Necessary Conditions on Realizable Two-Point Correlation Functions of Random Media†

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A fascinating inverse problem that has been receiving considerable attention is the construction of realizations of random two-phase heterogeneous media with a target two-point correlation function. However, not every hypothetical two-point correlation function corresponds to a realizable two-phase medium. Here, we collect all of the known necessary conditions on the two-point correlation functions scattered throughout a diverse literature and derive a new, but simple, positivity condition. We apply the necessary conditions to test the realizability of certain classes of proposed correlation functions.

1. Introduction

Random two-phase heterogeneous media abound in synthetic products and nature. Examples include composite materials, colloidal dispersions, gels, foams, wood, geologic media, and animal and plant tissue.[1−5] The effective transport, mechanical, and electromagnetic properties of such heterogeneous materials are known to be dependent on correlation functions that statistically characterize the microstructure.[3] It has recently been suggested that microstructure reconstruction problems can be posed as optimization problems.[6,7] A set of *target* correlation functions are prescribed, based on experiments or theoretical models. Starting from some initial realization of the random two-phase medium, the reconstruction method proceeds to find a realization by evolving the microstructure such that the calculated correlation functions best match the target functions. This intriguing inverse problem is solved by minimizing an *error* based on the distance between the target and calculated correlation functions. The two-phase medium can be a dispersion of particles in some matrix (liquid or solid)[6] or, more generally, a digitized image of a two-phase material.[7]

An effective reconstruction procedure enables one to generate accurate structures at will, and subsequent analysis can be performed on the image to obtain desired macroscopic properties (e.g., transport, electromagnetic, and mechanical properties) of the media. This becomes especially useful in generating three-dimensional structures from planar information when three-dimensional imaging techniques are not available (a "poor man's" tomography experiment).[3,8]

Interestingly, the same procedure has been used to "construct" realizations of two-phase media from a hypothetical target correlation function.[3,7,9,10] In this mode, the procedure is called a *construction* algorithm. There are many different types of statistical descriptors of two-phase media;[3] however, the most basic one is the two-point correlation function, which gives the probability of finding two points in one of the phases (see definition below) and is obtainable from small-angle X-ray scattering.[11] The construction algorithm can be used to determine if a prescribed two-point correlation function is, in fact, realizable. If such a two-point correlation function is realizable, then the procedure could be used to categorize classes of random microstructures, which would be a valuable accomplishment. However, not every hypothetical two-point correlation function corresponds to a realizable two-phase medium.[3] Therefore, it is of great fundamental and practical importance to determine the necessary conditions that realizable two-point correlation functions must possess.[3,12] We note, in passing, that this question is closely related to realizability issues of pair-correlation functions of many-particle systems.[13−15]

One objective of this paper is to gather all of the known necessary conditions on the two-point correlation function of two-phase random media, also known as "random closed sets" in the field of stochastic geometry.[16,17] Some of these conditions are well-known in the physical sciences literature, but others are more arcane and are contained in obscure mathematical technical reports and/or proceedings. We also derive a new but simple positivity condition on the two-point correlation function. We consider some illustrative examples of proposed correlation functions and test whether they can correspond to realizable two-phase random media.

2. Necessary Conditions

Here, we collect all of the known necessary conditions on the two-point correlation function of random media that are scattered throughout a diverse literature. We also derive a new positivity condition.

Each realization ω of the two-phase random medium occupies the region of d-dimensional Euclidean space $\mathcal{V} \in \mathcal{R}^d$ of volume V that is partitioned into two *random* sets or *phases*, whose interiors are disjoint: phase 1, a region $\mathcal{V}_1(\omega)$ of volume fraction ϕ_1, and phase 2, a region $\mathcal{V}_2(\omega)$ of volume fraction ϕ_2. For a given realization ω, the *indicator function* $\mathcal{I}^{(i)}(\mathbf{x}; \omega)$ for phase i at any position vector $\mathbf{x} \in \mathcal{V}$ is defined by

$$\mathcal{I}^{(i)}(\mathbf{x}; \omega) = \begin{cases} 1, & \text{if } \mathbf{x} \in \mathcal{V}_i(\omega) \\ 0, & \text{otherwise} \end{cases} \tag{1}$$

Thus, a two-phase random medium is described by a binary stochastic process $\{\mathcal{I}^{(i)}(\mathbf{x})\colon \mathbf{x} \in \mathcal{R}^d\}$. For statistically homogeneous but anisotropic media, the first two correlation functions are given by[3]

$$S_1^{(i)}(\mathbf{x}) = \langle \mathcal{I}^{(i)}(\mathbf{x}) \rangle = \phi_i \tag{2}$$

† It is a great pleasure and privilege for the author to contribute an article in a volume to honor the career of William B. Russel on the occasion of his 60th birthday.

