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Modeling of physical properties of composite materials

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Abstract

Recent progress in three different areas involving the modeling of the physical properties of composites is reviewed. These include: (i) theoretical approaches to microstructure/property relations; (ii) X-ray microtomography, an imaging technique that enables one to obtain high-resolution three-dimensional microstructural phase information of a composite sample in a non-intrusive manner; and (ii) topology optimization, a promising numerical technique that enables one to design composites with tailored material properties. Current limitations and future research needs are described.

1. Introduction

The problem of determining the macroscopic or effective physical properties of composite media is a classical one in science and engineering, attracting the attention of such luminaries as Maxwell (1873) and Einstein (1906). In the most general sense, a heterogeneous material consists of domains of different materials (phases) or the same material in different states. Attention here is focused on the many instances in which the 'microscopic' length scale (e.g., the average domain size) is much larger than the molecular dimensions (so that the domains possess macroscopic properties) but much smaller than the characteristic length of the macroscopic sample. In such circumstances, the heterogeneous material can be viewed as a continuum on the microscopic scale and macroscopic or 'effective' properties can be ascribed to it. Such heterogeneous media abound in nature and in man-made situations: examples include aligned and chopped fiber composites, porous and cracked media, polycrystals, polymer blends, foams, fluidized beds, photographic emulsions, cermets, soils, rocks, blood, and animal and plant tissue, to mention a few.

In light of the manifest technological importance of determining the effective parameters of disordered

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heterogeneous materials (e.g., composite and porous media), an enormous body of literature has evolved based upon direct measurement, empirical relations, and approximate as well as rigorous theoretical methods (see Beran, 1968; Christensen, 1979; Willis, 1981; Torquato, 1991; and references therein). Performing direct measurements on each material sample, for all possible phase property values and volume fractions, is prohibitive from a time and cost standpoint. Empirical relations are more useful for correlating data rather than predicting them. Since effective properties are sensitive to the details of the microstructure, a broader approach is to calculate the properties from the microstructure of the disordered material; one can then relate changes in the microstructure quantitatively to changes in the macroscopic parameters. This has important implications for the design of materials with tailored properties.

In this report, we survey developments in three different areas:

- theoretical approaches to microstructure/property relations;
- X-ray microtomography, an imaging technique that enables one to obtain high-resolution three-dimensional microstructural phase information of a composite sample in a nonintrusive manner; and
- topology optimization, a promising numerical technique that enables one to design composites with tailored material properties.

Considering the vastness of the literature, no attempt will be made to discuss all of the key developments. The physical properties that we will focus on include the elastic moduli, conductivity (thermal or electrical), thermal expansion coefficients, piezoelectric coefficients, and failure characteristics of composites. However, we point out that other seemingly different properties (fluid permeability and trapping rate) have been approached with same tools that will be described below (Torquato, 1991). In other words, it pays to view all types of physical properties of composites under the same general light.

2. Theoretical developments

2.1. Beyond volume fraction information

For simplicity, we will focus the discussion on composites consisting of two different phases designated as phases 1 and 2. Depending upon the physical context, the ith phase can be either solid, fluid, or void, and is characterized by a set of physical properties (elastic moduli, strength, conductivity, etc.) as well as a constant volume fraction ϕ_i, in the case of a statistically uniform systems. The volume fraction is the simplest but most important piece of microstructural information.

Many practitioners still insist on using simple mixture rules to predict the physical properties of composites. For example, two popular mixture rules for some arbitrary effective property K_e are the so-called arithmetic average

$$K_e = K_1\phi_1 + K_2\phi_2 \tag{1}$$

and the harmonic average

$$K_e = \frac{K_1K_2}{K_1\phi_1 + K_2\phi_2}, \tag{2}$$

where K_i is the property of phase i. It is seen that both the arithmetic average Eq. (1) and the harmonic average Eq. (2) only incorporate the phase volume fractions. Such mixture rules are not only used to estimate linear properties of composites, such as elastic moduli and conductivity, but nonlinear properties, such as strength. In the case of linear properties, it is well known that the arithmetic average

Fig. 1. Gray-scale digitized microscope image of a three-phase boron carbide/aluminum composite: white region is Al phase, black region is B_4C phase, and gray region is Al_4BC phase. The B_4C and Al phases are the dominant ones.

