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FUNCTIONAL SERIES AND HASHIN-SHTRIKMAN TYPE BOUNDS ON THE EFFECTIVE CONDUCTIVITY OF RANDOM MEDIA

K. Z. MARKOV[1] and Kr. D. ZVYATKOV[2]

[1]*Faculty of Mathematics and Informatics, "St. Kl. Ohridski" University of Sofia, 1126 Sofia, Bulgaria*

[2]*Institute of Mathematics and Informatics, "K. Preslavski" University, 9700 Schumen, Bulgaria*

A general method of placing variational bounds on the effective scalar conductivity of random heterogeneous solids is proposed. The method utilizes the Hashin-Shtrikman variational principle and trial fields which are obtained upon truncating the functional series expansion for the polarization field in the medium. It is shown how the earlier variational procedures due to Hashin and Shtrikman, Milton and Phan-Thien and Willis find natural places in the proposed general scheme. The new results reported include, for example, the fact of nonexistence of certain Gaussian-like random media and, for dispersions of spheres with volume fraction c, an exact $O(c^2)$ relation for the effective conductivity which contains absolutely convergent integrals only.

1 Introduction

In this paper we address the problem of variational bounding for the effective mechanical properties of random solids on the base of limited statistical information concerning their internal constitution. This problem has attracted considerable interest in the recent decades and one of the reasons is the fact that very little is usually known about the internal structure of a random medium of practical interest. The proposed variational techniques could be

roughly divided into two groups depending on whether the classical or Hashin-Shtrikman variational principles are used (cf. the survey of Willis (1981)). In each group the variational estimates are obtained by extremization of the respective functionals on certain subspaces of admissible trial fields and the success of the procedures depends heavily on their skillful choice.

In Markov (1987) a general class of trial fields has been proposed for the classical variational principle in the heat conductivity context. The fields are formed as truncated functional (Volterra-Wiener) series. These series appear in a natural way when representing the solution of the respective basic random problem as an infinite functional series, cf. Christov and Markov (1985) and Markov (1991), and we briefly recall the reasoning in Section 2. Let us note that such a choice of trial fields has led to the possibility to unify, simplify and generalize the earlier proposed variational techniques, based on the classical variational principles, due to Prager (1963), Beran (1965), Kröner (1977) et al., cf. Markov (1987) for details.

The aim of this paper is to trace and to identify, in a similar systematic manner, the various applications of truncated functional series as classes of trial polarization fields in the Hashin-Shtrikman variational principle. The outline of the paper is as follows. We first recall the principle in Section 2 and discuss the respective representations of polarization. The simplest class, for particulate media, is the choice of polarization as an arbitrary nonrandom function within the inclusions, but one and the same for all of them. For a dispersion of spheres, however, the best choice of the function is constant which leads to the classical Hashin-Shtrikman bounds (Section 3). The next approximation includes already a one-tuple term and, with a special choice of the integrand, it is a counterpart to the class admitted by Beran (1965). In the latter case the respective bounds were introduced and studied by Milton and Phan-Thien (1982) and Phan-Thien and Milton (1982) under the assumption of periodicity of the microstructure. We rederive these bounds for a general random medium and then specialize them to a medium of Gaussian type, for which the three-point moment vanishes and the four-point moment has an expression of Gaussian type through the two-point one. It turns out that such an assumption is unrealistic since the lower bound is greater than the upper (Section 5). For media of practical interest, say, for dispersions of spheres, the evaluation of the Phan-Thien–Milton bounds is extremely difficult, even to $O(c^2)$, where c is the volume fraction of the spheres. That is why we generalize first the class of trial polarizations, admitted by the Phan-Thien–Milton procedure and get in passing an exact expression to $O(c^2)$ for the effective conductivity of the dispersion which contains only absolutely convergent integrals (Section 6). We then modify the general class of polarizations and reach in a natural way the procedure of Willis (1978), see Section 7, where the correct final form of the Willis bound is given.

Let us point out finally that many details and a number of results will be deliberately skipped here in order to be able to concentrate on the basic ideas of the proposed variational procedures. A detailed exposition, containing in particular a discussion of the respective Hashin-Shtrikman type bounds on the elastic moduli for dispersions of spheres, will be given in the survey of the authors (Markov and Zvyatkov, 1994).

2 The Hashin-Shtrikman principle and the trial polarizations

We first recall the basic random problem in the theory of heterogeneous composite media, cf. Beran (1968). For simplicity we shall deal hereafter with the scalar conductivity case only:

$$\nabla \cdot \mathbf{q}(\mathbf{x}) = 0,\ \mathbf{q}(\mathbf{x}) = \kappa(\mathbf{x})\nabla\theta(\mathbf{x}),\ \langle \nabla\theta(\mathbf{x})\rangle = \mathbf{G}, \tag{2.1}$$

where $\kappa(\mathbf{x})$ is the given random conductivity field, $\theta(\mathbf{x})$—the temperature field, $\mathbf{q}(\mathbf{x})$—the heat flux vector, $\mathbf{G}$ is the prescribed temperature gradient. The brackets $\langle\cdot\rangle$ denote statistical averaging. Hereafter the media are assumed statistically homogeneous and isotropic. The solution of (2.1) is understood in a statistical sense, so that one is to get all multipoint moments (correlation functions) of $\theta(\mathbf{x})$ and the joint moments of $\kappa(\mathbf{x})$ and $\theta(\mathbf{x})$. Among the latter is the one-point moment

$$\langle \kappa(\mathbf{x})\nabla\theta(\mathbf{x})\rangle = \kappa^*\mathbf{G}, \tag{2.2}$$

where κ^* is the effective conductivity of the medium.

As noted by Christov and Markov (1985), the problem (2.1) defines implicitly a nonlinear operator $\mathfrak{F}$ that transforms the known field $\kappa(\mathbf{x})$ (the "input") into the temperature field $\theta(\mathbf{x})$ (the "output"). Following the general idea of the system theory, cf. e.g., Schetzen (1980), it is natural to expand the operator $\mathfrak{F}$ as a functional (Volterra-Wiener) series, generated by the input $\kappa(\mathbf{x})$

$$\theta(\mathbf{x}) = \mathbf{G}\cdot\mathbf{x} + \int T_1(\mathbf{x}-\mathbf{y})\kappa'(\mathbf{y})\,d^3\mathbf{y}$$
$$+\iint T_2(\mathbf{x}-\mathbf{y}_1,\mathbf{x}-\mathbf{y}_2)[\kappa'(\mathbf{y}_1)\kappa'\mathbf{y}_2) - M_2^\kappa(\mathbf{y}_1-\mathbf{y}_2)]\,d^3\mathbf{y}_1 d^3\mathbf{y}_2 + \cdots, \tag{2.3}$$

with certain nonrandom kernels T_i, $i = 0, 1, \ldots$, and to truncate this series afterwards. In (2.3) $\kappa'(\mathbf{x}) = \kappa(\mathbf{x}) - \langle\kappa\rangle$, $M_2^\kappa(\mathbf{x}-\mathbf{y}) = \langle\kappa'(\mathbf{x})\kappa'(\mathbf{y})\rangle$. (We assume the medium unbounded so that the integrals hereafter are taken over the whole $\mathbb{R}^3$ if the integration domain is not explicitly indicated.) Two types of applications for such truncated series could be envisaged. The first is to use them as approximate, in a certain sense, solutions of the problem (2.1). This possibility was discussed in more detail and worked out in the case of random dispersions of spheres in Markov (1989, 1991), see also Markov and Christov (1992). The second is to

employ them as classes of trial fields, say, for the classical variational principle, corresponding to (2.1), namely

$$W[\theta(\cdot)] = \Big\langle \kappa(\mathbf{x})|\nabla\theta(\mathbf{x})|^2 \Big\rangle \to \min,\ \langle\nabla\theta(\mathbf{x})\rangle = \mathbf{G}, \tag{2.4}$$

and $W_{\min} = \kappa^* G^2$. This idea was developed by Markov (1987), where it was shown how the earlier proposed variational techniques could be put into this frame. For example, the Beran method (1965) is a Ritz type procedure in which one truncates (2.3) after the one-tuple term and chooses the kernel T_1 in a special (Beran's) form:

$$\mathcal{K}_B = \Big\{ \theta(\mathbf{x}) \mid \theta(\mathbf{x}) = \mathbf{G}\cdot\mathbf{x} + \lambda\mathbf{G}\cdot\int \nabla\frac{1}{4\pi|\mathbf{x}-\mathbf{y}|}\kappa'(\mathbf{y})\,d^3\mathbf{y},\ \lambda\in\mathbb{R}\Big\}. \tag{2.5}$$

Let us recall now the Hashin-Shtrikman variational principle. To this end we introduce a homogeneous "comparison" medium, with conductivity κ_0, and define the so-called polarization field as

$$\mathbf{p}(\mathbf{x}) = \widetilde{\kappa}(\mathbf{x})\nabla\theta(\mathbf{x}),\ \widetilde{\kappa}(\mathbf{x}) = \kappa(\mathbf{x}) - \kappa_0. \tag{2.6}$$