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and

$$S_2^{(i)}(\mathbf{r}) = \langle \mathscr{I}^{(i)}(\mathbf{x}_1)\mathscr{I}^{(i)}(\mathbf{x}_2)\rangle \tag{3}$$

where $i = 1$ or 2, angular brackets denote an ensemble average, $\mathbf{r} = \mathbf{x}_1 - \mathbf{x}_2$, and the symbol ω is henceforth dropped for brevity. (The generalization to n-point correlation functions for $n \geq 1$ is straightforward.[3]) Clearly, ϕ_i lies in the closed interval [0, 1] and $\phi_1 + \phi_2 = 1$. The two-point or autocorrelation function $S_2^{(i)}(\mathbf{r})$ for statistically homogeneous media gives the probability of finding the end points of a vector $\mathbf{r}$ in phase i. Debye and Bueche[11] showed that the two-point correlation function of a porous medium can be obtained experimentally via small X-ray scattering. Note that the two-point function for phase 2 is simply related to the corresponding function for phase 1 via the expression

$$S_2^{(2)}(\mathbf{r}) = S_2^{(1)}(\mathbf{r}) - 2\phi_1 + 1 \tag{4}$$

and, thus, the *autocovariance* function

$$\chi(\mathbf{r}) \equiv S_2^{(1)}(\mathbf{r}) - {\phi_1}^2 = S_2^{(2)}(\mathbf{r}) - {\phi_2}^2 \tag{5}$$

for phase 1 is equal to that for phase 2. Generally, for $\mathbf{r} = 0$,

$$S_2^{(i)}(0) = \phi_i \tag{6}$$

and in the absence of any *long-range* order,

$$\lim_{|\mathbf{r}|\to\infty} S_2^{(i)}(\mathbf{r}) \to {\phi_i}^2 \tag{7}$$

An important necessary condition for the existence of a two-point correlation function $S_2^{(i)}(\mathbf{r})$ for a two-phase statistically homogeneous medium with d dimensions is that the d-dimensional Fourier transform of autocovariance $\chi(\mathbf{r})$, denoted by $\tilde{\chi}(\mathbf{k})$, must be non-negative for all wave vectors,[3] i.e.,

$$\tilde{\chi}(\mathbf{k}) = \int_{\mathscr{R}^d} \chi(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} \geq 0 \qquad \text{(for all } \mathbf{k}\text{)} \tag{8}$$

where $\chi(\mathbf{r})$ is given by eq 5. Physically, this non-negativity condition results because $\tilde{\chi}(\mathbf{k})$ is proportional to the scattered intensity, which must be positive.[3] This is sometimes called the Wiener−Khintchine condition,[3] which is necessary but not sufficient for the class B correlation functions that come from binary stochastic processes $\{\mathscr{I}^{(i)}(\mathbf{x}): \mathbf{x} \in \mathscr{R}^d\}$. The Wiener−Khinchtine condition is easily proved by exploiting a well-known theorem that states any continuous function $\chi(\mathbf{r})$ must be positive semi-definite (non-negative) in the sense that for any finite number of spatial locations $\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_m$ in $\mathscr{R}^d$ and arbitrary real numbers $a_1, a_2, ..., a_m$,

$$\sum_{i=1}^{m}\sum_{j=1}^{m} a_i a_j \chi(\mathbf{r}_i - \mathbf{r}_j) \geq 0 \tag{9}$$

if and only if it has a non-negative Fourier transform $\tilde{\chi}(\mathbf{k})$. Note that this property does not prevent $\chi(\mathbf{r})$ from being pointwise negative for certain values of $\mathbf{r}$. Importantly, whereas the real-space condition is difficult to check, the spectral version (eq 8) is straightforward to test. It is noteworthy that if the medium in d dimensions is both statistically homogeneous and isotropic, then the one-, two-, ..., and d-dimensional Fourier transforms of $\chi(\mathbf{r})$ must all be non-negative.[12] This is a consequence of the fact that $\chi(\mathbf{r})$ for such a random medium is an invariant in any m-dimensional subspace, where $m = 1, 2, ..., (d - 1)$.