Eq. (1) generally grossly overestimates the effective property, whereas the harmonic average Eq. (2) generally grossly underestimates the effective property.

Popular among more sophisticated practitioners are effective-medium or self-consistent approximations (Hill, 1965; Budiansky, 1965) for dispersions of inclusions in a matrix. The basic idea is to embed a *typical inclusion* in a matrix that has the unknown effective property. The resulting

expression for the effective property depends on the phase properties and volume fractions, and on the inclusion shape. Self-consistent approximations break down even for moderate to high phase contrast values (Christensen, 1979; Torquato, 1998) and, in particular, predict spurious percolation thresholds for dispersions. Indeed, it has been shown that self-consistent approximations are exact for media that possess a type of *topological symmetry* that typical particulate and fiber-reinforced composites do not possess. Thus, self-consistent approximations should not be applied to dispersions unless the phase contrast is small enough. Nonetheless, many continue to apply it to dispersions because of its appeal as a simple analytical expression.

In the case of dispersions of particles in a matrix, it crucial in a model to capture the fact that the matrix and particle phases are connected and disconnected, respectively. Composite-spheres models (Hashin, 1962; Christensen and Lo, 1979) attempt to incorporate such topological features while utilizing volume fraction information only. Resulting analytical expressions for the effective elastic moduli provide good agreement with experimental data on dispersions provided there is no significant clustering of the particles. When clustering is a factor, one must include microstructural information beyond that contained in the volume fractions.

Approaches to modeling effective properties of more complex microstructures with just volume fraction information must break down. For example, Fig. 1 shows a micrograph of the rather complex microstructure of a three-phase boron carbide/aluminum composite (Torquato et al., 1999). Here, both the boron carbide and aluminum phases are connected (although in two dimensions, only the boron carbide phase appears to be connected) and it is clear that one is hard-pressed to extract a simple unit cell (as is typically done for dispersions) that captures the overall behavior.

From these examples, we can see that the effective properties must depend upon microstructural information beyond that contained in phase volume fractions; i.e., what we will refer to as *higher-order* microstructural information. How do we precisely quantify this higher-order microstructural information, and can we incorporate this information to predict the effective properties? Clearly, we want to accomplish these tasks using first principles. It turns out that for linear effective properties (elastic moduli, conductivity, etc.) there are exact system-independent approaches as well as rigorous bounding techniques that systematically lead one to precise microstructural functions. These quantities take the form of various types of n-point statistical correlations, depending on the physical property of interest.

2.2. Bounds/microstructure relations

Unfortunately, in virtually all situations, the details of the microstructure (all of the correlation functions) are not completely known. This naturally leads one to attempt to estimate the effective properties from partial statistical information (lower-order correlation functions) and, in particular, to establish the range of possible values the effective properties can take given such limited microstructural information; i.e., to determine rigorous upper and lower bounds on the properties. Traditionally, minimum energy principles are used to generate bounds on effective properties.

Improved bounds are bounds that depend *nontrivially* upon two-point and high-order correlation functions and thus involve information beyond that contained in the volume fractions. In the cases of the conductivity and elastic moduli of isotropic materials, for example, improved bounds are those which are tighter than the Hashin–Shtrikman bounds (Hashin and Shtrikman, 1962, 1963). Improved bounds on a variety of different effective properties have been derived in terms of $S_n(\mathbf{x}^n)$, i.e., the probability of finding n points at positions $\mathbf{x}^n \equiv \mathbf{x}_1,\ldots, \mathbf{x}_n$ in one of the phases for linear materials (Beran, 1968; Milton, 1982; Milton and Phan-Thien, 1982; Torquato, 1991) as well as nonlinear materials (Willis, 1991; Ponte Castaneda and Suquet, 1998). Three- and four-point bounds on the elastic moduli and conductivity of various composites have been computed (Torquato, 1991). Although such three-

