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ON THE TWO-POINT CORRELATION FUNCTIONS IN RANDOM ARRAYS OF NONOVERLAPPING SPHERES

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For a random dispersion of identical spheres, the known two-point correlation functions like "particle-center," "center-surface," "particle-surface," etc., are studied. Geometrically, they give the probability density that two points, thrown at random, hit in various combinations a sphere's center, a sphere, or a sphere's surface. The basic result of the paper is a set of simple and integral representations of one and the same type for these correlations by means of the radial distribution function for the set of sphere's centers. The derivations are based on the geometrical reasoning, recently employed by Markov and Willis when studying the "particle-particle" correlation. An application, concerning the effective absorption strength of a random array of spherical sinks, is finally given.

Keywords: random media, dispersions of spheres, correlation variational bounds, absorption problem

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1. INTRODUCTION

In many cases of great practical interest the macroscopic behaviour of a two-phase medium is strongly influenced by the amount and the internal distribution of the interfacial surface. A classical problem of such a kind is supplied first of all by the theory of diffusion-controlled reactions, as initiated by Smoluchowski in 1916. Formally, this is equivalent to the problem, concerning a species (defects) diffusing in the presence of an array of ideally absorbing traps (sinks). Another classical problem is the quest for the permeability of porous solids. The reason is that in both problems the observed macroscopic response is ruled by the events that take place at the boundary between the phases: in the first case chemical reactants' encounter (or absorption of defects) happens there and in the second case the viscous fluid flows around the particle surfaces, where no-slip boundary condition is to be satisfied. Hence it is natural that in studying both these phenomena the interfacial statistics should essentially enter the appropriate theories. Perhaps the first example was provided by Doi [3] who derived bounds on both the effective sink strength and the permeability. These bounds were put on a firmer base and generalized by Torquato and co-authors [9, 16, 10, 1]. The bounds include integrals of the interfacial two-point statistical correlations, which later on were thoroughly studied within a more general framework by Torquato [15, 14]. An alternative approach in the absorption context has been proposed by Talbot and Willis [12] who, using a Hashin-Shtrikman's type variational principle, derived a bound on the effective sink strength for a dispersion of nonoverlapping spheres which eventually utilizes only an integral incorporating the total correlation function. At a first glance this bound is entirely different from Doi's one since no interfacial statistics is even mentioned in Talbot and Willis' reasoning. As we shall see below, the Talbot and Willis bound turns out, however, to be identical to that of Doi.

The evaluation of the interfacial statistical characteristics for realistic two-phase random models meets with considerable difficulties. Only for the simplest model of fully penetrable spheres (the Boolean model) the needed quantities can be comparatively easily evaluated, as done by Doi himself. For dispersions of nonoverlapping spheres — a model that very often is appropriate for particulate type media — such an evaluation is much more involving, and the reason can be well seen from the already mentioned paper of Torquato [15]. In the same paper the author notes that the needed interfacial correlations have a convolution structure which allows, in principle, to reduce them to single integrals containing the total correlation functions for the dispersions, provided the Fourier transform is employed in the statistically isotropic case. No further details are given in [14], however, apart from appropriate formulae valid for a dilute dispersion, and numerical results for the semi-empirical Verlet-Weis distribution [18], see also [13]. (Note that the dilute results have been derived by Berryman [2] by means of a different approach.)

In the recent paper [7], a simple geometrical reasoning was proposed, which allowed the authors to represent the two-point correlation function of the region, occupied by the spheres (that is, the "particle-particle" correlation), as a simple integral that contains the radial distribution function of the spheres. The aim of the present work is to demonstrate that the same geometrical reasoning can be straightforwardly applied when considering the two-point interfacial correlations, if combined with a formula, noted by Doi [3]. In this way the said correlations will be reduced to even simpler integrals of the *same* type as that for the "particle-particle" one. To accomplish this, the definitions of the three basic interfacial characteristics are first introduced in Section 2, preceded by that of the simple "particle-center" correlation. The investigation of the latter in Section 3 serves as a model for a similar treatment of the interfacial characteristics, performed in Sections 4 – 6 5 and 6. (The study of the "particle-center" correlation, detailed here, is outlined in the author's paper [6].) The formulae for all two-point correlations have a fully similar structure, which is summarized in Table 1 (Section 9). In Section 7 the first two moments of the various two-point correlations are directly evaluated by means of an alternative and simpler method which is applicable in the 2-D case as well. As an elementary application of the obtained formulae it is finally shown (Section 8) that the Doi's bound on the effective sink strength of the dispersion coincides with that of Talbot and Willis.