The task of determining the necessary and sufficient conditions that B must possess is very complex. It has been shown that autocovariance functions in B must not only meet the condition of eq 8 but another condition on "corner-positive" matrices.[3] Little is known about corner-positive matrices; therefore, this theorem is very difficult to apply in practice. Thus, a meaningful characterization of B remains an open and interesting problem, especially in the context of d-dimensional two-phase random media.

No attempt will be made to address the complete characterization of B here; instead, we summarize the known necessary conditions, in addition to the condition 8, that characterize B, most of which are described in ref 3. The two-point correlation function must satisfy the bounds

$$0 \leq S_2^{(i)}(\mathbf{r}) \leq \phi_i \qquad \text{(for all } \mathbf{r}\text{)} \tag{10}$$

The lower bound states that $S_2^{(i)}(\mathbf{r})$ must be non-negative for all $\mathbf{r}$, but in the discussion presented below, we show that either $S_2^{(1)}(\mathbf{r})$ or $S_2^{(2)}(\mathbf{r})$ must strictly be positive for $\phi_i \neq {}^1/_2$. The corresponding bounds on the autocovariance function are given by[3]

$$-\min({\phi_1}^2, {\phi_2}^2) \leq \chi(\mathbf{r}) \leq \phi_1\phi_2 \qquad \text{(for all } \mathbf{r}\text{)} \tag{11}$$

Another consequence of the binary nature of the process in the case of statistically homogeneous and isotropic media, i.e., when $S_2^{(i)}(\mathbf{r})$ is dependent only on the distance $r \equiv |\mathbf{r}|$, is that its derivative at $r = 0$ is strictly negative, or

$$\left.\frac{dS_2^{(i)}}{dr}\right|_{r=0} = \left.\frac{d\chi}{dr}\right|_{r=0} < 0 \qquad \text{(for all } 0 < \phi_i < 1\text{)} \tag{12}$$

This is a consequence of the fact that slope at $r = 0$ is proportional to the negative of the specific surface.[3] This means that $S_2^{(i)}(\mathbf{r})$ has a cusp at the origin, implying that the two-point function is nonanalytic at the origin. It is a property of binary processes that if $\chi_1(\mathbf{r})$ and $\chi_2(\mathbf{r})$ are in B, then $\chi_1(\mathbf{r})\cdot\chi_2(\mathbf{r})$ is in B and $\alpha\chi_1(\mathbf{r}) + (1 - \alpha\chi_2(\mathbf{r})$ is in B for every α in [0, 1]. This was proven by Shepp[18] in one dimension, but the proof should extend trivially to d dimensions.

A little-known necessary condition for statistically homogeneous media is the so-called "triangular inequality" that was first derived by Shepp[18] and later rediscovered by Matheron:[19]

$$S_2^{(i)}(\mathbf{r}) \geq S_2^{(i)}(\mathbf{s}) + S_2^{(i)}(\mathbf{t}) - \phi_i \tag{13}$$

where $\mathbf{r} = \mathbf{t} - \mathbf{s}$. The derivation of the triangular inequality 13 is straightforward. Following Shepp, we introduce the random variable $Y^{(i)}(\mathbf{x})$:

$$Y^{(i)}(\mathbf{x}) = 2\mathscr{I}^{(i)}(\mathbf{x}) - 1 = \begin{cases} 1 & (\text{if } \mathbf{x} \in \mathscr{V}_i) \\ -1 & (\text{otherwise}) \end{cases} \tag{14}$$

The mean of $Y^{(i)}(\mathbf{x})$ is $\langle Y^{(i)}(\mathbf{x})\rangle = 2\phi_i - 1$, which is equal to zero if $\phi_1 = \phi_2 = {}^1/_2$. Observe that $Y^{(i)}(\mathbf{x}_1) - Y^{(i)}(\mathbf{x}_2) + Y^{(i)}(\mathbf{x}_3)$ is an odd number (either -3, -1, 1, or 3) and, therefore,

$$\langle [Y^{(i)}(\mathbf{x}_1) - Y^{(i)}(\mathbf{x}_2) + Y^{(i)}(\mathbf{x}_3)]^2\rangle \geq 1 \tag{15}$$

Using the fact that $\langle Y^{(i)}(\mathbf{x}_1)Y^{(i)}(\mathbf{x}_2)\rangle = 4S_2^{(i)}(\mathbf{x}_1 - \mathbf{x}_2) - 4\phi_i + 1$, where we have invoked statistical homogeneity, we immediately obtain the triangular inequality 13.

