

Unified methodology to quantify the morphology and properties of inhomogeneous media

S. Torquato

Princeton Materials Institute, Princeton University, Princeton, NJ 08544, USA

Abstract

Recent progress that we have made on the problem of determining the effective properties of random heterogeneous media from the morphology is reviewed. A variety of different effective properties are considered, including the electrical conductivity and elastic moduli of composites, time scales associated with diffusion and reaction among traps, and fluid permeability of porous media. Studying seemingly disparate properties from a general viewpoint is shown to be fruitful.

1. Introduction

This paper describes recent progress that we have made on several aspects of the problem of determining effective properties of random heterogeneous materials from a knowledge of the microstructure or morphology. The random heterogeneous material is a domain of space $\mathcal{V}(\omega) \in R^d$ (where the realization ω is taken from some probability space) of volume V which is composed of two regions: a phase 1 region $\mathcal{V}_1(\omega)$ of volume fraction ϕ_1 and a phase 2 region $\mathcal{V}_2(\omega)$ of volume fraction ϕ_2 . Depending upon the physical context phase i can be either solid, fluid or void. We consider a variety of different physical properties such as the electrical conductivity and elastic moduli of composites, time scales associated with diffusion and reaction among sinks or traps, and fluid permeability of porous media. A number of topics are described, including *conventional* and *percolation-type* property bounds, quantitative characterization of the morphology, and rigorous *cross-property* relations. It is shown that it is quite fruitful to study seemingly disparate properties from a general viewpoint.

2. Improved variational bounds on effective properties

For general random media, the complexity of the microstructure prevents one from obtaining the effective properties of the system exactly. Therefore, any rigorous statement about the properties, *given limited morphological information*, must be in the form of an inequality, i.e., rigorous bounds on the effective properties. Bounds are useful since they: (i) enable one to test the merits of theories and computer experiments; (ii) as more microstructural information is incorporated successfully, the bounds become progressively narrower; and (iii) one of the bounds can typically provide a good estimate of the property for a wide range of conditions, even when the reciprocal bound diverges from it [1].

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 [2,3].

2.1. Conventional improved bounds

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 $\mathbf{x}^n \equiv x_1, \dots, x_n$ in one of the phases [4–9]. Other bounds on effective properties have been given in terms of other types of statistical quantities, including point/ q -particle functions G_n ($n = 1 + q$) [10] and surface-void F_{sv} and surface–surface F_{ss} correlation functions [8,9,11]. Until recently, a stumbling block to the evaluation of improved bounds has been the difficulty involved in ascertaining the correlation functions. This impasse was broken several years ago (see section 3), resulting in the first evaluation of improved bounds for nontrivial model microstructures [1,12].

All of the aforementioned bounds are referred to as *conventional* bounds because the lower-order statistical correlation functions involved do not reflect information about *percolating clusters or connected paths* in the system. Nonetheless, it is important to emphasize that it has been established [1] that one of the bounds can still provide a good estimate of the properties in high-contrast situations, depending on whether the system is above or below the *percolation threshold*, as shown below.

Improved upper and lower bounds on the effective conductivity σ_e of random suspensions of spheres [1,13], aligned cylinders [1,14–16], and aligned spheroids [21] have been computed for arbitrary phase conductivity ratio $\alpha = \sigma_2/\sigma_1$. These results have been compared to corresponding Brownian-motion simulation data [17–19]. Improved n -point bounds ($n \geq 3$) are generally found to provide significant improvement over bounds which just incorporate volume-fraction information. One of the bounds is always found to provide an accurate estimate of the data, even for large phase contrast. This key point is illustrated in Fig. 1

