Microstructure and conductivity of hierarchical laminate composites

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Certain hierarchical laminates with a wide separation of length scales are known theoretically to have optimal transport and mechanical properties. We derive analytical expressions for the $n$-point probability functions that statistically characterize the microstructure for more general hierarchical laminates with an arbitrary number of stages and a finite separation of length scales. Using two-point probability information, we rigorously bound the effective conductivity (or dielectric constant) tensor for macroscopically anisotropic laminates and study how the separation of length scales affects the effective properties.

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I. INTRODUCTION

Since the details of the microstructure of random materials are usually not completely known, researchers have, in lieu of an exact determination, either estimated or bounded the effective properties of random materials given limited microstructural information [1,2]. One interesting problem in the case of bounding approaches is finding the microstructures that saturate the bounds, i.e., determining the optimal microstructures. Certain laminate composites with structural hierarchy (structure at different length scales) are known to optimize the effective conductivity [3–6] as well as the effective elastic moduli [5–11]. Hierarchical composites are also of practical interest since they are abundant in nature [12]: tendon [13], bone [14], and mollusk shells [15] are excellent examples of hierarchical biological composites.

To our knowledge, the quantitative characterization of the microstructure (via statistical correlation functions) of hierarchical laminates has been lacking. Moreover, there are presently no rigorous estimates of the effective properties of hierarchical laminates when the separation between the length scales is finite. In this paper, we will address these issues in the context of finding the effective conductivity tensor of such materials.

In Fig. 1 we show a portion of a random laminate of second rank, i.e., one that possesses two levels of hierarchy. It is constructed in two stages. The first stage is simply a series of parallel strips of width $d_1$ in the $x$ direction generated by some one-dimensional random process. For this process we define $\phi_1^{(1)}$ and $\phi_2^{(1)}$ to be the volume fractions of the disconnected phase (phase 1) and the “slab” phase (phase 2), respectively. We also respectively define $\sigma_1$ and $\sigma_2$ to be the conductivities of phases 1 and 2. The second stage of lamination adds perpendicular strips of width $d_2$ in the gaps of the first stage. We define $\phi_1^{(2)}$ and $\phi_2^{(2)}$ to be the volume fractions of phases 1 and 2 for the second-stage processes, respectively. Clearly from this construction

$$\phi_1^{(1)} + \phi_2^{(1)} = \phi_1^{(2)} + \phi_2^{(2)} = 1. \quad (1)$$

Also, a point lies in phase 1 of the entire laminate exactly when its $x$ coordinate lies in phase 1 of the first stage and its $y$ coordinate lies in phase 1 of the second stage of lamination. Since these events are independent, we see that the volume fraction of phase 1 of the entire laminate is given by

$$\phi_1 = 1 - \phi_2 = \phi_1^{(1)} \phi_1^{(2)}. \quad (2)$$

By repeating this procedure one can create higher-rank laminates in the plane. We also can generalize this procedure to higher dimensions, although we restrict our attention to two dimensions in this paper. Finally, laminates in general do not necessarily need to have orthogonal stages; we only consider such laminates in this paper to facilitate our characterization of the microstructure. We will discuss how to apply our microstructural characterization to laminates without orthogonal stages.

Typical one-dimensional systems from which laminates are constructed are fully penetrable rods, totally impenetrable rods in thermal equilibrium, and one-dimensional “random checkerboards.” Realizations of these three systems are shown in Fig. 2; the systems depicted have equal rod lengths and volume fractions of the phases. Notice that the clusters could have width larger than $d$ in the systems which permit the individual rods to overlap. By extending these one-dimensional systems into two dimensions, hierarchical laminates are constructed.

Much research has been conducted on hierarchical laminates with a wide separation of length scales [3–6] (for laminates of second rank, this condition means that $d_1/d_2$ tends

FIG. 1. A portion of a typical second-rank laminate, and one way that seven points could fall within the gaps of the first stage of lamination.
FIG. 2. The three one-dimensional random systems considered in this paper: (a) fully penetrable rods, (b) totally impenetrable rods, and (c) a one-dimensional random checkboard process. The rods of the three systems have a common width $d$; however, the clusters in systems (a) and (c) can be longer than $d$ due to overlap. Laminates are generated by extending such systems into two-dimensional systems of gaps and slabs.

to infinity). For such laminates, the fields are piecewise uniform within the two phases of the composite, and so exact expressions for the effective properties can be obtained by using macroscopic methods. However, laminates with only a finite separation of length scales do not have piecewise uniform fields, and for this reason the macroscopic properties of such laminates cannot be calculated analytically. Some other technique must be employed to estimate or bound the effective properties.

To study laminates with a finite separation of length scales, we will use contrast expansion theory, which was formulated by Sen and Torquato [16,17]. They derived the following series expansion for the effective conductivity tensor $\boldsymbol{\sigma}_e$ for any $d$-dimensional two-phase random composite (in particular, random laminates):

$$
(\phi_1 \beta_{ij})^2 (\sigma_e - \sigma_{ij})^{-1} \left( (\sigma_e + (d-1) \sigma_1) I \right) = \phi_1 \beta_{ij} I - \sum_{n=2}^{\infty} \mathbf{A}_{n}^{(i)} \beta_{ij}^n,
$$

where $I$ is the identity tensor, $i,j = 1,2$, $i \neq j$,

$$
\beta_{ij} = \frac{\alpha_{ij} - \sigma_{ij}}{\alpha_1 + (d-1) \sigma_1},
$$

and the tensor coefficients $\mathbf{A}_{n}^{(i)}$ are functionals of $S_1, \ldots, S_n$, where $S_p(r')$ is the probability that $p$ given points $r' = r_1, \ldots, r_p$ all lie within phase $i$. (Bounds of arbitrary order can be obtained from (3); this will be discussed later.) Unlike the other tensor coefficients, $\mathbf{A}_{2}^{(i)} = \mathbf{A}_{2}^{(2)}$, and henceforth their common value will be denoted by $\mathbf{A}_{2}$. In two dimensions $\mathbf{A}_2$ is traceless and is explicitly given by

$$
\mathbf{A}_2 = \frac{1}{\pi \delta_{-0}} \int_\delta^{2\pi} \int_0^{2\pi} \frac{d\theta}{r} \begin{bmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{bmatrix} \left[ S_2(r, \theta) - \phi_1^2 \right]
$$

for statistically homogeneous media; see Ref. [16] for the integral expressions for the higher $\mathbf{A}_{n}^{(i)}$. The quantity $(r, \theta)$ in the integrand represents the separation between the two points that lie in phase 1 in polar coordinates.