The Hashin-Shtrikman principle governs, in a variational form, the field $\mathbf{p}(\mathbf{x})$; it states that the functional

$$U[\mathbf{p}(\cdot)] = \kappa_0 G^2 + \Big\langle 2\mathbf{p}(\mathbf{x})\cdot\mathbf{G} + \mathbf{p}(\mathbf{x})\cdot\nabla\theta'(\mathbf{x}) - \mathbf{p}(\mathbf{x})\cdot\mathbf{p}(\mathbf{x})/\widetilde{\kappa}(\mathbf{x})\Big\rangle \tag{2.7}$$

has a stationary value for the actual polarization field in the medium, i.e., for the field $\mathbf{p}(\mathbf{x}) = \widetilde{\kappa}(\mathbf{x})\nabla\theta(\mathbf{x})$, where $\theta(\mathbf{x})$ is the actual temperature field—the solution of the problem (2.1). Moreover,

$$U_{\text{ext}} = \kappa^* G^2 \tag{2.8}$$

and this is the maximum or minimum value of U whenever $\kappa(\mathbf{x}) \geq \kappa_0$ or $\kappa(\mathbf{x}) \leq \kappa_0$ respectively. In (2.7) $\theta'(\mathbf{x})$ is the solution of the equation $\kappa_0\Delta\theta'(\mathbf{x}) + \nabla\cdot\mathbf{p}(\mathbf{x}) = 0$, for which $\langle\nabla\theta'(\mathbf{x})\rangle = 0$; the prime denotes fluctuating parts.

The general form of the polarization field in the medium could be easily obtained if we insert the series (2.3) into (2.6)

$$\mathbf{p}(\mathbf{x}) = \widetilde{\kappa}(\mathbf{x})\Big\{\mathbf{G} + \int \mathbf{K}_1(\mathbf{x}-\mathbf{y})\kappa'(\mathbf{y})\,d^3\mathbf{y}$$

$$+\iint \mathbf{K}_2(\mathbf{x}-\mathbf{y}_1,\mathbf{x}-\mathbf{y}_2)[\kappa'(\mathbf{y}_1)\kappa'(\mathbf{y}_2) - M_2^{\kappa}(\mathbf{y}_1-\mathbf{y}_2)]\,d^3\mathbf{y}_1\,d^3\mathbf{y}_2 + \cdots\Big\}. \tag{2.9}$$

The first few kernels $\mathbf{K}_i$ could be specified, e.g., from the perturbation solution of the respective integral equation for the polarization field in the case of a weakly inhomogeneous medium. It appears, in particular, that

$$\mathbf{K}_1(\mathbf{x}) = \frac{1}{\langle\kappa\rangle}\mathbf{G}\cdot\nabla\left(\nabla\frac{1}{4\pi|\mathbf{x}|}\right), \tag{2.10}$$

which is proportional to the integrand gradient in the Beran class (2.5). However, instead of looking for the exact form of the kernels in (2.9), we could truncate this series and use the results, similarly to the classical principle (2.4), as classes of trial polarization fields in the Hashin-Shtrikman principle (2.7), introducing adjustable multipliers, varying the kernels and employing Ritz type procedures. All bounds obtained in this way will be called in what follows bounds of Hashin-Shtrikman type.

Let us illustrate the above in the simplest cases.

First, we could truncate the series (2.9) after the constant $\mathbf{G}$. Since no restrictions are imposed on the polarization field, we could multiply the result by an adjustable scalar $\lambda \in \mathbb{R}$. We are thus led to the class of trial fields

$$\mathcal{P}^{(1)} = \{\, \mathbf{p}(\mathbf{x}) \mid \mathbf{p}(\mathbf{x}) = \lambda\widetilde{\kappa}(\mathbf{x})\mathbf{G} \,\}, \tag{2.11}$$

to be considered in more detail in Section 3.

The truncation of the series (2.9) after the one-tuple term leads to the more general class of trial fields

$$\mathcal{P}^{(2)} = \Big\{\, \mathbf{p}(\mathbf{x}) \mid \mathbf{p}(\mathbf{x}) = \widetilde{\kappa}(\mathbf{x})\Big(\lambda\mathbf{G} + \int \mathbf{K}(\mathbf{x}-\mathbf{y})\kappa'(\mathbf{y})\, d^3\mathbf{y}\Big) \,\Big\}, \tag{2.12}$$

where now both λ and $\mathbf{K}(\mathbf{x})$ are adjustable. This class will be discussed in Section 4. Hereafter we drop the subscript '1' in the notation $\mathbf{K}_1$ for the kernel in the one-tuple term, since only the latter will be used and discussed.

3 The two-point bounds

Consider first the restriction of the functional U over the class of polarization fields (2.11). This restriction is obviously a quadratic function of λ. Its extremization yields, after some algebra,

$$\kappa^{(2)}_{HS} = \kappa_0 + \frac{\langle\widetilde{\kappa}\rangle^2}{\langle\widetilde{\kappa}\rangle + \dfrac{1}{3\kappa_0}\langle\kappa'^2\rangle}, \tag{3.1}$$

having used the assumption of statistical isotropy of the medium. On inserting here $\kappa_0 = k_1$ and $\kappa_0 = k_2$ we get a lower or upper bound on the effective conductivity κ^*, provided k_1 and k_2 are lower or upper bounds on the field $\kappa(\mathbf{x})$, respectively.

Since $\kappa^{(2)}_{HS}$ is a monotonically increasing function of κ_0, the best bounds are obtained if one chooses $k_1 = \inf \kappa(\mathbf{x})$ and $k_2 = \sup \kappa(\mathbf{x})$. The superscript '2' in the notation of the bounds (3.1) indicates that the two-point correlations for the field $\kappa(\mathbf{x})$ are only needed in their evaluation.

Let the medium be two-phase with conductivity of the constituents κ_f and κ_m whose volume fractions are respectively c and $1-c$. On taking $\kappa_0=\kappa_m$ and $\kappa_0=\kappa_f$, we get the familiar Hashin-Shtrikman bounds

$$\frac{\kappa^{(2)}_{HS}}{\kappa_m}=1+\frac{3\beta_m c}{1-\beta_m c},\quad \beta_m=\frac{[\kappa]}{\kappa_f+2\kappa_m}, \tag{3.2}$$

at $\kappa_0=\kappa_m$; the respective expression at $\kappa_0=\kappa_f$ is obtained upon interchanging the indices 'm' and 'f' and replacing c by $1-c$. As usual $[\kappa]=\kappa_f-\kappa_m$.

It is important to point out that the bounds (3.1) do not coincide and are less restrictive than the Hashin-Shtrikman ones for an N-phase medium at $N>2$. The reason is that in the latter case one introduces constant polarizations $\lambda_i\mathbf{G}$ in each phase, $i=1,\ldots,N$, so that the number of adjustable scalars is bigger than in the class (2.11). To get the Hashin-Shtrikman bounds for the N-phase medium, (2.11) should be replaced by the class of trial polarizations

$$\mathbf{p}(\mathbf{x})=\sum_{i=1}^{N-1}\lambda_i\widetilde{\kappa}^i(\mathbf{x})\mathbf{G}.$$

The restriction of the functional (2.7) on this class still involves only two-point correlation functions for the medium and yields, after extremization with respect to the λ's, the respective Hashin-Shtrikman bounds. Since two-phase media and, above all, random dispersions will be treated in what follows, we shall not give any more details here.

Let the medium be a random dispersion of equi-sized nonoverlapping spheres of conductivity κ_f and radii a, embedded into a matrix of conductivity κ_m. The polarization fields from the class $\mathcal{P}^{(1)}$ are obviously constant within the spheres and matrix. Moreover, if we take $\kappa_0=\kappa_m$, then $\mathbf{p}(\mathbf{x})$ vanishes in the matrix so that the field $\mathbf{p}(\mathbf{x})\in\mathcal{P}^{(1)}$ could be conveniently written as

$$\mathbf{p}(\mathbf{x})=\lambda\mathbf{G}\int h(\mathbf{x}-\mathbf{y})\psi(\mathbf{y})\,d^3\mathbf{y}, \tag{3.3}$$

where

$$\psi(\mathbf{x})=\sum_j\delta(\mathbf{x}-\mathbf{x}_j) \tag{3.4}$$

is the random density function for the random set $\mathbf{x}_j$ of sphere centers (Stratonovich, 1967), $h(\mathbf{x})$ denoting the characteristic function of a single sphere of radius a located at the origin and $\delta(\mathbf{x})$ standing for the Dirac delta function.

The representation (3.3) hints at the idea to consider the more general situation when

$$\mathbf{p}(\mathbf{x})=\int h(\mathbf{x}-\mathbf{y})\mathbf{F}(\mathbf{x}-\mathbf{y})\psi(\mathbf{y})\,d^3\mathbf{y}, \tag{3.5}$$

where $\mathbf{F}(\mathbf{x})$ is an adjustable function. This means that we allow now the polarization to vary, but in one and the same manner within each sphere. It could be shown, however, that

the best choice of $\mathbf{F}(\mathbf{x})$ is the constant, so that the Hashin-Shtrikman bounds (3.2) cannot be improved, if the polarization is admitted to vary in the class (3.5).

