INTRODUCTION

Composite materials can be generally defined as those materials having two or more distinct material phases. With the advent of advanced polymeric composite materials, the term composite became somewhat synonymous with engineered carbon-epoxy, Kevlar-epoxy or ceramic- or metal-matrix composites, though this term later came to refer to a broader set of materials; more recently, the descriptor heterogeneous has been used to characterize study of such materials. Porous materials may also be considered composite materials, with one phase composed of void or air spaces. Examples of composites include the familiar carbon-epoxy airframe skins, and glass/epoxy or glass/polyester structural materials, e.g., helicopter rotor blades, or even furniture. Sporting goods, e.g., golf clubs, tennis rackets, and skis are also often constructed of advanced composites. Even wood, which contains reinforcing cellulose fibers, bone, which may be considered a porous reinforcement, at a smaller scale, extracellular matrices, reinforced by structural proteins such as collagen, that are surrounded by ground substance (Fig. 1) constitute composites. There is a large body of literature available on both properties[1−5] and manufacturing[6,7] of many types of engineered composite materials, and much of this work has found, and will continue to find application in improved understanding of heterogeneous biomaterials and design of biocompatible materials.[8] As an example, of the 20–30% of the human body that is composed of proteins, up to 50% is collagen,[9] collagen’s precursors have been on the planet nearly as long as multicellular life.[10] Undoubtedly, the need for improved micro and nanoscale models for the behavior of such critically important fibrous biomaterials will continue, and will support new insights into biochemistry and evolutionary science.

HISTORICAL BACKGROUND

General modeling of the properties of heterogeneous materials is of great importance to almost all engineering and scientific disciplines, and can be traced to the mid-19th century (Table 1), in work on properties of gases.[10–53] Closed-form solutions for effective properties in gases led to similar analyses for conductivity and stiffness in composite solids. Determination of engineering properties, from conductivity to stiffness, was classically accomplished via solution of Laplace’s equation, whose linearizing field assumption allows simultaneous solution of a number of important problems using the same partial differential equations, rescaled using appropriate material constants (Tables 2 and 3, following the description in Ref. [54]). Other techniques that have been widely used to determine, or bound, properties of heterogeneous materials, include solutions of stress fields in representative volume elements (RVEs), models of anisotropic sheets, and models of continuum anisotropic phases. In this article, we do not attempt to survey each of these areas thoroughly; we aim, however, to give an overview of approaches in modeling composite materials, with specific results of classic models, and an eye toward the modeling of biological materials. Thus, we omit discussion of manufacture of composite materials (see, for example, Refs. [6,55,56]). Instead, we emphasize analysis of elastic and transport properties, both for their common roots in the literature, and also their importance in study of biomaterials. We begin with general formulations of anisotropic elasticity, and discuss simplifications for layered structures, which are abundant both in engineered and biological materials. Bounds on elastic properties are also discussed, since they allow estimation of material response (important in analysis of damage and growth modeling of bone, skin, and other tissues). And, a discussion of the role of phase geometry and percolation, relative to transport properties, is presented for its usefulness in estimation of both mechanical response and permeability of specific phases (e.g., structural proteins) in biomaterials.

CONTINUUM AND MICROMECHANICS OF COMPOSITE MATERIALS

Composite materials may be isotropic or anisotropic, depending on the shapes, locations, and relative sizes of the material phases. Many particulate, porous, or short-
fiber systems, for example, exhibit isotropic stiffness and conductivity; long-fiber and fabric-reinforced systems generally exhibit some degree of anisotropy.

Broadly, analysis of composite materials can be divided into two categories. Work that incorporates anisotropy into material models without detailed modeling of each phase is termed continuum mechanics, and can be used to predict effective properties of a heterogeneous material (see Ref. [57] for example). Work that directly models the shapes, locations, and relative sizes of model phases in a material is termed micromechanics, and more recently, nanomechanics, though the latter properly includes atomistic or molecular dynamics modeling and often is applied only to very small volumes due to its inherent computational intensiveness. Micromechanics is generally used to determine the details of stress, current, or other distributions (Table 2) within a heterogeneous material, along with effective properties (e.g., Refs. [1,58]). The units of the common parameters used in the derivation of effective properties and their governing equations are listed in Table 3 and Table 4. Though theories for failure of material have been developed using continuum mechanics,[59,60] understanding of specific failure mechanisms often requires analysis of the load sharing among the constituent materials, especially for brittle reinforcements. Statistical approaches have been

Fig. 1 Examples of composite materials, including (a) an anode of a Li-ion battery, containing carbon particles and polymeric binder, (b) trabecular bone (courtesy Dr. Scott Hollister, University of Michigan), (c) wood of an elm tree, and (d) collagen fibrils of the rat sciatic nerve perineurium, (e) carbon nanotube sheet, and (f) substrate of NiMH electrode. (View this art in color at www.dekker.com.)
Table 1  Contributions to heterogeneous mechanics, including work in disperse gases

<table>
<thead>
<tr>
<th>Disperse gases</th>
<th>Dielectrics</th>
<th>Disperse media</th>
</tr>
</thead>
<tbody>
<tr>
<td>1879 R. Clausius</td>
<td>1956 J.D. Eshelby</td>
<td>1973 W.B. Russel</td>
</tr>
<tr>
<td>1880 L.V. Lorenz</td>
<td>1956 E.H. Kerner</td>
<td>1975 K.S. Mendelson</td>
</tr>
<tr>
<td>1880 H.A. Lorentz</td>
<td>1957 J.D. Eshelby</td>
<td>1978 W.T. Doyle</td>
</tr>
<tr>
<td>1892 J.W. Rayleigh</td>
<td>1958 C. van der Pol</td>
<td>1978 R. Landauer</td>
</tr>
<tr>
<td>1912 O. Wiener</td>
<td>1962 Z. Hashin</td>
<td>1979 R.M. Christensen and K.H. Lo</td>
</tr>
<tr>
<td>1954 A.V. Hershey</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Gases are in italics, conductivity of solids are in normal type, and mechanics of solids are in bold. (Adapted from Ref. [54].)