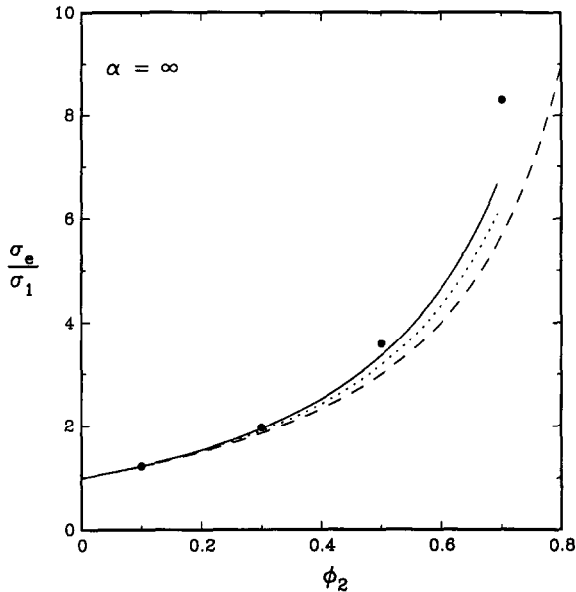


Fig. 1. Scaled effective conductivity σ_e/σ_1 of superconducting ($\alpha = \sigma_2/\sigma_1 = \infty$) random arrays of aligned cylinders versus cylinder volume fraction ϕ_2 . Comparison of two-point (dotted line), three-point (dashed line), and four-point (solid line) lower bounds to simulation data (filled circles).

which shows two-, three- and four-point lower bounds [5,6] on the effective conductivity σ_e a transversely isotropic composite consisting of a random array of *superconducting*, aligned, infinitely long, equisized, circular cylinders. These three- and four-point bounds were evaluated by Torquato and Lado [15,16] for fiber volume fractions ϕ_2 up to 70%. Note that even though the upper bounds diverge to infinity in this instance, the four-point lower bound provides a good estimate of the data since the cylindrical fibers do not form clusters [1].

Similar trends and conclusions were found for improved elastic moduli bounds. Three- and four-point bounds [5,6] were computed by Torquato and Lado [15,16] for the above cylinder model. Miller and Torquato [20] carried out corresponding calculations for cylinders with a polydispersivity in size.

Torquato and Lado [21] have obtained two-point upper bounds on the survival time τ for diffusion among aligned spheroidal traps of aspect ratio b/a with an infinite surface rate constant κ . These bounds were compared to “exact” simulation data determined by Miller, Kim and Torquato [22] and found to capture the essential dependence of τ upon b/a .

2.2. Toward percolation-type bounds

The aforementioned utility of conventional bounds in extreme contrast instances notwithstanding, is highly desirable to derive sharper bounds in terms of morphological quantities that better reflect percolation information. Such bounds

have been recently derived and computed by Torquato and Rubinstein [23] and by Bruno [24], using similar approaches, for the problem of conduction in particle suspensions. Letting σ_i be the conductivity of phase i , they were able to derive an upper bound on the effective conductivity σ_e which remained finite, in general, in the limit $\sigma_e/\sigma_1 \rightarrow \infty$ by incorporating information that the superconducting particles did not touch. Similarly, they found lower bounds on σ_e which did not necessarily vanish in the limit $\sigma_e/\sigma_1 \rightarrow 0$. Whereas Bruno's bounds involve the minimum distance between all particles pairs, the Torquato–Rubinstein bounds incorporate the nearest-neighbor distribution function $H_p(r)$. Bounds involving $H_p(r)$ have been also derived for the effective viscosity of a suspension [25], mean survival time [8], and the fluid permeability [9].

The Rubinstein–Torquato [8] variational principle for the lower bound on the mean survival time τ for $\kappa = \infty$ has been generalized by Torquato and Avellaneda [26] to treat the case of finite surface rate constant κ . Using this principle, they obtained the lower bound

$$\tau \geq \langle \delta \rangle^2 / D + \phi_1 / \kappa s, \quad (1)$$

where the general n th moment is defined by

$$\langle \delta^n \rangle = \int_0^\infty \delta^n P(\delta) d\delta, \quad (2)$$

and $P(\delta)$ is the *pore size distribution function*. $P(\delta) d\delta$ is the probability that a point in the pore region \mathcal{V}_1 lies at a distance between δ and $\delta + d\delta$ from the nearest point on the pore–solid interface $\partial\mathcal{V}$. This quantity contains some connectedness information (see section 3). Here s is the specific surface. Note that bound (1) is generally nontrivial (i.e., nonzero). These authors also derived lower bounds on the associated principal relaxation time T_1 . They [26] computed lower bounds on τ and T_1 for an interpenetrable-sphere model called the “cherry-pit” model [10] for several values of the *impenetrability index* λ . Fig. 2 compares the lower bounds (solid lines) on the dimensionless survival time $\tau D/a^2$ (where a is sphere radius) in the case $\kappa = \infty$ corresponding to simulation data [22] (dotted lines) for the model in the extreme limits $\lambda = 0$ and $\lambda = 1$ (corresponding to the cases of *fully penetrable* and *totally impenetrable* spheres, respectively). The lower bounds on τ become relatively sharper as the trap volume fraction ϕ_2 increases. To date, no one has derived an analogous nontrivial lower bound on the fluid permeability (i.e., a nonzero lower bound) for general porous media.