4 The four-point bounds

Consider now the larger class of trial polarization fields $\mathcal{P}^{(2)}$, cf. (2.12), that emerges in a natural way after truncation of the series (2.9) after the one-tuple term. The restriction of the Hashin-Shtrikman functional (2.7) over $\mathcal{P}^{(2)}$ is a functional of the adjustable quantities λ and $\mathbf{K}(\mathbf{x})$ for which the respective Euler-Lagrange equations could be written. They would include an integro-differential equation from which the "best" kernel $\mathbf{K}(\mathbf{x})$ could be sought for a given random constitution. If found, this kernel would allow to obtain the best, i.e., the most restrictive, bounds on the effective properties which utilize the Hashin-Shtrikman variational principle and statistical information given by the first ℓ-point correlation functions of the random conductivity field $\kappa(\mathbf{x})$ of the medium up to $\ell = 4$. In this sense the bounds so obtained would be four-points which will be reflected in their notations $\kappa^{(4)}_{HS}$. In a similar way the best three-point bounds were expressed in Markov (1987) by means of the solution of the respective Euler-Lagrange equation for the energy functional (2.4), restricted over the class of trial fields that represent the truncation of the series (2.3) after the one-tuple term. It is noteworthy that while in the latter case we could get the best three-point bounds, the bounds $\kappa^{(4)}_{HS}$ will not be here the best four-point ones in general. The reason can be well seen from the derivation of Hill (1963) of the Hashin-Shtrikman variational principle from the classical one, in which certain terms are omitted in the latter.

The equation for the "best" kernel $\mathbf{K}(\mathbf{x})$ would be however a complicated integro-differential equation. Its counterpart, derived and studied in Markov (1987) in the simpler case when the classical principle is employed, was solved only in some particular cases, namely, for cell materials and for dispersions of spheres to $O(c^2)$. That is why, without deriving explicitly the respective equation, we immediately resort to the Ritz type procedure in which $\mathbf{K}(\mathbf{x})$ is the gradient of the first perturbation kernel (2.10). Thus we introduce the class of trial polarization fields

$$\mathbf{p}(\mathbf{x}) = \widetilde{\kappa}(\mathbf{x})\Big\{\lambda_1\mathbf{G} + \lambda_2\mathbf{G}\cdot\int\nabla\left(\nabla\frac{1}{4\pi|\mathbf{x}-\mathbf{y}|}\right)\kappa'(\mathbf{y})\,d^3\mathbf{y}\Big\}, \tag{4.1}$$

where now $\lambda_1, \lambda_2 \in \mathbb{R}$ are two adjustable scalar parameters. As a matter of fact the class (4.1), in the scalar conductivity and elastic cases, was introduced by Phan-Thien and Milton (1982) and Milton and Phan-Thien (1982), who however used the Fourier transforms of the respective fields, having assumed the medium two-phase and with periodic internal constitution. But though the assumption of internal periodicity does not lead to any loss

of generality as far as the effective properties are concerned, it seems more logical to start with polarization fields of the form (4.1) if only because this fits naturally within the general framework of truncated functional series as a natural source of trial fields.

Let us point out immediately that the above choice of the kernel $\mathbf{K}(\mathbf{x})$ is not the best in general. Briefly, the explanation follows from the recent results of the authors (Markov and Zvyatkov, 1991a,b): As is clear from (2.6), a trial polarization field would be close to the true one when the associated temperature field is close to the true one. This means that the class (4.1) may lead to the best possible bounds, obtainable in the wider class (2.12), if the Beran kernel provides the best bounds obtainable from the classical variational principle over the class of trial temperature fields

$$\theta(\mathbf{x}) = \mathbf{G}\cdot\mathbf{x} + \int T(\mathbf{x}-\mathbf{y})\kappa'(\mathbf{y})\,d^3\mathbf{y},$$

in which the kernel T is varied. The latter holds indeed at least in two cases, namely, (i) for cell materials (Markov, 1987) and (ii) for dispersions of nonoverlapping spheres, but to $O(c^2)$ only, and not for higher orders of c (Markov and Zvyatkov, 1991a,b). Thus we can suspect that in these two cases (i) and (ii), the Phan-Thien–Milton bounds are the best, i.e., they cannot be improved if we try to optimize the Hashin-Shtrikman functional over the wider class (2.12). But even for random dispersions at higher than degree c^2 the said bounds are not optimal and may be improved at the price of a skillful choice of the kernel $\mathbf{K}(\mathbf{x})$ in (2.12). (This kernel should somehow "feel" the statistics of the dispersion and its form therefore should be variable, in contrast with the fixed Beran kernel simply multiplied by a scalar.) It may be shown, however, that the Phan-Thien–Milton bounds are not optimal for random dispersions even to $O(c^2)$, but the rigorous proof will be exposed elsewhere. The explanation of this fact could be again found in Hill's derivation of the Hashin-Shtrikman principle—the disregard of certain terms in the classical principle in this derivation indicates that a simple one-to-one correspondence between the optimal kernels in these two principles cannot be expected.

The restriction of the functional U, cf. (2.7), over the class (4.1) is the quadratic function

$$U(\lambda_1,\lambda_2) = \Big(a_0 + 2a_1\lambda_1 + 2a_2\lambda_2 + a_{11}\lambda_1^2 + 2a_{12}\lambda_1\lambda_2 + a_{22}\lambda_2^2\Big)\,G^2, \tag{4.2a}$$

where

$$a_0 = \kappa_0,\ a_1 = \langle\widetilde{\kappa}\rangle,\ a_2 = -\frac{1}{3}\langle\kappa'^2\rangle,\ a_{11} = -\frac{1}{3}\frac{\langle\kappa'^2\rangle}{\kappa_0} - \langle\widetilde{\kappa}\rangle,$$

$$a_{12} = \frac{1}{3}\Big\{\frac{1}{\kappa_0}\Big[\langle\kappa'^3\rangle I_\kappa^{(3)} + \langle\widetilde{\kappa}\rangle\langle\kappa'^2\rangle\Big] + \langle\kappa'^2\rangle\Big\}, \tag{4.2b}$$

$$a_{22} = \frac{1}{3}\Big\{\frac{1}{\kappa_0}\Big[\langle\kappa'^4\rangle I_\kappa^{(4)} - 2\langle\widetilde{\kappa}\rangle\langle\kappa'^3\rangle I_\kappa^{(3)} - \langle\widetilde{\kappa}\rangle^2\langle\kappa'^2\rangle + \frac{1}{9}\langle\kappa'^2\rangle^2\Big] - \Big[\langle\kappa'^3\rangle I_\kappa^{(3)} + \langle\widetilde{\kappa}\rangle\langle\kappa'^2\rangle\Big]\Big\};$$

here

$$I_\kappa^{(3)} = \frac{1}{\langle \kappa'^3 \rangle} \iint \left(\frac{1}{4\pi|\mathbf{z}|} \right)_{,ij} \left(\frac{1}{4\pi|\mathbf{w}|} \right)_{,ij} M_3^\kappa(\mathbf{z}, \mathbf{w})\, d^3\mathbf{z}\, d^3\,\mathbf{w}, \tag{4.3}$$

$M_3^\kappa = \langle \kappa'(\mathbf{0})\kappa'(\mathbf{z})\kappa'(\mathbf{w}) \rangle$, is the dimensionless statistical parameter that appears in Beran's bounds (Beran, 1965), and

$$I_\kappa^{(4)} = \frac{1}{\langle \kappa'^4 \rangle} \iiint \left(\frac{1}{4\pi|\mathbf{z}|} \right)_{,ij} \left(\frac{1}{4\pi|\mathbf{w}|} \right)_{,jk} \left(\frac{1}{4\pi|\mathbf{z}-\mathbf{v}|} \right)_{,ki} M_4^\kappa(\mathbf{z}, \mathbf{v}, \mathbf{w})\, d^3\mathbf{z}\, d^3\mathbf{v}\, d^3\mathbf{w} \tag{4.4}$$

is a new dimensionless statistical parameter, depending already on the four-point correlations in the medium; $M_4^\kappa(\mathbf{z}, \mathbf{v}, \mathbf{w}) = \langle \kappa'(\mathbf{0})\kappa'(\mathbf{z})\kappa'(\mathbf{v})\kappa'(\mathbf{w}) \rangle$,

The extremization of the function $U(\lambda_1, \lambda_2)$ yields

$$\operatorname{extr} U(\lambda_1, \lambda_2) = \kappa_{HS}^{(4)} G^2,$$

where

$$\kappa_{HS}^{(4)} = a_0 + \frac{2a_1a_2a_{12} - a_1^2a_{22} - a_2^2a_{11}}{a_{11}a_{22} - a_{12}^2}. \tag{4.5}$$

Due to the Hashin-Shtrikman variational principle the quantity $\kappa_{HS}^{(4)}$ so obtained is a lower or upper bound on the effective conductivity κ^* whenever $\kappa(\mathbf{x}) \geq \kappa_0$ or $\kappa(\mathbf{x}) \leq \kappa_0$ respectively. Obviously these bounds are the exact counterparts of the Beran bounds since they both utilize, as a matter of fact, one and the same class of trial fields but differ in the variational principle used in their derivation. In the case of a two-phase medium the bounds $\kappa_{HS}^{(4)}$ reduce to those obtained by Phan-Thien and Milton (1982). That is why we shall refer to them as Phan-Thien–Milton's in what follows.