shown to be useful in developing scaling rules for failure (e.g., Refs. [61–65]). The subject of failure of heterogeneous materials is quite broad and spans modeling of ductile failure, fracture, fatigue, and creep, to name a few key phenomena. Here, we introduce modeling of constitutive properties of elastic, heterogeneous materials, from

Table 2  Effective medium theories and solution using Laplace’s equation

<table>
<thead>
<tr>
<th>Linear problem of interest for a two-phase material</th>
<th>Quantity represented by ( q )</th>
<th>Quantity represented by ( E ) ( E_j = U_j )</th>
<th>Transport coefficient ( K )</th>
<th>Local differential equation satisfied in each phase (in steady state)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conduction</td>
<td>Heat flux</td>
<td>Temperature gradient</td>
<td>Thermal conductivity</td>
<td>( q_i = K_i E_j = K_i U_j )</td>
</tr>
<tr>
<td>Electrical conduction</td>
<td>Electric current</td>
<td>Electric field intensity</td>
<td>Electrical conductivity</td>
<td>( \nabla \cdot \vec{q} = 0 )</td>
</tr>
<tr>
<td>Electrical insulation</td>
<td>Electric displacement</td>
<td>Electric field intensity</td>
<td>Dielectric constant</td>
<td></td>
</tr>
<tr>
<td>Permeation of a porous medium consisting of a fixed array of small rigid particles with an incompressible Newtonian fluid</td>
<td>Force on particles in unit volume of mixture (=pressure gradient calculated from pressure drop between distant parallel planes)</td>
<td>Flux of fluid volume relative to particles (Darcy constant divided by ( \mu ))</td>
<td>Permeability (or rigidity and bulk moduli)</td>
<td>( \nabla p = \mu \nabla^2 \vec{u} ) ( \nabla \cdot \vec{u} = 0 ) where ( \vec{u} = ) velocity; ( p = ) pressure; ( \mu = ) viscosity</td>
</tr>
<tr>
<td>Elasticity of a medium containing elastic inclusions embedded in an elastic matrix</td>
<td>Stress</td>
<td>Strain</td>
<td>Lame constants (or rigidity and bulk moduli)</td>
<td>( \vec{q} = 2\mu \vec{E} + \lambda \vec{E} ) ( \nabla \cdot \vec{q} = 0 ) ( \mu, \lambda = ) local Lame constants</td>
</tr>
</tbody>
</table>

(Adapted from Ref. [54].)
Table 3  Common units for conversion of parameters in Table 2

<table>
<thead>
<tr>
<th>q</th>
<th>U</th>
<th>E</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>J/m²</td>
<td>K (temperature)</td>
<td>K/m</td>
<td>J/m · K</td>
</tr>
<tr>
<td>Amp/m²</td>
<td>V</td>
<td>V/m</td>
<td>S/m</td>
</tr>
<tr>
<td>C/m²</td>
<td>V</td>
<td>V/m</td>
<td>f/m</td>
</tr>
<tr>
<td>m/s</td>
<td>m</td>
<td>1</td>
<td>m/s</td>
</tr>
<tr>
<td>F/m²</td>
<td>m</td>
<td>1</td>
<td>F/m²</td>
</tr>
</tbody>
</table>

The continuum to microscale, and comment on applications for both constitutive and failure modeling.

CONTINUUM, ANISOTROPIC STIFFNESS

The number of stiffnesses required to fully characterize a material's response depends upon the degree of its anisotropy. Counterintuitively, tensorial stiffnesses are denoted $C_{ijkl}$, and tensorial compliances are denoted $S_{ijkl}$. An elastic constitutive relation (using the notation of Fig. 2) can be expressed as either

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl}$$  \hspace{1cm} (1)

or

$$\varepsilon_{ij} = S_{ijkl} \sigma_{kl}$$  \hspace{1cm} (2)

respectively, where $\varepsilon_{kl}$ is the infinitesimal strain tensor and $\sigma_{ij}$ is the stress tensor. We note that 2-D sections of the internal structure of a composite material depend on the plane examined, but models using 3-D ellipsoidal or cylindrical inclusions can be used to represent a wide range of reinforcement shapes (Fig. 3), from particles (2-D circles or ellipses, or 3-D spheres or ellipsoids) to fibers (1-D lines, 2-D ellipses or circles, or 3-D cylinders or ellipsoids).

