Mathematical Models and Methods in Applied Sciences,
Vol. 2 (1992), No. 3, 249–269.

ON THE PROBLEM OF HEAT CONDUCTION FOR RANDOM DISPERSIONS OF SPHERES ALLOWED TO OVERLAP

KONSTANTIN Z. MARKOV
Faculty of Mathematics and Informatics, University of Sofia,
5 blvd J. Boucher 1126 Sofia, Bulgaria

and

CHRISTO I. CHRISTOV
Laboratory of Informatics, Institute of Meteorology and Hydrology,
Bulgarian Academy of Sciences, 1184 Sofia, Bulgaria

We consider a random two-phase medium which represents a matrix containing an array of allowed to overlap spherical inclusions with random radii. A statistical theory of transport phenomena in the medium, on the example of heat propagation, is constructed by means of the functional (Volterra-Wiener) series approach. The functional series for the temperature is rendered virial in the sense that its truncation after the p-tuple term yields results for all multipoint correlation functions of the temperature field that are asymptotically correct to the order n^p, where n is the mean number of spheres per unit volume. The case $p = 2$ is considered in detail and the needed kernels of the factorial series are found to the order n^2. In this way the full statistical solution, i.e., all needed correlation functions, and not only the effective conductivity, can be expressed in a closed form, correct to the said order.

1. Introduction

Consider a system of random points $\mathbf{x}_\alpha$ in the three-dimensional space $\mathbb{R}^3$. Let us attach to each point $\mathbf{x}_\alpha$ a sphere V_a of radius a_α, i.e. let us consider a polydisperse rigid suspension of spheres centered at the points of the random system. When the spheres are forbidden to penetrate each other one has the well known dispersion of nonoverlapping spheres. An obvious generalization of such a model that corresponds in a sense better to the pure "point" nature of the generating set $\mathbf{x}_\alpha$ can be obtained in the following way.

Assume that the points $\mathbf{x}_\alpha$ serve as nuclei of spheres which start to grow simultaneously from zero radius to radius a_α. The growth of the spheres is independent, i.e. if a pair of points are closer than the sum of the final radii of spheres the latter penetrate each other without "noticing" the presence of the other sphere. Thus, the particles shown in Fig. 1 are formed. Next we suppose that each complex of spheres has a thermal conductivity κ_f. The reminder of the space is endowed with thermal conductivity κ_m. The so-designed material, see Fig. 1, is an idealized two-phase

composite, whose definition suggests that it may be quite adequate as a model for a number of random constitutions of practical and technological interest. Indeed, the model has been successfully used to describe such materials like catalysis silica gels for gel permeation chromatography, amberlite resin beads prepared by controlled suspension polymerization, freeze dried apple and beef, polyurethane foams, metal filled polymers, etc., see[9] for some details and references.

Fig. 1

We shall also distinguish in what follows monodisperse and polydisperse models in which the spheres have either constant or random radii respectively. It is important to note that the latter is akin to the so-called Boolean model introduced by Matheron[20] in order to describe the random structure of porous materials materials, see also[14] for further development and application to sintered materials. The Boolean model is based on the notion of a Poissonian point set to each point of which grains of random shape and size are attached. The grains grow without interacting among each other so that the overlapping is permitted. In the present paper we resort only to the case when the inclusions are spheres, but the resulting model is not a limiting case of the Boolean medium, because we relax the requirement for the generating point set to be Poissonian.

To the best of the authors' knowledge, the above introduced model was first employed by Weissberg[26] whose aim was to obtain a certain bound on the diffusion coefficient of a random porous medium. (In a footnote the said author mentioned that the model had been proposed to him by W.F.Brown.) The appealing simplicity of the model, especially for a Poisson generating set of random points $\mathbf{x}_\alpha$, from one hand, and its applicability to real random media from the other hand, has immediately inspired a number of studies.[9,26–28]

Recently Torquato *et al.*[23–25] devoted several papers on the statistical description and bulk properties of such dispersions of overlapping spheres, where the statistical theory of scalar conductivity phenomena in the monodisperse case was constructed. In particular, an analytic formula for the effective conductivity, κ^*, of the dispersion, correct to the order n^2, was derived. The method of Torquato is an extension of the cluster expansion approach, introduced and thoroughly developed by Felderhof

et al.[10] in the case of a dispersion of nonoverlapping spheres.

In this paper we propose to use an alternative statistical approach in which functional (Volterra-Wiener) series of a special kind—the so-called factorial series[19]—are employed. The method was successfully applied in[17,18] in the study of scalar conductivity problem for dispersions of nonoverlapping spheres, see also,[2,3,7] and it was able to reproduce in a coherent and rigorous way the n^2-formulas for the effective conductivity, found by Jeffrey[13] and Felderhof *et al.*[10]. The new and essential point, however, is that the factorial series approach is able as well to produce results, in an analytic form, for all multipoint correlation functions of the random fields of interest. (See,[18] where the n^2-formula for the two-point correlation function of the temperature field is given as an illustration.) Thus, unlike the cluster expansion method, concerned solely with the effective properties evaluation, our approach yields the full statistical solution of the random transport problem under study, which includes, as is well known,[1] the effective conductivity as a simplest one-point statistical characteristics.

The aim of the present paper is to demonstrate how the factorial series work in the scalar conductivity problem for dispersions of spheres in which overlapping is permitted. First, in Section 2, it is shown how to develop the conductivity coefficient of a dispersion of overlapping spheres into an infinite functional series, generated by the so-called factorials[19] of the random density function connected with the generating set of random points $\mathbf{x}_\alpha$. In Section 3 we develop the random temperature field as functional series with respect to the same factorial fields. Such series have the important property that, for a wide class of random sets $\mathbf{x}_\alpha$, they are virial in the sense that their truncation after the p-tuple term yields results that are asymptotically correct to the order n^p for all multipoint correlation functions of the temperature field. This fact, proved in[19] in the monodisperse case of nonoverlapping spheres, appears valid in the case of overlapping as well (Section 3). In Section 4 the procedure for identification of the kernels in the factorial series is given. It leads to a hierarchy of coupled integro-differential equations. The virial approximation to the solution of this system is proposed in Section 5, where the case $p = 2$ is considered in detail. The full statistical description of the temperature field, asymptotically correct to the order n^2, is given there in an analytical form which involves the yet unknown solution to the single-inclusion problem in the case when the inclusion is formed by two overlapping spheres. In this way we are able to express in a closed form all multipoint correlation functions for the temperature field in the dispersion, correct to the order n^2. As a simplest illustration we obtain an expression for the effective heat conductivity of the dispersion which could be shown to coincide with the respective n^2-formula of Torquato.[23]

2. Statistical Description of the Dispersion

In order to elucidate the main ideas we begin with the monodisperse case when all spheres have the radius a, so that the medium is completely described by a system of random points $\mathbf{x}_\alpha$—the centers of the spheres. The statistics of the system $\mathbf{x}_\alpha$

is conveniently represented by the multipoint distribution densities $f_k(\mathbf{y}_1, \ldots, \mathbf{y}_k)$, or probability density functions ρ_k, as denoted in.[24] They define the probability dP to simultaneously find a point of the random set $\mathbf{x}_\alpha$ per each of the infinitesimal volumes $\mathbf{y}_i < \mathbf{y} < \mathbf{y}_i + d\mathbf{y}_i$, $1, \ldots, k$, to be

$$dP = f_k(\mathbf{y}_1, \ldots, \mathbf{y}_k)\, d^3\mathbf{y}_1 \ldots d^3\mathbf{y}_k. \tag{2.1}$$

We assume that the system $\mathbf{x}_\alpha$ is statistically isotropic and homogeneous; then, in particular, $f_1 = n$ and $f_k = f_k(\mathbf{y}_{2,1}, \ldots, \mathbf{y}_{k,1})$, where $\mathbf{y}_{j,i} = \mathbf{y}_j - \mathbf{y}_i$ and n denotes the number density, i.e., the mean number of points per unit volume.

Let us imagine now that by means of a certain manufacturing process we produce random point systems $\mathbf{x}_\alpha$ with different number densities n. The statistics of the system $\mathbf{x}_\alpha$ will then depend on n as a parameter, i.e. $f_p = f_p(\mathbf{Y}_p; n), \mathbf{Y}_p = (\mathbf{y}_1, \ldots, \mathbf{y}_p)$. We shall assume, as usual, that $f_p \sim n^p$, i.e., f_p has the asymptotic order n^p at $n \to 0$, $p = 1, 2, \ldots$. In particular, for the two-point distribution density f_2 which most frequently appears in models and theoretical studies, we have

$$f_2(\mathbf{y}_1, \mathbf{y}_2) = n^2 g(r),\ \ g(r) = g_0(r) + O(n), \tag{2.2}$$

$r = |\mathbf{y}_2 - \mathbf{y}_1|$. (The point system $\mathbf{x}_\alpha$ hereafter will be assumed statistically isotropic as well.) Thus $g_0(r)$ is the zero-density limit of the radial distribution function $g(r)$ for the system $\mathbf{x}_\alpha$.