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 [1]. Until recently, application of such bounds (although in

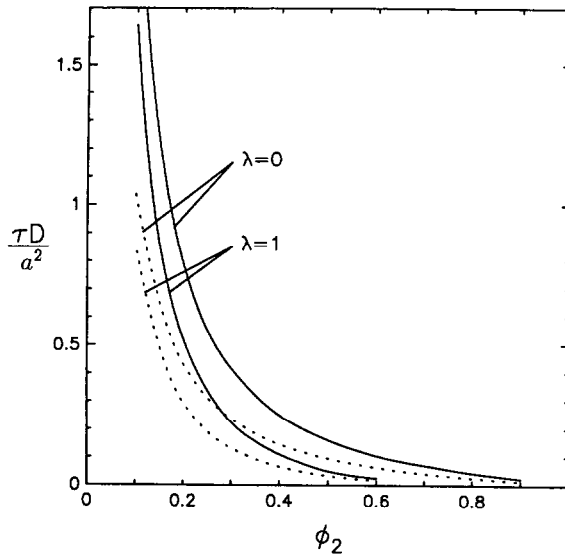


Fig. 2. Scaled mean survival time $\tau D/a^2$ versus trap volume fraction ϕ_2 in the extreme limits of the cherry-pit model [10] for traps of radius a at $\phi_2 = 0.5$.

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.

3.1. Unified theoretical approach

For statistically inhomogeneous systems of N identical d -dimensional spheres, Torquato [12] has introduced the general n -point distribution function $H_n(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q)$ which is defined to be the correlation associated with finding m points with positions \mathbf{x}^m on certain surfaces within the medium, $p-m$ with positions \mathbf{x}^{p-m} in certain spaces exterior to the spheres, and q sphere centers with positions \mathbf{r}^q , $n = p + q$. He also found a *series representation* of H_n which enables one to compute it. From the general quantity H_n one can obtain all of the aforementioned correlation functions and their generalizations [1,12]. This formalism has been generalized to treat polydispersed spheres [1,27], anisotropic media (e.g., aligned ellipsoids and cylinders) [1,14,21], and cell models [28].

3.2. Identification of essential morphological information

The goal ultimately is to ascertain the essential morphological information, quantify it theoretically or experimentally, and then employ the information to estimate the effective properties of the heterogeneous material. Practically

speaking, one is limited by the order of the correlation function; the lower the order, the easier it is to measure or obtain the correlation function. It is apparent that lower-order functions that reflect the topological property of *connectedness* of the phases are likely candidates for usage as essential signatures of the microstructure.

Lower-order S_n (such as S_2 and S_3) do not contain nontrivial connectedness information. By contrast, the aforementioned pore size distribution function $P(\delta)$ reflects some information about the connectedness of a spherical region of radius δ in phase 1. It is trivially related to the “void” nearest-neighbor distribution function [29]. In fig. 3, we depict $P(\delta)$ in the cherry-pit model for several values of the impenetrability index λ .

The “lineal-path function” $L(z)$ gives the probability of finding a line segment of length z wholly in phase 1 when randomly thrown into the sample. It is equivalent to the probability that a point can move along a *lineal path* of length z in phase i without passing through the other phase [30]. Hence, $L(z)$ contains *degenerate* connectedness information along a lineal path. $L(z)$ is a quantity of great stereological interest. We have exactly represented and computed $L(z)$ for various suspensions of monodispersed [30] as well as polydispersed spheres [31].

