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On the Optimal Third-Order Bounds on the Effective Conductivity of Random Dispersions of Spheres*

1. Introduction

The paper is devoted to the problem of estimating the effective scalar transport properties (in the context of thermal conductivity) for random dispersions of spheres, i. e. arrays of equisized (with radius a) nonoverlapping spheres haphazardly distributed throughout a matrix. Such dispersions, as is well known, have been considered by many authors starting perhaps with J. Maxwell [1] who has given a heuristic formula for their effective conductivity κ^* . After Maxwell many authors studied the effective properties of the random dispersions struggling with the profound problem how to account properly for the multi-particle interactions among the spheres, see, e. g., [2, 3]. The difficulties in calculating κ^* have made many authors consider the simplified problem in which, say, the effective conductivity κ^* , is to be evaluated to the order c^2 only, because this is the simplest situation in which the particle interaction shows up in a nontrivial way, see [4—6] et al.; hereafter c denotes the volume fraction of the spheres.

A problem, closely related to the evaluation of the effective properties, consists in bounding of their values making use of the limited statistical information concerning the random constitution. This problem appears in a natural way in practice since very little is usually known about the internal structure of a real heterogeneous material of technological interest, and of a random dispersion in particular. That is why the bounding problem has been considered by many authors, most of them making use of variational principles, see the survey [7] for details and references. It has appeared that the existing variational procedures can be conveniently unified making use of truncated functional series as classes of trial functions [8].

The outline of the paper is as follows. We first recall in § 2 the bounding procedure of [8] and its realization (§ 3) that leads to so-called Beran's bounds [9], and then we pose, after [10], the problem of optimality of the latter. Optimality is here understood in the sense that they should be the most restrictive ones under a given amount of statistical information; for Beran's bounds this information comprises the prescribed two- and three-point correlation functions for the medium. In this sense the

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said bounds are third-order. Having briefly recalled the methods of a statistical description for random dispersions, we modify in § 4 the variational procedure and introduce the so-called cluster bounds of Torquato [11]; they have appeared to coincide with Beran's as a simple consequence of the assumption of nonoverlapping. In § 5 it is shown that Beran's, and therefore Torquato's bounds as well, are optimal to the order c^3 ; however (§ 7), they are not optimal to the higher orders of c , and these are the central results of the paper.

2. The variational procedure

Consider for the moment an arbitrary random medium whose coefficient of thermal conductivity $\kappa(\mathbf{x})$ is a known statistically homogeneous and isotropic function. The temperature field, $\theta(\mathbf{x})$, in the medium, in the absence of body sources, is governed by the equations

$$(2.1a) \quad \nabla \cdot \mathbf{q}(\mathbf{x}) = 0, \quad \mathbf{q}(\mathbf{x}) = \kappa(\mathbf{x}) \nabla \theta(\mathbf{x}),$$

where $\mathbf{q}(\mathbf{x})$ is the opposite heat flux vector. We also prescribe the mean value of the temperature gradient to be constant

$$(2.1b) \quad \langle \nabla \theta(\mathbf{x}) \rangle = \mathbf{G}.$$

The brackets $\langle \cdot \rangle$ denote ensemble averaging.

The random problem (2.1) is the typical one for the theory of heterogeneous composite materials of random constitution. Let us recall [12] that to solve it means to evaluate all multipoint moments (correlation functions) of $\theta(\mathbf{x})$ and the joint moments of $\theta(\mathbf{x})$ and $\kappa(\mathbf{x})$, making use of the known moments of the field $\kappa(\mathbf{x})$. Among the joint moments of $\theta(\mathbf{x})$ and $\kappa(\mathbf{x})$ one has to evaluate, in particular, the one-point moment $\langle \kappa(\mathbf{x}) \nabla \theta(\mathbf{x}) \rangle = \kappa^* \langle \nabla \theta(\mathbf{x}) \rangle = \kappa^* \mathbf{G}$, where κ^* is the effective conductivity of the medium.

As is well known [12], the random problem (2.1) is equivalent to the variational principle

$$(2.2) \quad W[\theta(\cdot)] = \langle \kappa(\mathbf{x}) | \nabla \theta(\mathbf{x}) |^2 \rangle \rightarrow \min.$$

The functional W is considered over the class of trial fields that satisfy (2.1b). Moreover, $\min W = \kappa^* G^2$, $G^2 = \mathbf{G} \cdot \mathbf{G}$.