A convenient characteristics of the field created by a random point set is the so-called random density field

$$\psi(\mathbf{x}) = \sum_\alpha \delta(\mathbf{x} - \mathbf{x}_\alpha). \tag{2.3}$$

This field was systematically used by Stratonovich[22] in the one-dimensional case when the role of $\mathbf{x}$ is played by the time. The random function $\psi(\mathbf{x})$ is uniquely defined by the random set $\mathbf{x}_\alpha$. The respective formulas are derived in;[15] they read:

$$\begin{gathered}
\langle \psi(\mathbf{y}) \rangle = f_1(\mathbf{y}) = n, \\
\langle \psi(\mathbf{y}_1)\psi(\mathbf{y}_2) \rangle = f_1(\mathbf{y}_1)\delta(\mathbf{y}_{1,2}) + f_2(\mathbf{y}_1, \mathbf{y}_2), \\
\langle \psi(\mathbf{y}_1)\psi(\mathbf{y}_2)\psi(\mathbf{y}_3) \rangle = f_1(\mathbf{y}_1)\delta(\mathbf{y}_{1,2})\delta(\mathbf{y}_{1,3}) \\
+3\big\{\delta(\mathbf{y}_{1,2}) f_2(\mathbf{y}_1, \mathbf{y}_3)\big\}_s + f_3(\mathbf{y}_1, \mathbf{y}_2, \mathbf{y}_3),
\end{gathered} \tag{2.4}$$

etc., where $\{\cdot\}_s$ means symmetrization with respect to all different combination of indexes in the braces. The brackets $\langle \cdot \rangle$ hereafter denote ensemble averaging. The usefulness of the field $\psi(\mathbf{x})$ in the study of particulate random media was demonstrated by the authors;[2,3,7,8,17–19] it stems from the fact that the random conductivity field

$$\kappa(\mathbf{x}) = \begin{cases} \kappa_m, & \text{if } \mathbf{x} \in \text{matrix}, \\ \kappa_f, & \text{if } \mathbf{x} \in \text{spheres}, \end{cases} \tag{2.5}$$

has a simple integral representation by means of $\psi(\mathbf{x})$ in the case when the spheres are forbidden to overlap. In the dispersion under study, where the spheres can overlap, the adequate representation of $\kappa(\mathbf{x})$ through $\psi(\mathbf{x})$ is a crucial point in our analysis.

Let us introduce after Frish[11] the random field

$$I(\mathbf{x}) = \begin{cases} 1, & \text{if } \mathbf{x} \in \text{matrix}, \\ 0, & \text{if } \mathbf{x} \in \text{spheres}. \end{cases} \tag{2.6}$$

This function is convenient for describing two-phase media since it refers to both cases of non-overlapping or overlapping spheres; it has been frequently used in the literature.[26−28,23−24]

Due to definitions (2.5) and (2.6) we have[24]

$$\kappa(\mathbf{x}) = \kappa_m + [\kappa](1 - I(\mathbf{x})), \tag{2.7}$$

$$I(\mathbf{x}) = \prod_{\alpha} [1 - h(\mathbf{x} - \mathbf{x}_\alpha)], \tag{2.8}$$

where $[\kappa] = \kappa_f - \kappa_m$, and $h(\mathbf{x})$ is the indicator function of a single sphere of radius a located at the origin. Using the definition (2.3) of the random density field together with (2.7) and (2.8), it may be easily shown that the field $\kappa(\mathbf{x})$ can be expanded as the functional series

$$\kappa(\mathbf{x}) = \kappa_m + [\kappa] \sum_{k=1}^{\infty} \int \dots \int h(\mathbf{x} - \mathbf{y}_1) \dots h(\mathbf{x} - \mathbf{y}_k)$$

$$\times \, \Delta_\psi^{(k)}(\mathbf{y}_1, \dots, \mathbf{y}_k) \, d^3\mathbf{y}_1 \dots d^3\mathbf{y}_k, \tag{2.9}$$

where the so-called factorials[4,5] of the random density field are introduced as follows

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

$$\Delta_\psi^{(k)}(\mathbf{y}_1, \dots, \mathbf{y}_k) = \psi(\mathbf{y}_1)[\psi(\mathbf{y}_2) - \delta(\mathbf{y}_{2,1})] \dots \tag{2.10}$$

$$\times \, [\psi(\mathbf{y}_k) - \delta(\mathbf{y}_{k,1}) - \dots - \delta(\mathbf{y}_{k,k-1})], \quad k = 2, 3, \dots.$$

(Hereafter the integrals are over $\mathbb{R}^3$ if the integration domain is not explicitly indicated.)

When the spheres are forbidden to overlap, the products $h(\mathbf{x} - \mathbf{y}_1) \dots h(\mathbf{x} - \mathbf{y}_k)$ in (2.9) vanish, so that

$$I(\mathbf{x}) = 1 - \sum_j h(\mathbf{x} - \mathbf{x}_j) = 1 - \int h(\mathbf{x} - \mathbf{y}) \psi(\mathbf{y}) \, d^3\mathbf{y},$$

and (2.7) reduces to the simple linear transformation

$$\kappa(\mathbf{x}) = \kappa_m + [\kappa] \int h(\mathbf{x} - \mathbf{y}) \psi(\mathbf{y}) \, d^3\mathbf{y}, \tag{2.11}$$

widely used in the theory of transport phenomena in dispersions of nonoverlapping spheres, developed in.[2,3,7,8,16–19]

Note also the important formula

$$\left\langle \Delta_{\psi}^{(p)}(\mathbf{y}_1, \dots \mathbf{y}_p) \right\rangle = f_p(\mathbf{y}_1, \dots, \mathbf{y}_p),\ p = 1, 2, \dots. \tag{2.12}$$

This formula is announced in[4] and rigorously proved in,[5] see also.[19]

Let us denote by c the volume fraction of the filler (particulate) phase represented by the spheres and their intersections. Then, comparing the obvious formula $\langle \kappa(\mathbf{x}) \rangle = \langle \kappa \rangle = \kappa_m + c[\kappa]$ with the result of averaging both sides of (2.9), we get in virtue of (2.7) and (2.12)

$$c = \sum_{k=1}^{\infty} \frac{(-1)^{k+1}}{k!} \int \dots \int h(\mathbf{x} - \mathbf{y}_1) \dots h(\mathbf{x} - \mathbf{y}_k) \left\langle \Delta_{\psi}^{(k)}(\mathbf{y}_1, \dots, \mathbf{y}_k) \right\rangle$$

$$\times\, d^3\mathbf{y}_1 \dots d^3\mathbf{y}_k = \int h(\mathbf{x} - \mathbf{y}) f_1(\mathbf{y})\, d^3\mathbf{y} \tag{2.13}$$

$$-\frac{1}{2!} \int\int h(\mathbf{x} - \mathbf{y}) h(\mathbf{x} - \mathbf{y}_1) h(\mathbf{x} - \mathbf{y}_2) f_2(\mathbf{y}_1, \mathbf{y}_2)\, d^3\mathbf{y}_1 d^3\mathbf{y}_2 + \dots.$$

An equivalent to (2.13) formula is given in.[24,p.I,eq.(24)] The k-tuple terms in (2.13) can be easily calculated only for a Poissonian random set $\mathbf{x}_j$, for which $f_p = n^p$, $p = 1, 2, \dots$. In this case

$$c = \eta - \frac{1}{2!}\eta^2 + \frac{1}{3!}\eta^3 + \dots = 1 - e^{-\eta}, \quad \eta = nV_a, \tag{2.14}$$

$V_a = \frac{4}{3}\pi a^3$, which is a well known result, see[9,26] *et al.*

The representation (2.13) allows one also to calculate in a closed form all multipoint moments (correlation functions) of the random conductivity field $\kappa(\mathbf{x})$ of the dispersion in terms of the given probability densities f_p of the random set $\mathbf{x}_\alpha$. An alternative and more detailed analysis of these and various other statistical characteristics of dispersions of overlapping spheres is performed by Torquato and Stell.[24]

The generalization of the results previous results to the case of a polydisperse model is straightforward and essentially follows the reasoning in the case of nonoverlapping spheres.[4–6]

