–41, 1960.

[19] Marco Avellaneda and Graeme W. Milton. Optimal bounds on the effective bulk modulus of polycrystals. *SIAM J. Appl. Math.*, 49(3):824–837, June 1989.

[20] M. Beran and J. Molyneux. Use of classical variational principles to determine bounds for the effective bulk modulus in heterogeneous media. *Q. Appl. Math.*, 24:107–118, 1966.

[21] R. Zeller and P.H. Dederichs. Elastic constants of polycrystals. *Phys. Stat. Solidi (B)*, 55:831–842, 1973.

[22] M.W.M. Willemse and W.J. Caspers. Electrical conductivity of polycrystalline materials. *J. Math. Phys.*, 20(8):1824–1831, Aug. 1979.

[23] Melvin N. Miller. Bounds for effective bulk modulus of heterogeneous materials. *J. Math. Phys.*, 10(11):2005–2013, Nov. 1969.

[24] Marco Avellaneda and Oscar Bruno. Effective conductivity and average polarizability of random polycrystals. *J. Math. Phys.*, 31(8):2047–2056, Aug. 1990.

[25] H.-J. Bunge. *Texture Analysis in Materials Science.* Butterworths, Boston, 1982.

[26] E. Kröner. Statistical modelling. In John Gittus and Joseph Zarka, editors, *Modelling Small Deformations of Polycrystals*, chapter 8, pages 229–291. Elsevier Applied Science Publishers, New York, 1986.

[27] J.R. Willis. Bounds and self-consistent estimates for the overall properties of anisotropic composites. *J. Mech. Phys. Solids*, 25:185–202, 1977.

[28] D.J. Bacon, D.M. Barnett, and R.O. Scattergood. Anisotropic continuum theory of lattice defects. *Progress in Materials Science*, 23:51–262, 1979.

[29] I.M. Gel'fand and G.E. Shilov. *Generalized Functions.* Academic Press, 1964.

[30] I. Ekeland and R. Temam. *Convex Analysis and Variational Problems.* North-Holland, 1976.

[31] Robert V. Kohn and Graeme W. Milton. On bounding the effective conductivity of anisotropic composites. In J.L.Ericksen et al., editors, *Homogenization and Effective Moduli of Materials and Media*, pages 97–125. Springer-Verlag, 1986.

[32] M.J. Beran, T.A. Mason, B.L. Adams, and T. Olson. Bounding elastic constants of an orthotropic polycrystal from measurements of the microstructure. In revision, 1994.