The number of nonzero components of the stiffness tensor and the relationships among its components can be determined using material symmetry and equilibrium considerations. As a first cut, the 81 coefficients in the

Table 4  Common governing equations for modeling physical phenomena

<table>
<thead>
<tr>
<th>Equation</th>
<th>Formula</th>
<th>Phenomena</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wave</td>
<td>$\nabla^2 \nu = \kappa \frac{\partial \nu}{\partial t}$</td>
<td>1. Wave</td>
<td>1. Analytical solution by various transformations, e.g. Bäcklund transformation, Green's function, integral transform, Lax Pair, separation of variables</td>
</tr>
<tr>
<td>Diffusion</td>
<td>$\frac{\partial \nu}{\partial t} = \kappa \nabla^2 \nu$</td>
<td>1. Heat conduction</td>
<td>2. Numerical solution, e.g. finite element method</td>
</tr>
<tr>
<td>Poisson</td>
<td>$\nabla^2 \nu = -4\pi \rho$</td>
<td>1. Electrostatics with constant source or sink, 2. Thermal field with constant source or sink</td>
<td>2. Numerical solution, e.g. finite element method</td>
</tr>
</tbody>
</table>
The $C_{ijkl}$ tensor can be seen immediately to have only 36 independent coefficients due to the symmetry of $\sigma_{ij}$ and $\varepsilon_{kl}$, as

$$\sigma_{ij} = \sigma_{ji} \text{ and } \varepsilon_{kl} = \varepsilon_{lk}$$

We can then write the constitutive rule in matrix form (e.g., Refs. [66,67] for notation and general methods that follow) as

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix} \tag{3}$$

where $C_{ij}$ are the elastic stiffness coefficients, and

$$\begin{align*}
\sigma_1 &= \sigma_{11}; \sigma_2 = \sigma_{22}; \sigma_3 = \sigma_{33}; \sigma_4 = \sigma_{23}; \sigma_5 = \sigma_{32}; \sigma_6 = \sigma_{12} \\
\varepsilon_1 &= \varepsilon_{11}; \varepsilon_2 = \varepsilon_{22}; \varepsilon_3 = \varepsilon_{33}; \varepsilon_4 = 2\varepsilon_{23}; \varepsilon_5 = 2\varepsilon_{32}; \varepsilon_6 = 2\varepsilon_{12} \tag{4}
\end{align*}$$

The requirement of symmetry in $C_{ij}$ further reduces the number of independent coefficients to 21.

Further, nontrivial reductions of the stiffness tensor (i.e., for a number of independent coefficients greater than 2) can be obtained for aligned fibrous materials, wherein the transverse arrangement of fibers determines the degree of anisotropy (Fig. 4). Materials containing square-packed fibers (Fig. 4a) are termed orthotropic, since they contain at least two mutually orthogonal planes of symmetry; in this case, the number of elastic coefficients is reduced to 9, as

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix} \tag{5}$$

Materials containing aligned, hexagonally packed fibers or randomly arranged fibers (Figs. 4b and 4c) are termed transversely isotropic, since the elastic properties are invariant with respect to an arbitrary rotation about an axis parallel to the fibers’ axis; in this case, the number of independent stiffness coefficients is reduced to 5, as

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{11} - C_{12} \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{bmatrix} \tag{6}$$
Composites composed of layers of fibrous sheets, or laminae, are termed laminates or laminated composites. Analysis of the elastic properties of a stack of such layers (Fig. 5) requires modeling of both the in-plane properties of each layer and an assumed for an out-of-plane displacement function for the stack. Classically, this is accomplished using the well-known laminate theory, in which an elastic stiffness matrix, the ABBB matrix, is assembled for the stack. A standard notation is shown in Fig. 5; the laminate code is enclosed in brackets, with sequential plies designated by the in-plane orientation of their fibers. Subscripts $s$ and $t$ are used to denote sym-

Fig. 3 Cross-sections of (a) particulate and (b) fibrous composite materials.

Fig. 4 Several classical transverse arrangements assumed for aligned-fiber composites, including (a) square packing, (b) hexagonal close-packing and (c) random packing.

Fig. 5 Notation for laminated composites, with in-plane orientation of fibers in each layer designated in degrees. The example shown is a symmetric, quasi-isotropic laminate, [0/±45/90]_s.
metric or total, respectively. Symmetry in the orientations of the layers about the midplane prevents bend-twist coupling in the laminate, discussed later. Also, many laminates are designed to have in-plane properties that are independent of rotation (quasi-isotropy), as in the example of Fig. 5.

Plane stress is assumed in each layer. Normal stress resultants in the x-direction, \(N_x\), in the y-direction, \(N_y\), and in shear, \(N_{xy}\), are defined as

\[
N_x = \int_{-H/2}^{H/2} \sigma_x dz \\
N_y = \int_{-H/2}^{H/2} \sigma_y dz \\
N_{xy} = \int_{-H/2}^{H/2} \tau_{xy} dz
\]

and moment resultants, \(M_x\), \(M_y\), and \(M_{xy}\), are defined as

\[
M_x = \int_{-H/2}^{H/2} \sigma_z dz \\
M_y = \int_{-H/2}^{H/2} \sigma_z dz \\
M_{xy} = \int_{-H/2}^{H/2} \tau_{xy} dz
\]

The plane stress assumption (\(\sigma_3, \tau_{23}, \text{and} \tau_{13}=0\)) results in the 2-D reduction of Eq. 3 to

\[
\begin{bmatrix}
\sigma_1 \\
\sigma_2 \\
\tau_{12}
\end{bmatrix} =
\begin{bmatrix}
Q_{11} & Q_{12} & 0 \\
Q_{12} & Q_{22} & 0 \\
0 & 0 & Q_{66}
\end{bmatrix}
\begin{bmatrix}
\epsilon_1 \\
\epsilon_2 \\
\gamma_{12}
\end{bmatrix}
\]

where

\[
Q_{11} = C_{11} - \frac{C_{13}^2}{C_{33}} \\
Q_{12} = C_{12} - \frac{C_{13}C_{23}}{C_{33}} \\
Q_{22} = C_{22} - \frac{C_{23}^2}{C_{33}} \\
Q_{66} = Q_{66}
\]