Note that if the autocovariance $\chi(\mathbf{r})$ of a statistically homogeneous and isotropic medium is monotonically decreasing, nonnegative, and convex (i.e., $d^2\chi(r)/dr^2 \geq 0$), then it satisfies the triangular inequality 13.[20] The triangular inequality implies several pointwise conditions on the two-point correlation function. For example, for statistically homogeneous and isotropic media, the triangular inequality implies the condition 12, the fact that the steepest descent of the two-point correlation function occurs at the origin,[18] i.e.,

$$|S_2^{(i)}(0)| \geq |S_2^{(i)}(r)| \qquad \text{(for all } r\text{)} \tag{16}$$

and the fact that $S_2^{(i)}(\mathbf{r})$ must convex at the origin,[20] i.e.,

$$\left.\frac{d^2 S_2^{(i)}}{dr^2}\right|_{r=0} = \left.\frac{d^2\chi}{dr^2}\right|_{r=0} \geq 0 \tag{17}$$

From the "stochastic continuity" theorem for general stochastic processes,[21] it follows that if $S_2^{(i)}(r)$ is continuous at $r = 0$, then it is continuous for all r. This continuity condition can also be proven using the triangular inequality. Note that $S_2^{(i)}(r)$ can be discontinuous at the origin if the specific surface s is infinitely large.

The triangular inequality is actually a special case of the more-general condition[18]

$$\sum_{i=1}^{m}\sum_{j=1}^{m}\epsilon_i\epsilon_j\chi(\mathbf{r}_i - \mathbf{r}_j) \geq 1, \qquad (\text{for } \epsilon_i = \pm 1 \text{ (where } i = 1, ..., m \text{ and } m \text{ is odd)}) \tag{18}$$

This necessary condition is much stronger than expression 9, implying that there are other necessary conditions beyond those identified thus far. However, the condition 18 is difficult to check in practice, because it does not have a simple spectral analogue, in contrast to expression 9 (cf. eq 8). Note that the integers $\epsilon_i = \pm 1$ in expression 18 can be replaced with general integers, which would lead to an even more general condition on $\chi(\mathbf{r})$.

Here, we report a new simple consequence of the lower bound of expression 11. Because the autocovariance is the same for phase 1 and phase 2, then it immediately follows from the lower bound of expression 11 that

$$S_2^{(i)}(\mathbf{r}) \geq \max(0, 2\phi_i - 1) \qquad \text{(for all } \mathbf{r}\text{)} \tag{19}$$

Thus, for $\phi_i > 1/2$, $S_2^{(i)}(\mathbf{r})$ is strictly positive, such that it must be greater than $2\phi_i - 1$. Interestingly, the lower bound of expression 11 for the autocovariance $\chi(\mathbf{r})$, first obtained in ref 3, was derived from the trivial pointwise non-negativity condition $S_2^{(i)}(\mathbf{r}) \geq 0$. However, the consequences of going back to the two-point correlation function $S_2^{(i)}(\mathbf{r})$ were heretofore not examined. The nontrivial positivity condition 19 results because the statistics of phase 1 are not independent of the statistics of phase 2. Because ϕ_i^2 is the large-distance asymptotic limit of $S_2^{(i)}(\mathbf{r})$, its global minimum value or, more precisely, its infimum (greatest lower bound) must be less than or equal to ϕ_i^2. (Technically, one must consider the infimum and not the minimum, because the minimum may not actually be achieved, e.g., a monotonically decreasing function that only asymptotically approaches its minimum value of ϕ_i^2.) Clearly, the lower bound 19 holds for the infimum of $S_2^{(i)}(\mathbf{r})$, which will be denoted by $\inf[S_2^{(i)}(\mathbf{r})]$. In summary, the infimum of any two-point correlation function of a statistically homogeneous medium must satisfy the inequalities

$$\max(0, 2\phi_i - 1) \leq \inf[S_2^{(i)}(r)] \leq \phi_i^2 \tag{20}$$

(see Figure 1).