Recently, one of the authors has proposed a general bounding method which employs truncated functional series, generated by the conductivity field $\kappa(\mathbf{x})$, as classes of trial fields. We recall the method in the simplest nontrivial case when the class of such fields is

$$(2.3) \quad K^{(1)} = \left\{ \theta(\mathbf{x}) \mid \theta(\mathbf{x}) = \mathbf{G} \cdot \mathbf{x} + \int K(\mathbf{x} - \mathbf{y}) \kappa'(\mathbf{y}) d^3 \mathbf{y} \right\},$$

where $\kappa'(\mathbf{x}) = \kappa(\mathbf{x}) - \langle \kappa(\mathbf{x}) \rangle$ is the fluctuating part of $\kappa(\mathbf{x})$. Hereafter, the integrals are over the whole R^3 , if the integration domain is not explicitly indicated.

The energy functional (2.2), when restricted over the class (2.3), becomes a usual functional of the nonrandom kernel K , whose Euler-Lagrange equation reads [8]

$$(2.4) \quad \mathbf{G} \cdot \nabla M_2^\kappa(\mathbf{x}) + \langle \mathbf{x} \rangle \int \Delta K(\mathbf{x} - \mathbf{y}) M_2^\kappa(\mathbf{y}) d^3 \mathbf{y} + \int \nabla K(\mathbf{y}) \cdot \nabla_x M_3^\kappa(\mathbf{x}, \mathbf{y}) d^3 \mathbf{y} = 0.$$

This equation could be solved, if the first three moments $\langle \kappa \rangle$,

$$M_2^\kappa(\mathbf{x}) = \langle \kappa'(\mathbf{0}) \kappa'(\mathbf{x}) \rangle, \quad M_2^\kappa(\mathbf{x}, \mathbf{y}) = \langle \kappa'(\mathbf{0}) \kappa'(\mathbf{x}) \kappa'(\mathbf{y}) \rangle,$$

of the field $\kappa(\mathbf{x})$ are known. Moreover, it could be shown, employing simple convexity arguments that the solution does exist and is unique. The solution, $K(\mathbf{y})$, is to be inserted into the second equation of (2.1a) which, upon averaging, will bring forth an upper bound $\kappa^{(3)}$ on the effective conductivity:

$$(2.5) \quad \kappa^* \leq \kappa^{(3)}, \quad \kappa^{(3)} \mathbf{G} = \langle \kappa \rangle \mathbf{G} + \int \nabla K(\mathbf{y}) M_2^{\kappa}(\mathbf{y}) d^3 \mathbf{y}.$$

The superscript "3" indicates that evaluation of $\kappa^{(3)}$ requires knowledge of the r -point moments for the field $\kappa(\mathbf{x})$ up to $r=3$; in this sense $\kappa^{(3)}$ is called in [8] third-order. More important, it is shown in [8] that $\kappa^{(3)}$ is the optimal third-order bound in the sense that it is the best one which can be obtained making use of the said statistical information, i. e. the moments $\langle \kappa \rangle$, M_2^{κ} and M_3^{κ} only.

The construction of the optimal third-order lower bound is fully similar; it is based on the variational principle, dual to (2.2), see [8]. That is why only the evaluation of the lower bound will be treated in detail in what follows.

3. The Beran bounds

The explicit solution of the integrodifferential equation (2.4) is very difficult in general. That is why we introduce, after [10], a simpler procedure. Let $\tilde{K}(\mathbf{x})$ be a fixed kernel. Consider the set of trial fields

$$(3.1) \quad \tilde{K}^{(1)} = \left\{ \theta(\mathbf{x}) \mid \theta(\mathbf{x}) = \mathbf{G} \cdot \mathbf{x} + \alpha \int \tilde{K}(\mathbf{x}-\mathbf{y}) \kappa'(\mathbf{y}) d^3 \mathbf{y} \right\} \subset K^{(1)},$$

where $\alpha \in \mathbb{R}^1$ is adjustable parameter. The functional W , when restricted on $\tilde{K}^{(1)}$, becomes a quadratic function of α , whose minimization brings forth certain third-order bound $\tilde{\kappa}^{(3)} = \tilde{\kappa}^{(3)}[\tilde{K}(\cdot)]$ on both κ^* and $\kappa^{(3)}$: $\kappa^* \leq \tilde{\kappa}^{(3)} \leq \kappa^{(3)}$; we underline here that $\tilde{\kappa}^{(3)}$ depends on the choice of the kernel $\tilde{K}$. Due to obvious reasons, the bound $\tilde{\kappa}^{(3)}$ is called in [10] a Ritz's type bound. If $\tilde{\kappa}^{(3)} = \kappa^{(3)}$, we call, after [10], the kernel $\tilde{K}$ optimal. Since the solution of the Euler-Lagrange equation (2.4) is unique, the optimal kernels are always proportional to the solution of the latter. Therefore, the determination of an optimal kernel and the solution of Eq. (2.4) represent in general two equivalent problems.