If we omit the series in (3), we obtain the well-known Hashin-Shtrikman bounds on the effective conductivity of isotropic-two-phase composites in two and three dimensions [18]. These bounds are the best possible given only volume-fraction information, and hence optimal, since they can be realized for several classes of composites [3,4,18,19]. One such class of optimal structures (i.e., structures that achieve these bounds) are macroscopically isotropic laminates, which have a wide separation of length scales and satisfy the volume-fraction requirement [3,4]

$$
\phi_2^{(1)} = \phi_2^{(2)} / \phi_1^{(2)}.
$$

For macroscopically isotropic laminates, the tensor coefficients $\mathbf{A}_n^{(i)}$ must vanish [6].

If $S_2$ is independent of the direction $\theta$ (statistical isotropy), or is symmetric about the line $\theta = \pi/4$, then $\mathbf{A}_2$ is trivially zero in view of (5). However, from geometrical considerations (elaborated in Sec. II), $S_2$ is inherently statistically anisotropic for the hierarchical laminate of Fig. 1 and thus obeys neither of these symmetries, yet $\mathbf{A}_2$, as shall be shown, vanishes anyway when the laminate is macroscopically isotropic. To demonstrate this, we will first calculate the microstructure function $S_2$ for laminates and then use (5) to explicitly show, from the microstructure, that $\mathbf{A}_2 = 0$ for macroscopically isotropic laminates.

By taking certain Padé approximants of (3), Sen and Torquato obtained bounds of arbitrary order on the effective conductivity tensor in terms of the $\mathbf{A}_n^{(i)}$, which in turn depend on the $S_n$ [16]. In this paper we will study the second-order bounds obtained from a $[1,1]$ Padé approximant of (3). The bounds on the effective conductivity in the two principal directions are identical and equal to the Hashin-Shtrikman bounds whenever $\mathbf{A}_2 = 0$. However, when $\mathbf{A}_2$ is not equal to the zero tensor, the two sets of bounds are not identical but instead are directionally dependent. Therefore, when we take laminates which satisfy (6) and have an increasing separation of length scales, the bounds in the two principal directions both converge to the Hashin-Shtrikman bounds. Approaching laminates from the perspective of their microstructure therefore allows us to study how the separation of length scales (i.e., the nonuniformity of the fields within the phases) affects the effective conductivity tensor.

Summarizing, in this paper we study the following questions: What are the $S_n$ for laminates with any separation of length scales? Does the functional behavior of $S_n$ reflect the construction of the laminate? Can we bound the effective conductivity of laminates with a finite separation of length scales? How does the separation of length scales affect these bounds? How close are they to the bounds for laminates with an infinite separation of length scales? Are these results in agreement with known results as the separation of length scales tends to infinity? Finally, one outstanding unsolved problem: what are all classes of optimal composites; i.e., what form must the $S_n$ have so that the $\mathbf{A}_n^{(i)}$ vanish? A study of the microstructure of laminates may provide a first step toward answering this difficult last question.

In Sec. II we obtain analytical representations of the $S_n$ for fully penetrable laminates of arbitrary rank and $S_2$ for laminates of arbitrary rank and construction in terms of the microstructure of the one-dimensional generating processes.
We explicitly calculate $S_2$ for second-rank fully penetrable laminates, totally impenetrable laminates, and laminates generated by random checkerboards. Our expressions are valid for laminates with a finite separation of length scales. In Sec. III we use our expression for $S_2$ to calculate the two-point tensor coefficient $A_2$ and therefore bounds on $\sigma_2$ for laminates with a finite separation of length scales. Then we let the separation of length scales tend to infinity and verify that the bounds in the two principal directions indeed both converge to the Hashin-Shtrikman bounds for macroscopically isotropic hierarchical laminates.

II. MICROSTRUCTURE OF LAMINATES

To begin, we study the microstructure of laminates in the plane. We first define the $n$-point phase 1 probability functions $S_n$ and the lineal path function $L$. These functions are inherently anisotropic for laminates since the laminates themselves are statistically anisotropic. We develop a recursive equation valid for any $S_n$ for random laminates of arbitrary rank generated by systems of fully penetrable rods. Generalizations are then discussed, including an expression for $S_2$ for laminates of arbitrary rank and construction; this expression will be used in our numerical calculations of $A_2$ in Sec. III. We then use this expression to calculate $S_2$ for three types of second-rank laminates: fully penetrable laminates, totally impenetrable laminates, and laminates generated by random checkerboards. Finally, we study how $S_2$ reflects the structure of laminates on their multiple length scales. (In Appendix A we will consider the lineal path function for second-rank laminates.)

A. Definitions of microstructure functions

The probability that $n$ points with positions $\mathbf{r}^n$ all lie in phase 1 is denoted by $S_n(\mathbf{r}^n) = r_1, \ldots, r_n$ and can be explicitly written as [20]

$$S_n(\mathbf{r}^n) = \left( \prod_{j=1}^{n} I(r_j) \right),$$

(7)

where $I$ is the indicator function of phase 1; i.e.,

$$I(\mathbf{r}) = \begin{cases} 1, & \mathbf{r} \text{ in phase 1}, \\ 0, & \text{otherwise}. \end{cases}$$

(8)

The angular brackets denote an ensemble average over the possible realizations. For statistically homogeneous media, the $S_n$ are dependent only on the relative displacements so that, for example, $S_1 = \phi_1$, the volume fraction of phase 1.