2. DEFINITIONS OF THE BASIC TWO-POINT STATISTICAL CHARACTERISTICS

Consider a dispersion of equal and nonoverlapping spheres of radius a in $\mathbb{R}^3$, whose centers form the random set of points $\{x_\alpha\}$. The assumption of statistical isotropy and homogeneity is adopted henceforth. Introduce after Stratonovich [11] the so-called random density field for the dispersion

$$\psi(x) = \sum_\alpha \delta(x - x_\alpha), \tag{2.1}$$

$\delta(x)$ is the Dirac delta-function. All multipoint moments of the field $\psi(x)$ can be easily expressed by means of the multipoint probability densities of the random set $\{x_\alpha\}$, but in what follows only the first two simplest formulae of this kind will be needed, namely,

$$\langle \psi(x) \rangle = n, \quad F^{\rm cc}(x) = \langle \psi(x)\psi(0) \rangle = n\delta(x) + n^2 g(x), \tag{2.2}$$

where n is the number density of the spheres, and $g(x) = g(r)$, $r = |x|$, is their radial distribution function, see [11]. The brackets $\langle \cdot \rangle$ signify ensemble averaging. Note that the assumption of nonoverlapping implies that $g(x) = 0$ if $|x| \le 2a$. The notation $F^{\rm cc}(x)$ in (2.2) is justified by the interpretation of the quantity $\langle \psi(x)\psi(0) \rangle$ — this is the "center-center" correlation, in the sense that it obviously gives the probability densities of finding centers of particles both at the origin and at the point x.

Let

$$I_1(x) = \begin{cases} 1, & \text{if } x \in \mathcal{K}_1, \\ 0, & \text{otherwise,} \end{cases} \tag{2.3}$$

be the characteristic function of the region $\mathcal{K}_1$, occupied by the spheres. Then

$$I_1(x) = (h_a * \psi)(x) = \int h_a(x-y)\psi(y)\,{\rm d}y, \quad I_1'(x) = \int h_a(x-y)\psi'(y)\,{\rm d}y, \tag{2.4}$$

where $\psi'(y) = \psi(y) - n$ is the fluctuating part of the field $\psi(y)$ and $h_a(y)$ is the characteristic function of a single sphere of radius a, located at the origin. All integrals hereafter are over the whole $\mathbb{R}^3$ and, as usual, $f * g$ denotes the convolution of the functions f and g. The simple integral representation (2.4), combined with the formulae (2.2), serves as a basis for evaluating the needed interfacial statistical characteristics in what follows. Its simplest consequence reads

$$\eta_1 = \langle I_1(x) \rangle = nV_a, \quad V_a = \tfrac{4}{3}\pi a^3, \tag{2.5}$$

having taken averages of both sides of (2.4); η_1 is the volume fraction of the spheres.

In turn, the two-point correlation most often used is

$$F^{\rm pp}(x) = \langle I_1(0) I_1(x) \rangle\,. \tag{2.6}$$

The interpretation of $\langle I_1(0)I_1(x)\rangle$ is obvious — this is the probability that two points, separated by the vector x, when thrown into the medium both fall within a sphere. That is why $\langle I_1(0)I_1(x)\rangle$ can be called "particle-particle" correlation, which explains its notation $F^{\rm pp}(x)$ in (2.6).

Before introducing the interfacial characteristics, it is noted that another correlation, closely related to $F^{\rm pp}(x)$, will be useful as well. This is the "particle-center" one

$$F^{\rm pc}(x) = \langle I_1(x)\psi(0)\rangle\,, \tag{2.7}$$

which obviously gives the probability that for a pair of points, separated by the vector x, one hits a sphere's center while the other falls into a sphere.