Indeed, consider the system of marked random points $\{\mathbf{x}_\alpha; a_\alpha\}$, where the mark $a_\alpha \in (0, \infty)$ is the radius of the sphere centered at the random spatial position $\mathbf{x}_\alpha$. (For the general definition and basic properties of sets of marked random points see.[21]) Similarly to the monodisperse case, cf. (2.1), the system of marked random points is exhaustively described by the multipoint probability densities F_k such that

$$dP = F_k(\mathbf{y}_1, \dots, \mathbf{y}_k; a_1, \dots, a_k)\, d^3\mathbf{y}_1 \dots d^3\mathbf{y}_k\, da_1 \dots da_k \tag{2.15}$$

is the probability to simultaneously find in the vicinities $\mathbf{y}_i < \mathbf{y} < \mathbf{y}_i + d\mathbf{y}_i$ of the spatial positions $\mathbf{y}_i, k$ members of the system with marks (i.e., with radii) in the vicinities $a_i < a < a_i + da_i$ of the values a_i, respectively, $i = 1, \ldots, k$. Obviously

$$F_1 = nP(a), \tag{2.16}$$

where $P(a)$ is the one-dimensional probability density of the mark. It is convenient also to introduce the notation

$$F_k = \widetilde{f}_k(\mathbf{y}_1, \ldots, \mathbf{y}_k; a_1, \ldots, a_k) P_k(a_1, \ldots, a_k), \tag{2.17}$$

where $P_k(a_1, \ldots, a_k)$ are the multivariate probability densities of the mark of an object (a sphere), regardless to the particular spatial positions of the latter. In turn, the functions $\widetilde{f}_k$ in (2.17) reflect the statistical interrelation between the marks and the spatial positions. One easily sees that $\widetilde{f}_k$ play a role similar to that of the functions f_k from (2.1); here, however, $\widetilde{f}_k$ are referred to the subsets of points each of which has the specific value, a_1 to a_k respectively, of the mark. The decomposition (2.17) helps keeping the notations quite similar to those for the case of random points without marks, just replacing the functions f_k by $\widetilde{f}_k$.[4–6] For example, the radial distribution function in (2.2) is to be replaced by the more general one

$$g(\mathbf{y}_1, \mathbf{y}_2; a_1, a_2) = g(r; a_1 + a_2) = \frac{F_2(\mathbf{y}_1, \mathbf{y}_2; a_1, a_2)}{n^2 g_0(r; a_1 + a_2)} + O(n), \tag{2.18}$$

where $r = |\mathbf{y}_2 - \mathbf{y}_1|$ and g_0 is the zero-density limit of the function g.

In what follows we shall adopt the assumption of statistical independence of the mark distribution

$$P_k(a_1, \ldots, a_k) = P(a_1) \ldots P(a_k), \tag{2.19}$$

which is reasonable in the case of dilute set $\mathbf{x}_\alpha$, considered hereafter, when $n \to 0$.

The expressions (2.7), (2.8) for the random coefficient $\kappa(\mathbf{x})$ of thermal conductivity are easily generalized for the polydisperse case making use of the indicator function for a single sphere of radius located at the origin: $h(\mathbf{x}; a) = 1$ for $|\mathbf{x}| \le a$ and vanishes otherwise. Acknowledging the dependence of $h(\mathbf{x}; a)$ on the mark a in eqn (2.7), we recast (2.9) in the form

$$\kappa(\mathbf{x}) = \kappa_m + [\kappa] \sum_{k=1}^{\infty} \int \ldots \int h(\mathbf{x} - \mathbf{y}_1; a_1) \ldots h(\mathbf{x} - \mathbf{y}_k; a_k)$$

$$\times \, \Delta_\psi^{(k)}(\mathbf{y}_1, \ldots, \mathbf{y}_k; a_1, \ldots, a_k) \, d^3\mathbf{y}_1 \ldots d^3\mathbf{y}_k \, da_1 \ldots da_k, \tag{2.20}$$

where $\Delta_\psi^{(k)}$ are the generalized factorials

$$\Delta_\psi^{(0)}(\mathbf{y}; a) = 1, \;\; \Delta_\psi^{(1)}(\mathbf{y}; a) = \psi(\mathbf{y}; a),$$

$$\Delta_{\psi}^{(k)}(\mathbf{y}_1,\ldots,\mathbf{y}_k;a_1,\ldots,a_k)$$

$$= \psi(\mathbf{y}_1;a_1)[\psi(\mathbf{y}_2;a_2)-\delta(\mathbf{y}_{1,2})\delta(a_{2,1})]\ldots[\psi(\mathbf{y}_k;a_k) \tag{2.21}$$

$$-\delta(\mathbf{y}_{k,1})\delta(a_{k,1})-\ldots-\delta(\mathbf{y}_{k,k-1})\delta(a_{k,k-1})],$$

$k=2,3,\ldots$, $a_{i,j}=a_i-a_j$, of the marked random density function[4]

$$\psi(\mathbf{x};a)=\sum_{\alpha}\delta(\mathbf{x}-\mathbf{x}_\alpha)\delta(a-a_\alpha), \tag{2.22}$$

generated by the system of marked random points $\{\mathbf{x}_\alpha;a_\alpha\}$, cf. (2.10). The expressions, similar to (2.4), for the function $\psi(\mathbf{x};a)$ are easily derived from (2.21), see;[4–6] they read

$$\langle\psi(\mathbf{y};a)\rangle = F_1(\mathbf{y};a)=nP(a),$$

$$\langle\psi(\mathbf{y}_1;a_1)\psi(\mathbf{y}_2;a_2)\rangle = F_1(\mathbf{y}_1;a_1)\delta(\mathbf{y}_{1,2})\delta(a_{1,2}) \tag{2.23}$$

$$+F_2(\mathbf{y}_1,\mathbf{y}_2;a_1,a_2),\ \text{etc.}$$

3. Heat Conduction Through the Dispersion—Functional Expansion

Consider the typical problem of heat conduction through a random unbounded heterogeneous medium. The governing equations of the problem, at the absence of body sources, are

$$\nabla\cdot\mathbf{q}(\mathbf{x})=0,\ \mathbf{q}(\mathbf{x})=\kappa(\mathbf{x})\nabla\theta(\mathbf{x}), \tag{3.1a}$$

$$\langle\nabla\theta(\mathbf{x})\rangle=\mathbf{G}, \tag{3.1b}$$

where $\mathbf{q}(\mathbf{x})$ is the flux vector and $\theta(\mathbf{x})$ is the random temperature field. The existence and uniqueness theorem for the problem (3.1) is proved, e.g., in[12] under the natural condition $0<k_1\le\kappa(\mathbf{x})\le k_2<\infty$.

Let us recall now, see e.g.,[1] that solving the random problem (3.1) means to determine all r-point moments of the temperature field, namely, the averages

$$\langle\theta(\mathbf{x}_1)\ldots\theta(\mathbf{x}_r)\rangle \tag{3.2a}$$

and the joint moments of $\theta(\mathbf{x})$ and $\kappa(\mathbf{x})$, i.e., the averages

$$\langle\theta(\mathbf{x}_1)\ldots\theta(\mathbf{x}_s)\kappa(\mathbf{x}_{s+1})\ldots\kappa(\mathbf{x}_{s+l})\rangle,\ r,l,s=1,2,\ldots, \tag{3.2b}$$

by means of the known moments

$$\langle\kappa(\mathbf{x}_1)\ldots\kappa(\mathbf{x}_q)\rangle,\ q=1,2,\ldots, \tag{3.3}$$

of the given conductivity field. In particular, among the joint moments (3.2b), one is to evaluate the one–point moment

$$\langle \kappa(\mathbf{x}) \nabla \theta(\mathbf{x}) \rangle = \kappa^* \mathbf{G}, \tag{3.4}$$

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

Similarly to the representation (2.9) of the conductivity field, we develop the random temperature field in a functional series with respect to the factorials, i.e.,

$$\theta(\mathbf{x}) = T_0(\mathbf{x}) + \iint T_1(\mathbf{x} - \mathbf{y}; a) \Delta_\psi^{(1)}(\mathbf{y}; a)\, d^3\mathbf{y} da$$

$$+ \iiiint T_2(\mathbf{x} - \mathbf{y}_1, \mathbf{x} - \mathbf{y}_2; a_1, a_2) \Delta_\psi^{(2)}(\mathbf{y}_1, \mathbf{y}_2; a_1, a_2)\, d^3\mathbf{y}_1 d^3\mathbf{y}_2\, da_1 da_2 + \dots, \tag{3.5}$$

where $T_0, T_1, \dots$ are nonrandom kernels. Due to the symmetry of the factorials (2.14), the kernels T_p for $p \geq 2$ are also symmetric functions of their arguments. (Hereafter the integrals with respect to the mark a are over $(0, +\infty)$.)

The functional series of the type (3.5) are introduced, in the monodisperse case, in,[19] where they are called factorial. The central result of[19] states that for the class of point sets $\mathbf{x}_\alpha$ which comply with the assumption $f_p \sim n^p$, the factorial series (3.5) are virial in the following sense.