When we refer to the microstructure of laminates in this paper, $S_n$ will denote the microstructure function for the full laminate. We also define $S_n^{(i)}$ to be the $n$-point probability function for phase 1 for the one-dimensional process which determines the $i$th stage of lamination.

The probability that a vector $\mathbf{x}$ is wholly contained in phase 1 is called the lineal path function [21] and is denoted by $L(x)$. This probability is different than $S_2$, which requires that only the endpoints of the line lie in the same phase. We also define $L^{(i)}$ to be the one-dimensional lineal path function for the process which determines the $i$th stage of lamination.

We now characterize the microstructure of laminates by calculating $S_n$ in terms of the functions $S_n^{(i)}$ and $L^{(i)}$.

B. $S_n$ for fully penetrable laminates of arbitrary rank

By a fully penetrable laminate, we mean a laminate generated by fully penetrable (i.e., spatially uncorrelated) rods at each stage of lamination, so that the $i$th stage of lamination is probabilistically determined by the width of the laminates $d_i$ and the number density of lamination $\rho_i$. We allow the possibility that the strips overlap in general, so that the “slabs” generated by the strips of the $i$th stage may have width greater than $d_i$. We also assume the processes of the $i$th stage of lamination are identically distributed and independent both of each other and the processes of every other stage of lamination. This assumption also holds for the more general laminates considered later in this paper.

To calculate the probability that $n$ points $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$ all fall in the disconnected phase of a $k$th-rank fully penetrable laminate, we first order the $n$ points by their $x$-coordinates so that $x_1 \leq x_2 \leq \cdots \leq x_n$. Then we use a key property of random laminates: the laminates of order $k-1$ embedded in the gaps of the first stage of lamination are generated independently of each other.

To utilize this feature, we introduce some notation to enumerate the $2^{n-1}$ different ways that the ordered $n$ points could fall into the gaps of the first stage of lamination. Consider the set $A$ of $n$-tuples of the letters 0 and 1 whose $n$th element is 1. Then there is a one-to-one correspondence between the elements of this set and the permutations of the $n$ points in different gaps: if $p_0 = 0$ and $p_1, \ldots, p_m$ are the positions of the 1s in an element $a$ of $A$, we associate with this element $a$ the event that the sets of points $\{x_{p_1+1}, \ldots, x_{p_2+1}\}$ fall in the same gap and in a different gap than the set corresponding to any other $j$. (For brevity we suppress the dependence of the $p_j$ and $m$ on the $n$-tuple $a$.) We conclude from this bijection that there are indeed $2^{n-1}$ ways the ordered points could lie in the gaps.

To illustrate this notation, consider the event of seven points falling in the disconnected phase depicted in Fig. 1. From left to right, the first four points lie in one gap of the first stage of lamination, the next two points lie in another gap, while the last point lies a third gap. The sequence corresponding to this event is $a = \{0,0,0,1,0,1,1\}$, so that $m = 3$, $p_0 = 0$ (as always), $p_1 = 4$, $p_2 = 6$, and $p_3 = 7$ ($p_m = n$ always). Under this construction, $a_i = 1$ exactly when point $i$ is the rightmost point in a gap.

Since a Poisson distributed system has independent and stationary increments, the probability that the $n$ points will fall in the gaps of the first stage of lamination according to the arrangement associated with $a \in A$ is

$$P(a) = S_n^{(1)}(x_1, \ldots, x_n) \prod_{i=1}^{n-1} M(x_{i+1} - x_i; a_i),$$

(9)

where $a_i$ is the $i$th element of $a$,
\[
M(r,0) = \frac{L^{(1)}(r)}{S_2^{(1)}(r)} \begin{cases} 
1, & r \leq d_1, \\
e^{-p_i(r-d_i)}, & r > d_1,
\end{cases} 
\]

and

\[
M(r,1) = 1 - M(r,0).
\]

The functions \(S_2\) and \(L\) for fully penetrable rods are given explicitly in \((17)\) and \((18)\). The calculation of this probability is not so trivial for more general one-dimensional processes, as discussed in the next subsection.

Once we have isolated the \(x\) coordinates in the gaps of the first stage of lamination, we must now calculate the probability that the set \(\{r_{pj+1}, \ldots, r_{pj+k}\}\) (i.e., all the points that lie in an arbitrary gap) also lies in the disconnected phase. Since the processes within the gaps of the first stage are embedded laminates of rank \(k-1\) rotated 90° from the usual orientation, this conditional probability is just \(S_p^{(k-1)}(r_{pj+1}, \ldots, r_{pj+k})\), where \(r\) is the transpose of \(r\) and \(S_p^{(k)}\) is the \(p\)-point disconnected-phase probability function of the embedded laminates of rank \(k-1\).

Since the processes in the embedded laminates are assumed to be independent of each other and the first stage of lamination, we finally conclude using the law of total probability that

\[
S_n(r_1, \ldots, r_n) = S_n^{(1)}(x_1, \ldots, x_n) \sum_{a \in A} \prod_{i=1}^{n-1} M(x_{j+1} - x_i; a) \prod_{j=1}^m S_p^{(k-1)}(r_{pj+1}, \ldots, r_{pj+k}).
\]

Through repeated use of \((12)\) we can reduce \(S_n\) for a \(k\)-th rank laminate to the one-dimensional functions \(S_p^{(i)}\) for \(1 \leq p \leq n\) and \(1 \leq i \leq k\).

\[\text{C. } S_n \text{ for general random laminates}\]

In principle, the above approach could be applied to laminates of arbitrary rank generated by random processes other than fully penetrable rods. However, such a recursive relationship would require knowledge of microstructure functions never before considered in the literature. For example, determining \(S_3\) requires knowing the probability that, given three points, the first two lie in one gap and the third lies in another gap. While such probabilities can be computed explicitly for fully penetrable rods, and is done in \((9)\), they have not been considered for more general one-dimensional systems.