It is natural to represent the above introduced correlations as

$$F^{\rm cc}(x) = n^2 + \overline{F}^{\rm cc}(x), \quad F^{\rm pc}(x) = n\eta_1 + \overline{F}^{\rm pc}(x), \quad F^{\rm pp}(x) = \eta_1^2 + \overline{F}^{\rm pp}(x), \tag{2.8}$$

where, as it follows from (2.2), (2.4), (2.6) and (2.7) ,

$$\begin{aligned}
\overline{F}^{\rm cc}(x) &= \langle \psi'(0)\psi'(x)\rangle = n\delta(x) + n^2\nu_2(x),\\
\overline{F}^{\rm pc}(x) &= \langle I_1'(x)\psi'(0)\rangle = (h_a * \overline{F}^{\rm cc})(x) = nh_a(x) + n^2\int h_a(x-y)\nu_2(y)\,\mathrm{d}y,\\
\overline{F}^{\rm pp}(x) &= \langle I_1'(x)I_1'(0)\rangle = \big(h_a * \overline{F}^{\rm pc}\big)(x) = \big(h_a * h_a * \overline{F}^{\rm cc}\big)(x).
\end{aligned} \tag{2.9}$$

Here

$$\nu_2(y) = g(y) - 1 \tag{2.10}$$

is the so-called binary (or total) correlation function for the dispersion. Due to the no long-range assumption, all $\nu_2(x)$, $\overline{F}^{\rm cc}(x)$, $\overline{F}^{\rm pc}(x)$ and $\overline{F}^{\rm pp}(x)$ vanish as $x \to \infty$, since the constants in the right-hand sides of (2.8) are just their long-range values.

Let us recall now the definitions of the interfacial correlations. The first one,

$$F^{\rm sc}(x) = \langle\, |\nabla I_1(x)|\, \psi(0)\rangle\,, \tag{2.11}$$

can be called "surface-center." Since $|\nabla I_1(x)|$ and $\psi(x)$ are delta-functions, the former concentrated over the surface $\partial\mathcal{K}_1$ of the spheres and the latter over the set $\{x_\alpha\}$, the interpretation of $F^{\rm sc}(x)$ is obvious — this is the probability that if two points, separated by the vector x, are thrown into the medium, one of them falls on the surface of a sphere, while the other hits a center x_α of a sphere. This interpretation explains the terminology used here (note that it differs from that used by Torquato [15], where (2.11) is called "surface-particle" correlation).

The second interfacial correlation is

$$F^{\rm sp}(x) = \langle\, |\nabla I_1(x)|\, I_1(0)\rangle \tag{2.12}$$

— obviously the "surface-particle" one. The reason is that it gives the probability that one of the two points, separated by the vector x, when thrown into the medium, falls on the surface of a sphere, and the other falls within a sphere. (Note again the difference in terminology used here: Torquato [15] calls (2.11) “surface-particle" correlation, while (2.12) is very closely connected to the “surface-void" correlation of Doi [3].)

Finally, let

$$F^{\mathrm{ss}}(x) = \langle\, |\nabla I_1(x)|\, |\nabla I_1(0)|\, \rangle \tag{2.13}$$

be the “surface-surface" correlation, which gives the probability that the two points, separated by the vector x, thrown into the medium, both fall on the spheres' surfaces. (The terminology agrees here with that of Doi [3] and Torquato [15].)

Let now $h_b(x)$ be the characteristic function of the sphere of variable radius b, located at the origin. Then

$$\frac{\partial}{\partial b}\, h_b(x)\, \Big|_{\,b\,=\,a} = \delta(|x| - a). \tag{2.14}$$

As a matter of fact, the formula (2.14) was noted by Doi [3] who employed it for evaluating the interfacial correlations for the Boolean model of fully penetrable spheres. Coupled with Stratonovich density field (2.1), it gives

$$|\nabla I_1(x)| = \int \frac{\partial}{\partial b}\, h_b(x-y)\, \psi(y)\, \mathrm{d}y\, \Big|_{\,b\,=\,a}, \tag{2.15}$$

since $|\nabla I_1(x)|$ is a sum of delta functions, concentrated on the surfaces of the spheres. The formula (2.15) will play a central role in our study. Its first and simplest consequence is the formula for the specific surface, S, of the dispersion, i.e. the amount of the interface in a unit volume. Due to the nonoverlapping assumption, obviously $S = 4\pi a^{\,2} n$. Formally, the latter formula immediately follows after averaging (2.15):

$$S = \langle |\nabla I_1(x)| \rangle = n \frac{\partial}{\partial b} \int h_b(x-y)\, \mathrm{d}y\, \Big|_{\,b\,=\,a} = n \frac{\mathrm{d}}{\mathrm{d}b} \left(\tfrac{4}{3}\pi b^3\right) \Big|_{\,b\,=\,a} = 4\pi a^2 n. \tag{2.16}$$