and four-point bounds can provide significant improvement over two-point bounds, the bounds diverge as the contrast between the phase properties increases. The upper bound, for example, generally diverges to infinity when phase 2 is superrigid relative to phase 1, even if phase 2 is topologically disconnected. The reason for this behavior is that *lower-order* S_n do not reflect information about *percolating clusters or connected paths* in the system and, accordingly, bounds involving such lower-order information are referred to as *conventional* improved bounds. Nonetheless, it is important to emphasize that one of the bounds can still provide a good estimate of the properties in high-contrast situations (Torquato, 1991), depending on whether the system is above or below the *percolation threshold*; i.e., the point at which a disconnected phase becomes connected. Conventional bounds on effective properties have been given in terms of other types of statistical quantities, including point/q-particle functions G_n $(n = 1+q)$ (Torquato, 1986a) and surface–void F_{sv} and surface–surface F_{ss} correlation functions (Doi, 1976).

Although conventional bounds can still be valuable for extreme contrast situations, it highly desirable to derive sharper bounds in terms of morphological quantities that better reflect percolation or connectedness information. Such bounds have been recently derived and computed (Torquato and Rubinstein, 1991) for the problem of conduction in particle suspensions in terms of the nearest-neighbor distribution function H_P. Moreover, bounds on certain diffusion parameters for porous media have been expressed in terms of the pore-size distribution function $P(\delta)$ (Torquato and Avellaneda, 1991).

2.3. Microstructure characterization

The previous section described some of the different types of statistical correlation functions (S_n, G_n, F_{sv}, F_{ss}, H_P, P) that have arisen in rigorous bounds on effective properties. Until recently, application of such bounds (although in existence for almost thirty years in some cases) was virtually nonexistent because of the difficulty involved in ascertaining the correlation functions. Are these different functions related to one another? Can one write down a single expression that contains complete statistical information? The answers to these two queries are in the affirmative.

For statistically inhomogeneous systems of identical d-dimensional spheres, a general n-point distribution function H_n has been introduced and represented (Torquato, 1986b). From the general quantity H_n, one can obtain all of the aforementioned correlation functions and their generalizations. This formalism has been generalized to treat polydispersed spheres, anisotropic media (e.g., aligned ellipsoids and cylinders) and cell models (see Torquato, 1991). We should mention that quantities that are superb signatures of clustering and percolation have been studied and evaluated (Torquato, 1991).

In the last decade or so, considerable progress has been made on the determination of statistical correlation functions from computer simulations (Monte Carlo and molecular dynamics). From a theoretician's point of view, simulations may be regarded as 'experiments' that one may test theories against for specific models of heterogeneous media. Computer simulations also offer a means of studying model systems which may be too difficult to treat theoretically. Obtaining statistical measures, such as H_n, from simulations is a two-step process. First, one must generate realizations of the disordered medium. Second, one samples each realization for the desired quantity and then averages over a sufficiently large number of realizations.

2.4. Cross-property relations

An intriguing fundamental as well as practical question is the following: Can different properties of the heterogeneous material be *rigorously* linked to one another? Such cross-property relations would be of great utility in the *multifunctional* design of composites. In particular, can the overall thermal (electrical) response of a composite to an applied thermal (electrical) load be related rigorously to the overall linear mechanical response of the same medium to an applied mechanical load?

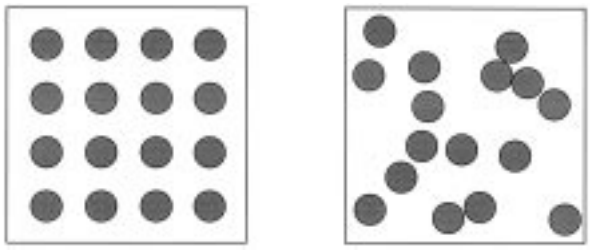

Fig. 2. Two systems at the same volume fraction but the right-most example has greater fluctuations. The failure characteristics of these systems can be dramatically different from one another.