The *chord-length distribution function* $p(z)$ is related to the second derivative of $L(z)$ [32,33]. Chord lengths measure the distances between the intersections that a line makes with the two-phase interface. Using measurements of $p(z)$, Krohn and Thompson [34] showed that certain sedimentary rocks were fractal structures. The function $p(z)$ is also of basic importance in transport problems involving “discrete free paths” (e.g., Knudsen diffusion and radiative transport) and in

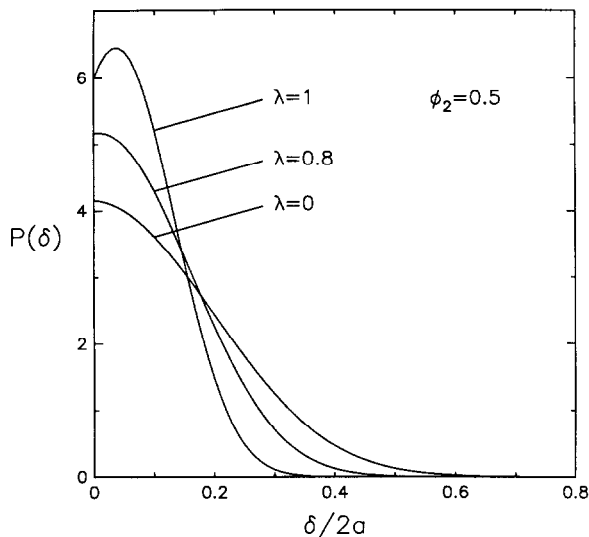


Fig. 3. Pore size distribution function $P(\delta)$ versus $\delta/2a$ for spheres of radius a in the cherry-pit model [10] for several values of the impenetrability index λ .

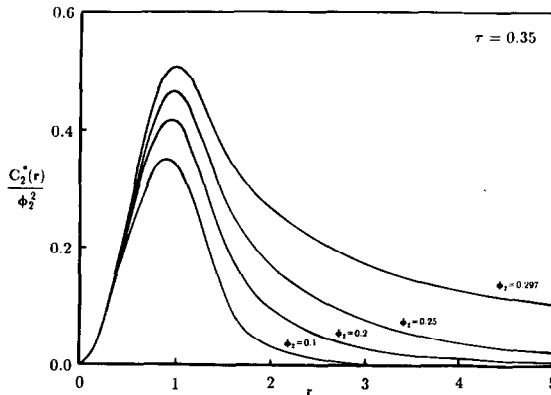


Fig. 4. Nontrivial part of the two-point cluster function $C_2^*(r)$ for “sticky spheres” of unit diameter and $\tau = 0.35$ at several sphere volume fractions: $\phi_2 = 0.1, 0.2, 0.25, 0.297$, respectively from left to right.

stereology. Using the relation between $p(z)$ and $L(z)$, we computed $p(z)$ for various sphere distributions [33].

Perhaps the most promising two-point morphological descriptor identified to date is the *two-point cluster function* $C_2(x_1, x_2)$ defined to be the probability of finding two points at positions x_1 and x_2 in one phase such that they have a connected path between them [35]. Thus, C_2 is the analogue of S_2 but reflects connectedness information. Torquato, Beasley and Chiew [35] obtained an exact series representation of C_2 for particle systems with an arbitrary interparticle potential. They applied their results by computing $C_2(r)$ (where $r = |x_2 - x_1|$) for distributions of “sticky” hard spheres parameterized by a stickiness index τ^{-1} . In fig. 4, the nontrivial part of the two-point cluster function $C_2^*(r)$ (divided by ϕ_2^2) is given for several values of the sphere volume fraction ϕ_2 up to the percolation threshold value for $\tau = 0.35$. For fixed r , $C_2^*(r)$ increases with increasing ϕ_2 , thus indicating the presence of increasingly larger clusters. At the threshold $\phi_2^c = 0.297$, $C_2^*(r)$ correctly becomes long-ranged because of the presence of an infinite cluster. Lee and Torquato [36] have computed C_2 for interpenetrable spheres in the *cherry-pit* model [10]. *The remaining challenge is to be able to incorporate $C_2(r)$ into a theory to predict effective properties for a wide range of conditions, even near the threshold.*

4. Rigorous cross-property relations

An intriguing fundamental as well as practical question in the study of heterogeneous materials is the following. Can different properties of the medium be *rigorously* linked to one another? Such cross-property relations become especially useful if one property is more easily measured than another property.

Since the effective properties of random media reflect certain morphological information on the medium, one might expect that one could extract useful information about one effective property given an exact determination of another property.