Similarly to (2.8), represent the interfacial correlations in the form

$$F^{\mathrm{sc}}(x) = nS + \overline{F}^{\mathrm{sc}}(x), \quad F^{\mathrm{sp}}(x) = \eta_1 S + \overline{F}^{\mathrm{sp}}(x), \quad F^{\mathrm{ss}}(x) = S^2 + \overline{F}^{\mathrm{ss}}(x), \tag{2.17}$$

where, as it follows from (2.11), (2.4), (2.12) and (2.13) ,

$$\begin{aligned}
\overline{F}^{\mathrm{sc}}(x) &= \langle |\nabla I_1(x)| \psi'(0) \rangle = n \frac{\partial}{\partial b}\, h_b(x)\, \Big|_{\,b\,=\,a} + n^2 \frac{\partial}{\partial b} \int h_b(x-y) \nu_2(y)\, \mathrm{d}y\, \Big|_{\,b\,=\,a}, \\
\overline{F}^{\mathrm{sp}}(x) &= \langle |\nabla I_1'(x)| I_1'(0) \rangle = (h_a * \overline{F}^{\mathrm{sc}})(x) = \int h_a(x-y) \overline{F}^{\mathrm{sc}}(y)\, \mathrm{d}y, \\
\overline{F}^{\mathrm{ss}}(x) &= \langle |\nabla I_1(x)|\, (|\nabla I_1(0)| - S) \rangle = (\frac{\partial}{\partial b}\, h_b * \overline{F}^{\mathrm{sc}})(x)\, \Big|_{\,b\,=\,a} \\
&= \int \frac{\partial}{\partial b} h_b(x-y) \overline{F}^{\mathrm{sc}}(y)\, \mathrm{d}y\, \Big|_{\,b\,=\,a}.
\end{aligned} \tag{2.18}$$

Similarly to (2.8), all $\overline{F}^{\mathrm{sc}}(x)$, $\overline{F}^{\mathrm{sp}}(x)$, $\overline{F}^{\mathrm{ss}}(x)$ vanish at infinity, since the constants in the right-hand sides of (2.17) are the appropriate long-range values.

It is noted after Torquato [15] that the “surface-center" correlation (2.11) is the most important in the sense of (2.18), i.e. the other two — $F^{\mathrm{sp}}(x)$ and $F^{\mathrm{ss}}(x)$ — can be easily represented by means of $F^{\mathrm{sc}}(x)$.

It should be pointed out also that all the correlation functions, mentioned in this section, are particular case of the much more general statistical characteristics for two-phase random media, as introduced by Torquato [15]. Our aim here will be however much more specific, namely, derivation of simple integral representations of these correlations by means of the total correlation function for the set $\{x_\alpha\}$ of sphere's centers of the type of Eq. (3.13) below.

3. THE “PARTICLE-CENTER" CORRELATION

Let us split the radial distribution function, $g(x)$, as

$$g(x) = g^{\mathrm{ws}}(x) + \widetilde{g}(x), \tag{3.1}$$

where

$$g^{\mathrm{ws}}(x) = 1 - h_{2a}(x) = \begin{cases} 0, & \text{if } |x| \le 2a, \\ 1, & \text{if } |x| > 2a, \end{cases} \tag{3.2}$$

corresponds to the simplest “well-stirred" distribution of spheres; $\widetilde{g}(x)$ is then the “correction" to the latter. In turn, the total correlation $\nu_2(x)$, defined in (2.10), is represented as

$$\nu_2(x) = -h_{2a}(x) + \widetilde{\nu}_2(x). \tag{3.3}$$

Moreover, one has

$$\begin{aligned} \nu_2(x) =& \widetilde{\nu}_2(x) = \widetilde{g}(x), \quad \text{if} \quad |x| \ge 2a, \\ \widetilde{\nu}_2(x) =& g(x), \quad \text{if} \quad |x| < 2a, \end{aligned} \tag{3.4}$$

as a consequence of the nonoverlapping assumption. The formula $(3.4)_1$ will allow us to replace below $\widetilde{g}(x)$ by the binary correlation $\nu_2(x)$ when $|x| = r \ge 2$.