Rigorous cross-property bounds that link conductivity and elastic moduli have been obtained (Milton, 1984; Berryman and Milton, 1988). Subsequently, these results were improved upon using the so-called *translation method* (Gibiansky and Torquato, 1996). How sharp are these cross-property estimates, given an exact determination of one of the effective properties? To examine this question, one can utilize exact results for the effective conductivity and effective bulk modulus K_e of hexagonal arrays of superconducting, superrigid inclusions (phase 2) in a matrix. Agreement between the cross-property bounds and the exact elastic-moduli data is remarkably good. It is noteworthy that *standard variational upper bounds* on the effective properties (such as Hashin–Shtrikman) here diverge to infinity as they do not incorporate information that the *superrigid phase is in fact disconnected*. By contrast, the cross-property upper bound uses the fact that the *infinite-contrast phase is disconnected via conductivity information*.

2.5. Influence of spatial variability on failure of composites

The field of failure in composites is a huge one and cannot be covered in the limited space of this report. The reader is referred to the contributions of Dvorak et al. (1992), Budiansky et al. (1995), Zhou and Curtin (1995) and Christensen (1997) on the failure of various fiber composites, Haubensack et al. (1995) on crack propagation in brittle composites, and the paper by Dvorak (2000) who reviews developments in the inelastic response of composites. Our limited focus here will be on the utility of statistical mechanics to characterize microstructure fluctuations and failure in composites.

It is of great practical interest to understand how spatial variability in the microstructure of composites affects the failure characteristics of the heterogeneous materials (see Fig. 2). It is useful to discuss several examples reported in the literature that illustrate this point. Barsoum et al. (1992) reported data on strength versus fiber spacing for borosilicate glass reinforced with SiC fibers under three-point bending. Matrix cracks initiated at a lower stress as the local fiber spacing increased. Thus, the important length scale is the largest interfiber spacing, i.e., the extreme statistics govern the strength. This implies that naive attempts to estimate the strength using a simple rule of mixture relation Eq. (1) must necessarily fail since volume fraction information is equivalent to average fiber spacing. Botsis et al. (1997) subsequently showed that a Griffith-type scaling relation for the strength involving the largest interfiber spacing provided good correlation with the data.

In another experimental study, MacKay (1990) investigated cracking in unidirectional metal matrix composites under thermal cycling. It was found that residual stresses caused matrix cracks and interfacial debonding. Cracking was related to the fiber distribution; more cracking occurred between the more closely spaced fibers within a row. Finally, in a theoretical study on the compressive strength of unidirectional composites by Chung and Weitsman (1994), it was found that random fiber spacing

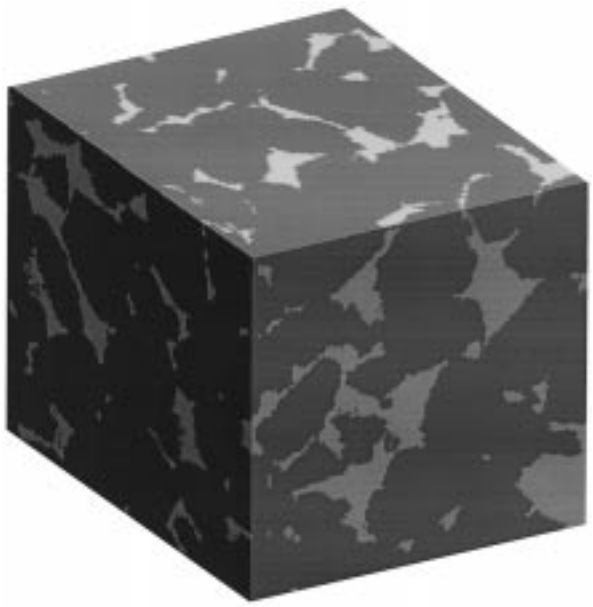

Fig. 3. Fountainebleau sandstone: lighter shade is void and darker shade is solid.

instigated the formation of severe transverse loadings on the fibers. The analysis required the probability density of fiber spacing.