We note that for the 2-D case, these relations apply to both transversely isotropic or orthotropic laminae. Transformation of stiffnesses (Eq. 9) to a global coordinate system is required for each layer, where the transformed stiffnesses are denoted \(\overline{Q}_{ij}\), as in

\[
\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\tau_{xy}
\end{bmatrix} =
\begin{bmatrix}
\overline{Q}_{11} & \overline{Q}_{12} & \overline{Q}_{16} \\
\overline{Q}_{12} & \overline{Q}_{22} & \overline{Q}_{26} \\
\overline{Q}_{16} & \overline{Q}_{26} & \overline{Q}_{66}
\end{bmatrix}
\begin{bmatrix}
\epsilon_x \\
\epsilon_y \\
\gamma_{xy}
\end{bmatrix}
\]

and are obtained from the \(Q_{ij}\) by

\[
\begin{align*}
\overline{Q}_{11} &= Q_{11} \cos^4 \theta + 2(Q_{12} + 2Q_{66}) \sin^2 \theta \cos^2 \theta + Q_{22} \sin^4 \theta \\
\overline{Q}_{12} &= (Q_{11} + Q_{22} - 4Q_{66}) \sin^2 \theta \cos^2 \theta + Q_{12}(\sin^4 \theta + \cos^4 \theta) \\
\overline{Q}_{16} &= (Q_{11} - Q_{12} - 2Q_{66}) \sin \theta \cos \theta \\
&\quad + (Q_{12} - Q_{22} - 2Q_{66}) \sin \theta \cos \theta \\
\overline{Q}_{22} &= Q_{11} \sin^4 \theta + 2(Q_{12} + 2Q_{66}) \sin^2 \theta \cos^2 \theta + Q_{22} \cos^4 \theta \\
\overline{Q}_{26} &= (Q_{11} - Q_{22} - 2Q_{66}) \sin^3 \theta \cos \theta \\
&\quad + (Q_{12} - Q_{22} + 2Q_{66}) \sin \theta \cos^3 \theta \\
\overline{Q}_{66} &= (Q_{11} + Q_{22} - 2Q_{12} - 2Q_{66}) \sin^2 \theta \cos^2 \theta + Q_{66}(\sin^4 \theta + \cos^4 \theta)
\end{align*}
\]

Use of the Kirchhoff–Love hypothesis, that plane transverse sections remain plane during loading, results in

\[
\begin{align*}
u &= u_o - z \frac{\partial w_o}{\partial x} \\
v &= v_o - z \frac{\partial w_o}{\partial y} \\
w &= w_o
\end{align*}
\]

for the displacement \((u, v, w)\) of a point at \((x, y, z)\), given midplane displacements \((u_o, v_o, w_o)\). The strains can then be calculated via

\[
\begin{align*}
\epsilon_x &= \frac{\partial u}{\partial x} - 2z \frac{\partial^2 w_o}{\partial x^2} = \epsilon_x' - z \frac{\partial^2 w_o}{\partial x^2} \\
\epsilon_y &= \frac{\partial v}{\partial y} - 2z \frac{\partial^2 w_o}{\partial y^2} = \epsilon_y' - z \frac{\partial^2 w_o}{\partial y^2} \\
\gamma_{xy} &= \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} + \frac{\partial w_o}{\partial x} - 2z \frac{\partial^2 w_o}{\partial x \partial y} = \gamma_{xy}' - 2z \frac{\partial^2 w_o}{\partial x \partial y}
\end{align*}
\]
Assuming small rotations, displacements $u$ and $v$ in Eq. 13, the strains, can expressed as

\[
\varepsilon_x = \frac{\partial u}{\partial x} = \frac{\partial u_0}{\partial x} - \frac{\partial^2 w}{\partial x^2} = \varepsilon_x^0 + z \kappa_x^0
\]

\[
\varepsilon_y = \frac{\partial v}{\partial y} = \frac{\partial v_0}{\partial y} - \frac{\partial^2 w}{\partial y^2} = \varepsilon_y^0 + z \kappa_y^0
\]

\[
\gamma_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} = \frac{\partial u_0}{\partial y} + \frac{\partial v_0}{\partial x} - 2z \frac{\partial^2 w}{\partial x \partial y}
= \gamma_{xy}^0 + z \gamma_{xy}^0
\]  

and Eq. 11 can be rewritten as

\[
\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\tau_{xy}
\end{bmatrix} =
\begin{bmatrix}
\bar{Q}_{11} & \bar{Q}_{12} & \bar{Q}_{16} \\
\bar{Q}_{12} & \bar{Q}_{22} & \bar{Q}_{26} \\
\bar{Q}_{16} & \bar{Q}_{26} & \bar{Q}_{66}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_x^0 + z \kappa_x^0 \\
\varepsilon_y^0 + z \kappa_y^0 \\
\gamma_{xy}^0 + z \gamma_{xy}^0
\end{bmatrix}
\]  