However, the probability that only two points do or do not lie in the same gap is determined by the defined one-dimensional two-point phase 1 probability functions \(S_2^{(1)}\) and the lineal path functions \(L^{(i)}\), and so \(S_2\) can be calculated for general random laminates of arbitrary rank. Our analysis of conditioning of the positions of the two points relative to the first stage of lamination is particularly self-evident in determining \(S_2\) for second-rank laminates of arbitrary construction. If the two \(x\) coordinates lie in the same gap, then the \(y\) coordinates both must lie in phase 1 of the second-stage one-dimensional process in that gap. On the other hand, if they lie in different gaps, then the two \(y\) coordinates need to lie in phase 1 of two independent processes. Using the law of total probability and this analysis, we conclude that

\[
S_2(x,y) = L^{(1)}(x)S_2^{(2)}(y) + [S_2^{(1)}(x) - L^{(1)}(x)](\phi_1^{(2)})^2,
\]

where \((x,y)\) is the displacement between the two points. The complexity of the general expression \((12)\) is thus greatly simplified when \(n=k=2\). Similar expressions for \(S_2\) can be developed for laminates of higher rank. As expected, \(S_2(x,y)\) tends to its long-range value of \(\phi_1^2\) as \(x,y \to \infty\). This will be used in the integrations of the next section.

Finally, we can use our analysis to calculate \(S_n\) for laminates that do not have orthogonal stages. For example, a second-rank laminate whose second stage is at angle \(\theta\) from horizontal can be transformed to a topologically equivalent orthogonal laminate via the linear transformation

\[
(x,y) \to (x,y - x \tan \theta).
\]

To calculate \(S_n\) for this slanted laminate, we would first project the points to their images under the above transformation and then calculate \(S_n\) for this orthogonal laminate.

\[\text{D. Calculation of } S_2 \text{ for second-rank laminates}\]

In this section we will use \((13)\) to calculate \(S_2(x,y)\) for second-rank fully penetrable laminates, totally impenetrable laminates, and laminates generated by random checkerboards. We will also show that \(S_2\) reflects the behavior of laminates on their multiple length scales.

\[\text{I. Fully penetrable laminates}\]

We now explicitly state \(S_2\) for fully penetrable second-rank laminates in terms of the generating one-dimensional processes. The microstructure of fully penetrable rods (an example of which is shown in Fig. 2) on a line is very well understood. If the rods have diameter \(d\) and number density \(p\), and we define the reduced density \(\eta\) by

\[
\eta = \rho d,
\]

then we have [22]

\[
S_1 = \phi_1 = e^{-\eta}.
\]

For two points separated by a distance \(x\), the two-point phase 1 probability function is given by
where \( u = |x|/d \) is dimensionless distance.

The lineal path function for fully penetrable rods is given by [21]

\[
S_2(u) = \begin{cases} 
  e^{-\eta(1+u)}, & u \leq 1, \\
  e^{-2\eta}, & u > 1,
\end{cases}
\]

so that, not surprisingly, \( L(u) = S_2(u) \) for \( u \leq 1 \).

Substitution of these results into (13) and use of dimensionless units \( u = |x|/d_1 \) and \( v = |y|/d_2 \) yields

\[
S_2(u,v) = \begin{cases} 
  \phi_1 e^{-\eta_1 u - \eta_2 v}, & u \leq 1, v \leq 1, \\
  \phi_1 e^{-\eta_1 u - \eta_2}, & u \leq 1, v > 1, \\
  \phi_1 [e^{-\eta_1 u}(e^{-\eta_2 v} - e^{-\eta_1}) + \phi_1], & u > 1, v \leq 1, \\
  \phi_1^2, & u > 1, v > 1,
\end{cases}
\]

as usual, and \( w = r/d_1 \). [From geometric considerations,

\( S_2(w, \theta) \) is symmetric about \( \theta = \pi/2 \) and is periodic with period \( \pi \).] As we see, our simulation data is in excellent agreement with (19). We also note that, as expected, \( S_2 \) is not symmetric about \( \theta = \pi/4 \).

2. Totally impenetrable laminates

We now consider second-rank laminates which are constructed by systems of hard rods of equal diameter \( d \) in thermal equilibrium. A possible realization of such a system was given in Fig. 2. As before, we need the quantities \( S_2^{(i)}(x) \) and \( L^{(i)}(x) \) for the one-dimensional processes that generate the laminate to determine \( S_2 \) for the full laminate. Torquato and Lado [23] calculated \( S_2 \) explicitly for a system of hard rods in equilibrium. After some simplification their expression can be written in terms of the dimensionless distance \( u = |x|/d \) as

\[
S_2(u) = (1 - \eta) \sum_{k=0}^{j} \frac{\exp(-[u-k]/a)}{k!} \left( \frac{u-k}{a} \right)^k,
\]

where \( j \leq u \leq j+1 \) and

\[
a = \frac{1 - \eta}{\eta}.
\]

As before, \( \eta \) is the reduced density. Since the rods do not overlap,

\[
\phi_1 = 1 - \eta.
\]

For sufficiently large \( u \), \( S_2(u) \) can be accurately approximated using the method of subtracted singularities, as explained in Appendix B. This asymptotic approximation will turn out to be useful in numerically computing the tensor coefficient \( A_2 \), as described in Sec. III.

Also, Lu and Torquato [21] calculated the lineal path function \( L \) exactly for a system of hard rods in equilibrium and found that

\[
L(u) = (1 - \eta) \exp(-u/a).
\]
As before, \( L(u) = S_2(u) \) for \( u \leq 1 \).

Therefore, to calculate \( S_2 \) for totally impenetrable laminates, we substitute (22) and (25) with appropriate \( \eta_1 \) and \( \eta_2 \) into (13). As with fully penetrable laminates, this expression is also in agreement with computer simulations.