We see from these three examples that spatial fluctuations in the microstructure can have important consequences for the failure characteristics of composites. Microstructure fluctuations is a topic of long-standing interest in the statistical physics community, but much of this work has not permeated the applied mechanics or materials science communities. For example, using the machinery of statistical mechanics, the *statistics of interfiber spacing* (Torquato and Lu, 1993) and *local volume fraction fluctuations* within an 'observation' window (Quintanilla and Torquato, 1997) have been quantified. Such statistical measures are of direct relevance to all three of the aforementioned problems since they contain information about all of the statistical moments.

3. X-ray microtomography

Much of the early work on characterizing the microstructure of heterogeneous materials was done via sectioning. This approach is unsatisfactory, especially in biomedical applications, not only because it destroys the sample but it often also causes the sections themselves to be altered during the sectioning process. Non-invasive techniques needed to be developed. Transmission microscopy and scanning tunneling electron microscopy are now well-established non-invasive techniques but are limited to two-dimensional information.

It is well established that the physical properties of composites are generally sensitive to the full three-dimensional structure of the samples. X-ray microtomography (Flannery et al., 1987), and confocal microscopy (Fredrich et al., 1995) are relatively new noninvasive techniques that provide three-dimensional phase information.

Computer-aided tomography (CAT) scans are a common way to obtain three-dimensional phase information, especially in the medical field. However, the resolution obtained is limited to approximately

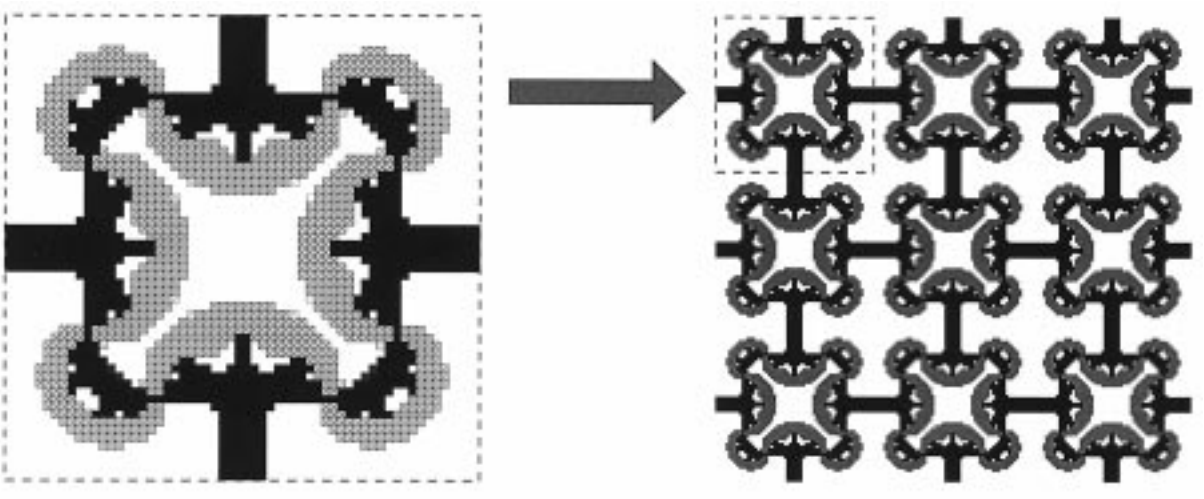

Fig. 4. Optimal microstructure for minimization of effective thermal expansion coefficient (Sigmund and Torquato, 1997). White regions denote void, black regions consist of low expansion material and cross-hatched regions consist of high expansion material.