Let us recall now the well-known formula for the common volume of two spheres of radii b and ξ, the first centered at the origin, the other at the point x, $|x| = r$:

$$\big(h_b * h_\xi\big)(x) = \int h_b(x-y) h_\xi(y)\,\mathrm{d}y = V_a \begin{cases} \tau^3, & \text{if } 0 \le \rho \le \mu - \tau, \\ \Psi(\rho;\mu,\tau), & \text{if } \mu - \tau \le \rho \le \mu + \tau, \\ 0, & \text{if } \rho > \mu + \tau, \end{cases} \tag{3.5}$$

where

$$\Psi(\rho;\mu,\tau) = \frac{1}{16\rho}(\mu+\tau-\rho)^2(\rho^2 + 2(\mu+\tau)\rho - 3(\mu-\tau)^2), \tag{3.6}$$

with the dimensionless variables

$$\rho = r/a, \quad \mu = \xi/a, \quad \tau = b/a. \tag{3.7}$$

It is assumed in (3.5) that $\xi \geq b$, i.e. $\mu \geq \tau$. The elementary formulae (3.5) and (3.6) will play a central role in the sequel.

From (2.8), (3.1) and (3.2) it now follows

$$\overline{F}^{\mathrm{pc}}(x) = \overline{F}^{\mathrm{pc}}_{\mathrm{ws}}(x) + \widetilde{F}^{\mathrm{pc}}(x), \tag{3.8}$$

where

$$\begin{aligned} \overline{F}^{\mathrm{pc}}_{\mathrm{ws}}(x) &= nh_a(x) - n^2(h_a * h_{2a})(x) \\ &= n\eta_2 h_a(x) - \frac{n\eta_1}{16\rho}(3-\rho)^2(\rho^2+6\rho-3)\big[\,h_{3a}(x) - h_a(x)\,\big], \end{aligned} \tag{3.9}$$

$$\widetilde{F}^{\mathrm{pc}}(x) = n^2 \int h_a(x-y)\widetilde{g}(y)\,\mathrm{d}y. \tag{3.10}$$

This formula implies that

$$\widetilde{F}^{\mathrm{pc}}(x) = 0, \quad \text{if} \quad |x| \leq a, \tag{3.11}$$

since $\widetilde{g}(x) = 0$ at $|x| \leq 2a$, see $(3.4)_2$.

To represent $\widetilde{F}^{\mathrm{pc}}(x)$ as a simple one-tuple integral, containing the function $\widetilde{g}(x)$, write down the latter as

$$\widetilde{g}(y) = \int_{2a}^{\infty} \widetilde{g}(A)\,\frac{\partial}{\partial A} h_A(y)\,\mathrm{d}A, \tag{3.12}$$

which follows from (2.14). Then, in virtue of (3.5) (at $\tau = 1$) and $(3.4)_2$,

$$\begin{aligned} \widetilde{F}^{\mathrm{pc}}(x) &= n^2 \int_2^{\infty} \mathrm{d}\mu\,\widetilde{g}(\mu)\frac{\partial}{\partial\mu}\big(h_a * h_\xi\big)(r) \\ &= \frac{3n\eta_1}{4\rho}\int_{\max\{2,\rho-1\}}^{\rho+1}\left[1-(\mu-\rho)^2\right]\mu\nu_2(\mu)\,\mathrm{d}\mu. \end{aligned} \tag{3.13}$$

The obtained simple representation of $F^{\mathrm{pc}}(x)$ by means of the total correlation allows one to interconnect the moments

$$\theta_k^{\mathrm{pc}} = \int_0^{\infty} \rho^k\,\overline{F}^{\mathrm{pc}}(r)\,\mathrm{d}\rho, \quad k = 0, 1, \ldots, \tag{3.14}$$

of $F^{\mathrm{pc}}(r)$ on the semiaxis $(0, \infty)$ with the appropriate moments of the total correlation. Indeed, due to (3.8) and (3.9),

$$\theta_k^{\mathrm{pc}} = \theta_{k,\mathrm{ws}}^{\mathrm{pc}} + \widetilde{\theta}_k^{\mathrm{pc}}. \tag{3.15}$$

The first term in (3.15) corresponds to the well-stirred distribution when $\overline{F}^{\mathrm{pc}}(r) = \overline{F}^{\mathrm{pc}}_{\mathrm{ws}}(x)$ is given in (3.9); the appropriate integration is elementary. In turn, $\widetilde{\theta}_m^{\mathrm{pc}}$ corresponds to the deviation $\widetilde{g}(r)$ of the radial distribution function from the well-stirred statistics. Using (3.13) and changing the order of integration give

$$\begin{aligned} \widetilde{\theta}_k^{\mathrm{pc}} &= n\eta_1 \int_2^{\infty} H_k^{\mathrm{pc}}(\mu)\mu\nu_2(\mu)\mathrm{d}\mu, \\ H_k^{\mathrm{pc}}(\mu) &= \frac{3}{4}\int_{\mu-1}^{\mu+1}\rho^{k-1}\left[1-(\mu-\rho)^2\right]\,\mathrm{d}\rho. \end{aligned} \tag{3.16}$$