3. Random checkerboard laminates

A third type of laminate is constructed by one-dimensional checkerboard processes, also depicted in Fig. 2, in which the plane is divided into equisized sections of width \( d \). Each section, independent of the other sections, belongs to phase 1 with probability \( \phi_1 \) and phase 2 with probability \( \phi_2 \). The required microstructure functions for phase 1 are then given by

\[
S_2(u) = \begin{cases} 
(1-u) \phi_1 + u \phi_1^2, & u \leq 1, \\
\phi_1^2, & u > 1,
\end{cases}
\]  
(26)

and

\[
L(u) = (1-z) \phi_1^n + z \phi_1^{n+1},
\]  
(27)

where the dimensionless distance is decomposed as \( u = (n-1) + z \) with \( 0 \leq z < 1 \). Substitution of these into (13) gives \( S_2 \) for the full laminate. We note that for sufficiently large \( x \) and \( y \), \( S_2(x,y) \) is identically equal to \( \phi_1^2 \), just as in the case of the one-dimensional checkerboard model.

4. Behavior of \( S_2 \) on different length scales

To conclude this section we discuss how the graph of \( S_2 \) can reflect the processes which construct the laminate. In particular, we show that \( S_2 \) reflects microstructural information about a composite on its different length scales.

In Fig. 4 we plot \( S_2(w, \pi/6 \) ), where again we use polar coordinates with \( w = r/d_1 \), for a laminate constructed by two different one-dimensional processes. The first stage is generated by a system of fully penetrable rods with \( \eta_1 = 0.4 \). The second stage is generated by systems of totally impenetrable rods in thermal equilibrium with \( \eta_2 = 0.8 \) and \( d_2 = 0.1d_1 \).

As we see, \( S_2 \) for this laminate reflects properties of the functional behavior of \( S_2 \) for the one-dimensional processes. On the length scale \( w = O(1) \), \( S_2 \) decays exponentially and then more or less flattens, just like it does for “pure” fully penetrable rods [see (17)]. However, on the length scale \( w = O(0.1) \), we see a sharp cusp and dampened oscillations, just like \( S_2 \) for “pure” totally impenetrable rods in thermal equilibrium [see (22)]. While we cannot conclude decisively from this graph the precise components of the laminate, we see that the structure of the laminate on both length scales is reflected in \( S_2 \).

III. EFFECTIVE CONDUCTIVITY TENSOR OF LAMINATES

A laminate with a finite separation of length scales has fields which are not piecewise uniform, and so its effective conductivity cannot be calculated analytically. We will use rigorous second-order bounds on \( \sigma_e \) that depend on \( S_2 \) (which was calculated in the previous section) and the phase conductivities \( \sigma_1 \) and \( \sigma_2 \) to estimate the effective conductivity for laminates with a finite separation of length scales. We verify that these bounds converge to the Hashin-Shtrikman bounds for macroscopically isotropic laminates, i.e., laminates that satisfy (6) and have an infinite separation of length scales.

A. Second-order contrast bounds

By taking certain Padé approximants of (3), Sen and Torquato [16] obtained bounds of arbitrary order on the effective conductivity tensor \( \sigma_e \). The second-order bounds on \( \sigma_e \) are given by

\[
\frac{\sigma_e}{\sigma_j} = 1 + \frac{\phi_1 (\sigma_1 - \sigma) \sigma_j}{\sigma_j} \left[ 1 - \frac{\phi_1 (\sigma_j - \sigma)}{\sigma_j} \right]^{-1},
\]  
(28)

and \( \mathbf{A}_2 \) is given by (5). For \( \sigma_2 > \sigma_1 \), we obtain a lower bound from (28) for \( j = 1 \) and \( i = 2 \), and we obtain an upper bound for \( j = 2 \) and \( i = 1 \).

We note in passing that one can eliminate the parameter \( \mathbf{a}_2 \) by utilizing the property that \( \text{Tr} \mathbf{a}_2 = -\phi_1 \phi_2 \) (since \( \mathbf{A}_2 \) is traceless) to yield the simpler bounds on the eigenvalues \( \lambda_1 \) and \( \lambda_2 \) of \( \sigma_e \) obtained by Lurie and Cherkaev [3,9] and by Tartar [4]:

\[
\frac{1}{\sigma_1} + \frac{1}{\lambda_1 - \sigma_1} + \frac{1}{\lambda_2 - \sigma_1} \leq \frac{1}{\phi_2} \left( \frac{1}{\sigma_1} + \frac{2}{\sigma_2 - \sigma_1} \right),
\]  
(30)

\[
\frac{1}{\sigma_2} + \frac{1}{\lambda_1 - \sigma_2} + \frac{1}{\lambda_2 - \sigma_2} \geq \frac{1}{\phi_1} \left( \frac{1}{\sigma_2} + \frac{2}{\sigma_1 - \sigma_2} \right),
\]  
(31)

where \( \sigma_2 > \sigma_1 \).
When \( A_2 = 0 \), the bounds (28) coincide with the Hashin-Shtrikman bounds on macroscopically isotropic two-phase composites, which are known to be optimal for several classes of composites. One such class is a geometry of space-filling, singly-coated circular cylinders [18], where the inner core is one phase and the outer shell is the other phase. Another example is the Vigdergauz construction [19]. Also, the bounds (28) are realized for \( A_2 \neq 0 \) by space-filling, singly coated ellipsoids [4, 24, 25].

Second-rank laminates with a wide separation of length scales have also been shown by macroscopic methods to achieve the bounds (28) and thus are optimal composites [3, 4]. We conclude again that \( A_2 \) must be the zero tensor for macroscopically isotropic laminates. However, this previous research does not determine \( A_2 \) and hence the bounds (28) for laminates with a finite separation of length scales.