$\sim$100 μm. Synchrotron-based X-ray microtomography (Flannery et al., 1987) provides a means to have both high resolution ($\approx$1 μm) and non-destructive evaluation of three-dimensional structural information. Recently, microtomographic methods have been used to study the structure and properties of sandstones (Coker et al., 1996). The microtomography data and reconstructed three-dimensional maps of the samples X-ray opacity were collected using beamline X2B located at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory.

In the case of sandstone, the digitized image is stored as a $512 \times 512 \times 512$ matrix of voxel values. The values stored in these voxels (which corresponded to the electron densities in the sample) are then binned, and the two phases show up as two peaks in a histogram of the electron density values. Once a cutoff value is determined to distinguish the phases, the sample is stored as a matrix of bits, corresponding to values of either 0 (matrix phase) or 1 (void phase). Fig. 3 shows a surface cut of a Fountainebleau sandstone. Note the complexity of the void space. One can now extract the microstructural functions that determine the property behavior from this image using the simulation techniques discussed in the previous section. In this way, the fluid permeability and the trapping constant were estimated for this sample.

4. Topology optimization

A promising new method for the systematic design of composites as well as smart material systems is the *topology optimization method*. The topology optimization method was developed a decade ago by Bendsøe and Kikuchi (1988) and was originally intended for the design of mechanical structures. It is being used not only to solve structural problems but also in smart and passive material design, mechanism design, MicroElectroMechanical Systems (MEMS) design and many other design problems (Sigmund, 1994; Larsen et al., 1997; Sigmund and Torquato, 1997; Sigmund et al., 1998).

The basic topology optimization problem can be stated as follows: *distribute a given amount of material in a design domain such that an objective function is extremized* (Bendsøe and Kikuchi, 1988; Bendsøe, 1995). The objective function can be any combination of the individual components of the