3. Illustrative Examples

It is convenient to introduce the scaled autocovariance function $f(\mathbf{r})$, which is defined as

$$f(\mathbf{r}) \equiv \frac{\chi(\mathbf{r})}{\phi_1\phi_2} = \frac{S_2^{(i)}(\mathbf{r}) - \phi_i^2}{\phi_1\phi_2} \qquad (\text{for } 0 \leq r < +\infty) \tag{21}$$

From expression 19, we obtain the triangular inequality for f:

$$f(\mathbf{r}) \geq f(\mathbf{s}) + f(\mathbf{t}) - 1 \tag{22}$$

Moreover, the bounds of expression 19 become

$$-\min\left[\frac{\phi_1}{\phi_2}, \frac{\phi_2}{\phi_1}\right] \leq f(\mathbf{r}) \leq 1 \qquad \text{(for all } \mathbf{r}\text{)} \tag{23}$$

Our focus in this paper will be hypothetical continuous functions $f(r)$ that are dependent on the distance $r = |\mathbf{r}|$ and could potentially correspond to statistically homogeneous and isotropic media without long-range order, such that $f(0) = 1$ and $f(r)$ tends toward zero as $r \rightarrow \infty$ sufficiently fast, so that the Fourier transform of $\chi(r) = S_2^{(i)}(\mathbf{r}) - \phi_i^2$ exists. The latter two properties of $f(r)$ ensure that $S_2^{(i)}(r)$ obeys its proper asymptotic limiting behaviors, as specified by expressions 6 and 7, respectively. When the scaled autocovariance $f(r)$ is dependent only on the magnitude $r = |\mathbf{r}|$, then the Fourier transform condition 8 on $\tilde{f}(k)$ can be written in any space dimension d as[22]

$$\tilde{f}(k) = (2\pi)^{d/2}\int_0^\infty r^{d-1} f(r)\frac{J_{(d/2)-1}(kr)}{(kr)^{(d/2)-1}}\,dr \geq 0 \tag{24}$$

where $k = |\mathbf{k}|$ and $J_\nu(x)$ is the Bessel function of order ν. The bounds defined by expression 20 are equivalent to

$$-\min\left[\frac{\phi_1}{\phi_2}, \frac{\phi_2}{\phi_1}\right] \leq f_{\inf} \leq 0 \tag{25}$$

where $f_{\inf}$ is the infimum of $f(r)$. Note that when function $f(r)$ is independent of the volume fraction ϕ_1, it would correspond, if realizable, to a two-phase medium with *phase-inversion symmetry*.[3] A two-phase random medium possesses phase-inversion symmetry if the geometry of phase 1 at volume fraction ϕ_1 is

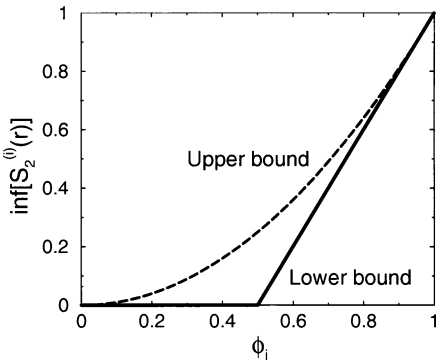


Figure 1. Graphs of the upper bound (dashed curve) and lower bound (solid lines) of expression 20 on the infimum of $S_2^{(i)}(r)$ for a statistically homogeneous medium.

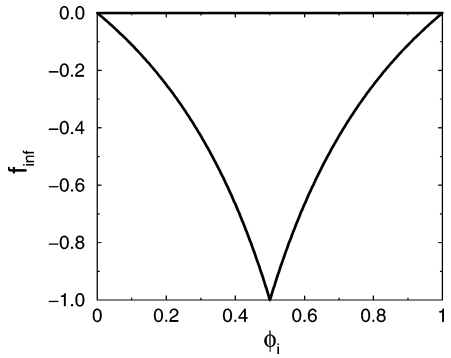


Figure 2. Graphical depiction of the bounds described by expression 25 on the infimum (f_{inf}) for volume-fraction-independent $f(r)$. The quantity f_{inf} must lie within the region delineated by the heavy solid lines.