A special choice of the kernel $\tilde{K}$ is proposed, as a matter of fact, by Beran [9]

$$(3.2) \quad \tilde{K}(\mathbf{x}) = K_B(\mathbf{x}) = \mathbf{G} \cdot \nabla \frac{1}{4\pi |\mathbf{x}|}.$$

This kernel appears in a natural way in the perturbation solution of the random problem (2.1); the evaluation of the respective bound $\tilde{\kappa}^{(3)} = \kappa_B$, called Beran's, is somewhat simpler and can be explicitly performed in certain cases, see, e. g., [13, 14]. Here we shall be interested in the problem of optimality of Beran's bounds for random dispersions of spheres.

The condition of optimality for Beran's bounds easily follows from (2.4) if there we insert a kernel, proportional to (3.2):

$$(3.3) \quad (1-\alpha) \mathbf{G} \cdot \nabla M_2^{\kappa}(\mathbf{x}) + \frac{\alpha}{\langle \kappa \rangle} \mathbf{G} \cdot \int \nabla \nabla \frac{1}{4\pi |\mathbf{y}|} \cdot \nabla_{\mathbf{x}} M_3^{\kappa}(\mathbf{x}, \mathbf{y}) d^3 \mathbf{y} = 0,$$

for a certain $\alpha \in R$ and all $\mathbf{G}$. This condition has been derived in [8] where it has been shown that it holds for Miller's cell materials. We shall show that (2.4) does not hold for random dispersions whatever be the random distribution of the spheres.

4. Alternative variational procedure for the dispersion

Let $\mathbf{x}_j$ be the set of random points that serve as centers of spheres in the dispersion. We introduce the usual multipoint probability densities $f_p(\mathbf{y}_1, \dots, \mathbf{y}_p)$ that give the probability $dP = f_p(\mathbf{y}_1, \dots, \mathbf{y}_p) d^3\mathbf{y}_1 \dots d^3\mathbf{y}_p$ simultaneously to find a point from the set $\mathbf{x}_j$ in each of the infinitesimal volumes $\mathbf{y}_i < \mathbf{y} < \mathbf{y}_i + d\mathbf{y}_i$, $i=1, \dots, p$, see [15]. Due to the assumed statistical homogeneity, $f_1 = n$, where $n = c/V_a$ is the number density of the spheres, $V_a = \frac{4}{3}a^3$. We also assume that $f_k \sim n^k$, $k=2, \dots$, see [8]. In particular, for the two-point density function we have

$$f_2(\mathbf{y}_1, \mathbf{y}_2) = f_2(\mathbf{y}_2 - \mathbf{y}_1) = n^2 g_0(\mathbf{y}_2 - \mathbf{y}_1) + o(n^2),$$

where g_0 is the zero-density limit of the so-called radial distribution function $f_2(\mathbf{y}_1, \mathbf{y}_2)/n^2$.

The set of random points $\mathbf{x}_j$ generates the field

$$(4.1) \quad \psi(\mathbf{x}) = \sum_j \delta(\mathbf{x} - \mathbf{x}_j),$$

called random density field [15]. This field describes the set $\mathbf{x}_j$ in the statistical sense, i. e. all multipoint moments of $\psi(\mathbf{x})$ can be expressed by means of the probability densities f_p and vice versa, e. g.,

$$(4.2) \quad \langle \psi(\mathbf{y}) \rangle = n, \quad \langle \psi(\mathbf{y}_1) \psi(\mathbf{y}_2) \rangle = n \delta(\mathbf{y}_2 - \mathbf{y}_1) + f_2(\mathbf{y}_1, \mathbf{y}_2), \text{ etc.}$$

Moreover, the random conductivity field of the dispersion, $\kappa(\mathbf{x})$, has a simple integral representation by means of $\psi(\mathbf{x})$:

$$(4.3) \quad \kappa(\mathbf{x}) = \kappa_m + [\kappa] \int h(\mathbf{x} - \mathbf{y}) \psi(\mathbf{y}) d^3\mathbf{y}, \quad \kappa'(\mathbf{x}) = [\kappa] \int \int h(\mathbf{x} - \mathbf{y}) \psi'(\mathbf{y}) d^3\mathbf{y},$$

where $h(\mathbf{x})$ is the characteristic (indicator) function for a single sphere of radius a located at the origin.