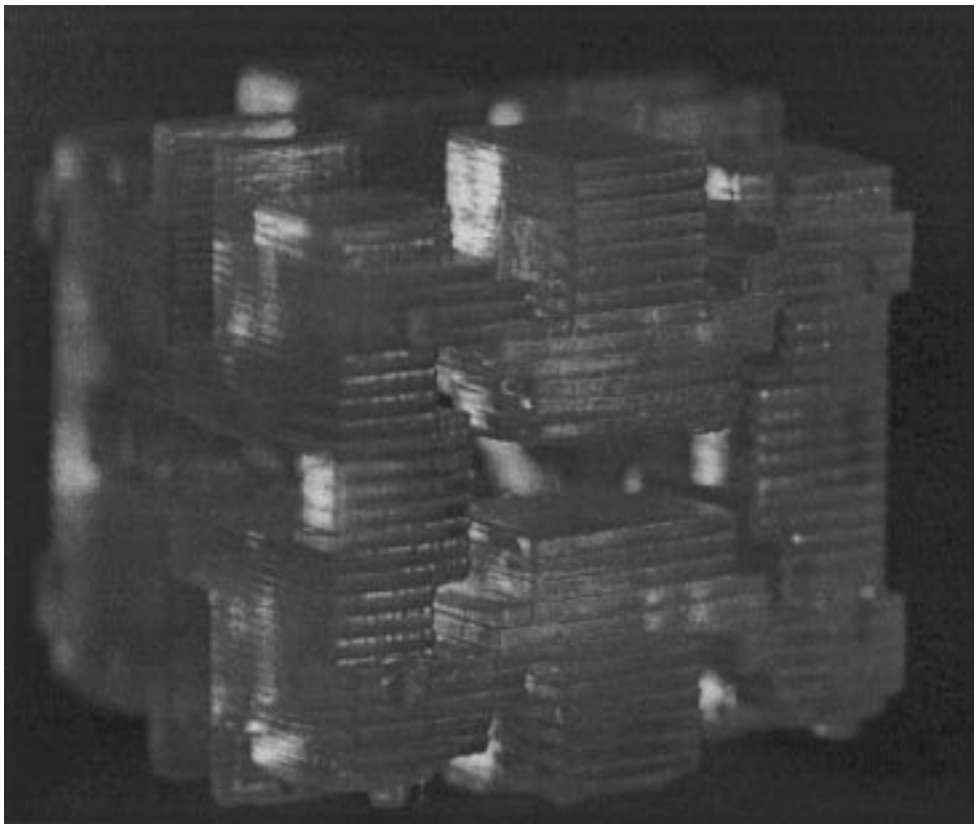

Fig. 5. Prototype of one base cell made by stereolithography. This special porous solid has negative Poisson's ratio and, when used as a matrix in a piezocomposite, maximizes hydrophone performance.

relevant effective property tensor subject to certain constraints. The design domain is the periodic base cell and is initialized by discretizing it into a large number of finite elements. The problem consists in finding the optimal distribution of the base materials and/or void, such that the objective function is minimized. The optimization procedure solves a sequence of finite element problems followed by changes in material type (density) of each of the finite elements, based on sensitivities of the objective function and constraints with respect to design changes (Sigmund and Torquato, 1997).

The topology procedure has been employed to design composite materials with extreme elastic (Larsen et al., 1997), thermal (Sigmund and Torquato, 1997) or piezoelectric properties (Sigmund et al., 1998). Materials with extreme or unusual thermal expansion behavior are of interest from both a technological and fundamental standpoint. Zero thermal expansion materials are needed in structures subject to temperature changes such as space structures, bridges and piping systems. Materials with large thermal displacement or force can be employed as 'thermal' actuators. A negative thermal expansion material has the counterintuitive property of contracting upon heating. A fastener made of a negative thermal expansion material, upon heating, can be inserted easily into a hole. Upon cooling, it will expand, fitting tightly into the hole. All three types of expansion behavior have been designed (Sigmund and Torquato, 1997).

To illustrate the capability of the method, we discuss the negative expansion case for which we must consider a three-phase material: high expansion material, low expansion material, and void region. Fig.

4 shows the two-dimensional optimal design that we found; the main mechanism behind the negative expansion behavior is the *reentrant cell structure* having bimaterial components which bend (into the void space) and cause large deformation when heated.

In the case of piezoelectricity, actuators that maximize the delivered force or displacement can be designed. Moreover, one can design piezocomposites (consisting of an array of parallel piezoceramic rods embedded in a polymer matrix) that maximize the sensitivity to acoustic fields. The topology optimization method has been used to design piezocomposites with optimal performance characteristics for hydrophone applications (Sigmund et al., 1998). When designing for maximum hydrostatic charge coefficient, the optimal transversally isotropic matrix material has negative Poisson's ratio in certain directions. This matrix material itself turns out be a composite, namely, a special porous solid. Using an AutoCAD file of the three-dimensional matrix material structure and a stereolithography technique, such three-dimensional negative Poisson's ratio materials have actually been fabricated (Sigmund et al., 1998). Such a prototype cell (cellular solid made from a polymer) is shown in Fig. 5.

5. Research needs

- The intersection of solid mechanics with biology will play a major role in the future. Virtually all biological material systems are composites that are found to have at least one distinct structural feature at a variety of length scales. A formalism to predict the effective properties of such complex multi-scale composites is currently lacking.
- The machinery of statistical mechanics has yet to be fully exploited in the study of composites. Outstanding problems where such tools can be fruitfully applied include the characterization of the microstructure of statistically inhomogeneous media (such as functionally graded materials) as well as the toughness and strength of composites.
- Presently, three-dimensional imaging techniques are limited by resolution and/or the types of materials that can be imaged. Experimental methods must be developed that will enable us to image in three dimensions a wide class of materials and over a wide spectrum of length scales. Such information can be read into a computer and then analyzed and visualized as one desires.
- The topology optimization procedure is in its infancy and its potential has yet to be realized in optimal design applications involving linear properties, not to mention nonlinear properties. This computational method combined with improved fabrication techniques will make optimal design of real composite materials (including multifunctional design) a reality in the future.

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