Let us denote by $\theta^{(p)}(\mathbf{x})$ the series (3.5) truncated after the p–tuple term, namely

$$\theta(\mathbf{x}) = \theta^{(p)}(\mathbf{x}) + R_p(\mathbf{x}), \tag{3.6}$$

$$R_p(\mathbf{x}) = \sum_{k=p+1}^{\infty} \iint T_k(\mathbf{x} - \mathbf{y}_1, \dots, \mathbf{x} - \mathbf{y}_k; a_1, \dots, a_k)$$

$$\times\, \Delta_\psi^{(k)}(\mathbf{y}_1, \dots, \mathbf{y}_k; a_1, \dots, a_k)\, d^3\mathbf{y}_1 \dots d^3\mathbf{y}_k\, da_1 \dots da_k. \tag{3.7}$$

Accordingly, we truncate also the series (2.9) after the p–tuple term

$$\kappa(\mathbf{x}) = \kappa^{(p)}(\mathbf{x}) + r_p(\mathbf{x}),$$

$$r_p(\mathbf{x}) = \sum_{k=p+1}^{\infty} \frac{(-1)^{(k+1)}}{k!} \iint h(\mathbf{x} - \mathbf{y}_1; a_1) \dots h(\mathbf{x} - \mathbf{y}_k; a_k)$$

$$\times\, \Delta_\psi^{(k)}(\mathbf{y}_1, \dots, \mathbf{y}_k; a_1, \dots, a_k)\, d^3\mathbf{y}_1 \dots d^3\mathbf{y}_k\, da_1 \dots da_k. \tag{3.8}$$

Then it appears that

$$\langle \theta(\mathbf{x}_1) \dots \theta(\mathbf{x}_r) \rangle = \langle \theta^{(p)}(\mathbf{x}_1) \dots \theta^{(p)}(\mathbf{x}_r) \rangle + o(n^p), \tag{3.9a}$$

$$\langle \theta(\mathbf{x}_1) \dots \theta(\mathbf{x}_m) \kappa(\mathbf{x}_{m+1}) \dots \kappa(\mathbf{x}_{m+r}) \rangle$$

$$= \langle \theta^{(p)}(\mathbf{x}_1) \dots \theta^{(p)}(\mathbf{x}_m) \kappa^{(p)}(\mathbf{x}_{m+1}) \dots \kappa^{(p)}(\mathbf{x}_{m+r}) \rangle + o(n^p). \tag{3.9b}$$

The relations (3.9) just represent the definition of the virial property of a functional series as introduced in.[7,17–19] This means that if the kernels $T_0, T_1, \ldots, T_p$ are properly identified, the truncation after the p–tuple term gives the full statistical description of $\theta(\mathbf{x})$ asymptotically correct to the order n^p; moreover, it suffices to replace the conductivity field $\kappa(\mathbf{x})$ in (2.9) by its truncation $\kappa^{(p)}(\mathbf{x})$, see (3.8).

A general method for identification of the kernels in the series (3.5) will be displayed only in the case $p = 2$, which suffices to demonstrate the required technique and allows us to make a comparison with the respective Torquato's expression[23] for the effective conductivity of the dispersion to the order n^2.

To facilitate the analysis we first render the series (3.5) n^2–orthogonal in the sense that the averaged values of the products of terms with different orders are $o(n^2)$–small. To this end we introduce after[18,19] the following linear combinations of the factorials

$$D_\psi^{(0)} = 1,\ D_\psi^{(1)}(\mathbf{y}; a) = \Delta_\psi^{(1)}(\mathbf{y}; a) - nP(a) = \psi'(\mathbf{y}; a),$$

$$\begin{gathered} D_\psi^{(2)}(\mathbf{y}_1, \mathbf{y}_2; a_1, a_2) = \Delta_\psi^{(2)}(\mathbf{y}_1, \mathbf{y}_2; a_1, a_2) \\ -ng_0(\mathbf{y}_1, \mathbf{y}_2; a_1, a_2)\big[P(a_2)\psi'(\mathbf{y}_1; a_1) + P(a_1)\psi'(\mathbf{y}_2; a_2)\big] \\ -n^2 P(a_1, a_2) g_0(\mathbf{y}_1, \mathbf{y}_2; a_1, a_2), \end{gathered} \tag{3.10}$$

$$D_\psi^{(k)}(\mathbf{y}_1, ..., \mathbf{y}_k; a_1, ..., a_k) = \Delta_\psi^{(k)}(\mathbf{y}_1, ..., \mathbf{y}_k; a_1, ..., a_k),$$

$k = 3, 4, \ldots$, and g_0 is given in (2.18).

As a consequence of (2.4) and (3.10) it can be easily verified that

$$\left\langle D_\psi^{(1)} \right\rangle = 0,\ \left\langle D_\psi^{(2)} \right\rangle = o(n^2), \tag{3.11a}$$

$$\left\langle D_\psi^{(1)}(\mathbf{y}_1; a_1) D_\psi^{(2)}(\mathbf{y}_2, \mathbf{y}_3; a_2, a_3) \right\rangle = o(n^2). \tag{3.11b}$$

These relations suffice to claim that the fields (3.10) form a n^2–orthogonal system. Henceforth, the following, correct to the order $o(n^2)$, formulas for their moments are needed

$$\begin{gathered} \left\langle D_\psi^{(1)}(\mathbf{y}_1; a_1) D_\psi^{(1)}(\mathbf{y}_2; a_2) \right\rangle = nP(a)\delta(\mathbf{y}_{1,2})\delta(a_{1,2}) \\ -n^2 P(a_1)P(a_2)R_{12}, \end{gathered} \tag{3.12a}$$

$$\begin{gathered} \left\langle D_\psi^{(1)}(\mathbf{y}_1; a_1) D_\psi^{(1)}(\mathbf{y}_2; a_2) D_\psi^{(1)}(\mathbf{y}_3; a_3) \right\rangle \\ = nP(a_1)\delta(\mathbf{y}_{1,2})\delta(\mathbf{y}_{1,3})\delta(a_{1,2})\delta(a_{1,3}) \\ -n^2 3 \left\{\delta(\mathbf{y}_{1,2})\delta(a_{1,2})P(a_1)P(a_3)R_{13}\right\}_s, \end{gathered} \tag{3.12b}$$

$$\left\langle D_\psi^{(2)}(\mathbf{y}_1, \mathbf{y}_2; a_1, a_2) D_\psi^{(1)}(\mathbf{y}_3; a_3) D_\psi^{(1)}(\mathbf{y}_4; a_4) \right\rangle$$

$$= n^2 P(a_1)P(a_2)(1-R_{12})[\delta(\mathbf{y}_{1,3})\delta(\mathbf{y}_{2,4}) \tag{3.12c}$$
$$\times\ \delta(a_{1,3})\delta(a_{2,4}) + \delta(\mathbf{y}_{1,4})\delta(\mathbf{y}_{2,3})\delta(a_{1,4})\delta(a_{2,3})],$$
$$\left\langle D_\psi^{(2)}(\mathbf{y}_1,\mathbf{y}_2;a_1,a_2)D_\psi^{(2)}(\mathbf{y}_3,\mathbf{y}_4;a_3,a_4)D_\psi^{(1)}(\mathbf{y}_5,a_5)\right\rangle$$
$$= n^2 P(a_1)P(a_2)(1-R_{12})[\delta(\mathbf{y}_{1,5})\delta(a_{1,5}) + \delta(\mathbf{y}_{2,5})\delta(a_{2,5})] \tag{3.12d}$$
$$\times\ [\delta(\mathbf{y}_{1,3})\delta(\mathbf{y}_{2,4})\delta(a_{1,3})\delta(a_{2,4}) + \delta(\mathbf{y}_{1,4})\delta(\mathbf{y}_{2,3})\delta(a_{1,4})\delta(a_{2,3})],$$

$$\left\langle D_\psi^{(2)}(\mathbf{y}_1,\mathbf{y}_2;a_1,a_2)D_\psi^{(2)}(\mathbf{y}_3,\mathbf{y}_4;a_3,a_4)D_\psi^{(2)}(\mathbf{y}_5,\mathbf{y}_6;a_5,a_6)\right\rangle$$
$$= n^2 P(a_1)P(a_2)(1-R_{12})[\delta(\mathbf{y}_{1,3})\delta(\mathbf{y}_{2,4})\delta(a_{1,3})\delta(a_{2,4})$$
$$+\delta(\mathbf{y}_{1,4})\delta(\mathbf{y}_{2,3})\delta(a_{1,4})\delta(a_{2,3})[\delta(\mathbf{y}_{1,5})\delta(\mathbf{y}_{2,6}) \tag{3.12e}$$
$$\times\ \delta(a_{1,5})\delta(a_{2,6}) + \delta(\mathbf{y}_{1,6})\delta(\mathbf{y}_{2,5})\delta(a_{1,6})\delta(a_{2,5})],$$

where $R_{ij} = R(|\mathbf{y}_i - \mathbf{y}_j|; a_i + a_j)$ and

$$R(|\mathbf{y}_1 - \mathbf{y}_2|; a_1 + a_2) = 1 - g_0(|\mathbf{y}_1 - \mathbf{y}_2|; a_1 + a_2). \tag{3.13}$$

Note that in the case of a compound Poisson system[21] one has, in particular, $R_{ij} = 0$ and the functions $D_\psi^{(i)}$, $i = 0, 1, 2$, coincide with the first three generalized Charlier polynomials.[4–6]

Note also that the validity of the formulas (3.12) is not connected with properties like overlapping or nonoverlapping; they hold for an arbitrary set of points $\mathbf{x}_\alpha$, for which $f_p \sim n^p$,$p = 1, 2, \ldots$. The said properties, to the order n^2, can be described by an appropriate choice of the function R, defined in (3.13). If, for instance, $R = 1$ at $|\mathbf{y}| \le A$ and vanishes otherwise, we have a dispersion of "partially penetrable" spheres, which have impenetrable cores with radii whose sum is A. Such dispersions have been considered by Torquato[23,p.III] who derived certain n^2-bounds on their effective conductivity in the monodisperse case.