The practical application of the bounds $\kappa_{HS}^{(4)}$ for a random constitution at hand obviously depends on the possibility to evaluate the parameters $I_\kappa^{(3)}$ and $I_\kappa^{(4)}$. However, even the evaluation of the simpler parameter $I_\kappa^{(3)}$ for media of practical and theoretical interests poses great problems only recently overcome for dispersions of spheres (both nonoverlapping and overlapping), see Felderhof (1982), Torquato and Stell (1985), Beasley and Torquato (1986), et al. As a matter of fact, no attempts to calculate the parameter $I_\kappa^{(4)}$ have been undertaken in the literature. That is why we shall start with the discussion of a mathematically simple, but unrealistic as it will appear, random medium for which the latter parameter can be explicitly calculated.

5 The four-point bounds for a Gaussian-type medium

Let us assume that the conductivity fluctuation, $\kappa'(\mathbf{x})$, of the medium obeys the normality assumption up to four-point moments. This means that

$$M_3^\kappa(\mathbf{x},\mathbf{y}) = 0, \tag{5.1}$$

$$M_4^\kappa(\mathbf{x},\mathbf{y},\mathbf{z}) = M_2^\kappa(\mathbf{x}-\mathbf{y})M_2^\kappa(\mathbf{z}) + M_2^\kappa(\mathbf{y}-\mathbf{z})M_2^\kappa(\mathbf{x}) + M_2^\kappa(\mathbf{z}-\mathbf{x})M_2^\kappa(\mathbf{y}). \tag{5.2}$$

These assumptions somewhat resemble Finkel'berg's "approximation of random phases", though the latter dealt with the field

$$\tau(\mathbf{x}) = \frac{\kappa(\mathbf{x})-\kappa_0}{\kappa(\mathbf{x})+2\kappa_0} \tag{5.3}$$

and required it to be Gaussian in order to be able to evaluate the first few cluster integrals in the respective expansion of the effective conductivity, cf. Finkel'berg (1964).

Due to (4.3) and (5.1), the Beran parameter $I_\kappa^{(3)}$ vanishes. In turn, it can be shown that under the assumption (5.2) the second statistical parameter $I_\kappa^{(4)}$ is

$$I_\kappa^{(4)} = \frac{4}{3}\Big(\frac{\langle\kappa'^2\rangle^2}{\langle\kappa'^4\rangle} + \frac{3}{\langle\kappa'^4\rangle}\int_0^\infty \chi_2(r)\,dM_2^\kappa(r)\Big), \tag{5.4a}$$

where

$$\chi_2(r) = -\frac{1}{r^3}\int_0^r s^2 M_2^\kappa(s)\,ds = -\frac{1}{3}\int_0^1 M_2^\kappa(r\sqrt[3]{p})\,dp. \tag{5.4b}$$

As usual, we represent the two-point correlation function $M_2^\kappa(r)$ as

$$M_2^\kappa(r) = \langle\kappa'^2\rangle\varphi(r),\ \varphi(0)=1, \tag{5.5}$$

and assume that $\varphi(r)$ is strongly monotonically decreasing, tending to zero when $r\to\infty$. In this case the parameter $I_\kappa^{(4)}$ becomes

$$I_\kappa^{(4)} = \gamma\frac{\langle\kappa'^2\rangle^2}{\langle\kappa'^4\rangle},\ \gamma = \frac{4}{3}\Big\{1+\int_0^1\int_0^1 \varphi(\sqrt[3]{p}\varphi^{-1}(t))\,dt\,dp\Big\}. \tag{5.6}$$

Since $\varphi(r)$ is monotonically decreasing, (5.6) immediately yields the estimate

$$\frac{4}{3}\frac{\langle\kappa'^2\rangle^2}{\langle\kappa'^4\rangle} \le I_\kappa^{(4)} \le \frac{8}{3}\frac{\langle\kappa'^2\rangle^2}{\langle\kappa'^4\rangle}, \tag{5.7}$$

whatever be the two-point correlation function $M_2^\kappa(r)$.

Consider now the perturbation expansion of the bounds (4.5) in the case of a weakly inhomogeneous medium for which

$$\omega = \frac{\langle\kappa'^2\rangle}{\langle\kappa\rangle^2} \ll 1.$$

In this case (4.5) yields, after some algebra,

$$\frac{\kappa_{HS}^{(4)}}{\langle\kappa\rangle} = 1 - \frac{1}{3}\omega + A_2(k_i)\omega^2 + o(\omega^2), \tag{5.8}$$

where

$$A_2(k_i) = \frac{1+9\gamma}{27M_i},\ M_i = \frac{k_i}{\langle\kappa\rangle}, \tag{5.9}$$

having taken into account (5.6). We recall that (5.8) provides, respectively, a lower or upper bound on the effective conductivity if $k_1 \leq \kappa(\mathbf{x})$ or $\kappa(\mathbf{x}) \leq k_2$.

The first consequence of (5.9) is that both bounds coincide to the order ω giving the exact value of the effective conductivity to the same order

$$\frac{\kappa^*}{\langle\kappa\rangle} = 1 - \frac{1}{3}\omega + o(\omega). \tag{5.10}$$

This is however a well-known result, valid for an arbitrary weakly inhomogeneous and statistically isotropic medium, cf. Brown (1955).

Moving now to the ω^2-coefficient in (5.9), we notice that we should have $A_2(k_1) \leq A_2(k_2)$, if we choose $k_1 = \inf\kappa(\mathbf{x})$ and $k_2 = \sup\kappa(\mathbf{x})$. But the latter inequality is obviously violated since both k_1 and k_2 should be non-negative for a real medium. Thus we can conclude that there exist no random media for which the assumptions (5.1) and (5.2) hold and $\kappa(\mathbf{x}) \geq 0$. This result warrants several remarks and comments.

First, to demonstrate the nonexistence of such media the four-point bounds (4.5) are necessary. The reason is that the three-point upper bound of Beran (1965) in this case yields solely

$$\frac{\kappa^*}{\langle\kappa\rangle} \leq 1 - \frac{1}{3}\omega,$$

since $I_\kappa^{(3)} = 0$ here. Nothing could be said, however, for the lower Beran bound because the compliance field $1/\kappa(\mathbf{x})$ is not obliged in general to obey the requirements (5.1) and (5.2). (The medium under study is not necessarily two-phase.)

Second, Gaussianity of $\kappa(\mathbf{x})$ for a two-phase medium is equivalent to Gaussianity of the field $\tau(\mathbf{x})$, cf. (5.3), assumed by Finkel'berg (1964). The latter assumption has led him to some unusual values of the second cluster integral for a dispersion so that he concluded that caution is needed when applying it to real dispersions. Our result of nonexistence of Gaussian-type random media sheds light upon this conclusion of Finkel'berg and justifies his warning.

Third, the failure of the Gaussian assumption is not at all unexpected for particulate media. The only explanation, though somewhat weak and not entirely satisfactory, that the authors are able to offer at the moment for such media, is the following. As argued

by Christov and Markov (1985), the Gaussian assumption in this case implies a very dense population of point-like inclusions and thus it is unable to take allowance for their finite size. But the dimensionless effective conductivity $\kappa^*/\langle\kappa\rangle$ cannot be expressed by the number density solely for the usually treated unbounded medium (since the characteristic length—the mean size of the inclusions—is now missing). More curious is perhaps the fact that even if we reject the requirement that the medium is two-phase and relax the Gaussian assumption to the three- and four-point moments only, cf. (5.1) and (5.2), we find again no such media for which $\kappa(\mathbf{x}) \geq 0$.