4.1. Link between permeability and diffusion properties

In the context of transport in porous media, rigorous links between the effective properties have been explored only very recently [26,37,38]. (It should be noted that a very useful approximate cross-property relation for the permeability was derived by Johnson, Koplik and Schwartz [39].) Torquato [37] derived the first rigorous relation connecting the permeability tensor to the mean survival time τ of a porous medium containing perfectly absorbing pore walls ($\kappa = \infty$). For d -dimensional isotropic media of arbitrary topology the following scalar relation holds:

$$k \leq D\phi_1\tau, \quad (3)$$

where D is the diffusion coefficient. Relation (3) becomes an equality for transport interior to parallel tubes of arbitrary cross section (in the direction of the tubes). The bound (3) is relatively sharp for flow around dilute arrays of obstacles. Moreover, for any *disconnected* pore space, k is zero while τ is nonzero, implying that τ does not reflect nontrivial topological information. For finite relation κ , (3) still holds. It is important to note that τ can be determined from a nuclear magnetic resonance (NMR) experiment [40].

More recently, Avellaneda and Torquato [38] derived the first rigorous relation connecting the permeability to the *effective electrical conductivity* σ_e of any isotropic porous medium, containing a conducting fluid of conductivity σ_1 and an insulating solid phase. Specifically, they found that

$$k = L^2/8F, \quad F = \sigma_1/\sigma_e, \quad (4)$$

where F is the *formation factor* and L is a length parameter which is a weighted sum over the *viscous relaxation times* associated with the time-dependent Stokes equations. The parameter L^2 reflects information about the “effective throat area for the fluid dynamically connected part of the pore space.” The quantity $L^2/8$ was bounded from above by DT_1 and thus [38]

$$k \leq DT_1/F, \quad (5)$$

where T_1 is the *principal diffusion relaxation time*. T_1 can also be obtained from NMR measurements.

It has been recently conjectured that for a wide class of isotropic media of arbitrary topology with formation factor F , the following relation holds [41]:

$$k \leq D\tau/F. \quad (6)$$

It is clear that because $F^{-1} \leq \phi_1$ and $\tau \leq T_1$ [26], the relation (6) for the

permeability will always be below or equal to either bound (3) or (5). The bound (6) is obeyed for a wide class of porous media but is not perfectly general [41].

Now we will apply eq. (5) in the vicinity of the threshold ϕ_1^c at which the fluid phase 1 becomes disconnected. It is believed that both the permeability and effective conductivity near the connectivity threshold (i.e., as $\phi_1 \rightarrow \phi_1^{c+}$) vanish as

$$k \sim (\phi_1 - \phi_1^c)^e, \quad \sigma_e \sim (\phi_1 - \phi_1^c)^t. \tag{7a,b}$$

Since the principal diffusion time T_1 does not vanish at the connectivity threshold ϕ_1^c but rather is a nonzero constant, then substitution of (7a,b) into (6) immediately yields the following critical-exponent relation which holds for any isotropic porous medium:

$$e \geq t. \tag{8}$$

Inequality (8) is borne out by many theoretical and simulation studies for specific model microstructures (see, e.g., ref. [42] and references therein). For example, for the “Swiss-cheese” model (randomly overlapping spheres), Feng, Halperin and Sen have shown [42] that

$$e - t = 3/2, \quad d = 2, \quad e - t = 2, \quad d = 3. \tag{9}$$

Finally, we note that in the vicinity of the threshold, the above relations imply that $L^2 \sim (\phi_1 - \phi_1^c)^\beta$, where $\beta = e - t$. Thus, generally $\beta \geq 0$.

The cross-property relations (3), (5) and (6) have been applied for a variety of of different model microstructures [37,38,41]. As an example, fig. 5 compares the cross-property inequalities (3) and (6) to permeability data (filled circles) [43] for fully penetrable or randomly overlapping spheres for a wide range of porosities ϕ_1 . (Relation (5) is not shown since T_1 is infinitely large for this model [26,41].) The