Let us truncate the series (3.5) after the two-tuple term. Due to the virial property of (3.5) we can obtain in this way the n^2-solution to the random problem (3.1), provided the kernels are properly identified. In the truncated series we rearrange the terms making use of the n^2-orthogonal fields from (3.10):

$$\theta(\mathbf{x}) = \mathbf{G}\cdot\mathbf{x} + \int\int T_1(\mathbf{x}-\mathbf{y};a)D_\psi^{(1)}(\mathbf{y};a)\,d^3\mathbf{y}da$$
$$+\int\int\int\int T_2(\mathbf{x}-\mathbf{y}_1,\mathbf{x}-\mathbf{y}_2;a_1,a_2)D_\psi^{(2)}(\mathbf{y}_1,\mathbf{y}_2;a_1,a_2)\,d^3\mathbf{y}_1 d^3\mathbf{y}_2\,da_1 da_2. \tag{3.14}$$

The new kernels T_1 and T_2 here (no new notations are introduced for them) are linear combinations of the kernels T_0, T_1, T_2 from (3.5). The zeroth-order kernel in (3.14) is indeed $\mathbf{G}\cdot\mathbf{x}$, since $D_\psi^{(1)}$ and $D_\psi^{(2)}$ are centered stochastic variables (see (3.11a)), and since $\theta(\mathbf{x})$ is to satisfy (3.1b).

Thus the n^2-solution of the basic random problem (3.1) requires only to identify the nonrandom kernels T_1 and T_2 in the truncated functional series (3.14).

4. Identification of the Kernels T_1 and T_2

As far as our aim is the n^2-solution to the random problem (3.1), we first truncate the series (2.20) for the conductivity field $\kappa(\mathbf{x})$ of the dispersion of overlapping spheres after the two-tuple term and then rearrange the terms so as to replace $\Delta_\psi^{(1)}$ and $\Delta_\psi^{(2)}$ by the above introduced n^2-orthogonal quantities $D_\psi^{(1)}$ and $D_\psi^{(2)}$, see (3.10). Eventually we get

$$\kappa(\mathbf{x}) = K_0 + [\kappa]\iint K_1(\mathbf{x}-\mathbf{y};a)D_\psi^{(1)}(\mathbf{y};a)\,d^3\mathbf{y}da$$

$$+[\kappa]\iiiint K_2(\mathbf{x}-\mathbf{y}_1,\mathbf{x}-\mathbf{y}_2;a_1,a_2)D_\psi^{(2)}(\mathbf{y}_1,\mathbf{y}_2;a_1,a_2)\,d^3\mathbf{y}_1d^3\mathbf{y}_2\,da_1da_2, \quad (4.1)$$

where

$$K_1(\mathbf{x};a) = h(\mathbf{x};a)\left\{1 - n[V_a - F(\mathbf{x};a)]\right\}, \quad (4.2)$$

$$K_2(\mathbf{x},\mathbf{y};a,b) = -\frac{1}{2}h(\mathbf{x};a)h(\mathbf{y};b), \quad (4.3)$$

$$F(\mathbf{x};a) = \iint h(\mathbf{x}-\mathbf{y};a)R(\mathbf{y};b)\,d^3\mathbf{y}db, \quad (4.4)$$

$$K_0 = \kappa_m + [\kappa]\eta(1-\frac{1}{2}\eta)$$

$$+\frac{1}{2}[\kappa]n^2\iint h(\mathbf{y};b)F(\mathbf{y};b)\,d^3\mathbf{y}db, \quad \eta = n\overline{V}. \quad (4.5)$$

$$\overline{V} = \frac{4}{3}\pi\int a^3P(a)\,da,$$

so that $\overline{V}$ is the mean volume of the spheres, embedded into the matrix. Obviously,

$$K = \langle\kappa\rangle + \ o(n^2), \quad (4.6)$$

since $D_\psi^{(1)}$ and $D_\psi^{(2)}$ are n^2-centered, cf. (3.11a).

To specify the needed kernels T_1 and T_2 in the representation (3.14) for the temperature field, a scheme descending to that devised in[3,7] and many times employed later by the authors,[2,4–6,17–19] is used. Namely, we substitute (4.1) and (3.14) into (3.1a), multiply by $D_\psi^{(1)}(\mathbf{0};a)$ and take the ensemble average. (Note, however, the following: here a is a fixed value of the mark, $a > 0$; in the one-tuple terms of (3.14) and (4.1) a is a "mute" variable and it should be renamed, say, as a_1 and a_2 respectively, before averaging.) In virtue of (3.11) and (3.12) this procedure yields the first equation for the kernels T_1 and T_2:

$$K_0\Delta S(\mathbf{x};a) + [\kappa]\nabla\cdot\Big\{K_1(\mathbf{x};a)[\mathbf{G}+\nabla S(\mathbf{x};a)] - nF_1(\mathbf{x};a)[\mathbf{G}+\nabla T_1(\mathbf{x};a)]$$

$$-n\iint K_1(\mathbf{x}-\mathbf{y};b)R(\mathbf{y};b)\nabla T_1(\mathbf{x}-\mathbf{y};b)\,d^3\mathbf{y}db$$

$$+2n\iint g_0(\mathbf{y};b)K_1(\mathbf{x}-\mathbf{y};b)+2K_2(\mathbf{x}-\mathbf{y};a,b)] \tag{4.7a}$$

$$\times\ \nabla T_2(\mathbf{x}-\mathbf{y},\mathbf{x};a,b)\,d^3\mathbf{y}d^3b$$

$$+2n\iint g_0(\mathbf{y};b)K_2(\mathbf{x}-\mathbf{y},\mathbf{x};a,b)\nabla T_1(\mathbf{y};b)\,d^3\mathbf{y}db\Big\}=0,$$

where

$$S(\mathbf{x};a)=T_1(\mathbf{x};a)-n\iint T_1(\mathbf{x}-\mathbf{y};b)R(\mathbf{y};b)\,d^3\mathbf{y}db, \tag{4.8}$$

$$F_1(\mathbf{x};a)=\iint K_1(\mathbf{x}-\mathbf{y};b)R(\mathbf{y};b)\,d^3\mathbf{y}db. \tag{4.9}$$

A similar procedure, based on multiplying by $D_\psi^{(2)}(\mathbf{0},\mathbf{z};a,b)$ and acknowledging (3.12), gives the second equation for T_1 and T_2:

$$2K_0\Delta T_2(\mathbf{x}-\mathbf{y},\mathbf{x};a,b)+[\kappa]\nabla\cdot\Big\{K_1(\mathbf{x};a)\nabla T_1(\mathbf{x}-\mathbf{y};b).$$

$$+2K_2(\mathbf{x}-\mathbf{y},\mathbf{x};a,b)[\mathbf{G}+\nabla T_1(\mathbf{x};a)+\nabla T_1(\mathbf{x}-\mathbf{z};b)$$

$$+2\nabla T_2(\mathbf{x}-\mathbf{y},\mathbf{x};a,b)]+K_1(\mathbf{x}-\mathbf{y};b)\nabla T_1(\mathbf{x};a) \tag{4.7b}$$

$$+2[K_1(\mathbf{x};a)+K_1(\mathbf{x}-\mathbf{y};b)]\nabla T_2(\mathbf{x}-\mathbf{y},\mathbf{x};a,b)\Big\}=0.$$

Everywhere in (4.7) the differentiation is with respect to $\mathbf{x}$, so that $\mathbf{y}, a$ and b play the role of parameters.

Thus, (4.7) form a system of integro-differential equations for the unknowns T_1 and T_2. Instead of boundary conditions we require for the latter to be bounded over the entire $\mathbb{R}^3$ in order to secure the existence of all multi-point correlation functions of the random solution $\theta(\mathbf{x})$ of the problem (3.1) for the dispersion under study.

5. Virial Solution to the Basic System (4.7)

Since we are interested in the n^2-solution to the random problem (3.1) for the dispersion of overlapping spheres, it suffices to look for the solution of the system (4.7) in the form

$$T_1(\mathbf{x};a)=T_{10}(\mathbf{x};a)+nT_{11}(\mathbf{x};a),$$

$$T_2(\mathbf{x},\mathbf{y};a,b)=T_{20}(\mathbf{x},\mathbf{y};a,b); \tag{5.1}$$

the reason is that T_1 will always appear scaled by n, and T_2—scaled by n^2, when calculating the needed statistical characteristics (3.2) and (3.3) of the temperature field $\theta(\mathbf{x})$, cf. (3.14), (2.23) and (3.12).