Finally, a global stiffness matrix for both in-plane displacements and out-of-plane moments can be expressed in terms of the ABBD matrix as

\[
\begin{bmatrix}
N_x \\
N_y \\
N_{xy}
\end{bmatrix} =
\begin{bmatrix}
A_{11} & A_{12} & A_{16} \\
A_{12} & A_{22} & A_{26} \\
A_{61} & A_{26} & A_{66}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_x^0 \\
\varepsilon_y^0 \\
\gamma_{xy}^0
\end{bmatrix}
\]

\[
+ \begin{bmatrix}
B_{11} & B_{12} & B_{16} \\
B_{12} & B_{22} & B_{26} \\
B_{16} & B_{26} & B_{66}
\end{bmatrix}
\begin{bmatrix}
\kappa_x^0 \\
\kappa_y^0 \\
\kappa_{xy}
\end{bmatrix}
\]  

\[
\begin{bmatrix}
M_x \\
M_y \\
M_{xy}
\end{bmatrix} =
\begin{bmatrix}
B_{11} & B_{12} & B_{16} \\
B_{12} & B_{22} & B_{26} \\
B_{16} & B_{26} & B_{66}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_x^0 \\
\varepsilon_y^0 \\
\gamma_{xy}^0
\end{bmatrix}
\]

\[
+ \begin{bmatrix}
D_{11} & D_{12} & D_{16} \\
D_{12} & D_{22} & D_{26} \\
D_{16} & D_{26} & D_{66}
\end{bmatrix}
\begin{bmatrix}
\kappa_x^0 \\
\kappa_y^0 \\
\kappa_{xy}
\end{bmatrix}
\]
where

\[ A_i = \int_{-H/2}^{H/2} \overline{Q}_i \, dz \approx \sum_{k=1}^{N} \overline{Q}_{ik} (z_k - z_{k-1}) \]

\[ B_i = \int_{-H/2}^{H/2} \overline{Q}_i z \, dz \approx \sum_{k=1}^{N} \overline{Q}_{ik} \left( z_k^2 - z_{k-1}^2 \right) \]

\[ D_i = \int_{-H/2}^{H/2} \overline{Q}_i z^2 \, dz \approx \frac{1}{3} \sum_{k=1}^{N} \overline{Q}_{ik} \left( z_k^3 - z_{k-1}^3 \right) \]  

(19)

The matrices represent extensional stiffness (A), bending (D), and bend-twist coupling (B). If each layer of laminate is thin, the terms \( A_{ij}, B_{ij}, \) and \( D_{ij} \) can be approximated from the sums shown in Eq. 19, and we can write the laminate constitutive law as

\[
\begin{bmatrix}
N_x \\
N_y \\
N_{xy} \\
M_x \\
M_y \\
M_{xy}
\end{bmatrix} =
\begin{bmatrix}
A_{11} & A_{12} & A_{16} & B_{11} & B_{12} & B_{16} \\
A_{12} & A_{22} & A_{26} & B_{12} & B_{22} & B_{26} \\
A_{16} & A_{26} & A_{66} & B_{16} & B_{26} & B_{66} \\
B_{11} & B_{12} & B_{16} & D_{11} & D_{12} & D_{16} \\
B_{12} & B_{22} & B_{26} & D_{12} & D_{22} & D_{26} \\
B_{16} & B_{26} & B_{66} & D_{16} & D_{26} & D_{66}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_x \\
\varepsilon_y \\
\gamma_{xy} \\
\kappa_x \\
\kappa_y \\
\kappa_{xy}
\end{bmatrix}
\]  

(20)

We note that the dimensions of these parameters are scaled per unit length of the laminate, i.e., \( N_i \) and \( A_{ij} \) are expressed in force per unit length, \( M_i \) and \( B_{ij} \), in force, and \( D_{ij} \) as force \( \times \) length. As usual, \( \varepsilon \) is dimensionless; curvature \( \kappa \) is dimensioned as inverse length.

These relations have been widely implemented in free and commercially available codes, and are a cornerstone of laminate design. However, though laminate theory can satisfactorily model the behavior of the composite at the lamina or laminate scale, the details of load sharing among the constituent materials and many aspects of failure require more detailed modeling of the phases.

**MICROMECHANICS OF ORDERED AND DISORDERED COMPOSITES**

Micromechanical approaches take specific account of each phase in modeling. Classical approaches (Fig. 6a) span simple strength-of-materials series\(^{68}\) and parallel\(^{69}\) models, to early 2-D elastic field solutions for stresses around elliptical particles (e.g., Ref. [70]). All of these stemmed, along with much other work in the field, from the classical work of Eshelby.\(^{27}\) To model polymeric systems having viscoelastic behavior, elements in each model can be replaced with Voigt–Kelvin (parallel spring-dashpot) or Maxwell (series spring-dashpot) elements, as illustrated in Fig. 6b. In present applications, modeling of the details of even elastic load transfer in constituent phases (with engineering fibers of O(10–100 \( \mu \)m)) in a simulation of structural properties (of components of O(1 cm)) is still somewhat beyond computational capability, though detailed finite element analyses of load transfer have found great utility in informing less-detailed models of structural response and failure (e.g., Ref. [67]). Here, we emphasize the classical work in analytical elasticity (Fig. 7), employing simplifying assumptions for the shapes of the phases in composite media in order to directly perform energy and mechanics of materials analyses to derive field solutions for stresses, strains, and stiffnesses.

Though many fibers are anisotropic, especially with regard to thermal expansion (e.g., many carbon fibers have a slightly negative axial coefficient of thermal expansion and a positive transverse CTE), the classical micromechanics models view each phase as isotropic. Thus, we complete the reduction of the stiffness tensor described earlier for single, isotropic phases to (see below) for which there are only two independent components of \( C_{ij} \). Engineering constants, such as Young’s modulus \( E \), shear modulus \( \mu \), and bulk modulus \( K \) can be readily obtained from these tensorial stiffnesses. For example, if we specify

\[ \varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \varepsilon \]  

(22)

and

\[ \sigma_1 = \sigma_2 = \sigma_3 = \sigma \]  

(23)

we can find from the definition of bulk modulus \( K \),

\[ \sigma = 3K\varepsilon \]  