The existence of a convenient description of the random dispersion by means of the density field $\psi(\mathbf{x})$ makes possible an alternative variational procedure. Indeed, let us introduce the class of trial fields

$$(4.4) \quad T^{(1)} = \left\{ \theta(\mathbf{x}) \mid \theta(\mathbf{x}) = \mathbf{G} \cdot \mathbf{x} + \int T(\mathbf{x} - \mathbf{y}) \psi'(\mathbf{y}) d^3\mathbf{y} \right\}$$

— the counterpart of the class (2.3). Due to (4.3), the classes (2.3) and (4.4) are isomorphic: if the transition from $\kappa'(\mathbf{x})$ to $\psi'(\mathbf{x})$ is performed according to (4.3), the kernel K is transformed into the kernel T by means of the convolution

$$(4.5) \quad T(\mathbf{x}) = (h * K)(\mathbf{x}) = \int h(\mathbf{x} - \mathbf{y}) K(\mathbf{y}) d^3\mathbf{y}.$$

The functional W , when restricted over the class (4.4), becomes

$$(4.6) \quad W|_{T^{(1)}} = W[T(\cdot)] = \langle \kappa \rangle G^2 + \int \int \{ 2[\kappa] h(\mathbf{x} - \mathbf{y}_1) \mathbf{G} + \langle \kappa \rangle \nabla T(\mathbf{x} - \mathbf{y}_1) \}$$

$$\cdot \nabla T(\mathbf{x}-\mathbf{y}_2) \langle \psi'(\mathbf{y}_1) \psi'(\mathbf{y}_2) \rangle d^3 \mathbf{y}_1 d^3 \mathbf{y}_2 \\ + 2[\kappa] \int \int \int h(\mathbf{x}-\mathbf{y}_1) \nabla T(\mathbf{x}-\mathbf{y}_2) \cdot \nabla T(\mathbf{x}-\mathbf{y}_3) \langle \psi'(\mathbf{y}_1) \psi'(\mathbf{y}_2) \psi'(\mathbf{y}_3) \rangle d^3 \mathbf{y}_1 d^3 \mathbf{y}_2 d^3 \mathbf{y}_3$$

and the eventual form of its Euler-Lagrange equation reads [8]:

$$(4.7) \quad \begin{aligned} & \kappa_m \Delta S + [\kappa] \nabla \cdot \left\{ h(\mathbf{x}) [\mathbf{G} + \nabla S(\mathbf{x})] - n F(\mathbf{x}) \mathbf{G} \right. \\ & + n [V_a - F(\mathbf{x})] \nabla S(\mathbf{x}) - n \int \nabla S(\mathbf{x}-\mathbf{y}) h(\mathbf{x}-\mathbf{y}) R(\mathbf{y}) d^3 \mathbf{y} \\ & + n^2 \int \int h(\mathbf{x}-\mathbf{y}) R(\mathbf{y}_1) R(\mathbf{y}_1-\mathbf{y}_2) [1-R(\mathbf{y}_1)] \nabla T(\mathbf{x}-\mathbf{y}_2) d^3 \mathbf{y}_1 d^3 \mathbf{y}_2 \\ & \left. + \frac{1}{n} \int \int h(\mathbf{x}-\mathbf{y}_1) \Lambda(\mathbf{0}, \mathbf{y}_1, \mathbf{y}_2) \nabla T(\mathbf{x}-\mathbf{y}_2) d^3 \mathbf{y}_1 d^3 \mathbf{y}_2 \right\} = 0, \end{aligned}$$

where $V_a = \frac{4}{3} \pi a^3$ is the volume of a single sphere and

$$(4.8) \quad \begin{aligned} S(\mathbf{x}) &= T(\mathbf{x}) - n \int R(\mathbf{x}-\mathbf{y}) T(\mathbf{y}) d^3 \mathbf{y}, \\ F(\mathbf{x}) &= \int h(\mathbf{x}-\mathbf{y}) R(\mathbf{y}) d^3 \mathbf{y}, \quad R(\mathbf{y}) = 1 - f_2(\mathbf{0}, \mathbf{y})/n^2, \\ \Lambda(\mathbf{y}_1, \mathbf{y}_2, \mathbf{y}_3) &= f_3(\mathbf{y}_1, \mathbf{y}_2, \mathbf{y}_3) - f_2(\mathbf{y}_{12}) f_2(\mathbf{y}_{23}) f_2(\mathbf{y}_{31})/n^3, \end{aligned}$$

so that the function Λ is the deviation of f_3 from the so-called superposition approximation, see [11].