On introducing (5.1) into (4.7), making use of (4.1) to (4.5), and equaling the coefficients of the same order of n, one gets

$$\kappa_m \Delta S_0(\mathbf{x}) + [\kappa]\nabla \cdot \{h(\mathbf{x};a)[\mathbf{G} + \nabla S_0]\} = 0, \tag{5.2a}$$

$$\begin{aligned}
&\kappa_m \Delta S_1(\mathbf{x};a) + [\kappa]\nabla \cdot \Big\{ h(\mathbf{x};a)\nabla S_1 + [V_a - F(\mathbf{x};a)]\nabla S_0 \\
&\quad -F(\mathbf{x};a)\mathbf{G} - h(\mathbf{x};a)(\mathbf{G} + \nabla S_0)[V_a - F(\mathbf{x};a)] \\
&\quad -\iint h(\mathbf{x}-\mathbf{y};b)R(\mathbf{y};a+b)\nabla T_{10}(\mathbf{x}-\mathbf{y};b)\, d^3\mathbf{y}db \\
&\quad -h(\mathbf{x};a)\iint g_0(\mathbf{y};a+b)h(\mathbf{x}-\mathbf{y};b)\nabla T_{10}(\mathbf{x}-\mathbf{y};b)\, d^3\mathbf{y}db \\
&\quad +2\iint g_0(\mathbf{y};a+b)h(\mathbf{x}-\mathbf{y};b)[1-h(\mathbf{x};a)]\nabla T_{20}(\mathbf{x}-\mathbf{y},\mathbf{x};a,b)\, d^3\mathbf{y}db \Big\} = 0,
\end{aligned} \tag{5.2b}$$

$$\begin{aligned}
&2\kappa_m \Delta T_{20}(\mathbf{x}-\mathbf{y},\mathbf{x};a,b) + [\kappa]\nabla \cdot \Big\{ 2[h(\mathbf{x};a) + h(\mathbf{x}-\mathbf{y};b) \\
&\quad -h(\mathbf{x};a)h(\mathbf{x}-\mathbf{y};b)]\nabla T_{20}(\mathbf{x}-\mathbf{y},\mathbf{x};b,a) \\
&\quad +h(\mathbf{x};a)\nabla T_{10}(\mathbf{x}-\mathbf{y};b) + h(\mathbf{x}-\mathbf{y};b)\nabla T_{10}(\mathbf{x};a) \\
&\quad +h(\mathbf{x};a)h(\mathbf{x}-\mathbf{y};b)[\mathbf{G} + \nabla T_{10}(\mathbf{x};a) + \nabla T_{10}(\mathbf{x}-\mathbf{y};b)] \Big\} = 0.
\end{aligned} \tag{5.2c}$$

Here S_0 and S_1 are the first two virial coefficients of the function $S(\mathbf{x};a)$ introduced in (4.8), i.e.,

$$S = S_0 + nS_1 + \ldots, \tag{5.3}$$

so that

$$S_0(\mathbf{x};a) = T_{10}(\mathbf{x};a), \tag{5.4}$$

$$S_1(\mathbf{x};a) = T_{11}(\mathbf{x};a) - \iint T_{10}(\mathbf{x}-\mathbf{y};b)R(\mathbf{y};a+b)P(b)\, d^3\mathbf{y}db. \tag{5.5}$$

Eqn (5.2a) is obviously the equation for the disturbance field superimposed by a single inclusion of radius a on a temperature field with constant gradient $\mathbf{G}$. The bounded solution, $T^{(1)}(\mathbf{x};a)$, to the last problem is well known

$$S_0(\mathbf{x};a) = T_{10}(\mathbf{x};a) = T^{(1)}(\mathbf{x};a) = \begin{cases} -\beta\mathbf{G}\cdot\mathbf{x}, & \text{if } |\mathbf{x}| \le a, \\ -\beta\dfrac{a^3}{|\mathbf{x}|^3}\mathbf{G}\cdot\mathbf{x}, & \text{if } |\mathbf{x}| > a, \end{cases} \tag{5.6}$$

$\beta = [\kappa]/(\kappa_f + 2\kappa_m)$. It is readily seen that the gradient of T_{10} is constant within the sphere $|\mathbf{x}| \le a$, i.e.,

$$h(\mathbf{x};a)\nabla T_{10}(\mathbf{x};a) = -\beta h(\mathbf{x};a)\mathbf{G}. \tag{5.7}$$

By means of (5.2a) and (5.4) the equation (5.2c) can be recast as

$$\kappa_m \Delta T^{(2)}(\mathbf{x},\mathbf{y};a,b) + [\kappa]\left\{h_W(\mathbf{x},\mathbf{y};a,b)[\mathbf{G}+\nabla T^{(2)}]\right\} = 0, \tag{5.8}$$

where

$$T^{(2)}(\mathbf{x},\mathbf{y};a,b) = 2T_{20}(\mathbf{x}-\mathbf{y},\mathbf{x};b,a) + T_{10}(\mathbf{x};a) + T_{10}(\mathbf{x}-\mathbf{y};b), \tag{5.9}$$

$$h_W(\mathbf{x},\mathbf{y};a,b) = h(\mathbf{x};a) + h(\mathbf{x}-\mathbf{y};b) - h(\mathbf{x};a)h(\mathbf{x}-\mathbf{y};b). \tag{5.10}$$

The last equality means that (5.8) is the equation for the disturbance $T^{(2)}(\mathbf{x}) = T^{(2)}(\mathbf{x},\mathbf{y}\,;a,b)$ to the linear (with constant gradient $\mathbf{G}$) temperature field introduced by a single inhomogeneity whose characteristic function is $h_W(\mathbf{x}) = h_W(\mathbf{x},\mathbf{y};a,b)$ is given in (5.10). (Let us recall that $\mathbf{y}$, a and b play the role of parameters.) Obviously the region $W(\mathbf{y};a,b)$ defined by the characteristic function $h_W(\mathbf{x})$, is formed by the common volume of the pair of spheres of radii a and b, the first centered at the origin, the second at the point $\mathbf{y}$. When $|\mathbf{y}| > a+b$, the region $W(\mathbf{y};a,b)$ is simply a pair of nonoverlapping spheres and the field $T^{(2)}(\mathbf{x},\mathbf{y};a,b)$ can be found analytically, see[13,10] *et al.* If, however, $|\mathbf{y}| < a+b$, the said spheres overlap and form inclusions of intricate shape, shown in Fig. 1 in two dimensions. The overlapping case poses a very difficult inhomogeneity problem; this problem, to the best of the authors' knowledge, first appeared in Torquato's analysis[23,p.I] of the effective conductivity for dispersions of overlapping spheres to the order n^2.

Thus the coefficients T_{10} and T_{20} do not depend on the statistics of the medium and they are the same as in the case of nonoverlapping spheres.[17,18] The only difference is that the spheres could intersect here. Moreover, a simple inspection shows that ∇T_{10} and $\frac{1}{2}\nabla T_{20}$ are just the one- and two-point cluster operators used by Felderhof *et al.*[10] and Torquato.[23,p.I]

Due to (5.7), the equation (5.2b) simplifies

$$\kappa_m \Delta S_1 + [\kappa]\nabla\cdot\big\{h(\mathbf{x};a)\nabla S_1 + [V_a - F(\mathbf{x};a)]\nabla T_{10}$$

$$-(1-\beta)F(\mathbf{x};a)\mathbf{G} - \underline{h(\mathbf{x};a)(1-2\beta)[V_a - F(\mathbf{x};a)]\mathbf{G}} + 2\mathbf{I}_{20}(\mathbf{x};a)\big\} = 0, \tag{5.11}$$

where

$$\mathbf{I}_{20}(\mathbf{x};a) = \int\!\!\int g_0(\mathbf{y};a+b)h(\mathbf{x}-\mathbf{y};b)$$

$$\times\,[1-h(\mathbf{x};a)]\nabla T_{20}(\mathbf{x},\mathbf{x}-\mathbf{y};a,b)P(b)\,d^3\mathbf{y}da. \tag{5.12}$$

The underlined terms in (5.11) are additional when compared to those in the respective equation (4.7) in[18] for a monodisperse medium. These additional terms result from overlapping of the spheres. If the spheres do not overlap then $g_0(\mathbf{y};a+b) = 0$ for $|\mathbf{y}| < a+b$ and the respective integral vanishes. Moreover, for the case of nonoverlapping, one has $F(\mathbf{x};a) = V_a$ at $|\mathbf{x}| < a$ and therefore $h(\mathbf{x};a)[V_a - F(\mathbf{x};a)] = 0$. In the monodisperse case eqn (5.11) reduces then to the respective equation (4.7) from[18] for dispersions of nonoverlapping spheres.