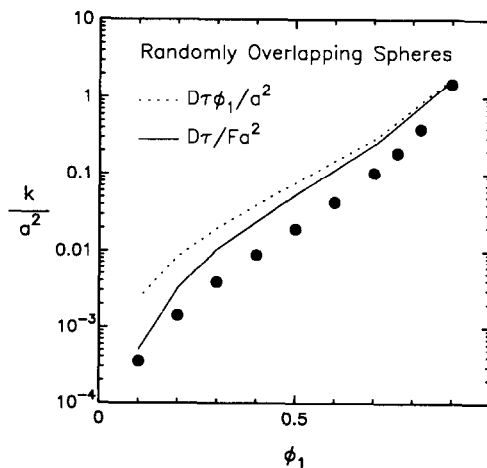


Fig. 5. Cross-property relations for the scaled fluid permeability k/a^2 versus porosity ϕ_1 for fully penetrable spheres of radius a . Circles are simulation data of ref. [43].

inequality (6) provides the better estimate of the data and is quite sharp at low porosities: a common situation in practice.

4.2. Link between conductivity and elastic moduli

Milton [44] showed that if the phase bulk moduli K_i equal the phase conductivities σ_i , then the effective bulk modulus K_e is bounded from above by the effective conductivity σ_e . It is trivial to extend Milton's result to the more general situation in which $K_2/K_1 \leq \sigma_2/\sigma_1$ as follows [45]:

$$K_e(K_1, K_2, G_1, G_2)/K_1 \leq \sigma_e(\sigma_1, \sigma_2)/\sigma_1, \quad K_2/K_1 \leq \sigma_2/\sigma_1, \quad (10)$$

where G_i is the shear modulus of phase i . This relation holds for any d -dimensional, isotropic, two-phase medium with positive phase Poisson's ratios ν_i .

Now using the relationship between G_e/K_e and the effective Poisson's ratio ν_e and the above result, it is easily shown [45] that the effective shear modulus G_e is bounded as

$$\frac{G_e(K_1, K_2, G_1, G_2)}{K_1} \leq \frac{\sigma_e(\sigma_1, \sigma_2)}{\sigma_1} \frac{d[1 - \nu_e(d-1)]}{2(1 + \nu_e)}, \quad K_2/K_1 \leq \sigma_2/\sigma_1. \quad (11)$$

A corollary of this relation for media characterized by a positive ν_e is the following weaker bound on G_e involving just the conductivity [45]:

$$\frac{G_e(K_1, K_2, G_1, G_2)}{K_1} \leq \frac{1}{2} \frac{d\sigma_e(\sigma_1, \sigma_2)}{\sigma_1}. \quad (12)$$

We now apply relations (10) and (12) to obtain relations among the critical exponents for elasticity and conduction. Consider the case in which phase 1 is an elastic material with nonzero values of K_1 , G_1 and E_1 , and phase 2 is a void phase. It is believed that the effective elastic moduli near the connectivity threshold (i.e., as $\phi_1 \rightarrow \phi_1^{c+}$) vanish as

$$K_e \sim (\phi_1 - \phi_1^c)^f, \quad G_e \sim (\phi_1 - \phi_1^c)^g, \quad (13a,b)$$

It is believed that $f = g$ for a wide class of random media. If this is the case, then it implies that the effective Poisson's ratio ν_e is generally a nonvanishing constant near ϕ_1^c .

Use of expressions (13a,b) yields the following critical-exponent relations valid for any isotropic d -dimensional two-phase medium:

$$f \geq t, \quad g \geq t. \quad (14a,b)$$

Again, these relations are borne out by theoretical and numerical studies on specific microgeometries [42].

More recently, Gibiansky and Torquato [46,47] have found the sharpest known cross-property bounds on the sets of pairs (σ_e, K_e) and (σ_e, G_e) that correspond to two-dimensional, isotropic composites of all possible microgeometries at a prescribed or unspecified volume fraction ϕ_i . These bounds enclose certain regions in the σ_e – K_e and σ_e – G_e planes, portions of which are realizable by certain microgeometries and thus optimal. For fixed volume fraction, the conductivity-bulk modulus bounds are defined by a *lens-shaped region* in the σ_e – K_e plane, whereas the conductivity-shear modulus bounds are represented by a *curvilinear trapezium* in the σ_e – G_e plane. The reader is referred to refs. [46,47] for further details. Some of these results are currently being extended to three dimensions. Interestingly, although the Gibiansky–Torquato upper bounds are generally sharper than (10) and (11), they cannot improve upon the critical-exponent bounds (14a,b).