In order to quantify the degree of anisotropy of laminates with a finite separation of length scales, we introduce the parameter

\[
\gamma = \frac{\max(|A_{11}|, |A_{22}|)}{\phi_1 \phi_2},
\]

where \( \Lambda_1 \) and \( \Lambda_2 \) are the eigenvalues of \( A_2 \). This is a purely microstructural parameter, independent of the conductivities \( \sigma_1 \) and \( \sigma_2 \). Since \(-\phi_1 \phi_2 \leq A_{11} \leq \phi_1 \phi_2 \) [16], we see that \( 0 \leq \gamma \leq 1 \). When \( \gamma = 0 \), the system is macroscopically isotropic. However, when \( \gamma = 1 \) (achieved by a system of aligned needles), the system is quite anisotropic. In the next section we will study the dependence of \( \gamma \) on the separation of length scales.

**B. Calculation of bounds for laminates**

We now directly calculate \( A_2 \) for laminates with any separation of length scales by numerically integrating (5) using (13), and explicitly verify that \( A_2 \) indeed tends to zero for second-rank laminates which obey (6) as the separation of length scales tends to infinity. While this result is expected, it is not at all obvious from the perspective of the microstructure since \( S_z(r, \theta) \) is not symmetric about \( \theta = \pi/4 \) for laminates, as discussed in the Introduction. We then calculate bounds on the effective conductivity tensor using (28).

To begin our analysis, laminates are symmetric about \( \theta = \pi/2 \); therefore, in view of (5), the off-diagonal components of \( A_2 \) are zero. Our calculation of \( A_2 \) thus reduces to calculating only one of the diagonal components.

We now consider fully penetrable laminates with a wide separation in length scales and substitute (19) into (5) to calculate \( A_2 \) asymptotically for fixed \( \eta_1 \) and \( \eta_2 \) as the separation of length scales \( q = d_1/d_2 \rightarrow \infty \). We find that

\[
(A_2)_{\eta \eta} = -\phi_1 (1 - 2 \phi_1^{(2)} + \phi_1) + O(\ln q/q)
\]

as \( q \rightarrow \infty \). Recall that \( \phi_1^{(2)} \) is the volume fraction of phase 1 of the one-dimensional process which determined the second stage of lamination, which is

\[
\phi_1^{(2)} = e^{-\eta_2} = e^{-\rho_2 d_2}
\]

for fully penetrable laminates from (16). The calculation of (33) is described in Appendix C. We conclude from this asymptotic result that \( A_2 \) tends to zero as the separation of length scales tends to infinity whenever (6) is satisfied. We also conclude that fully penetrable laminates with a wide separation of length scales achieve the anisotropic bounds of (28).

We now numerically calculate \( A_2 \) and hence \( \gamma \) for laminates with a finite separation of length scales. In Fig. 5 we plot numerical evaluations of \( \gamma \) for laminates which satisfy (6) at various \( \phi_1 \) and \( q \). We again see that \( \gamma \rightarrow 0 \) as \( q \rightarrow \infty \). We also see that, for constant \( q \), \( \gamma \) decreases as \( \phi_1 \) increases. This makes heuristic sense: for small \( \phi_1 \), the laminate will resemble a system of aligned needles, while for large \( \phi_1 \) there will be very few slabs in both the \( x \) and \( y \) directions, and hence the laminate will have similar structure in both directions.

From our numerical evaluation of \( A_2 \), we now obtain bounds on \( \sigma_{\eta} \) by using (28). In Figs. 6, 7, and 8 we show the \( x \) and \( y \) components of \( \sigma_{\eta} \) for fully penetrable laminates of second rank which satisfy \( \sigma_2/\sigma_1 = 10 \) and (6) for \( q = 1, 10 \), and \( \infty \), respectively. We see that as the separation of length scales increases, the bounds in the \( x \) and \( y \) directions converge until they are identical and equal to the two-dimensional Hashin-Shtrikman bounds when the laminate is macroscopically isotropic. Using (28) and (13), we are also able to calculate bounds on \( \sigma_{\eta} \) for second-rank laminates of arbitrary construction.

When \( d_1/d_2 = 1 \), we see that the bounds on the effective conductivity in the \( x \) direction are somewhat smaller than the bounds in the \( y \) direction; in fact, for sufficiently small \( \phi_1 \), the lower bound on \( (\sigma_{\eta})_{\eta} \) is larger than the upper bound on \( (\sigma_{\eta})_{\eta} \), regardless of which phase has a higher conductivity. A physical explanation of this phenomenon when the disconnected phase is a better conductor than the connected phase is trivial: even for very small \( \phi_1 \), the volume fraction requirement (6) still requires that \( \phi_1^{(2)} \) will be no smaller than 0.5. Therefore, the laminate will resemble a system of highly conducting needles aligned in the \( y \) direction. On the other
hand, if the slabs are better conductors, then current will be able to flow in the y direction in a straight line unimpeded, while current in the x direction will tend to flow around the needles. Such heuristic explanations, however, do not explain the behavior of the bounds for all possible length scales, phase conductivities and phase volume fractions.

IV. CONCLUSIONS

We have calculated \( S_n \) for fully penetrable laminates and \( S_2 \) for general laminates of arbitrary rank in terms of their constituent processes. We have explicitly given \( S_2 \) for three different types of second-rank laminates: fully penetrable, totally impenetrable, and random checkerboard. Using our expression for \( S_2 \), we have calculated the tensor coefficient \( A_2 \) numerically for general second-rank laminates, thereby obtaining estimates on the effective conductivity tensor in the form of bounds. We have done this for laminates with an arbitrary separation of length scales. We have also explicitly verified that \( A_2 \) indeed vanishes for optimal, macroscopically isotropic laminates, even though \( S_2 \) for laminates does not have symmetry about \( \theta = \pi/4 \).