In order to facilitate finding the function $S_1(\mathbf{x};a)$ we exclude from (5.12) the complicated integral $I_{20}(\mathbf{x};a)$, given in (5.12), making use of the reasoning presented again in[17,18] for the nonoverlapping case. Namely, let us multiply (5.2c) by $g_0(\mathbf{y};a,b)$ and rewrite the result in the form

$$\begin{aligned}
&2[\kappa]\nabla\cdot\big\{g_0(\mathbf{y};a,b)h(\mathbf{x}-\mathbf{y};b)[1-h(\mathbf{x};a)]\nabla T_{20}(\mathbf{x},\mathbf{x}-\mathbf{y};a,b)\big\}\\
&\quad=-g_0(\mathbf{y};a,b)\nabla\cdot\big\{2[\kappa_m+[\kappa]h(\mathbf{x};a)]\nabla T_{20}(\mathbf{x},\mathbf{x}-\mathbf{y};a,b)\\
&\qquad+[\kappa][h(\mathbf{x};a)\nabla T_{10}(\mathbf{x}-\mathbf{y};b)+h(\mathbf{x}-\mathbf{y};b)\nabla T_{10}(\mathbf{x};a)\\
&\qquad-h(\mathbf{x};a)h(\mathbf{x}-\mathbf{y};b)\{\mathbf{G}+\nabla T_{10}(\mathbf{x};a)+\nabla T_{10}(\mathbf{x}-\mathbf{y};b)\}\big\}.
\end{aligned}\tag{5.13}$$

Due to the presence of $h(\mathbf{x}-\mathbf{y};b)$, the left-hand side of (5.13) is absolutely integrable with respect to $\mathbf{y}$, over the entire space $\mathbb{R}^3$, and thus the same is true for the right-hand side. That is why we may chose the mode of integration as we wish; due to reasons to become clear a bit later, we select the following one:

$$\int\cdot\,d^3\mathbf{y}=\lim_{R\to\infty}\int_{Y_R}\cdot\,d^3\mathbf{y};\ \int_{Y_R}\cdot\,d^3\mathbf{y}=\int_0^R r^2dr\int_\Omega\cdot\,d\Omega,\tag{5.14}$$

where $Y_R=\big\{\,\mathbf{y}\mid 0\le|\mathbf{y}|\le R\,\big\}$. This means that in the integral over Y_R we first integrate with respect to the angular coordinates, i.e., on the unit sphere $\Omega=\big\{\,\mathbf{y}\mid|\mathbf{y}|=1\,\big\}$, and then with respect to the radial coordinate $r=|\mathbf{y}|$.

We introduce now the functions

$$\mathbf{L}_{10}(\mathbf{x};a)=\iint g_0(\mathbf{y};a+b)\nabla T_{10}(\mathbf{x}-\mathbf{y};b)P(b)\,d^3\mathbf{y}db,\tag{5.15}$$

$$L_{20}(\mathbf{x};a)=\iint g_0(\mathbf{y};a+b)T_{20}(\mathbf{x},\mathbf{x}-\mathbf{y};a,b)P(b)\,d^3\mathbf{y}db.\tag{5.16}$$

Both integrals in (5.15) and (5.16) are not absolutely convergent because their integrands are of order $|\mathbf{y}|^{-3}$ at $|\mathbf{y}|\gg1$, see.[13,17,18] However, they both exist in the sense (5.14) as shown in.[17,18] Thus, we can integrate both sides of (5.13) with respect to $\mathbf{y}\in\mathbb{R}^3$, taking the integrals in the sense (5.14), when necessary. We obtain

$$\begin{aligned}
&2\kappa_m\Delta L_{20}(\mathbf{x};a)+[\kappa]\nabla\cdot\big\{2h(\mathbf{x};a)\nabla L_{20}(\mathbf{x};a)+2\mathbf{I}_{20}(\mathbf{x};a)\\
&+h(\mathbf{x};a)\mathbf{L}_{10}(\mathbf{x};a)-[V_a-F(\mathbf{x};a)][(1-2\beta)\mathbf{G}h(\mathbf{x};a)-\nabla T_{10}(\mathbf{x};a)]\big\}=0,
\end{aligned}\tag{5.17}$$

taking into account (5.7) and (4.4).

Thus having introduced the conditionally convergent integrals (5.15) and (5.16), we combine them in such a manner which cancels out the contributions of the nonconvergent parts of the two integrals and obtain the relation (5.17), containing the absolutely convergent integral $\mathbf{I}_{20}(\mathbf{x};a)$.

We next subtract (5.17) from (5.11) and write down the result in the form

$$\kappa_m\Delta H(\mathbf{x};a)+[\kappa]\nabla\cdot\{h(\mathbf{x};a)\nabla H(\mathbf{x};a)+(\beta-1)F(\mathbf{x};a)\mathbf{G}$$

$$-h(\mathbf{x};a)\iint g_0(\mathbf{y};a+b)[\beta h(\mathbf{x}-\mathbf{y};b)\mathbf{G}+\nabla T_{10}(\mathbf{x}-\mathbf{y};b)]P(b)\,d^3\mathbf{y}db$$

$$-h(\mathbf{x};a)\mathbf{L}_{10}(\mathbf{x};a)]\}=0,$$

where

$$H(\mathbf{x};a)=S_1(\mathbf{x};a)-2L_{20}(\mathbf{x};a) \tag{5.19}$$

is the new unknown function introduced instead of $S_1(\mathbf{x};a)$.

A simple check, based on eqn (5.2a), shows that the solution of (5.19) is

$$H(\mathbf{x};a)=\beta V_a T_{10}(\mathbf{x};a)-\iint T_{10}(\mathbf{x}-\mathbf{y};b)R(\mathbf{y};a+b)\,d^3\mathbf{y}db \tag{5.20}$$

and thus, in virtue of (5.5), we have eventually

$$T_{11}(\mathbf{x};a)=\beta V_a T_{10}(\mathbf{x};a)+2L_{20}(\mathbf{x};a). \tag{5.21}$$

It could be shown that the kernel T_{11} is the same as in the nonoverlapping case,[18] and again the only difference here is that the spheres are allowed to intersect when evaluating the integral $L_{20}(\mathbf{x};a)$, cf. (5.16).

Eqn (5.21) terminates the solution of the basic stochastic problem (3.1) for the dispersion of overlapping spheres to the order n^2. Indeed the kernels $T_{10}(\mathbf{x};a)$ and $T_{20}(\mathbf{x},\mathbf{x}-\mathbf{y};a,b)$ are already determined in principle through the solutions of the one- and two-sphere inhomogeneity problems (5.8)-(5.10). Introducing T_{10},T_{11},T_{20} into (5.1) we obtain the kernels $T_1(\mathbf{x};a)$ and $T_2(\mathbf{x}_1,\mathbf{x}_2;a_1,a_2)$ of the truncated series (3.14), which gives the full stochastic solution of the problem (3.1) to the order n^2, as explained at the end of Section 3. The situation is thus completely similar to that for a dispersion of nonoverlapping spheres. The only difference is that the kernel $T_{20}(\mathbf{x},\mathbf{y};a,b)$ needs not vanish for $|\mathbf{x}-\mathbf{y}|\leq a+b$. As a result, the solution of the inclusion problem for two intersecting spheres appears in the n^2-solution of the stochastic problem (3.1) for the case of overlapping spheres. The limiting case of nonoverlapping spheres is readily deduced from the present solution simply setting $g_0(r,a+b)=0$, if $r<a+b$.

It is important to point out that the basic equation (5.11) for the function $S_1(\mathbf{x};a)$ contains the absolutely convergent integral $\mathbf{I}_{20}(\mathbf{x};a)$ only, so that $S_1(\mathbf{x};a)$, and thus $T_{11}(\mathbf{x};a)$ as well, could be evaluated, at least numerically, without introducing any conditionally convergent integrals, like (5.15) and (5.16). That is why the latter are not inherent in our approach; they play here an auxiliary role allowing to represent the n^2-solution of the basic random problem (3.1) in a convenient and simple form, as it is well seen from (5.21).