How sharp are the Gibiansky–Torquato [46,47] conductivity-elastic moduli estimates given an exact determination of one of the effective properties? To examine this question we employ exact results for the effective conductivity [48] and effective elastic moduli [49] of hexagonal arrays of superconducting, superrigid inclusions (phase 2) in a matrix such that $K_2/K_1 = \infty$, $G_1/K_1 = G_2/K_2 = 0.4$ and $\sigma_2/\sigma_1 = \infty$. The conductivity-elastic moduli bounds are calculated using the conductivity data of ref. [48]. As Table 1 shows, the agreement between the bounds and the elastic-moduli data [49] is quite good, especially in the case of the bulk modulus. 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, our cross-property upper bound uses the fact that the infinite-contrast phase is disconnected via conductivity information.

Table 1

Comparison of the cross-property bounds with exact data for the bulk and shear moduli of a hexagonal array of superrigid, superconducting circular inclusions with $G_1/K_1 = G_2/K_2 = 0.4$. The moduli lower bounds K_e^L , G_e^L and upper bounds K_e^U , G_e^U are calculated from the Gibiansky–Torquato cross-property relations [46,47] and the exact conductivity data [48]. The exact elastic moduli K_e , G_e are obtained from ref. [49].

ϕ_2	K_e^L/K_1	K_e^L/K_1	K_e^U/K_1	G_e^L/G_1	G_e^L/G_1	G_e^U/G_1
0.10	1.16	1.16	1.16	1.17	1.17	1.25
0.20	1.35	1.35	1.35	1.39	1.39	1.56
0.30	1.60	1.60	1.60	1.67	1.68	1.96
0.40	1.93	1.93	1.93	2.04	2.08	2.50
0.50	2.40	2.40	2.40	2.56	2.69	3.26
0.60	3.10	3.11	3.12	3.33	3.69	4.41
0.70	4.27	4.33	4.37	4.63	5.54	6.41
0.80	6.60	7.15	7.27	7.22	10.00	11.08
0.85	8.93	11.00	11.27	9.81	16.30	17.50

5. Conclusions

It is the morphology that provides the link between seemingly disparate physical properties of heterogeneous materials. An effective property is a functional of the relevant local fields weighted with certain correlation functions that statistically characterize the morphology. Generally, the type of correlation function involved depends on the specific physical problem that one studies. However, it has been shown that all of the apparently different types of correlation functions can be obtained from a single, grand function called H_n and, consequently, can be shown to be related to one another. When viewed in this unified light, it is not surprising that knowledge of one effective property of an heterogeneous material (a reflection of the morphology) generally places constraints (upper and lower bounds) on the allowable values of other properties. This paper demonstrates that such a unified approach to study macroscopic properties of heterogeneous media is both natural and very powerful.

Acknowledgements

I am deeply indebted to my collaborators who have made invaluable contributions to much of the research described here. I gratefully acknowledge the support of the US Department of Energy under Grant DE-FG05-92ER14275.

References

- [1] S. Torquato, *Appl. Mech. Rev.* 44 (1991) 37.
- [2] Z. Hashin and S. Shtrikman, *J. Appl. Phys.* 33 (1962) 1514.
- [3] Z. Hashin and S. Shtrikman, *J. Mech. Phys. Solid* 11 (1963) 127.
- [4] M.J. Beran, *Statistical Continuum Theories* (Wiley, New York, 1968).
- [5] G.W. Milton, *J. Appl. Phys.* 52 (1981) 5294.
- [6] G.W. Milton, *J. Mech. Phys. Solids* 30 (1982) 177.
- [7] J.G. Berryman and G.W. Milton, *J. Chem. Phys.* 83 (1985) 754.
- [8] J. Rubinstein and S. Torquato, *J. Chem. Phys.* 88 (1988) 6372.
- [9] J. Rubinstein and S. Torquato, *J. Fluid Mech.* 206 (1989) 25.
- [10] S. Torquato, *J. Chem. Phys.* 84 (1986) 6345.
- [11] M. Doi, *J. Phys. Soc. J.* 40 (1976) 567.
- [12] S. Torquato, *J. Stat. Phys.* 45 (1986) 843.
- [13] C.A. Miller and S. Torquato, *J. Appl. Phys.* 68 (1990) 5486.
- [14] S. Torquato and A.K. Sen, *J. Appl. Phys.* 67 (1990) 1145.
- [15] S. Torquato and F. Lado, *Proc. R. Soc. London A* 417 (1988) 59.
- [16] S. Torquato and F. Lado, *J. Appl. Mech.* 59 (1992) 1.
- [17] I.C. Kim and S. Torquato, *J. Appl. Phys.* 68 (1990) 3892.
- [18] I.C. Kim and S. Torquato, *J. Appl. Phys.* 69 (1991) 2280.
- [19] I.C. Kim and S. Torquato, *J. Appl. Phys.* 74 (1993) 1844.
- [20] C.A. Miller and S. Torquato, *J. Appl. Phys.* 69 (1991) 1948.
- [21] S. Torquato and F. Lado, *J. Chem. Phys.* 94 (1991) 4453.