The solution $T(\mathbf{x})$ to Eq. (4.7) is uniquely defined by the optimal kernel $K(\mathbf{x})$ by means of convolution with the characteristic function $h(\mathbf{x})$, see (4.5); we shall call $T(\mathbf{x})$ also optimal. If found, the optimal bound $\kappa^{(3)}$ has the form

$$(4.9) \quad \kappa^{(3)} \mathbf{G} = \langle \kappa \rangle \mathbf{G} + n [\kappa] \int h(\mathbf{x}) \nabla S(\mathbf{x}) d^3 \mathbf{x}.$$

5. The cluster bounds of Torquato

The explicit solution of Eqn (4.7), similarly to that of its counterpart (2.4) seems very difficult in general. That is why we shall again employ a Ritz's type procedure and introduce the class of trial fields

$$(5.1) \quad \tilde{T}^{(1)} = \left\{ \theta(\mathbf{x}) \mid \theta(\mathbf{x}) = \mathbf{G} \cdot \mathbf{x} + \int \tilde{T}(\mathbf{x}-\mathbf{y}) \psi'(\mathbf{y}) d^3 \mathbf{y} \right\} \subset T^{(1)},$$

where $\alpha \in R$ and $\tilde{T}(\mathbf{x})$ is a fixed kernel. Similarly to § 3, we shall thus obtain a certain Ritz's type bound on κ^* which will coincide with the optimal one, $\kappa^{(3)}$, if $\tilde{T}(\mathbf{x})$ is proportional to the optimal kernel $T(\mathbf{x})$ — the solution to Eqn (4.7). A choice, intuitively appealing, is to take $\tilde{T}(\mathbf{x}) = T^{(1)}(\mathbf{x})$, where $T^{(1)}(\mathbf{x})$ is the disturbance to the temperature field in an unbounded matrix, introduced by a single spherical inhomogeneity, when the temperature gradient at infinity equals $\mathbf{G}$, i. e.,

$$(5.2) \quad T^{(1)}(\mathbf{x}) = 3\beta \mathbf{G} \cdot \nabla \phi(\mathbf{x}) = -\beta \mathbf{G} \cdot \mathbf{x} \begin{cases} 1, & \text{if } |\mathbf{x}| \leq a \\ a^3/|\mathbf{x}|^3, & \text{if } |\mathbf{x}| > a, \end{cases}$$

where $\beta = [\kappa]/(\kappa_f + 2\kappa_m)$, and

$$(5.3) \quad \varphi = h * \frac{1}{4\pi|\mathbf{x}|}, \quad \text{i. e.,} \quad \varphi(\mathbf{x}) = \int \frac{h(\mathbf{y})}{4\pi|\mathbf{x}-\mathbf{y}|} d^3\mathbf{y},$$

is the Newtonian potential for a single sphere of radius a located at the origin. The bound $\tilde{\kappa}^{(3)}$ which corresponds to this choice of $\tilde{T}(\mathbf{x})$ was introduced by Torquato [11] who called it first-order cluster bound and later on evaluated it in some cases.

Due to (4.5), the classes of trial fields (3.1) and (5.1) coincide, and therefore the respective Ritz's type bounds also coincide, iff

$$(5.4) \quad \tilde{T}(\mathbf{x}) = \gamma(h * \tilde{K})(\mathbf{x})$$

for a certain $\gamma \in \mathbb{R}$. Obviously, (5.4) holds for the kernels (3.2) and (5.2) which means that for dispersions of nonoverlapping spheres the Beran bounds always coincide with the first-order cluster bounds. This conclusion has been made in [13] on the base of a direct check.

6. Virial expansion of the optimal kernel

Consider the functional (4.6). Through the moments $\langle \psi'(\mathbf{y}_1) \psi'(\mathbf{y}_2) \rangle$ and $\langle \psi'(\mathbf{y}_1) \psi'(\mathbf{y}_2) \psi'(\mathbf{y}_3) \rangle$ it depends on the number density of the spheres, or, equivalently, on their volume fraction $c = nV_a$: $W[T(\cdot)] = W[T(\cdot); n]$ and therefore, the optimal kernel which minimizes the functional also depends on n . At dilute concentrations c , $c \ll 1$, we seek this kernel in the virial form:

$$(6.1) \quad T(\mathbf{x}) = T(\mathbf{x}; n) = T_0(\mathbf{x}) + nT_1(\mathbf{x}) + n^2T_2(\mathbf{x}) + \dots$$

Since the minimizing element $T(\mathbf{x})$ for the functional (4.6) is unique, the virial coefficients $T_i(\mathbf{x})$ in (6.1) are uniquely defined as well.

