VII. Porous Media

Lecture 33: Macroscopic Conductivity of Composites

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An authoritative reference for effective properties of composite materials is *Random Heterogeneous Materials* by S. Torquato (Springer, 2002)

1. Conductivity of Composite Media

We consider a volume of a composite material subjected to a 1-D applied electric field, and giving rise to a potential difference, $\Delta \phi$:



Figure 1: Macroscopic composite volume element subjected to a 1-D electric field.

By Ohm's Law, V = IR and the average (macroscopic) current density is $\overline{J} = I/A$. Substituting for *I*, these can be combined to give:

$$\overline{J} = \frac{L}{AR} \frac{V}{L} = \frac{L}{AR} \frac{\Delta\phi}{L} = \overline{\sigma}\overline{E}$$
(1)

where $\overline{\sigma} = \frac{L}{AR}$ is the mean macroscopic conductivity of the volume, and $\overline{E} = \frac{\Delta \phi}{L}$ is the mean electric field. We are interested in how we can relate $\overline{\sigma}$ to the microscopic conductivity, $\sigma(\vec{x})$.

Consider steady conduction in composite media consisting of N "phases" with isotropic constant conductivities σ_i (i = 1,2,...N) and volume fractions Φ_i (Figure 2), where each domain



Figure 2: Piecewise composite material with domain conductivities σ_{i} .

satisfies Poisson's equation and suitable boundary conditions enforcing continuity of normal current between domains i and j:

$$\nabla^2 \phi = 0$$
Boundary conditions: $\hat{n} \cdot j_i = \hat{n} \cdot j_j$
(2)

(We can justify the use of Poisson's equation by noting the definition of microscopic current density, $j_i = -\sigma_i \nabla \phi$. Since conservation of charge requires $\nabla \cdot j_i = 0$, this implies that $\nabla^2 \phi = 0$).

2. Anisotropic Composites

We will show in this section that the effective conductivity of an anisotropic composite, $\overline{\sigma}$, lies within the Wiener bounds:

$$\langle \sigma^{-1} \rangle^{-1} \le \overline{\sigma} \le \langle \sigma \rangle$$
 (3)

where generally,

$$\langle c \rangle = \sum_{i=1}^{N} \Phi_{i} c_{i} \,. \tag{4}$$

The left-hand term $\langle \sigma^{-1} \rangle^{-1}$ is the harmonic mean of conductivity, while the right-hand term $\langle \sigma \rangle$ is the arithmetic mean.

We can gain physical understanding of these bounds by considering certain "striped" (laminated) microstructures that attain the maximum and minimum conductivities that are possible in anisotropic composite materials. The microstructure that achieves maximum conductivity is shown in Figure 3a and consists of laminated stripes parallel to the applied field, each stripe having cross-sectional area A_i and conductivity σ_i . Note that the arrangement of different phases is arbitrary, as long as the total volume fractions of phases *i* are consistent with the composite material being considered. In this model, the current passing through the material element sees a clear path of "least resistance" (the lowest conductivity stripe).

In contrast, the lowest possible conductivity is attained by a series of laminated stripes arranged perpendicular to the applied field, as shown in Figure 3b. In this case, all current must pass through the lowest-conductivity phase.



Figure 3: Striped laminated composite structures achieving the upper (a) and lower (b) Wiener bounds for macroscopic conductivity.



Figure 4: Equivalent circuits describing conduction pathways in striped laminates from Figure 3. (a) Corresponds to the Wiener upper bound, and (b) is the Wiener lower bound.

We can model the laminated structures as electrical networks consisting of resistors arranged in parallel (Wiener upper bound, Figure 4a) or in series (Wiener lower bound, Figure 4b). In the case of the upper bound, the lowest conductivity material provides a fast pathway for current, but in the case of the lower bound, all current must flow through an identical pathway that sees each layer, and therefore the lowest conductivity material will limit the macroscopic conductivity.

For a network of resistors in parallel, the effective conductivity is given as a summation over all conductivities, where each conductivity is weighted by the volume fraction of the corresponding phase in the composite:

$$\overline{\sigma}_{\max} = \langle \sigma \rangle = \sum_{i} \Phi_{i} \sigma_{i} \,. \tag{5}$$

For resistors in series, the effective inverse conductivity is given as a weighted sum of all the inverse conductivities:

$$\overline{\sigma}_{\min} = \left\langle \sigma^{-1} \right\rangle^{-1} = \frac{1}{\sum_{i} \frac{\Phi_{i}}{\sigma_{i}}}.$$
(6)

(5) and (6) are the Wiener upper and lower bounds, respectively.

Note that for a general case, where the applied field is neither parallel nor perpendicular to the stripes, but is instead applied at an angle θ (Figure 5), we can describe the conductivity as a tensor $\underline{\sigma}$ that is positive definite and symmetric, with eigenvalues σ_{\parallel} and σ_{\perp} , where $\sigma_{\parallel} > \sigma_{\perp}$:

$$\underline{\underline{\sigma}} = Q_{\theta} \begin{pmatrix} \sigma_{\parallel} & 0 \\ 0 & \sigma_{\perp} \end{pmatrix} Q_{-\theta}$$
(7)

where Q_{θ} is the 2-D rotation matrix,

$$Q_{\theta} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}.$$
 (8)

(7) and (8) are combined to give

$$\underline{\underline{\sigma}} = \begin{pmatrix} \sigma_{\parallel} \cos^2 \theta + \sigma_{\perp} \sin^2 \theta & (\sigma_{\parallel} - \sigma_{\perp}) \sin \theta \cos \theta \\ (\sigma_{\parallel} - \sigma_{\perp}) \sin \theta \cos \theta & \sigma_{\parallel} \sin^2 \theta + \sigma_{\perp} \cos^2 \theta \end{pmatrix}.$$
(9)



Figure 5: For the general case, an applied electric field can result in currents that flow in a transverse direction to the field, depending on the orientation of the composite material (described by angle θ).