(24)
Fig. 7 Micromechanical models of ordered composite materials, including representative volume elements for the effective medium theories of (a) Maxwell’s model (see Ref. [14]), (b) Rayleigh’s rectangular array (see Ref. [15]), (c) Hashin’s composite sphere model (see Ref. [31]) and (d) Christiansen and Lo’s three phases model (see Ref. [46]).

that

\[ K = \frac{1}{3} (C_{11} + 2C_{12}) \]  \hspace{1cm} (25)

The shear moduli are defined as

\[ \mu = \mu_{12} = \mu_{33} = \mu_{23} = \frac{1}{2} (C_{11} - C_{12}) \]  \hspace{1cm} (26)

and Young’s modulus and Poisson’s ratio can be then determined by bulk modulus \( K \) and shear modulus \( \mu \) as

\[ E = \frac{9K\mu}{3K + \mu} \]  \hspace{1cm} (27)

and

\[ \nu = \frac{3K - 2\mu}{2(3K + \mu)} \]  \hspace{1cm} (28)

Both somewhat realistic and purely theoretical constructs have been used to derive effective properties (both conductive and mechanical) using micromechanical analyses, and both classes of RVEs have contributed to literature on the bounding of effective properties. In the first category, wherein fibers or particles are somewhat literally represented in 2-D as circles or ellipsoids (see Fig. 3), the derivations of Maxwell\(^{[14]}\) and Rayleigh\(^{[15]}\) were among the first to allow calculation of effective conductive properties based on relative fraction of materials packed in a regular fashion. Later, Bruggeman analyzed both a “symmetric effective medium” and an “asymmetrical effective medium” by assuming a wide distribution for the sizes of inclusions.\(^{[22]}\)

In 1962, Hashin introduced a composite sphere model (Fig. 7c) using Eshelby’s energy approach (Fig. 6b) to develop a closed-form solution for effective stiffness of a continuous matrix phase infused with a variable-diameter sphere.\(^{[31]}\) The ratio of radii \( a/b \) for the phases was taken as a constant, proportional to the volumetric ratio of each composite sphere and independent of their absolute size.

Schemes involving theoretical material constructs have also allowed for solution of the field equations to estimate effective properties; these so-called self-consistent domains are analyzed by matching average stress and strain in the inclusion phases and the uniform stress and strain in the surrounding, infinite, isotropic medium. The first self-consistent formulations were developed by Hershey\(^{[71]}\) and Kröner\(^{[72]}\) in modeling polycrystalline media (Fig. 7d).
Table 5  Summary of the rigorous bounds of physical properties for transverse isotropic composites materials

<table>
<thead>
<tr>
<th>Property</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1$</td>
<td>$E_1^L = \nu^L E_1^L + \nu^m E_1^m + \frac{4(\nu_{12}^L - \nu_{12}^m)^2 k^l k^m G_{12}^m}{[k^l k^f + G_{12}^m (\nu^L k^f + \nu^m k^m)]}$</td>
<td>$E_1^U = \nu^L E_1^L + \nu^m E_1^m + \frac{4(\nu_{12}^L - \nu_{12}^m)^2 k^l k^m G_{12}^m}{[k^m k^f + G_{12}^m (\nu^L k^f + \nu^m k^m)]}$</td>
</tr>
<tr>
<td>$\nu_{12}=\nu_{13}$</td>
<td>$\nu_{12}^L = \nu_{13}^L = \nu^m \nu_{12}^m + \nu^L \nu_{12}^L + \frac{(\nu_{12}^m - \nu_{12}^L)(k^l - k^m)}{[k^m k^f + G_{12}^m (\nu^L k^m + \nu^m k^f)]}$</td>
<td>$\nu_{12}^U = \nu_{13}^U = \nu^m \nu_{12}^m + \nu^L \nu_{12}^L + \frac{(\nu_{12}^m - \nu_{12}^L)(k^m - k^l)}{[k^m k^f + G_{12}^m (\nu^L k^m + \nu^m k^f)]}$</td>
</tr>
<tr>
<td>$G_{12}$</td>
<td>$G_{12}^L = \frac{G_{12}^m [k^f (G_{12}^f + G_{12}^m) + \nu^L (G_{12}^L - G_{12}^m)]}{[k^f (G_{12}^f + G_{12}^m) - \nu^L (G_{12}^L - G_{12}^m)]}$</td>
<td>$G_{12}^U = \frac{G_{12}^m [k^f (G_{12}^f + G_{12}^m) + \nu^L (G_{12}^L - G_{12}^m)]}{[k^f (G_{12}^f + G_{12}^m) - \nu^L (G_{12}^L - G_{12}^m)]}$</td>
</tr>
<tr>
<td>$G_{23}$</td>
<td>$G_{23}^L = \frac{G_{23}^m [k^f (G_{23}^f + G_{23}^m) + 2k^m G_{23} + \nu^L (G_{23}^L - G_{23}^m)]}{[k^f (G_{23}^f + G_{23}^m) + 2k^m G_{23} - \nu^L (G_{23}^L - G_{23}^m)]}$</td>
<td>$G_{23}^U = \frac{G_{23}^m [k^f (G_{23}^f + G_{23}^m) + 2k^m G_{23} + \nu^L (G_{23}^L - G_{23}^m)]}{[k^f (G_{23}^f + G_{23}^m) + 2k^m G_{23} - \nu^L (G_{23}^L - G_{23}^m)]}$</td>
</tr>
<tr>
<td>$k$</td>
<td>$k^L = \frac{k^m (k^f + G_{23}^m)}{[k^f + G_{23}^m]} + \nu^L G_{23}^m (k^f - k^m)}{[k^f + G_{23}^m]}$</td>
<td>$k^U = \frac{k^m (k^f + G_{23}^m)}{[k^f + G_{23}^m]} + \nu^L G_{23}^m (k^f - k^m)}{[k^f + G_{23}^m]}$</td>
</tr>
<tr>
<td>$E_2=E_3$</td>
<td>$E_2^L = E_3^L = \frac{1}{4G_{23}^L} + \frac{1}{4k^L} + \frac{(\nu_{12}^L)^2}{E_1^L}$</td>
<td>$E_2^U = E_3^U = \frac{1}{4G_{23}^U} + \frac{1}{4k^U} + \frac{(\nu_{12}^U)^2}{E_1^U}$</td>
</tr>
<tr>
<td>$\nu_{23}$</td>
<td>$\nu_{23}^L = \frac{2E_1^L k^L - E_1^L E_2^L - 4(\nu_{12}^L)^2 k^L E_2^L}{2E_1^L k^L}$</td>
<td>$\nu_{23}^U = \frac{2E_1^U k^U - E_1^U E_2^U - 4(\nu_{12}^U)^2 k^U E_2^U}{2E_1^U k^U}$</td>
</tr>
</tbody>
</table>