Let us insert (6.1) into the functional (4.6) and expand the result in powers of n , making use of the respective relations for the two- and three-point moments of $\psi'(\mathbf{x})$ that follow from (4.2)

$$(6.2) \quad W[T(\cdot)] = \langle \kappa \rangle G^2 + nW_1[T_0(\cdot)] + n^2W_2[T_0(\cdot), T_1(\cdot)] + o(n^3).$$

The functionals W_1 and W_2 depend on the indicated virial coefficients as follows:

$$(6.3) \quad W_1[T_0(\cdot)] = \kappa_m \int |\nabla T_0(\mathbf{x})|^2 d^3\mathbf{x} + [\kappa] \int h(\mathbf{x}) \{ |\nabla T_0(\mathbf{x})|^2 + 2\mathbf{G} \cdot \nabla T_0(\mathbf{x}) \} d^3\mathbf{x},$$

$$(6.4) \quad W_2[T_0(\cdot), T_1(\cdot)] = \bar{W}_2[T_0(\cdot)] + 2 \int \nabla \cdot \{ \kappa_m \nabla T_0(\mathbf{x}) + [\kappa] h(\mathbf{x}) [\mathbf{G} + \nabla T_0(\mathbf{x})] \} \nabla T_1(\mathbf{x}) d^3\mathbf{x},$$

$$(6.5) \quad \begin{aligned} \bar{W}_2[T_0(\cdot)] = & [\kappa] \int |\nabla T_0(\mathbf{x})|^2 d^3\mathbf{x} \\ & - [\kappa] \int \int h(\mathbf{x}-\mathbf{y}_1) R_0(\mathbf{y}_1-\mathbf{y}_2) [2\mathbf{G} + 2\nabla T_0(\mathbf{x}-\mathbf{y}_1) + \nabla T_0(\mathbf{x}-\mathbf{y}_2)] \\ & \cdot \nabla T_0(\mathbf{x}-\mathbf{y}_2) d^3\mathbf{y}_1 d^3\mathbf{y}_2 - \kappa_m \int \nabla T_0(\mathbf{x}-\mathbf{y}_1) \cdot \nabla T_0(\mathbf{x}-\mathbf{y}_2) R_0(\mathbf{y}_1-\mathbf{y}_2) d^3\mathbf{y}_1 d^3\mathbf{y}_2; \end{aligned}$$

here $R_0(\mathbf{y}) = 1 - g_0(\mathbf{y})$.

The minimizing kernel satisfies the equation $\delta W = 0$ so that we have, in particular,

$\delta W_1[T_0(\cdot)] = 0$, $\delta W_2[T_0(\cdot), T_1(\cdot)] = 0$. The first of these equations yields straightforwardly

$$(6.6) \quad \kappa_m \Delta T_0(\mathbf{x}) + [\kappa] \nabla \cdot \{h(\mathbf{x})[\mathbf{G} + \nabla T_0(\mathbf{x})]\} = 0$$

which is just the equation for the above mentioned disturbance, $T^{(1)}(\mathbf{x})$, to the temperature field in an unbounded matrix, introduced by a single spherical inhomogeneity, when the temperature gradient at infinity equals $\mathbf{G}$:

$$(6.7) \quad T_0(\mathbf{x}) = T^{(1)}(\mathbf{x});$$

the field $T^{(1)}(\mathbf{x})$ is given in (5.2).

With $T_0(\mathbf{x})$ already found, one should vary only $T_1(\mathbf{x})$ in the functional (6.4) in order to derive the Euler-Lagrange equation for the latter. This is however not possible, because (6.6) yields

$$(6.8) \quad W_2[T_0(\cdot), T_1(\cdot)] = \bar{W}_2[T_0(\cdot)].$$

Equation (6.8) has three important implications. First, we can conclude that to calculate the optimal bound $\kappa^{(3)}$ to the order c^2 we need only know the field $T^{(1)}(\mathbf{x})$; the explicit form of $T_1(\mathbf{x})$ is not required at all, see (6.4), (6.6) and (6.7). Second, the kernel $T(\mathbf{x})$ is optimal to the order c^2 iff its leading coefficient $T_0(\mathbf{x})$ in the virial expansion (6.1) is proportional to the single-sphere disturbance field $T^{(1)}(\mathbf{x})$. As is shown in §§ 3, 5 this is just the case with the Beran and Torquato bounds so that we can conclude that they are the optimal third-order bounds for the dispersions of nonoverlapping spheres to the order c^2 . Third, the coefficient $T_1(\mathbf{x})$ in the expansion (6.1) cannot be found within the frame of the above performed n^2 -analysis of the functional W and thus higher degrees of n should be taken into account in the series (6.2).