3. Isotropic Composites

Consider a 2nd-rank (two phases), laminated, isotropic structure with $\sigma_1 > \sigma_2$, and where phase 1 percolates, but phase 2 does not (Figure 6).



Figure 6: 2nd rank laminated microstructure with percolation of only one phase.

The total volume fraction of phase 1 and phase 2 in the composite are given by

$$\Phi_1 = \Phi_1^{(1)} + \Phi_2^{(1)} \Phi_1^{(2)} \tag{10}$$

$$\Phi_2 = \Phi_2^{(1)} \Phi_2^{(2)} \tag{11}$$

with

$$\Phi_1^{(1)} + \Phi_2^{(1)} = \Phi_1^{(2)} + \Phi_2^{(2)} = 1.$$
(12)

We can analyze the composite's macroscopic conductivity in the same manner as before by constructing an equivalent resistor circuit describing the conduction pathways. For conduction parallel to the primary stripes (in the vertical direction in Figure 6), the resulting conductivity is given by

$$\sigma_{\parallel} = \Phi_1^{(1)} \sigma_1 + \frac{\Phi_2^{(1)}}{\frac{\Phi_1^{(2)}}{\sigma_1} + \frac{\Phi_2^{(2)}}{\sigma_2}}$$
(13)

and along the perpendicular direction (horizontal direction in Figure 6),

$$\sigma_{\perp} = \frac{1}{\frac{\Phi_{1}^{(1)}}{\sigma_{1}} + \frac{\Phi_{2}^{(1)}}{\Phi_{1}^{(2)}\sigma_{1} + \Phi_{2}^{(2)}\sigma_{2}}}.$$
(14)

Since we are modeling an isotropic material at the macroscale, $\sigma_{\parallel} = \sigma_{\perp}$ and therefore (after some algebra),

$$\Phi_2^{(1)} = \frac{\Phi_2^{(2)}}{\Phi_1^{(2)}}.$$
(15)

By combing the above equations, we can derive a bound on the mean macroscopic conductivity:

$$\overline{\sigma} = \sigma_{\parallel} = \sigma_{\perp} = \langle \sigma \rangle - \frac{(\sigma_1 - \sigma_2)^2 \Phi_1 \Phi_2}{\langle \tilde{\sigma} \rangle + \sigma_1} , \qquad (16)$$

where $\sigma_1 > \sigma_2$, $\langle \sigma \rangle = \Phi_1 \sigma_1 + \Phi_2 \sigma_2$, $\langle \tilde{\sigma} \rangle = \Phi_1 \sigma_2 + \Phi_2 \sigma_1$. This is an upper bound on the conductivity for all isotropic two-phase microstructures. In instead phase 2 (lower conductivity) is the percolating structure, then we exchange '1' and '2' in the above equation, and $\overline{\sigma}$ is a minimum.

In a more general case for an isotropic two-component media in *d* dimensions, the macroscopic conductivity (for $\sigma_1 > \sigma_2$) obeys Hashin-Shtrikman bounds:

$$\langle \boldsymbol{\sigma} \rangle - \frac{\left(\boldsymbol{\sigma}_{1} - \boldsymbol{\sigma}_{2}\right)^{2} \boldsymbol{\Phi}_{1} \boldsymbol{\Phi}_{2}}{\left\langle \tilde{\boldsymbol{\sigma}} \right\rangle + \boldsymbol{\sigma}_{2} (d-1)} \leq \overline{\boldsymbol{\sigma}} \leq \langle \boldsymbol{\sigma} \rangle - \frac{\left(\boldsymbol{\sigma}_{1} - \boldsymbol{\sigma}_{2}\right)^{2} \boldsymbol{\Phi}_{1} \boldsymbol{\Phi}_{2}}{\left\langle \tilde{\boldsymbol{\sigma}} \right\rangle + \boldsymbol{\sigma}_{1} (d-1)}$$
(17)

for *d* higher than two dimensions.

The Hashin-Shtrikman bounds are attained by space-filling isotropic patterns of coated spheres, where the volume fraction of the core and shell are the same as the macroscopic material. The HS upper bound is attained when the outer/shell component has larger conductivity, and the HS lower bound is attained when the inner/core has larger conductivity.



Figure 7: Isotropic composite consisting of coated spheres (σ_1 and σ_2), which achieves the maximum conductivity ($\sigma_2 > \sigma_1$) or minimum conductivity ($\sigma_2 < \sigma_1$) for a two-phase configuration with consistent volume fractions Φ_1 and Φ_2 .



Figure 8: Comparison of different conductivity limits.

10.626 Electrochemical Energy Systems Spring 2014

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