This last observation leads to the natural question raised in the Introduction: what symmetries must the \( S_n \) for optimal, macroscopically isotropic composites possess so that all of the tensor coefficients \( A_n \) vanish? This is a very difficult question to answer generally. We have shown explicitly that a sufficient condition for \( A_2 \) to vanish is an \( S_2 \) of the form

\[
\sim_{13}
\]

for any choice of \( S_2^{(1)}, L^{(1)}, \text{and } S_2^{(2)} \), as long as condition (6) is satisfied and the separation of length scales between the two stages tends to infinity. From (5), another sufficient condition is symmetry of \( S_2 \) about \( \theta = \pi/4 \). We have not shown, however, that these conditions are necessary. We have also not considered conditions which would ensure that the higher \( A_n \) vanish.

From a practical point of view, laminates with an infinite separation of length scales cannot be constructed. A natural question is thus determining how large the separation of length scales should be so that, for all intents and purposes, the laminate is an optimal structure. Judging by the convergence of the bounds, we suggest that a reasonable condition for declaring a second-rank laminate to be macroscopically isotropic is \( \gamma < 0.05 \). This is achieved at most volume fractions when \( q > 30 \).

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APPENDIX A: LINEAL PATH FUNCTION FOR SECOND-RANK LAMINATES

To characterize their microstructure, we determined \( S_n \) for laminates in Sec. II. We continue this characterization by
determining the lineal path function for second-rank laminates, i.e., the probability that the line connecting two points lies entirely in one of the phases. Using the independence of successive stages, the probability that the line between two points lies entirely in phase 1 is given by

\[ L_1(x,y) = L^{(1)}(x)L^{(2)}(y). \]  

(A1)

The corresponding probability for phase 2 is not nearly as trivial to calculate; a full expression for \( L_2(x,y) \) would require knowledge of the joint distribution of the size of the clusters and the number of gaps in a given interval. However, in the \( y \) direction, the connected-phase lineal path function is given by

\[ L_2(0,y) = \phi^{(1)}_2 + \phi^{(1)}_1 C^{(2)}_2(y), \]  

(A2)

where \( C^{(2)}_2 \) is the two-point cluster function [26] for the second stage of lamination. In the \( x \) direction we have

\[ L_2(x,0) = \sum_{r=0}^{\infty} N_r(x)(\phi^{(2)}_2)' \]  

(A3)

where \( N_r(x) \) is the probability that, for the one-dimensional process which generates the first stage of lamination, a given interval of length \( x \) contains exactly \( r \) gaps (including gaps at the beginning and the end of the interval).

The probability \( N_r \) for fully penetrable rods was calculated by Domb [27]. In terms of the dimensionless distance \( u = x/d_1 \), where as before we take \( j \leq u \leq j+1 \), \( N_r \) is given by

\[ N_0(u) = 1 + \sum_{k=0}^{j} (-1)^{j+k} k! \left( \sum_{k=1}^{j} \left( \frac{\eta(u-k)}{k!} + \frac{\eta(u-k)}{(k+1)!} \right) \right) \]  

(A4)

for \( r = 0 \) and by

\[ N_r(u) = \sum_{k=0}^{j-r+1} (-1)^k k! \left( \sum_{k=1}^{j} \left( \frac{\eta(u-j-k+1)}{(j-k)!} + \frac{\eta(u-j-k+1)}{(j+k)!} \right) \right) \]  

(A5)

for \( 1 \leq r \leq j + 1 \), while \( N_r(u) = 0 \) otherwise. In these expressions \( \eta \) is again the reduced density defined by (15). In one dimension, the probability that a given interval has no gaps is the two-point cluster function \( C^{(2)}_2 \), which was independently calculated by Çınlar and Torquato [28]. Substitution of \( N_r \) into (A3) gives \( L_2(x,0) \) for second-rank laminates whose first stage is generated by fully penetrable rods.

**APPENDIX B: ASYMPTOTIC APPROXIMATION OF \( S_2 \) FOR HARD RODS IN EQUILIBRIUM**

We develop an asymptotic approximation for \( S_2(u) \) as the dimensionless distance \( u \to \infty \) for a one-dimensional system of hard rods of unit diameter in equilibrium. This approximation is useful when numerically calculating \( A_2 \) using (5).

To obtain this approximation, we find a generating function whose coefficients give \( S_2(u) \). We then use the method of subtracted singularities to determine the asymptotic behavior of the coefficients [and hence \( S_2(u) \)] for large \( u \).

We first state the main theorem behind the method of subtracted singularities [29,30].

**Theorem.** Let the function \( f \) be meromorphic for \( |z| = R \) and analytic for \( |z| = R \) and \( z = 0 \), with simple poles inside this circle at \( z_i \) with residues \( c_i \), \( i = 1, \ldots, m \). Then the coefficients \( f_n \) defined by

\[ f(z) = \sum_{n=0}^{\infty} f_n z^n \]  

(B1)

satisfy

\[ f(z) = \sum_{n=0}^{\infty} f_n z^n \]  

(B2)

(This theorem can be generalized to functions with poles of finite order greater than one, but for the present purpose this generalization is not needed.)

To apply this theorem to the present problem, we restrict \( 0 \leq y < 1 \) and define the sequence \( \{a_j(y)\} \) by

\[ a_j(y) = S_2(j + y). \]  

(B3)

Recall that \( S_2 \) for hard rods in equilibrium is given by (22).