statistically identical to that of phase 2 in the system where the volume fraction of phase 1 is ϕ_2 and, hence,

$$S_2^{(1)}(\mathbf{r}, \phi_1, \phi_2) = S_2^{(2)}(\mathbf{r}, \phi_2, \phi_1) \tag{26}$$

By construction, the upper bound of expression 25 is always satisfied. All of the functions $f(r)$ considered below are taken to be independent of the volume fraction ϕ_1, and, therefore, any violation of the lower bound of expression 25 implies that a two-phase statistically homogeneous and isotropic medium cannot exist for the following volume-fraction intervals:

$$0 < \phi_i < \frac{|f_{inf}|}{1 + |f_{inf}|} \tag{27a}$$

and

$$\frac{1}{1 + |f_{inf}|} < \phi_i < 1 \tag{27b}$$

Figure 2 depicts the bounds of expression 25 on f_{inf} for $f(r)$ that are independent of volume fraction.

First, we note that, for any $f(r)$ that monotonically decreases in r to its long-range value of zero, the pointwise non-negativity condition 23 is obeyed for $0 \le \phi_i \le 1$. However, as some examples below will demonstrate, such an $f(r)$ function does not necessarily obey the triangular inequality 22. A natural example of a monotonic scaled autocovariance function $f(r)$ is the simple exponentially decaying function, i.e.,

$$f(r) = \exp\left(-\frac{r}{a}\right) \tag{28}$$

where a is a positive parameter that we call the "correlation length". This function was first proposed by Debye and coworkers,[11,23] who believed that it should correspond to structures in which one phase consists of "random shapes and sizes" but presented no proof that such was the case. The function described by eq 28 obeys the necessary non-negativity condition 24 on the spectral function $\tilde{f}(k)$ for any d, as well as the triangular inequality 22. The satisfaction of these necessary conditions does not ensure that such a correlation is realizable. However, the aforementioned inverse optimization construction technique[3,7] was applied to generate a two-dimensional digitized realization corresponding to eq 28 (see Figure 3). This leads one to believe that eq 28 is exactly realizable. Indeed, there are specific two-phase microstructures that achieve the "Debye" random-medium function (eq 28) in the plane.[16] The function described by eq

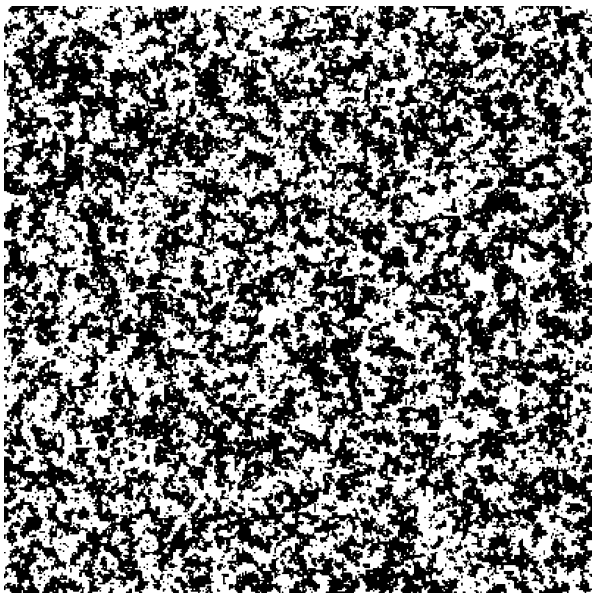


Figure 3. Construction of a digitized two-dimensional realization of a "Debye" random medium (400 pixels × 400 pixels).[3,7] Here, the volume fractions are $\phi_1 = \phi_2 = 0.5$ and the correlation length is $a = 2$ pixels.

28 is a special case of a more-general realizable subclass of B, given by the *completely monotonic functions*,[18] i.e.,

$$f(r) = \int_0^\infty \exp(-\lambda r)\, \mathrm{d}F(\lambda) \tag{29}$$

where $F(\lambda)$ is a non-negative bounded measure (bounded and nonincreasing function on $(0, \infty)$), i.e., $\mathrm{d}F \ge 0$ and $\int_0^\infty \mathrm{d}F(\lambda) = 1$. We see that if $F = \Theta(\lambda - a^{-1})$, then $\mathrm{d}F = \delta(\lambda - a^{-1})$ and eq 28 is recovered, where $\Theta(x)$ and $\delta(x)$ are the Heaviside and Dirac delta functions, respectively.