The functions $H_k^{\mathrm{pc}}(\mu)$ in (3.16) are polynomials whose explicit evaluation is straightforward. In particular,

$$H_1^{\mathrm{pc}}(\mu) = 1, \quad H_2^{\mathrm{pc}}(\mu) = \mu, \quad \text{etc.} \tag{3.17}$$

Hence, if

$$m_k = \int_2^\infty \rho^k \nu_2(\rho)\,\mathrm{d}\rho, \quad k = 0, 1, \ldots, \tag{3.18}$$

are the moments on $(2, \infty)$ of the binary correlation $\nu_2(\rho)$ or, which is the same, of the "correction" $\widetilde{g}(\rho)$ to the radial distribution function, then the formulae (3.16) and (3.17), together with (3.9), imply

$$\theta_1^{\mathrm{pc}} = n\eta_1 \left(\frac{5 - 19\eta_1}{10\eta_1} + m_1 \right), \quad \theta_2^{\mathrm{pc}} = n\eta_1 \left(\frac{1 - 8\eta_1}{3\eta_1} + m_2 \right), \quad \text{etc.} \tag{3.19}$$

4. THE "SURFACE-CENTER" CORRELATION

Inserting (3.3) into $(2.18)_1$ gives

$$\overline{F}^{\mathrm{sc}}(x) = \overline{F}^{\mathrm{sc}}_{\mathrm{ws}}(x) + \widetilde{F}^{\mathrm{sc}}(x), \tag{4.1}$$

where

$$\overline{F}^{\mathrm{sc}}_{\mathrm{ws}}(x) = n\delta(r-a) - n^2 \frac{\partial}{\partial b} \int h_b(x-y) h_{2a}(y)\,\mathrm{d}y \,\Bigg|_{b=a}, \tag{4.2}$$

$$\widetilde{F}^{\mathrm{sc}}(x) = n^2 \frac{\partial}{\partial b} \int h_b(x-y) \widetilde{g}(y)\,\mathrm{d}y \,\Bigg|_{b=a}. \tag{4.3}$$

Hence, the first term, $F^{\mathrm{sc}}_{\mathrm{ws}}(x)$, in (4.1) corresponds to the well-stirred distribution, while the second one, $\widetilde{F}^{\mathrm{sc}}(x)$, is due to the deviation, $\widetilde{g}(x)$, of the radial distribution function from the latter.

Combining $(2.18)_1$ and (4.2), and using (4.3) (at $\xi = 2a$) give eventually the "surface-center" correlation (2.11) in the well-stirred case:

$$\overline{F}^{\mathrm{sc}}_{\mathrm{ws}}(x) = n\delta(|x| - a) - nS \begin{cases} 0, & \text{if } 0 \le \rho \le 1, \\ \dfrac{(\rho+1)(3-\rho)}{4\rho}, & \text{if } 1 < \rho \le 3, \\ 0, & \text{if } \rho > 3. \end{cases} \tag{4.4}$$

To evaluate the deviation $\widetilde{F}^{\mathrm{sc}}(x)$ from (4.3), we shall use once again the representation (3.12):

$$\widetilde{F}^{\mathrm{sc}}(x) = n^2 \int_{2a}^\infty \mathrm{d}\xi\, \widetilde{g}(\xi) \left\{ \frac{\partial^2}{\partial b \partial \xi} \int h_b(x-y) h_\xi(y)\,\mathrm{d}y \right\}_{b=a}. \tag{4.5}$$

Applying (3.5) yields the needed formula

$$\widetilde{F}^{\mathrm{sc}}(x) = \frac{nS}{2\rho} \begin{cases} 0, & \text{if } 0 \le \rho \le 1, \\ \displaystyle\int_{\max\{2, \rho-1\}}^{\rho+1} \mu\nu_2(\mu)\,\mathrm{d}\mu, & \text{if } \rho > 1. \end{cases} \tag{4.6}$$