Note finally that the above reasoning also yields nonexistence of media for which $\kappa(\mathbf{x})$ obeys (5.1) and (5.2) and is bounded from below: $\kappa(\mathbf{x}) \geq K$, $K > -\infty$. Indeed, we could immediately replace $\kappa(\mathbf{x})$ by the field $\kappa(\mathbf{x}) - K$ which is nonnegative and also obeys the conditions (5.1) and (5.2) (because they include the fluctuation of the field $\kappa(\mathbf{x})$ only). That is why the result of this section may be formulated in the following way: *A stationary and isotropic random field $\kappa(\mathbf{x})$ that obeys the conditions (5.1) and (5.2) is necessarily not bounded from below.*

6 The four-point bounds for dispersions of spheres

Consider now the four-point bounds for a more realistic medium—the dispersion of nonoverlapping spheres, briefly discussed in Section 3. We first note that the random conductivity field of the dispersion, $\kappa(\mathbf{x})$, has a simple integral representation through the random density field (3.4), namely,

$$\kappa(\mathbf{x}) = \kappa_m + [\kappa]\int h(\mathbf{x}-\mathbf{y})\psi(\mathbf{y})\, d^3\mathbf{y}, \;\; [\kappa] = \kappa_f - \kappa_m. \tag{6.1}$$

The last formula allows the calculation of all needed correlation functions of the field $\kappa(\mathbf{x})$ to be calculated by means of the k-point probability densities f_k of the random set $\mathbf{x}_j$ of the sphere centers (see, e.g., Stratonovich, 1967). Afterwards one could to try to evaluate the needed statistical parameters (4.3) and (4.4) for the dispersion through the multi-point densities f_k up to $k = 4$. The calculation can be easily performed for the three-point parameter $I_\kappa^{(3)}$ to $O(c^2)$ (Markov, 1987), where c is the volume fraction of the spheres. However, a similar evaluation of the four-point parameter $I_\kappa^{(4)}$ is much more involved even to the same order c^2. That is why we shall try to analyze the structure of the trial fields (2.12) and to modify them accordingly in order to derive certain explicit bounds of Hashin–Shtrikman type for the dispersion, valid to $O(c^2)$.

Let us make the transition in (2.12) from the field $\kappa(\mathbf{x})$ to the field $\psi(\mathbf{x})$, i.e., let us

introduce (6.1) into (2.12). The trial fields (2.12) then become

$$\mathbf{p}(\mathbf{x}) = \widetilde{\kappa}(\mathbf{x})\Big(\mathbf{W} + [\kappa]\int \mathbf{\Phi}(\mathbf{x}-\mathbf{z})\psi(\mathbf{z})\, d^3\mathbf{z}\Big), \tag{6.2}$$

where

$$\mathbf{W} = \lambda\mathbf{G} - n[\kappa]\int \mathbf{\Phi}(\mathbf{x})\, d^3\mathbf{x}, \quad \mathbf{\Phi}(\mathbf{x}) = (\mathbf{K} * h)(\mathbf{x}) = \int \mathbf{K}(\mathbf{x}-\mathbf{y})h(\mathbf{y})\, d^3\mathbf{y}. \tag{6.3}$$

Hereafter we choose $\kappa_0 = \kappa_m$, i.e., the comparison medium is the matrix. Then

$$\widetilde{\kappa}(\mathbf{x}) = \kappa(\mathbf{x}) - \kappa_0 = [\kappa]\int h(\mathbf{x}-\mathbf{y})\psi(\mathbf{y})\, d^3\mathbf{y} = [\kappa]\sum_j h(\mathbf{x}-\mathbf{x}_j). \tag{6.4}$$

Upon inserting (6.4) into (6.2) and taking the definition (3.4) of $\psi(\mathbf{x})$ into account, we recast the trial fields (6.2) as

$$\mathbf{p}(\mathbf{x}) = [\kappa]\Big\{\sum_i h(\mathbf{x}-\mathbf{x}_i)[\mathbf{W} + \mathbf{\Phi}(\mathbf{x}-\mathbf{x}_i)] + \sum_{\substack{i,j \\ i\neq j}} h(\mathbf{x}-\mathbf{x}_i)\mathbf{\Phi}(\mathbf{x}-\mathbf{x}_j)\Big\}. \tag{6.5}$$

It is now obvious that the polarization fields (6.5) in the dispersion, corresponding to the class (2.12), have the following structure. They vanish inside the matrix (due to the choice $\kappa_0 = \kappa_m$) and in the spheres they are sums of two components: The first is a function, one and the same for all inclusions; the second depends on the position of the point $\mathbf{x}$ within the inclusion and on the location of the rest of them.

Let us recall that the special choice (2.10) of Beran (1965) of the kernel $\mathbf{K}(\mathbf{x})$ is of particular interest in our study (see Section 4). In this case the kernel, according to (6.3), is

$$\mathbf{\Phi}(\mathbf{x}) = \lambda_2\mathbf{G}\cdot\nabla\nabla\varphi(\mathbf{x}), \tag{6.6}$$

where $\varphi(\mathbf{x}) = h(\mathbf{x}) * \dfrac{1}{4\pi|\mathbf{x}|}$ is the Newtonian potential for a single sphere located at the origin. The field (6.6), let us recall, is proportional to the disturbance, $T^{(1)}(\mathbf{x})$, to the temperature field $\mathbf{G}\cdot\mathbf{x}$ in an unbounded matrix of conductivity κ_m, introduced by a single spherical inhomogeneity of conductivity κ_f. Hence for dispersions of spheres the class (6.5), with the special choice (6.6) of the kernel $\mathbf{\Phi}(\mathbf{x})$, coincides with the class introduced by Phan-Thien and Milton (1982).

Note that a transition from the field $\kappa(\mathbf{x})$ to the random density field $\psi(\mathbf{x})$, similar to that made above, was applied in Markov and Zvyatkov (1988, 1991a) for the classical variational principle. In this way it has been directly shown that the Beran bounds for dispersions of nonoverlapping spheres coincide with the so-called first-order cluster bounds of Torquato (1986).

The polarizations (6.5) can be represented in a more convenient "factorial" form if we introduce, after Christov (1985) and Markov (1991), the so-called factorial fields, generated by the random point set $\mathbf{x}_j$, namely:

$$\Delta_\psi^{(0)} = 1, \quad \Delta_\psi^{(1)}(\mathbf{y}_1) = \psi(\mathbf{y}_1),$$

$$\Delta_\psi^{(2)}(\mathbf{y}_1, \mathbf{y}_2) = \psi(\mathbf{y}_1)[\psi(\mathbf{y}_2) - \delta(\mathbf{y}_{2,1})], \quad \text{etc..} \tag{6.7}$$

The multipoint moments of the factorials that are needed in what follows can easily be expressed by means of the k-point probability densities f_k for the set $\mathbf{x}_j$ of sphere centers, see, Stratonovich (1967) or Markov and Christov (1992). For instance,

$$\left\langle \Delta_\psi^{(2)}(\mathbf{y}_1, \mathbf{y}_2)\Delta_\psi^{(1)}(\mathbf{y}_3) \right\rangle = n^2 g_0(\mathbf{y}_{1,2})[\delta(\mathbf{y}_{1,3}) + \delta(\mathbf{y}_{2,3})] + o(n^2),$$

$$\left\langle \Delta_\psi^{(2)}(\mathbf{y}_1, \mathbf{y}_2)\Delta_\psi^{(2)}(\mathbf{y}_3, \mathbf{y}_4) \right\rangle = n^2 g_0(\mathbf{y}_{1,2})[\delta(\mathbf{y}_{1,3})\delta(\mathbf{y}_{2,4}) + \delta(\mathbf{y}_{1,4})\delta(\mathbf{y}_{2,3})] + o(n^2), \tag{6.8}$$

etc., where $\mathbf{y}_{i,j} = \mathbf{y}_i - \mathbf{y}_j$, n stands for the number density of the spheres, and $g_0(\mathbf{y}_{1,2}) = f_2(\mathbf{y}_{1,2})/n^2 + o(n^2)$ is the zero-density limit of their radial distribution function.

The fields (6.5) can now be recast as

$$\mathbf{p}(\mathbf{x}) = [\kappa]\Big\{ \int h(\mathbf{x} - \mathbf{y})\mathbf{F}(\mathbf{x} - \mathbf{y})\psi(\mathbf{y})\, d^3\mathbf{y}$$

$$+ \iint h(\mathbf{x} - \mathbf{y}_1)\mathbf{\Phi}(\mathbf{x} - \mathbf{y}_2)\Delta_\psi^{(2)}(\mathbf{y}_1, \mathbf{y}_2)\, d^3\mathbf{y}_1\, d^3\mathbf{y}_2 \Big\}, \tag{6.9}$$

where

$$\mathbf{F}(\mathbf{x}) = \mathbf{W} + \mathbf{\Phi}(\mathbf{x}). \tag{6.10}$$

Thus the original trial fields (2.12), after making this transition, become truncated factorial series. Such series were introduced by Markov (1991): they represent functional series of the form (2.3), generated by the random density field $\psi(\mathbf{x})$ whose terms are rearranged so that the products $\psi(\mathbf{y}_1) \ldots \psi(\mathbf{y}_k)$ are replaced by the factorial fields (6.7). In the same paper of Markov it was argued that such series should be of primary importance in the theory of random particulate media since their truncations generate asymptotically correct stochastic solutions with any desired degree of accuracy. The representation (6.9) once more indicates the importance of the factorial series in the theory of particulate random media and random dispersions in particular.

In all cases to be treated below it suffices to replace the one-tuple term in (6.9) by the simpler one $\lambda\widetilde{\kappa}(\mathbf{x})\mathbf{G}$, with an adjustable λ. (As already mentioned in Section 3, the latter is the best choice in the two-point bounds of Hashin-Shtrikman type, so that a decisive improvement in the case of the four-point bounds should be expected from the two-tuple term in (6.9).)