Superscripts "L" and "U" indicate lower and upper bounds, respectively, for corresponding physical properties. Superscripts "f" and "m" indicate fiber and matrix phases, respectively. All formulae adapted from Ref. [76].
Table 6  Summary of rigorous bounds physical properties for particulate-filled composite materials

<table>
<thead>
<tr>
<th>Property</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k^L$</td>
<td>$k^m(k^f(1 + (\psi^f)^2(2\psi^f - 2\psi^m) + \psi^m) + 2k_m((\psi^f)^2 - 1)(\psi^m - \psi^f))$</td>
<td>$k^U = \frac{k^f{2k^f(\psi^f)^2(\psi^f - \psi^m) + k^m[(2\psi^f + \psi^m)(3\psi^m - 3\psi^f + 4(\psi^f)^2)]}}{-k^m\psi^f(\psi^m + 2\psi^f) + k^f/\psi^f(5\psi^f + 4\psi^m) - 3}$</td>
</tr>
<tr>
<td>$G^L$</td>
<td>$G^m\left[\frac{G^m(\psi^m)(7\psi^f + 2\psi^m) + G^f(8 + 7\psi^f - 5(2 + \psi^f)\psi^m)}{2G^f(\psi^m)(\psi^m - 4\psi^f)} + G^m(-7\psi^f - 2\psi^m + 2\psi^f(\psi^m - 4\psi^f))\right]$</td>
<td>$G^U = \frac{G^f\left[G^f(7\psi^m - 2\psi^f) + G^m(15 + 7\psi^f(5\psi^f - 22))\right]}{2G^m\psi^f(4\psi^m - 2\psi^f) + G^f(15 + \psi^f(10\psi^f - 23))}$</td>
</tr>
<tr>
<td>$E^L$</td>
<td>$\frac{9k^L G^L}{3k^L + G^L}$</td>
<td>$E^U = \frac{9k^U G^U}{3k^U + G^U}$</td>
</tr>
<tr>
<td>$\nu^L$</td>
<td>$\frac{3k^L - 2G^L}{2(3k^L + G^L)}$</td>
<td>$\nu^U = \frac{3k^U - 2G^U}{2(3k^U + G^U)}$</td>
</tr>
</tbody>
</table>

Superscripts "L" and "U" indicate lower and upper bounds, respectively, for corresponding physical properties. Superscripts "f" and "m" indicate filler and matrix phases, respectively. Physical properties of filler phase are assumed to be superior to those of the matrix phase. All formulae adapted from Ref. [76].
Later, Budansky extended their work in order to determine bounds on shear and bulk moduli of multiphase materials. Hashin and Shtrikman used a variational method to minimize potential energy in a model domain and provide rigorous bounds on effective magnetic permeability, shear, and bulk moduli of multiphase materials. Christensen and Lo later devised a three-phase self-consistent approach to calculate effective shear moduli of materials containing spherical and cylindrical inclusions.

Importantly, many classical results for effective conductivity and effective bulk modulus coincide for both physical and self-consistent RVEs. Effective elastic properties can be found for these arrangements via minimization of potential energy, or minimization or work principles, expressing stored elastic energy as either

\[
U_C = \frac{1}{2} \sum_{i=1}^{6} \sum_{j=1}^{6} \epsilon_i C_{ij} \epsilon_j
\]

or

\[
U_S = \frac{1}{2} \sum_{i=1}^{6} \sum_{j=1}^{6} \sigma_i (S_{ij}/p_i m_j) \sigma_j
\]

These two expressions result in different magnitudes for the total stored elastic energy in heterogeneous domains due to simplifying assumptions regarding stress and strain fields. Together, they allow calculation of bounds on properties of anisotropic fields of fibrous (Table 5) and particulate (Table 6) materials, with assumed geometry and volume fraction of phases (summarized in compact form, for example, by McCullough, following work by Hashin and Shtrikman). These estimates are useful for design for stiffness, in both fibrous and particulate materials, and can be readily used to model a wide range of materials, and compare well with elastic finite element simulations in prediction of stiffnesses we note that these models assume transverse isotropy in the composite, with isotropic fiber and matrix.