To demonstrate the performance of the above obtained n^2-solution, we shall calculate explicitly the effective conductivity of the dispersion of overlapping spheres to the same order n^2. To this end we insert (3.1b) and (4.1) into (3.4) and making use of (2.19), (4.4), (4.9), (5.1), (5.6), (5.7), (5.16), (5.17) and (5.21), we get eventually

$$\frac{\kappa^*}{\kappa_m}=1+k_1\eta+k_2\eta^2+o(\eta^2),\ \eta=n\overline{V}, \tag{5.22}$$

$$k_1 = 3\beta, \tag{5.23}$$

$$k_2\mathbf{G} = \frac{[\kappa]}{\kappa_m}\Bigg\{\frac{1}{\overline{V}^2}\iint h(\mathbf{x};a)\nabla S_1(\mathbf{x};a)P(a)\,d^3\mathbf{x}da - (1-2\beta)I\mathbf{G}$$

$$-\frac{1}{\overline{V}^2}\iiiint g_0(|\mathbf{y}_1-\mathbf{y}_2|;a_1+a_2)h(\mathbf{y}_1;a_1)h(\mathbf{y}_2;a_2) \tag{5.24}$$

$$\times\ \nabla T_{20}(\mathbf{y}_1,\mathbf{y}_2;a_1,a_2)P(a_1)P(a_2)\,d^3\mathbf{y}_1 d^3\mathbf{y}_2\,da_1da_2\Bigg\};$$

here

$$I = \frac{1}{2\overline{V}^2}\iiiint g_0(|\mathbf{y}_1-\mathbf{y}_2|,a_1+a_2)h(\mathbf{y}_1;a_1)h(\mathbf{y}_2;a_2)$$

$$\times\ P(a_1)P(a_2)\,d^3\mathbf{y}_1 d^3\mathbf{y}_2 da_1da_2 = \frac{1}{2}\left[1-\frac{1}{\overline{V}^2}\iint h(\mathbf{x};a)F(\mathbf{x};a)P(a)\,d^3\mathbf{x}da\right] \tag{5.25}$$

is the polydisperse generalization of the parameter introduced by Torquato[23,p.I] in the monodisperse case. It could be easily shown that in the latter case our formula (5.24) coincides with the n^2-expression of Torquato[23,p.I] for the effective conductivity of the dispersion of overlapping spheres.

With the same ease one could calculate in a closed form the rest of the needed multipoint correlations (3.2) to the order n^2. Of course, the explicit evaluation of these correlations and, in particular, the integrals that enter (5.24), is not an easy task. However, the difficulties to be encountered concern already deterministic problems and have purely analytical nature.

6. Discussion

We have presented a systematic statistical theory, based on the factorial functional series, for a special class of two-phase random media—random dispersion of spheres of random radii allowed to overlap. The theory is alternative to the cluster expansion approach of Felderhof *et al.*[10] which also yields asymptotic results for the effective scalar transport properties in nonoverlapping[10] and overlapping[23] cases. The comparison shows that as far as the effective conductivity is concerned, both approaches lead to the same results to the order n^2. The explanation of this fact needs a thorough and detailed comparison between the above mentioned approaches in the theory of random particulate media—cluster expansions and factorial series—which goes beyond the scope of this paper and will be done elsewhere. Our approach allowed us however to obtain the full statistical solution as well, i.e., to get unambiguous expressions, in an analytic form, for all needed multipoint correlation functions in the transport problem under study, and not only for the effective conductivity.

One more remark is finally warranted. It was yet Weissberg[26] who acknowledged the fact that the dispersion of overlapping spheres is, in a sense, simpler than the one of nonoverlapping spheres. In particular, one can take the simplest

system of random points—the Poissonian—when the multipoint probability densities are simply $F_k = n^k P(a_1) \dots P(a_k)$. It turned out that the last assumption did simplify the calculations when evaluating bounds on the effective conductivity κ^*, see.[26] However, if the rigorous evaluation of κ^* is aimed, the full statistical solution is to be carried out and the foregoing analysis shows that "overlapping" has no specific advantages when compared to "nonoverlapping", in a sense that the statistical theory, based on the functional series with respect to the factorials of random density function makes no difference, in principle, whether spheres can overlap or not. When solved to the order n^p the statistical problem in both cases reduces to solving deterministic inclusion problems for aggregates of up to p spheres and to consecutive integration with respect to the relative positions of spheres. The latter is demonstrated in details in Section 5 for $p = 2$. The crucial difference is that the inclusions are allowed to overlap in the dispersion under study and that makes the respective inclusion problems for $p \geq 2$ extremely difficult and analytical solution can not be expected. At the same time, in the two- and three-dimensional case of nonoverlapping dispersions an analytic solution for the two-sphere inclusion problem can be obtained. Thus one can conclude that in the framework of the full statistical theory of transport phenomena in dispersions of overlapping spheres, the plausible simplicity in the choice of the multipoint probability densities F_k is heavily paid for by the difficulties in solving the respective inclusion problems for sets of overlapping spheres.

Acknowledgement

The support of this work by the Bulgarian Ministry of Science and Education is acknowledged.

References

1. M. Beran, *Statistical Continuum Theories* (John Wiley, New York, 1968).
2. C. I. Christov, *Toward a statistical theory of emulsions*–In: *Proc. 13th Conf. Bulg. Math. Union* (Bulg. Acad. Sci., Sofia, 1984 473-481).
3. C. I. Christov, *Poisson-Wiener expansion in non-linear stochastic systems, Ann. Univ. Sofia, Fac. Mat. Mec., Livre 2, Mécanique* **75/1981**(1985) 143-165.
4. C. I. Christov, *A further development of the concept of random density function with application to Volterra-Wiener expansions, C. R. Acad. bulg. sci.* **38(1)** (1985) 35-38.
5. C. I. Christov, *Mechanical and Mathematical Modelling of Continuous Media with Random Structure* (Dr. Sci. thesis, Sofia, 1986). (in Bulgarian.)
6. C. I. Christov, *Determination of the interaction between the particulate and continous phase in an emulsion ..., Ann. Univ. Sof., Fac. Math. Mec., Livre 2, Mécanique* **77/1983**(1987) 115-128.
7. C. I. Christov and K. Z. Markov, *Stochastic functional expansion for random media with perfectly disordered constitution, SIAM J. Appl. Math.* **45**(1985) 289-311.

8. C. I. Christov and K. Z. Markov, *Stochastic functional expansion in elasticity of heterogeneous solids, Int. J. Solids Structures* **21** (1985) 1197-1211.
9. A. L. DeVera ,Jr., and W. Strieder, *Upper and lower bounds on the effective thermal conductivity of a random, two-phase material, J. Phys. Chem.* **81**(1977) 1783-1790.
10. B. U. Felderhof, G. W. Ford and E. G. D. Cohen, *Two-particle cluster integral in the expansion of the dielectric constant, J. Stat. Phys.***28**(1982) 649-672.
11. H. L. Frish, *Statistics of random media, Trans. Soc. Rheol.* **9**(1965) 293-312.
12. K. Golden and G. Papanicolaou, *Bounds for effective properties of heterogeneous media by analytic continuation, Comm. Math. Phys.* **90**(1983) 473-491.
13. D. J. Jeffrey, *Conduction through a random suspension of spheres, Proc. Roy. Soc. London* **A335**(1973) 355-367.
14. D. Jeulin, *Random structure analysis and modelling by mathematical morphology*– In: *Continuum Models of Discrete Systems* (A. J. M. Spencer, ed., Balkema, Rotterdam, 1987, 217-225.)
15. P. P. Kuznetzov and R. L. Stratonovich, *On the mathematical theory of correlated random points, Izv. AN SSSR, ser. mat.* **20**(1956) 167-178. (in Russian.)
16. K. Z. Markov, *Application of Volterra-Wiener series for bounding the overall conductivity of heterogeneous media. I. General procedure. II. Suspensions of equi-sized spheres, SIAM J. Appl. Math.* **47**(1987) 831-850, 851-870.
17. K. Z. Markov, *A virial stochastic expansion for a random suspension of spheres*– In: *Continuum Models of Discrete Systems* (A.J.M. Spencer, ed., Balkema, Rotterdam, 1987, 97-105).
18. K. Z. Markov, *On the heat propagation problem for random dispersions of spheres, Math. Balkanica (New Series)* **3**(1989) 399-417.
19. K. Z. Markov, *On the factorial functional series and their application to random media, SIAM J. Appl. Math.* **51**(1991) 128-139.
20. G. Matheron, *Elements pour une Theorie des Milieu Poreux* (Masson, Paris, 1967).
21. D. Snyder, *Random Point Processes* (John Wiley, New York, 1975).
22. R. L. Stratonovich, *Topics in Theory of Random Noises* (Gordon and Breach, New York, 1967, vol.1.)
23. S. Torquato, *Bulk properties of two-phase disordered media. I. Cluster expansion for the dielectric constant of dispersion of penetrable spheres. II. Effective conductivity of a dilute dispersion of penetrable spheres. III. New bounds on the effective conductivity of dispersions of penetrable spheres, J. Chem. Phys.* **81**(1984) 3079-3088. **83**(1985) 4776-4785. **84**(1986) 6345-6359.
24. S. Torquato and G. Stell, *Microstructure of two-phase random media. I. The n-point probability functions, J. Chem. Phys.* **77**(1982) 2071-2077.
25. S. Torquato and G. Stell, *Bounds on the effective thermal conductivity of a dispersion of fully penetrable spheres, Lett. Appl. Engng Sci* **23**(1985) 375-383.
26. H. L. Weissberg, *Effective diffusion coefficients in porous media, J. Appl. Phys.* **34**(1963) 2636-2639.

27. H. L. Weissberg, S. Prager, *Viscosity of concentrated suspensions, Trans. Rheology Soc.* **9**(1965) 321-338.
28. H. L. Weissberg and S. Prager, *Viscous flow through porous media. III. Upper bounds on the permeability for a simple random geometry, Phys. Fluids* **13**(1970) 2958-2965.