Before modifying the class of trial polarizations (6.5) in order to extract calculable bounds, at least to $O(c^2)$, we should first generalize this class. Such a generalization, which is natural enough, is the class

$$\mathbf{p}(\mathbf{x}) = \lambda\widetilde{\kappa}(\mathbf{x})\mathbf{G} + \sum_{\substack{i,j \\ i\neq j}} h(\mathbf{x}-\mathbf{x}_i)\mathbf{\Phi}(\mathbf{x}\,;\,\mathbf{x}_i,\mathbf{x}_j), \tag{6.11a}$$

where now $\mathbf{\Phi}(\mathbf{x}\,;\,\mathbf{x}_i,\mathbf{x}_j)$ is an arbitrary function such that

$$\mathbf{\Phi}(\mathbf{x};\mathbf{x}_i,\mathbf{x}_j) = \mathbf{\Phi}(\mathbf{x}-\mathbf{x}_i\,;\mathbf{x}_i-\mathbf{x}_j), \tag{6.11b}$$

due to the homogeneity of the dispersion. This means that we allow the polarization to vary in arbitrary manner within the reference inclusion 'i' (different in each inclusion); this is described by the dependence of $\mathbf{\Phi}$ on its first argument $\mathbf{x}-\mathbf{x}_i$, while the influence of the rest of the inclusions, labeled 'j', $j\neq i$, also varies arbitrarily, being described by the dependence of $\mathbf{\Phi}$ on its second argument $\mathbf{x}_i-\mathbf{x}_j$.

By means of the factorials (6.7) we rewrite the fields (6.11) as

$$\mathbf{p}(\mathbf{x}) = \lambda\widetilde{\kappa}(\mathbf{x})\mathbf{G} + [\kappa]\iint h(\mathbf{x}-\mathbf{y}_1)\mathbf{\Phi}(\mathbf{x}-\mathbf{y}_1;\mathbf{y}_1-\mathbf{y}_2)\Delta_{\psi}^{(2)}(\mathbf{y}_1,\mathbf{y}_2)\,d^3\mathbf{y}_1\,d^3\mathbf{y}_2, \tag{6.12}$$

where now both λ and $\mathbf{\Phi}$ are adjustable.

The restriction of the Hashin-Shtrikman functional (2.7) over the class of trial polarization fields (6.12) is a functional, $U[\lambda,\mathbf{\Phi}(\cdot\,;\,\cdot)]$, of λ and $\mathbf{\Phi}$. The Euler-Lagrange equation for the latter can be explicitly solved to $O(c^2)$, yielding

$$\operatorname{extr} U[\lambda,\mathbf{\Phi}(\cdot\,;\,\cdot)] = \widetilde{\kappa}_{HS}^{(4)}G^2,$$

$$\widetilde{\kappa}_{HS}^{(4)}G^2 = 1+3\beta+3\beta^2(1+S)c^2+o(c^2), \tag{6.13}$$

where $S=S[g_0(\cdot)]$ is a certain statistical parameter for the dispersion, defined as

$$3\beta^2 S[g_0(\cdot)]G^2 = a_2'G^2$$

$$= \frac{[\kappa]}{\kappa_m}\frac{1}{V_a^2}\int h(\mathbf{x})\,d^3\mathbf{x}\int g_0(\mathbf{y})\nabla T^{(1)}(\mathbf{x}-\mathbf{y})\cdot\left[\nabla T^{(2)}(\mathbf{x};\mathbf{y})-\nabla T^{(1)}(\mathbf{x})\right]d^3\mathbf{y}. \tag{6.14}$$

It can be directly shown that $a_2'+3\beta^2$ coincides with the exact value of the c^2-coefficient a_2 in the virial expansion of the effective conductivity κ^* of the dispersion, as given by Jeffrey (1973). This means that the formula (6.14) for a_2' can be recast as

$$3\beta^2 S[g_0(\cdot)]G^2 = a_2'G^2$$

$$= \frac{[\kappa]}{\kappa_m}\frac{1}{V_a^2}\mathbf{G}\cdot\int h(\mathbf{x})\,d^3\mathbf{x}\int g_0(\mathbf{y})\left[\nabla T^{(2)}(\mathbf{x};\mathbf{y})-\nabla T^{(1)}(\mathbf{x})\right]d^3\mathbf{y}, \tag{6.15}$$

where $T^{(2)}(\mathbf{x};\mathbf{z})$ denotes the disturbance to the temperature field $\mathbf{G}\cdot\mathbf{x}$ in an unbounded matrix of conductivity κ_m, introduced by a pair of nonoverlapping spherical inhomogeneities of conductivity κ_f, centered at the origin and at the point $\mathbf{z}$ respectively. The underlying reason for this coincidence is that the class (6.12) is rich enough to include the real polarization field to $O(c^2)$. Thus

$$\kappa^* = \widetilde{\kappa}^{(4)}_{HS} + o(c^2). \tag{6.16}$$

The representation (6.14) of a_2' seems to be novel and deserves some comments.

Let us recall that the integral in Jeffrey's formula (6.15) for a_2' is conditionally convergent with respect to $\mathbf{y}$. The reason is that the function $\mathbf{U}(\mathbf{x};\mathbf{y}) = \nabla T^{(2)}(\mathbf{x};\mathbf{y}) - \nabla T^{(1)}(\mathbf{x})$ has the order $|\mathbf{y}|^{-3}$ at $|\mathbf{y}| \gg 1$. A formal and rigorous justification of the mode of integration that leads to convergence in (6.15) was given in Markov (1987b, 1989). Jeffrey himself performed a "renormalization", subtracting from $\mathbf{U}(\mathbf{x};\mathbf{y})$ the term $\beta\nabla T^{(1)}(\mathbf{x})$ which contributes nothing to the value of the integral, but makes the resulting function absolutely integrable. The important point here is that the function $\mathbf{U}(\mathbf{x};\mathbf{y})$ appears multiplied by $\nabla T^{(1)}(\mathbf{x}-\mathbf{y})$ in our expression (6.14) for a_2' which makes the integral absolutely convergent, with the integrand having asymptotic order $|\mathbf{y}|^{-6}$ at $|\mathbf{y}| \gg 1$ (the same as in Jeffrey's renormalized formula). Thus, curiously and a bit unexpectedly, the Hashin-Shtrikman variational principle has led us to an exact formula for the c^2-coefficient a_2 of the dispersion conductivity which contains only absolutely convergent integrals. This fact confirms once again our view that the conditionally convergent integrals are not inherent in the theory of random dispersions. Though they admit an interesting and appealing physical interpretation (Jeffrey, 1978), such integrals could play an auxiliary role there, allowing in some cases only a convenient representation of the needed kernels in the functional series for the random fields of interest. Moreover, the mode of integration in the latter cases is unambiguously defined as a part of the full statistical solution of the problem, see Markov (1987b, 1989), Markov and Christov (1992).

In virtue of (6.16), there is no need to evaluate the bound $\widetilde{\kappa}^{(4)}_{HS}$, because the well-known results of Jeffrey (1973) and Felderhof *et al.* (1982), concerning the c^2-term of the effective conductivity, can be directly used to identify the said value. (The calculation required in their works is nontrivial, however.) That is why the class (6.12) should somehow be narrowed.

7 The bounds of Willis

Let us try now to narrow the class (6.12) of trial polarization fields in order to get certain useful bounds on the effective conductivity of the dispersion. The first thing to notice along this line is that the class (6.9) corresponds to the special choice of the functions $\mathbf{\Phi}(\mathbf{u};\mathbf{v})$ in

(6.12) for which

$$\mathbf{\Phi}(\mathbf{u};\mathbf{v}) = \mathbf{\Phi}(\mathbf{u}+\mathbf{v}). \tag{7.1}$$

As already mentioned, the kernel $\mathbf{\Phi}(\mathbf{u})$, given in (6.6), is of special interest. It corresponds to the Beran or (which is the same in our context), to the Phan-Thien–Milton) choice. In this case the trial fields (6.12) become simply

$$\mathbf{p}(\mathbf{x}) = \lambda_1\widetilde{\kappa}(\mathbf{x})\mathbf{G} + \lambda_2\mathbf{G}\cdot\iint h(\mathbf{x}-\mathbf{y}_1)\nabla\nabla\varphi(\mathbf{x}-\mathbf{y}_2)\Delta_{\psi}^{(2)}(\mathbf{y}_1,\mathbf{y}_2)\,d^3\mathbf{y}_1\,d^3\mathbf{y}_2, \tag{7.2}$$

where $\lambda_1,\ \lambda_2 \in \mathbb{R}$ are adjustable constants. Thus the polarization is now a sum of an adjustable constant vector and a term that depends, in a fixed way, on the position $\mathbf{x}$ of the point within the reference inclusion and on the locations of the rest of them, multiplied by another adjustable scalar. However, it is exactly the dependence of the function $\nabla\nabla\varphi(\mathbf{x}-\mathbf{y}_2)$ on $\mathbf{x}$ that makes the evaluation of the respective Hashin-Shtrikman type bounds for the dispersion extremely difficult even to $O(c^2)$, as already pointed out. That is why we could try to modify the class (7.2), noticing that $\mathbf{x}-\mathbf{y}_1 \approx \mathbf{y}_1-\mathbf{y}_2$ at $|\mathbf{y}_1-\mathbf{y}_2| \gg a$ and $|\mathbf{x}-\mathbf{y}_1| < a$, so that

$$h(\mathbf{x}-\mathbf{y}_1)\mathbf{\Phi}(\mathbf{x}-\mathbf{y}_2) \approx h(\mathbf{x}-\mathbf{y}_1)\mathbf{\Phi}(\mathbf{y}_1-\mathbf{y}_2). \tag{7.3}$$