To see whether the Beran bounds are also optimal to the order c^p at $p > 2$, we shall argue as follows. If this is so, the solution Eqn (4.6) should be proportional to $T^{(1)}(\mathbf{x})$, i. e.

$$T(\mathbf{x}) = T(\mathbf{x}; n) = a(n) T^{(1)}(\mathbf{x}) = a_0 T^{(1)}(\mathbf{x}) + a_1 n T^{(1)}(\mathbf{x}) + \dots,$$

and therefore all virial coefficients $T_i(\mathbf{x})$, $i = 0, 1, \dots$, should be proportional to $T^{(1)}(\mathbf{x})$ as well. To see in turn whether this is the case, we shall consider in the next § 7 the virial solution (6.1) of the Euler-Lagrange equation (4.6) and obtain explicitly $T_1(\mathbf{x})$; so that we shall be compelled to conclude that the Beran bounds are not the optimal third-order bounds for the dispersion.

7. Virial solution of Eq. (4.6) for the optimal kernel

We shall look for the solution of Eqn (4.6) in the virial form (6.1):

$$(7.1) \quad T(\mathbf{x}) = \sum_{p=0}^{\infty} n^p T_p(\mathbf{x}), \quad S(\mathbf{x}) = \sum_{p=0}^{\infty} n^p S_p(\mathbf{x}).$$

As is readily follows from (4.8)₁, we have

$$(7.2) \quad S_0(\mathbf{x}) = T_0(\mathbf{x}), \quad S_1(\mathbf{x}) = T_1(\mathbf{x}) = \int R_0(\mathbf{x} - \mathbf{y}) T_0(\mathbf{y}) d^3\mathbf{y},$$

etc. On introducing (7.1) into (4.7), we get for the first two functions S_0 and S_1 the following equations

$$(7.3) \quad \kappa_m \Delta S_0 + [\kappa] \nabla \cdot \{h(\mathbf{x})[\mathbf{G} + \nabla S_0(\mathbf{x})]\} = 0,$$

$$(7.4) \quad \kappa_m \Delta S_1 + [\kappa] \nabla \cdot \{h(x) \nabla S_1(x)\} - F_0(x) \mathbf{G} + [V_a - F(x)] \nabla S_0(x) - \int \nabla S_0(x-y) h(x-y) R_0(y) d^3y = 0,$$

where

$$(7.5) \quad F_0(x) = \int h(x-y) R_0(y) d^3y, \quad R_0(y) = 1 - g_0(y),$$

so that $F_0(x)$ and $R_0(x)$ are the leading terms (zero-density limits) in the virial expansions of the functions $F(x)$ and $R(x)$, defined in (4.8)₂.

Naturally enough, Eq. (7.3) coincides with (6.6) and thus

$$(7.6) \quad S_0(x) = T_0(x) = T^{(1)}(x) = 3\beta \mathbf{G} \cdot \nabla \varphi(x),$$

see (5.2) and (6.7). In particular, $\nabla S_0(x)$ is constant within the sphere $V_a = \{x \mid |x| \leq a\}$: $h(x) \nabla S_0(x) = -\beta \mathbf{G} h(x)$, which allows to simplify Eq. (7.4):

$$(7.7) \quad \kappa_m \Delta S_1 + [\kappa] \nabla \cdot \{h(x) \nabla S_1(x)\} - (1-\beta) F_0(x) \mathbf{G} + [V_a - F(x)] \nabla S_0(x) = 0.$$

The solution of this equation may be easily found making use of the respective continuity conditions at $|x|=a$ for the function $S_1(x)$ and the normal component of its "flux" $\kappa(x) \nabla S(x)$. The eventual result reads

$$(7.8a) \quad S_1(x) = \lambda_1 \mathbf{G} \cdot \mathbf{x}, \quad \text{if } r \leq a,$$

$$(7.8b) \quad S_1(x) = \mathbf{G} \cdot \mathbf{x} \left\{ \lambda_2 \frac{a^3}{r^3} + \frac{3\beta}{r^3} \int_a^r \rho^2 F_0(\rho) d\rho - \frac{[\kappa]}{\kappa_m} \frac{2\beta a^3}{r^3} \int_a^r \rho^2 \Phi_0(\rho) d\rho \right\}, \quad \text{if } r > a;$$

here $r = |x|$ and

$$(7.8c) \quad \lambda_1 = \lambda_2 = \frac{3\kappa_m}{\kappa_f + 2\kappa_m} \beta V_a + 3\beta^2 m_2 V_a, \quad \Phi_0(r) = \int_r^\infty \frac{F'_0(\rho)}{\rho^3} d\rho,$$

$$m_2 = -\frac{1}{2\pi} \Phi_0(a) = \frac{2}{3} - \frac{3}{2\pi} \int_a^\infty \frac{F_0(\rho)}{\rho^4} d\rho.$$