We now seek the generating function for this sequence, i.e., the function that satisfies

\[ f(z;y) = \sum_{j=0}^{\infty} a_j(y)z^j. \]  

(B4)

Straightforward algebraic manipulation verifies that this function is given by

\[ f(z;y) = \left( 1 - \frac{(z-1)\exp((z-1)y/a)}{1-z \exp((z-1)y/a)} \right). \]  

(B5)

Recall that \( a \) is defined by (23). To use the method of subtracted singularities to determine the asymptotic growth of the coefficients of \( f \) [and hence the growth of \( S_2(j + y) \) as \( j \to \infty \)], we must first find the poles and associated residues of \( f \). Clearly \( z_0 = 1 \) is a pole of \( f \) with residue
For $\eta<1$ there are no poles with modulus less than one. Therefore, as $u=j+y \to \infty$, (B2) implies that

$$S_2(u) = \frac{1-\eta}{1+1/\alpha} 1^{-j+1} \quad \text{as} \quad j \to \infty$$

$$= (1-\eta)^2.$$  

(B7)

as expected. When $\eta=0.5$ this limit reduces to the remarkable identity

$$\lim_{j \to \infty} \sum_{k=0}^{j} \frac{e^{-k} k^{j-k}}{(j-k)!} = \frac{1}{2}.$$  

(B8)

To determine the oscillations around the long-range value, other complex poles must be calculated numerically; they will depend on the value of $\eta$ for the system. Every pole of $f$ can be shown to be simple and the residue at a pole $\tilde{z}$ is given by

$$c = \frac{(1-\eta) \exp((z-1)/\alpha)}{(1+\alpha) \exp((z-1)/\alpha)}.$$  

(B9)

In summary, once we have numerically calculated the poles of smallest modulus of $f$, we can use the above theorem and (B9) to determine the asymptotic behavior of $S_2(u)$.

To see how useful the above procedure is, we now take $\eta=0.5$. The first four nontrivial poles of $f$ for this choice of $\eta$ are approximately

$$z_{1,2} = -0.532092 \pm 4.597158i \quad \text{and} \quad $$

$$z_{3,4} = -1.393982 \pm 10.868006i,$$

with residues

$$c_k = -\exp((z_k-1)y) (0.489044 \pm 0.107648i)$$  

(B10) and

$$c_k = -\exp((z_k-1)y) (0.501655 \pm 0.0459462i)$$  

(B11)

for $k=1,2$ and

$$c_k = -\exp((z_k-1)y) (0.501655 \pm 0.0459462i)$$  

(B12)

for $k=3,4$. We now substitute these values into (B2) and compare with the exact result of (22) for $\eta=0.5$. We see in Fig. 9 that this “asymptotic” expression is in fact very close to the actual value of $S_2(u)$ for small $u$ using only the first four nontrivial poles. We also can use this expression for $S_2$ at large distances to accurately and quickly calculate the integrand of (5) when calculating $A_2$ for totally impenetrable laminates.

**APPENDIX C: ASYMPTOTIC BEHAVIOR OF $A_2$ FOR LAMINATES WITH A WIDE SEPARATION OF LENGTH SCALES**

We discuss how (33) can be derived for fully penetrable laminates. Combining (19) and (5), we find that, when $d_1>2d_2$,

$$(A_2)_{yy} = I_1 + I_2 + I_3 + I_4 + I_5,$$  

(C1)

where

$$I_1 = \frac{4}{\pi} \int_{d_2}^{d_1} \int_0^{\infty} \frac{y^2 - x^2}{(x^2 + y^2)^2} (e^{-\rho_1(x+d_1) - 2\rho_2d_2 - \phi_1^2}) \, dx \, dy,$$  

(C2)

$$I_2 = \frac{4}{\pi} \int_0^{d_2} \int_0^{\infty} \frac{y^2 - x^2}{(x^2 + y^2)^2} \rho_1 e^{-\rho_1x} (e^{-\rho_2y} - e^{-\rho_2d_2}) \, dx \, dy,$$  

(C3)

$$I_3 = -\frac{4}{\pi} \lim_{\delta \to 0} \int_{\delta}^{d_2} \int_0^{\infty} \frac{\pi^2 \cos2\theta}{r} (e^{-\rho_1r \cos \theta - \rho_2 \sin \theta - \phi_1^2}) \, d\vartheta \, dr,$$  

(C4)

$$I_4 = -\frac{4}{\pi} \int_0^{d_2} \int_{2d_2-y^2(x^2+y^2)}^{2d_2} (e^{-\rho_1x - \rho_2y - \phi_1^2}) \, dx \, dy,$$  

(C5)

and

$$I_5 = \frac{4}{\pi} \int_0^{d_2} \int_{2d_2(y^2+x^2)}^{2d_2} (e^{-\rho_1x - \rho_2y - \phi_1^2}) \, dx \, dy.$$  

(C6)
We have converted to rectangular coordinates for each of
these expressions except $I_1$. We have also used the symme-
ty of $S_2$ to calculate $A_2$ in terms of integrals on the first
quadrant.

As $q = d_1/d_2 \rightarrow \infty$ for fixed $\eta_1$ and $\eta_2$, we use the domi-
nated convergence theorem [31] to replace the integrands by
a series in $1/q$; depending on the domain we expand either
the exponential term or the term $(y^2 - x^2)/(x^2 + y^2)^2$. Evalu-
ation of the resulting integrals yields (33).

A similar analysis shows that (33) is satisfied for lamina-
tes constructed by one-dimensional random checker-
boards. In fact, since all laminaes with an infinite separation
of length scales must achieve the Padé bounds on effective
conductivity, (33) must be true to leading order, regardless of
how the laminate is constructed. This is not at all obvious
from the perspective of the microstructure.

[5] G. W. Milton, in Homogenization and Effective Moduli of Ma-
terials and Media, edited by J. L. Erickson et al. (Springer-
307 (1986).
(1988).
331 (1988).
line, Mechanical Design in Organisms (Princeton University
Assembly of Polymers, edited by S. Case (Springer-Verlag,
Hashin, in Mechanics of Composite Materials (Pergamon
typographical error in (3.4) of this reference; the third case
should be $\sigma - a + A(r) - 2B(r) + C(r)$.
Problems, edited by G. Papanicolaou (SIAM, Philadelphia,
88, 6540 (1988).
[29] P. Flajolet and R. Sedgewick, Institut National de Recherche
en Informatique et en Automatique Report No. 2026, 1993
(unpublished).
[31] H. Royden, Real Analysis, 3rd ed. (Macmillan, New York,