Though effective properties can be estimated and bounded using these simplified elastic estimates, however, the importance of disorder in material geometry at the scale at which the material is used must frequently be considered. Such disorder can create internal nonuniformities in material response, and thus variability among devices or structures created from the material. Also, variability in location of reinforcement phases can result in higher stress concentrations in the material, producing earlier-than-expected failure (Fig. 8[77–79]).
Indeed, real, disordered, or stochastic materials exhibit a range of values in material response, and attempts have been made for various geometries (e.g., randomly laid fibers or particles, as in Fig. 9) to bound these properties. Work of this type models disorder in a material specifically, rather than through use of an energy approach, as described in the previous section, to simply bound properties of an ordered, representative arrangement. In early work, Bergman devised an analytical method to determine bounds for dielectric conductivity. Lurie and Cherkaev presented bounds for macroscopically anisotropic media by extending the work of Hashin and Shtrikman. Gibiansky and Torquato used a "translation method" to determine the rigorous bounds for the relation between conductivity and elastic moduli of two-dimensional, globally isotropic composite materials. Later, Torquato and coworkers used a discrete network and homogenization theory to determine the effective mechanical and transport properties of cellular solids. Studying fibrous materials, Lu, Carlsson, and Andersson used a micromechanical approach to obtain rigorous bounds on elastic properties. And Ostoj-Starzewski et al. developed network techniques to simulate effective properties of generalized composites by changing the spring constants of individual springs within the network to model multiphase material properties.

Sastry and coworkers studied the stochastic fibrous networks to determine both conductivity and variance in conductivity in battery materials. This work was later extended to model fiber type bonding conditions, and failure mechanisms in greater detail and was also extended to include the effects of fiber waviness on material mechanical properties to model variance in electrical conductivity of porous networks with elliptical particles.

PHASE CONTINUITY AND PERCOLATION IN DISORDERED COMPOSITES

All of these efforts further underscored the importance of variance in properties in real materials. Indeed, a key requirement in producing dramatic changes in material transport properties (e.g., thermal and electrical conduction) is percolation of the additive phase. We can define percolation as the formation of at least one, continuous, domain-spanning path of the percolating phase in the material. Dramatic improvements in computing speeds from the 1980s to the present have allowed direct, stochastic simulation of transport in disordered arrays.

Key features of such models include physically realistic simulation domains and use of many statistically equivalent realizations, i.e., domains in which the statistical parameters describing particles, sizes, etc. are the same for all, but the locations, sizes, etc. are different in each. As a result, the minimum amount of a phase required to produce dramatic improvements in composite properties can be determined, along with discrete and averaged predictions of material properties. Percolation concepts have been used not only in design of materials for mechanical properties, but also in filtration and conductive properties.

Classic work by Kirkpatrick, who studied site and bond percolation using a resistor network, pointed out the importance of the percolation threshold, or threshold.

![Fig. 10 Percolating and non-percolating arrays of circles, with volume fractions (a) 32.7%, (b) 51.2%, and (c) 64.0%.](image-url)
Fig. 11  Two-dimensional percolating and nonpercolating arrays of ellipses of aspect ratio 6 and volume fractions (a) 17.9%, (b) 31.6%, and (c) 50.7%. Three-dimensional percolating and nonpercolating arrays of ellipsoids are also shown, of aspect ratio 10, and volume fraction (d) 6%, and (e) 20%.

Fig. 12  Probability of percolation in 2D arrays, for various particle-fiber geometrics. (Adapted from Ref. [106].)

Fig. 13  Simulation results for percolation probability versus particle size, for arrays of overlapping ellipsoids of revolution. In this figure, 'a' represents the semi-axis length, and the aspect ratio of the ellipsoids is 10. (Adapted from Ref. [107].)

Seager also examined conduction and percolation phenomena in stick networks (among others), using 2-D and 3-D Monte Carlo simulations.\cite{103}

Recently, analytical approximations of the percolation points have been developed for both 2-D and 3-D arrays of generalized ellipses and ellipsoids of uniform shape and size,\cite{106,107} which verified and extended earlier results on simulation of simpler 2-D networks of 1-D fiber percolation,\cite{97,98} 3-D networks of 2-D ellipsoids, and other analytical approaches for determination of percolation of circular arrays;\cite{108,109,110,111,112,113,114} combined results\cite{91,106} are shown in Fig. 11. These illustrate that the percolation point in realistic materials is probabilistic (i.e., only a statistical estimation of percolation point can be made, for any given volume fraction of particles), and also that 2-D fiber models in models are quite satisfactory for determining percolation properties for aspect ratios greater than 100, as shown in Fig. 12. Similarly, Fig. 13 shows that percolation probability of ellipsoid models in 3-D model is also strongly dependent upon aspect ratio.

APPICATION OF COMPOSITE THEORIES TO BIOMATERIALS

Modeling of the shapes and effects of various phases in materials is tremendously important in understanding the combined mechanical and physiological role of biomaterials. Natural materials exhibit a high degree of variability, and use of statistical theories touched upon in
this chapter can be helpful in anticipating differences in clinical results of both in-vitro and in-vivo tissue response. Generalized domains, particularly fields of ellipses and ellipsoidal particles, can be used to describe a wide variety of materials and bound a number of important effective engineering properties. Percolative properties have important implications for understanding the role of particulates (either voids or material phases) and fibers, both adaptation and selection, in biomaterials (Fig. 12).

Thus, in conclusion, the modeling of heterogeneous domains performed by the composites community has broad application in modeling biomaterials. Elasticity provides an initial estimate of properties, and percolation theories provide a method of determining the connectivity of phases, and thus their importance in transport.

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ARTICLES OF FURTHER INTEREST

Alumina, p. 19
Degradable Polymer Composites, p. 423
Finite Element Analysis, p. 621

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