Another natural monotonic scaled autocovariance function $f(r)$ to consider is the Gaussian function, i.e.,

$$f(r) = \exp\left[-\left(\frac{r}{a}\right)^2\right] \tag{30}$$

Although any such Gaussian function has a non-negative spectral function $\tilde{f}(k)$, it cannot correspond to a two-phase random medium in $\mathscr{R}^d$, because the slope of $S_2^{(i)}(r)$ at $r = 0$ is zero (i.e., the specific surface is zero) and, therefore, violates the condition 12 or, more generally, the triangular inequality 22. For precisely the same reasons, the class of monotonic functions

$$f(r) = \exp\left[-\left(\frac{r}{a}\right)^\alpha\right] \qquad (\text{for any } \alpha > 1) \tag{31}$$

and

$$f(r) = \frac{1}{[1 + (r/a)^2]^{\beta - 1}} \qquad (\text{for any } \beta \ge d) \tag{32}$$

cannot correspond to a two-phase random medium in d dimensions. These specific examples, some of which are illustrated in Figure 4, show that the non-negativity condition 24 and the triangular inequality 13 are independent necessary conditions.

The final monotone function that we test is the simple linear function

$$f(r) = \begin{cases} 1 - (r/a) & (\text{if } r \le a) \\ 0 & (\text{otherwise}) \end{cases} \tag{33}$$

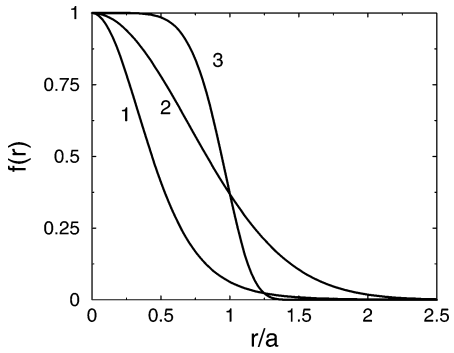


Figure 4. Examples of scaled autocovariance functions that cannot correspond to statistically homogeneous and isotropic two-phase random media: $f(r) = 1/(1 + r^2)^4$ for $d \leq 5$ (curve 1); $f(r) = \exp(-r^2)$ for any d (curve 2); and $f(r) = \exp(-r^6)$ for any d (curve 3).

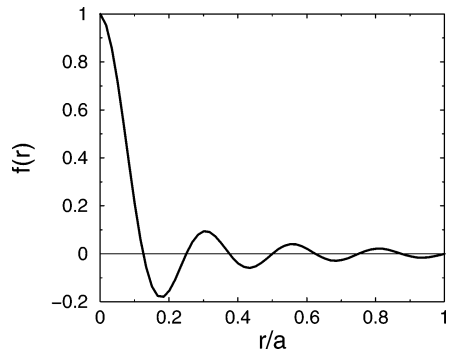


Figure 5. Graphical depiction of the damped sinusoidal function defined by eq 34, with $qa = 8\pi$.

Shepp[18] proved that such a scaled autocovariance is realizable by a statistically homogeneous two-phase medium in one dimension. However, this autocovariance is not realizable in higher dimensions, because its spectral function $\tilde{f}(k)$ can take on negative values for certain values of k. It is noteworthy that it has been shown that, for any positive definite $f(r)$ in one dimension, the function $2\arcsin(f)/\pi$, as well as $8\pi^{-2}\sum_k(2k + 1)^2 f((2k + 1)r)$ are in B.[18]

A generalization of the Debye random-medium function (eq 28) that is nonmonotone and would be characterized by short-range order is the following expression:[9]