Accordingly, we could replace the trial fields (6.9) with the fields

$$\mathbf{p}(\mathbf{x}) = \lambda\widetilde{\kappa}(\mathbf{x})\mathbf{G} + \iint h(\mathbf{x}-\mathbf{y}_1)\mathbf{\Phi}(\mathbf{y}_1-\mathbf{y}_2)\Delta_{\psi}^{(2)}(\mathbf{y}_1,\mathbf{y}_2)\,d^3\mathbf{y}_1\,d^3\mathbf{y}_2. \tag{7.4}$$

Hence the polarization within each inclusion is constant, similarly to the Hashin-Shtrikman choice, but this constant depends now on the presence of the remainder of the inclusions. These are, however, just the trial polarization fields, introduced by Willis (1978), which allowed him to obtain certain bounds on the effective conductivity, and also on the effective elastic moduli later (Willis, 1980). Thus we arrive here to this idea in a natural way, having analyzed the structure of the truncated polarization fields in the dispersion and trying to modify them in order to make the respective (Phan-Thien–Milton) bounds calculable. Note that Willis' assumption corresponds, in our notations, to the requirement

$$\mathbf{\Phi}(\mathbf{u};\mathbf{v}) = \mathbf{\Phi}(\mathbf{v}) \tag{7.5}$$

for the kernel $\mathbf{\Phi}$ in the class (6.9).

We shall start first with some remarks, concerning the nature and the sense of the assumption (7.3).

First, it is clear that the farther apart the spheres are, the more exact the assumption (7.3) becomes. Thus the latter should be expected to reflect correctly the influence of the remote spheres on the reference one. Conversely, the closer the spheres are, the more conspicuous becomes the inhomogeneity of the polarization within the reference sphere.

But the neighbouring spheres should have the predominant effect on the latter field which indicates that the assumption (7.3) is rather severe and makes us suspect that the relative simplicity in calculating Willis' bounds is to be paid for in the sense that the respective bounds would bring little improvement, if any, when compared to the known ones. A real improvement could be expected only when the polarization variation within the inclusions is not strongly pronounced; this should be the case when the spheres are "rigid", i.e., the ratio $\alpha = \kappa_f/\kappa_m \gg 1$. Indeed, we shall see below that the bounds of Willis, though they are four-point, are worse than the three-point bounds of Beran for a weakly inhomogeneous dispersion. The improvement on the latter shows up only when the ratio α of constituent conductivities is big enough.

Let us start now with the calculations. The Hashin-Shtrikman functional (2.7), when restricted over the class (7.4), becomes

$$\begin{aligned} U[\lambda, \boldsymbol{\Phi}(\cdot)] &= \kappa_m G^2 + [\kappa]\mathcal{E}(\lambda) c G^2 \\ &+ 2\mathbf{G} \cdot \left[\boldsymbol{\mathcal{D}}_\Phi^{(1)} + \lambda \frac{[\kappa]}{\kappa_m} \left(\boldsymbol{\mathcal{K}}_\Phi^{(1)} - \frac{1}{3\beta} \boldsymbol{\mathcal{D}}_\Phi^{(1)} \right) \right] c^2 \\ &+ \frac{1}{\kappa_m} \left[K_\Phi^{(2)} - \frac{1}{3\beta} D_\Phi^{(2)} \right] c^2 + o(c^2), \end{aligned} \tag{7.6}$$

where

$$\begin{aligned} \mathcal{E}(\lambda) &= 2\lambda + \left(\frac{[\kappa]}{3\kappa_m}(c-1) - 1 \right) \lambda^2, \quad \boldsymbol{\mathcal{D}}_\Phi^{(1)} = \frac{1}{V_a} \int \boldsymbol{\Phi}(\mathbf{y}) g_0(\mathbf{y})\, d^3\mathbf{y}, \\ D_\Phi^{(2)} &= \frac{1}{V_a} \int |\boldsymbol{\Phi}(\mathbf{y})|^2 g_0(\mathbf{y})\, d^3\mathbf{y}, \\ \boldsymbol{\mathcal{K}}_\Phi^{(1)} &= \frac{1}{V_a} \int \boldsymbol{\omega}(\mathbf{y}) \cdot \boldsymbol{\Phi}(\mathbf{y}) g_0(\mathbf{y})\, d^3\mathbf{y}, \\ K_\Phi^{(2)} &= \frac{1}{V_a} \int \boldsymbol{\Phi}(\mathbf{y}) \cdot \boldsymbol{\omega}(\mathbf{y}) \cdot \boldsymbol{\Phi}(-\mathbf{y}) g_0(\mathbf{y})\, d^3\mathbf{y}, \\ \boldsymbol{\omega}(\mathbf{y}) &= \frac{1}{V_a} \int h(\mathbf{y}-\mathbf{z}) \nabla\nabla\varphi(\mathbf{z})\, d^3\mathbf{z}. \end{aligned} \tag{7.7}$$

Consider first the simplified situation in which the kernel $\boldsymbol{\Phi}(\mathbf{y})$ in (7.4) has the form (6.6). This means that we introduce the trial polarizations of the form

$$\mathbf{p}(\mathbf{x}) = \lambda_1 \widetilde{\kappa}(\mathbf{x}) \mathbf{G} + \lambda_2 \mathbf{G} \cdot \iint h(\mathbf{x}-\mathbf{y}_1) \nabla\nabla\varphi(\mathbf{y}_1-\mathbf{y}_2) \Delta_\psi^{(2)}(\mathbf{y}_1, \mathbf{y}_2)\, d^3\mathbf{y}_1\, d^3\mathbf{y}_2, \tag{7.8}$$

where $\lambda_1, \lambda_2 \in \mathbb{R}$ are adjustable constants. The class (7.8) obviously corresponds to the Phan-Thien–Milton choice of the kernel $\boldsymbol{\Phi}$ in which the simplifying assumption of Willis—constant polarization within the inclusions—is made. The restriction of the functional $U = U(\lambda_1, \lambda_2)$ over the class (7.8) is a quadratic function of λ_1 and λ_2 of the form (4.2a), with the coefficients

$$a_0 = \kappa_m, \quad a_1 = [\kappa], \quad a_2 = 0,$$

$$a_{11} = c\left(\frac{[\kappa]}{3\kappa_m}(c-1)-1\right), \quad a_{12} = \frac{2}{3}a^3\frac{[\kappa]}{\kappa_m}\int_{2a}^{\infty}\frac{g_0(r)}{r^4}\,dr, \tag{7.9}$$

$$a_{22} = \frac{2a^3}{9\kappa_m}\left\{a^3\int_{2a}^{\infty}\frac{g_0(r)}{r^7}\,dr - \frac{1}{\beta}\int_{2a}^{\infty}\frac{g_0(r)}{r^4}\,dr\right\}.$$

These coefficients are found by means of (7.7), in which the kernel $\mathbf{\Phi}$ from (6.6) is inserted. Due to the presence of $g_0(\mathbf{y})$, only the values of the tensor function $\boldsymbol{\omega}(\mathbf{y})$ at $|\mathbf{y}| > 2a$ are needed in the calculations, since $g_0(\mathbf{y})$ vanishes otherwise (the spheres are forbidden to overlap). It is then easy to show that

$$\boldsymbol{\omega}(\mathbf{y}) = \rho^3\left(\mathbf{e}_r\mathbf{e}_r - \frac{1}{3}\mathbf{I}\right), \quad \rho = \frac{a}{r}, \tag{7.10}$$

$\mathbf{e}_r = \mathbf{y}/r$, $r = |\mathbf{y}|$, because the convolution $h * \varphi = (h * h) * \dfrac{1}{4\pi r}$ is harmonic in the region $|\mathbf{y}| > 2a$ and depends on r only. Thus it has the form C/r there, with $C = V_a/3$.