- [22] C.A. Miller, I.C. Kim and S. Torquato, *J. Chem. Phys.* 94 (1991) 5592.
- [23] S. Torquato and J. Rubinstein, *J. Appl. Phys.* 69 (1991) 7118.
- [24] O.P. Bruno, *Proc. R. Soc. Lond. A* 433 (1991) 353.
- [25] J.B. Keller, L. Rubinfeld and J. Molyneux, *J. Fluid Mech.* 30 (1967) 97.
- [26] S. Torquato and M. Avellaneda, *J. Chem. Phys.* 95 (1991) 6477.
- [27] B. Lu and S. Torquato, *Phys. Rev. A* 43 (1991) 2078.
- [28] B. Lu and S. Torquato, *Phys. Rev. B* 42 (1990) 4453.
- [29] S. Torquato, B. Lu and J. Rubinstein, *Phys. Rev. A* 41 (1990) 2059.
- [30] B. Lu and S. Torquato, *Phys. Rev. A* 45 (1992) 5530.
- [31] B. Lu and S. Torquato, *Phys. Rev. A* 45 (1992) 7292.
- [32] G. Matheron, *Elements Pour Une Theorie Des Milieux Poreux* (Masson, Paris, 1967).
- [33] S. Torquato and B. Lu, *Phys. Rev. E* 47 (1993) 2950.
- [34] C.E. Krohn and A.H. Thompson, *Phys. Rev. A* 32 (1985) 280.
- [35] S. Torquato, J.D. Beasley and Y.C. Chiew, *J. Chem. Phys.* 88 (1988) 6540.
- [36] S.B. Lee and S. Torquato, *J. Chem. Phys.* 91 (1989) 1173.
- [37] S. Torquato, *Phys. Rev. Lett.* 64 (1990) 2644.
- [38] M. Avellaneda and S. Torquato, *Phys. Fluids A* 3 (1991) 2529.
- [39] D.L. Johnson, J. Koplik and L.M. Schwartz, *Phys. Rev. Lett.* 57 (1986) 2564.
- [40] D.J. Wilkinson, D.L. Johnson and L.M. Schwartz, *Phys. Rev. B* 44 (1991) 4960.
- [41] S. Torquato and I.C. Kim, *J. Appl. Phys.* 72 (1992) 2612.
- [42] S. Feng, B.I. Halperin and P.N. Sen, *Phys. Rev. B* 35 (1987) 197.
- [43] A. Cancelliere, C. Chang, E. Foti, D. Rothman and S. Succi, *Phys. Fluids A* 2 (1990) 2085.
- [44] G.W. Milton, in: *Physics and Chemistry of Porous Media*, eds D.L. Johnson and P.N. Sen (American Institute of Physics, New York, 1984).
- [45] S. Torquato, in: *Macroscopic behavior of Heterogeneous Materials from the Microstructure*, eds S. Torquato and D. Krajcinovic (ASME) AMD 147 (1992) 53.
- [46] L.V. Gibiansky and S. Torquato, in: *Homogenization and Constitutive Modeling for Heterogeneous Materials*, eds C.S. Chang and J.W. Ju (ASME) AMD 166 (1993).
- [47] L.V. Gibiansky and S. Torquato, *Phys. Rev. Lett.* 71 (1993) 2927.
- [48] W.T. Perrins, D.R. McKenzie and R.C. McPhedran, *Proc. R. Soc. London A* 329 (1979) 207.
- [49] J.W. Eischen and S. Torquato, *J. Appl. Phys.* 74 (1993) 159.