$$f(r) = \mathrm{e}^{-r/a}\,\frac{\sin(qr)}{qr} \tag{34}$$

where q is an inverse length scale that controls oscillations in the term $\sin(qr)/(qr)$. The spectral function $\tilde{f}(k)$ of eq 34 in one, two, and three dimensions obeys the non-negativity condition 24. Interestingly, Torquato[3] observed that, although eq 34 satisfies the upper bound of the binary condition, as described by expression 11, it does not necessarily satisfy the lower bound of expression 11 or, equivalently, the lower bound of expression 23 for all ϕ_1, depending on the values of a and q. In other words, there are values of the infimum $f_{\inf}$ (which, in this case is a true global minimum) that violate the lower bound of expression 25. Let r_0 be the radial distance at which $f(r)$ achieves its global minimum. The minima of $f(r)$ are solutions to the transcendental equation $q(a + r)\tan(qr) = q^2ar$. The extremum value qr_0 can be shown to lie in the interval $[\pi, 3\pi/2)$ for arbitrary a and q. For example, for $aq = 8\pi$, $r_0 \approx 5.671a$ and $f_{\min} \approx -0.1818$ (see Figure 5) and, for $aq = 8\pi$, $r_0 \approx 0.1772a$ and $f_{\min} \approx -0.1818$ (see Figure 4), and therefore, according to expression 27, eq 34 is not realizable for the volume-fraction intervals

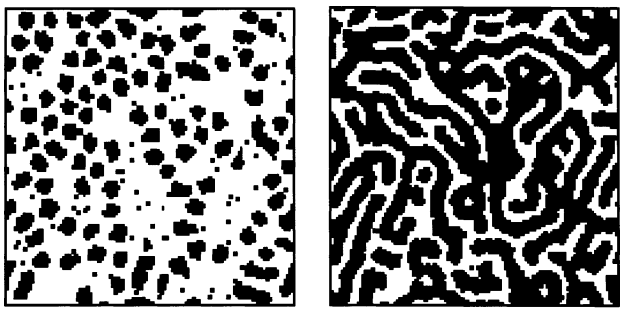


Figure 6. Construction of digitized two-dimensional realizations (400 pixels × 400 pixels) that computatively correspond to the target function given by eq 34 for $\phi_2 = 0.2$ and 0.5.[3,9] Here, $a = 32$ pixels and $q = 8\pi/a$. We now know that this function is not exactly realizable, because even though the construction technique matched eq 34 for almost all r, it could not yield the necessary convex behavior in the vicinity of the origin.

$$0 < \phi_i < 0.1538 \tag{35a}$$

and

$$0.8461 < \phi_i < 1 \tag{35b}$$

Interestingly, two realizations of digitized two-dimensional two-phase media were previously constructed[3,9] that putatively correspond to the scaled autocovariance function (eq 34) for $\phi_2 = 0.2$ and 0.5, respectively, and the aforementioned choice of a and q are shown in Figure 6. At $\phi_2 = 0.2$, the system resembles a *dilute particle suspension* with "particle" diameters of order b. At $\phi_2 = 0.5$, the resulting pattern is *labyrinthine*, such that the characteristic sizes of the "patches" and "walls" are of the order of a and $2\pi/q$, respectively. For these sets of parameters, all of the aforementioned necessary conditions on the function are met, except for the triangular inequality. Although eq 34 satisfies the negative slope condition 12 at the origin, it only satisfies the convexity condition 17 for $qa \leq \sqrt{3}$, which we see is violated in these instances, implying that the triangular inequality must be violated. As it turned out, the construction procedure matched the target function (eq 34) for almost all r, but it could not yield convex behavior in the vicinity of the origin. The triangular inequality was not known at the time; therefore, it was difficult to ascertain whether the slight discrepancy in the curvature of the function at the origin was numerical imprecision. We now know, in retrospect, that the construction technique revealed that a two-phase medium with a scaled autocovariance function (eq 34) cannot be exactly realized, which is a testament to the power of this method.

4. Conclusions

We have identified all of the known necessary conditions on the two-point correlation function $S_2^{(i)}(\mathbf{r})$ of statistically homogeneous two-phase media, and we have derived a new but simple positivity condition that it must satisfy. Using these conditions, we were able to ascertain the realizability of certain classes of proposed correlation functions. In future work, it will be important to identify other checkable necessary conditions. The stochastic optimization construction technique[3] appears to be a very powerful numerical tool in guiding such a search. Finally, we note that the analogous realizability problem for the pair correlation function g_2 of point processes[13−15,24,25] offers

many interesting challenges. It has recently been conjectured that the known standard non-negativity conditions on g_2 are sufficient to ensure the existence of point processes at and above some sufficiently high space dimension.[26,27] Application of this conjecture implies the possibility that the densest sphere packings in sufficiently high dimensions are disordered rather than periodic, implying the existence of disordered classical ground states for some continuous potentials. In future work, it would be interesting to investigate whether an analogous conjecture applies to binary stochastic processes.

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