The statistical parameter m_2 depends on the zero-density limit, $g_0(r)$, of the radial distribution function only. It was introduced and studied in [8, p. II] where it was shown that

$$(7.9) \quad m_2 = 2 \int_2^\infty \frac{\lambda^2}{(\lambda^2 - 1)^3} g_0(\lambda a) d\lambda, \quad \lambda = r/a.$$

It is to be noted that the function $S_1(x)$ within the sphere V_a was evaluated in [8, Eq. (9.16)] and this obviously suffices to obtain the bound $\kappa^{(3)}$ to the order c^2 , see (4.9). Thus we have, in virtue of (7.8) and (4.9), that

$$(7.10a) \quad \frac{\kappa^{(3)}}{\kappa_m} = 1 + 3\beta c + 3\beta^2 \left(1 + \frac{[\kappa]}{\kappa_m} m_2 \right) c^2 + o(c^2),$$

and a similar expression for the lower bound

$$(7.10b) \quad \frac{k^{(3)}}{k_m} = 1 + 3\beta c + 3\beta^2 \left(1 + \frac{[k]}{k_m} m_2\right) c^2 + o(c^2),$$

where $k=1/\kappa$ are the respective compliances.

The c^2 -bounds (7.10) are optimal in the class of trial fields (4.4). Moreover, as shown in § 6, the Beran bounds are c^2 -optimal and this fact explains why the direct c^2 -evaluation of the latter in [10] has led to the same expressions (7.10).

To calculate the field $T_1(\mathbf{x})$, in order to check on whether or not it is proportional to $T^{(1)}(\mathbf{x})$, we invoke (7.2)₂ and the formula

$$\begin{aligned} \int R_0(\mathbf{y}) T_0(\mathbf{x}-\mathbf{y}) d^3\mathbf{y} &= -\frac{3\beta}{r^3} \int_a^r \rho^2 F_0(\rho) d\rho \mathbf{G} \cdot \mathbf{x} \\ &= -\mathbf{G} \cdot \mathbf{x} \begin{cases} \beta V_a, & \text{if } r \leq a \\ \beta V_a \frac{a^3}{r^3} + \frac{3\beta}{r^3} \int_a^r \rho^2 F_0(\rho) d\rho, & \text{if } r > a, \end{cases} \end{aligned}$$

which can be easily deduced if one performs a convolution with $R_0(\mathbf{y})$ on both sides of Eq. (7.3). The eventual result reads

$$(7.11a) \quad T_1(\mathbf{x}) = -\mathbf{G} \cdot \mathbf{x} \begin{cases} \lambda, & \text{if } r \leq a \\ \lambda \frac{a^3}{r^3} - \frac{2[\kappa]\beta a^3}{\kappa_m r^3} \int_a^r \rho^2 F_0(\rho) d\rho, & \text{if } r > a, \end{cases}$$

where

$$(7.11b) \quad \lambda = 3\beta \left(\frac{2}{3} + \beta m_2 \right) V_a.$$

The crucial point now is the comparison between (7.11) and the single-sphere disturbance field $T^{(1)}(\mathbf{x})$, given in (5.2). A simple inspection shows that $T_1(\mathbf{x})$ and $T^{(1)}(\mathbf{x})$ are never proportional, since $\Phi_0(\mathbf{x})$ never vanishes, cf. (7.5) and (7.8c), and thus the second term in the r. h. side of (7.11a) at $r > a$ never vanishes as well. As already pointed out (§ 6), this fact implies that the Beran bounds are never optimal for the dispersions under study to the order c^2 at $p > 2$. In turn, this means that the condition of optimality (3.3) does not hold for the dispersions.

8. Concluding remarks

The foregoing analysis clearly shows that for dispersions of spheres and, more generally, for random particulate media, it is not possible to find a fixed optimal kernel $T(\mathbf{x})$, which is independent of the statistics of the medium and which leads to the best third-order bound. For the dispersions of nonoverlapping spheres we may only say that $T(\mathbf{x})$ resembles the single-sphere disturbance field $T^{(1)}(\mathbf{x})$ in that its gradient is constant within the sphere V_a and it decays as $\mathbf{G} \cdot \mathbf{x}/|\mathbf{x}|^3$ at infinity. However, at the intermediate distances, $a < |\mathbf{x}| < \infty$, the optimal kernel is sensitive to the statistics of the dispersion and to reveal the exact form of $T(\mathbf{x})$ through the solution of Eq. (4.7) seems very difficult. We may therefore conclude that though the Beran bounds have turned out not to be optimal they, unlike the optimal ones, can be eva-

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uated, at least numerically, for all admissible values of c , see [13, 14] and not only to the order c^2 .

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