The extremization of the quadratic function $U(\lambda_1, \lambda_2)$ with the coefficients (7.9) yields $\operatorname{extr} U = \widetilde{\kappa}_w G^2$, where

$$\frac{\widetilde{\kappa}_w}{\kappa_m} = 1 + 3\beta c + 3\beta^2(1 + \widetilde{S}_w)c^2 + o(c^2),$$

and

$$\widetilde{S}_w = \frac{6\beta\left(\displaystyle\int_0^{\frac{1}{2}}\rho^2 g_0(a/\rho)\,d\rho\right)^2}{\displaystyle\int_0^{\frac{1}{2}}\rho^2 g_0(a/\rho)\,d\rho - \beta\int_0^{\frac{1}{2}}\rho^5 g_0(a/\rho)\,d\rho}. \tag{7.11}$$

Thus the value

$$\widetilde{a}_w = 3\beta^2(1 + \widetilde{S}_w) \tag{7.12}$$

is an upper or lower bound on the c^2-coefficient a_2 for the dispersion, whenever $\kappa_f < \kappa_m$ or $\kappa_f > \kappa_m$ respectively. The bound (7.12) was announced by Zvyatkov (1992).

In the simplest well-stirred case $g_0(r) = 1$ and the bound (7.12) becomes:

$$\widetilde{a}_w = 3\beta^2\left(1 + \frac{4\beta}{16 - \beta}\right). \tag{7.13}$$

Let us now try to improve on the bound (7.12) by allowing the kernel $\mathbf{\Phi}(\mathbf{y})$ in (7.4) to vary, which is exactly the procedure of Willis (1978). The only difference, purely formal, is that Willis worked with double sums while here we employ the truncated factorial series (6.12), something that makes the calculations easier; in our notations his choice of trial fields corresponds to the requirement (7.5). The solution of the Euler-Lagrange equations

$$\frac{dU}{d\lambda} = 0, \quad \delta_\Phi U = 0 \tag{7.14}$$

for the functional (7.6) is sought in the virial form

$$\lambda^{\rm ext} = \lambda_0 + \lambda_1 c + \cdots , \quad \mathbf{\Phi}^{\rm ext}(\mathbf{x}) = \mathbf{\Phi}_0(\mathbf{x}) + \mathbf{\Phi}_1(\mathbf{x})c + \cdots .$$

The needed extremum value $U^{\rm ext}$ to $O(c^2)$ is defined by the zero-density terms λ_0 and $\mathbf{\Phi}_0(\mathbf{x})$. Moreover, $\lambda_0 = 3\beta\kappa_m/[\kappa]$. The equation for $\mathbf{\Phi}_0(\mathbf{x})$ that follows from (7.14), reads

$$3\beta\mathbf{G}\cdot\boldsymbol{\omega}(\mathbf{y})g_0(\mathbf{y}) + \frac{1}{\kappa_m}\Big\{\mathbf{\Phi}_0(-\mathbf{y})\cdot\boldsymbol{\omega}(\mathbf{y}) - \frac{1}{3\beta}\mathbf{\Phi}_0(\mathbf{y})\Big\}g_0(\mathbf{y}) = 0. \tag{7.15}$$

We shall suppose that the kernel $\mathbf{\Phi}(\mathbf{y})$ is even, so that $\mathbf{\Phi}_0(-\mathbf{y}) = \mathbf{\Phi}_0(\mathbf{y})$ in particular. This reflects the natural assumption that the influence of the sphere 'i' on the polarization within the spheres 'j' is the same of that of the sphere 'j' on that within 'i'. (It is interesting that the unnatural assumption that $\mathbf{\Phi}(\mathbf{y})$ is odd is immediately "punished"—the best choice then is $\mathbf{\Phi}_0(\mathbf{y}) = 0$ which yields the Hashin-Shtrikman bounds (3.2) to $O(c^2)$.) The solution of (7.15) is now obvious

$$\mathbf{\Phi}_0(\mathbf{y}) = 3\beta\kappa_m\mathbf{G}\cdot\boldsymbol{\omega}(\mathbf{y})\cdot\mathbf{T}^{-1}(\mathbf{y}), \tag{7.16a}$$

where

$$\mathbf{T}(\mathbf{y}) = \frac{1}{3\beta}\mathbf{I} - \boldsymbol{\omega}(\mathbf{y}). \tag{7.16b}$$

Having introduced the value of λ_0 already found, together with (7.16), into the functional (7.6), we obtain the extremum value of the latter: $\operatorname{extr} U[\lambda,\, \mathbf{\Phi}(\cdot)] = \kappa_w G^2$, where

$$\frac{\kappa_w}{\kappa_m} = 1 + 3\beta c + 3\beta^2(1 + S_w)c^2 + o(c^2). \tag{7.17}$$

Here $S_w = S_w[g_0(\cdot)]$ is a statistical parameter for the dispersion, defined as

$$S_w[g_0(\cdot)]G^2 = 3\mathbf{G}\cdot\frac{1}{V_a}\int g_0(\mathbf{y})\boldsymbol{\omega}(\mathbf{y})\cdot\mathbf{T}^{-1}(\mathbf{y})\cdot\boldsymbol{\omega}(\mathbf{y})\, d^3\mathbf{y}\cdot\mathbf{G}. \tag{7.18}$$

As a consequence of (7.10), we have immediately

$$\mathbf{T}(\mathbf{y}) = \frac{1}{3\beta}(1 + \beta\rho^3)\mathbf{I} - \rho^3\mathbf{e}_r\mathbf{e}_r, \tag{7.19}$$

so that $\mathbf{T}^{-1}(\mathbf{y})$ has the same structure, namely

$$\mathbf{T}^{-1}(\mathbf{y}) = \xi(\rho)\mathbf{I} + \eta(\rho)\mathbf{e}_r\mathbf{e}_r,$$

$$\xi(\rho) = \frac{3\beta}{1 + \beta\rho^3}, \quad \eta(\rho) = \frac{3\beta\rho^3}{1 - 2\beta\rho^3}\xi(\rho). \tag{7.20}$$

After simple algebra, based on (7.10) and (7.20), we get eventually the parameter S_w in the closed form

$$S_w = 6\beta\int_0^{1/2} g_0(a/\rho)\frac{\rho^2\, d\rho}{(1 + \beta\rho^3)(1 - 2\beta\rho^3)}. \tag{7.21a}$$

Hence, the value

$$a_2^w = 3\beta^2(1 + S_w), \tag{7.21b}$$

with S_w given in (7.18), is an upper or lower bound on the c^2-coefficient a_2 for the dispersion, whenever $\kappa_f < \kappa_m$ or $\kappa_f > \kappa_m$ respectively. We shall call (7.21) the bound of Willis.

The first thing to be pointed out about this bound is that our final result (7.21) differs from that of Willis (1978) (see his equation (51) in which, by the way, the multiplier 24π is misprinted as 8π). At the same time our expression (7.16) for the function $\mathbf{\Phi}_0$ agrees with the general formula of Willis, eqn (47), in the scalar conductivity case. Similarly, the general expression for the bound of Willis, eqn (48), agrees with our result (7.18). The difference in the final forms seems to be due to the fact that Willis has taken the tensor $\mathbf{T}(\mathbf{y})$, see (7.19), in the incorrect form $\dfrac{1}{3\beta}(1 + \beta\rho^3)\mathbf{I} + \rho^3\mathbf{e}_r\mathbf{e}_r$, which leads immediately to his eqn (51). By chance the latter equation predicts reasonable values, deviating but slightly from the correct expression (7.21), which may explain why the above said remained unnoticed by the author. The correct form (7.21) of Willis' bound has been first reported by Markov and Zvyatkov (1990).

In the simplest well-stirred case $g_0(r) = 1$ and the integration in (7.21a) is elementary:

$$a_2^w = 3\beta^2 \left(1 + \frac{2}{3} \ln \frac{8 + \beta}{2(4 - \beta)}\right). \tag{7.22}$$

Simple inspection demonstrates, as expected, that the bound of Willis (7.21) improves on the respective Beran bound (as calculated to $O(c^2)$ in Markov (1987)) only if the ratio $\alpha = \kappa_m/\kappa_f$ is big enough, $\alpha \geq \alpha_0$. (In the well-stirred case $\alpha_0 \approx 2.5$.) For $\alpha < \alpha_0$ and, in particular, for a weakly inhomogeneous dispersion, the bounds of Willis, though four-point, are worse than the three-point bounds of Beran due to reasons already discussed at the beginning of this section. Interestingly enough, the simplified bound (7.13) predicts values which are extremely close to the bound (7.21) in the well-stirred case.

Conclusions

A new aspect of application of truncated functional series in the theory of transport phenomena in heterogeneous media of random constitution was proposed and discussed in this paper. Namely, such series were systematically employed here as classes of trial polarizations fields for the Hashin–Shtrikman variational principle. In this way it turned out possible to unify and explore in more detail the existing variational procedures due to Hashin and Shtrikman, Phan-Thien and Milton, and Willis. In the resulting bounds a new four-point statistical parameter appeared (cf. (4.4)), whose evaluation for realistic and general enough

random constitutions is an open and difficult problem. In particular, certain analytical $O(c^2)$-formulae for random dispersions of spheres were proposed, as well as an exact $O(c^2)$ expression for their effective conductivity that contains convergent integrals only. In general, the obtained results indicate once again that the functional series, especially in their factorial form, represent a well-adapted and powerful tool in the mathematical theory of transport phenomena in random heterogeneous media.

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