Similarly to Section 3, consider the evaluation of the moments of $F^{\,\mathrm{sc}}(x)$, i.e. the quantities

$$\theta_k^{\mathrm{sc}} = \int_0^\infty \rho^k \, \overline{F}^{\mathrm{sc}}(r) \mathrm{d}\rho, \quad k = 0, 1, \ldots \tag{4.7}$$

Due to (4.1), again

$$\theta_k^{\mathrm{sc}} = \theta_{k,\mathrm{ws}}^{\mathrm{sc}} + \widetilde{\theta}_k^{\mathrm{sc}} \tag{4.8}$$

— the first term in (4.8) corresponds to the well-stirred distribution and its evaluation is elementary; the second is due to the “deviation" $\widetilde{g}(r)$. To evaluate the latter, insert (4.6) into (4.7) and change again the order of integration:

$$\begin{aligned}\widetilde{\theta}_k^{\mathrm{sc}} &= nS \int_2^\infty H_k^{\mathrm{sc}}(\mu) \widetilde{g}(\mu) \mathrm{d}\mu, \\ H_k^{\mathrm{sc}}(\mu) &= \frac{1}{2} \int_{\mu-1}^{\mu+1} \rho^{k-1} \, \mathrm{d}\rho = \frac{(\mu+1)^k - (\mu-1)^k}{2k}.\end{aligned} \tag{4.9}$$

Hence $H_1^{\mathrm{sc}}(\mu) = 1$, $H_2^{\mathrm{sc}}(\mu) = \mu$, etc. Together with (4.8), (4.4) and (4.9), this implies

$$\theta_1^{\mathrm{sc}} = nS \left(\frac{1 - 11\eta_1/2}{3\eta_1} + m_1 \right), \quad \theta_2^{\mathrm{sc}} = nS \left(\frac{1 - 8\eta_1}{3\eta_1} + m_2 \right), \quad \text{etc.} \tag{4.10}$$

5. THE “SURFACE-PARTICLE" CORRELATION

First, let us evaluate $F^{\mathrm{sp}}(0)$:

$$\begin{aligned}F^{\mathrm{sp}}(0) = \langle \, |\nabla I_1(0)| \, I_1(0) \rangle &= \frac{\partial}{\partial b} \iint h_a(y_1) h_b(y_2) \, \langle \psi(y_1) \psi(y_2) \rangle \, \mathrm{d}y_1 \mathrm{d}y_2 \, \Big|_{\,b\,=\,a} \\ &= \frac{\partial}{\partial b} \int h_a(y) h_b(y) \, \mathrm{d}y \, \Big|_{\,b\,=\,a},\end{aligned} \tag{5.1}$$

having used (2.2) and the fact that $g(y_1 - y_2) = 0$, if $|y_1 - y_2| \le 2a$, due to the nonoverlapping assumption. But

$$\frac{\partial}{\partial b} \int h_a(y) h_b(y) \, \mathrm{d}y = \frac{\partial}{\partial b} \begin{cases} \frac{4}{3}\pi a^3, & \text{if } b > a, \\ \frac{4}{3}\pi b^3, & \text{if } b < a, \end{cases} \tag{5.2}$$

which equals 0 if $b > a$ and $4\pi b^2$, if $b < a$. Hence, a question appears, which of the two values, 0 or $S = 4\pi a^2 n$, should be attributed to $F^{\mathrm{sp}}(0)$ when putting $b = a$ in (5.1) and (5.2). The correct answer is *one-half* of these two values, i.e.

$$F^{\mathrm{sp}}(0) = \frac{1}{2} \, S. \tag{5.3}$$

This will be confirmed by the formal calculations below. Roughly speaking, 1/2 in (5.3) means that the boundary $\partial\mathcal{K}$ is “equally shared" between the constituents. We imagine, in other words, that if a point lies in $\partial\mathcal{K}$, “half" of it belongs to $\mathcal{K}_1$ and the other “half" to $\mathcal{K}_2$.

To evaluate $\overline{F}^{\mathrm{sp}}(x)$, employ its definition from (2.18) and the formula (2.2):

$$\overline{F}^{\mathrm{sp}}(x) = \frac{\partial}{\partial b} \iint h_a(y_1)h_b(x-y_2)\ \langle \psi'(y_1)\psi'(y_2)\rangle\ \mathrm{d}y_1\mathrm{d}y_2 \Big|_{b=a} = A_1 n + A_2 n^2, \quad (5.4)$$

where

$$A_1 = \frac{\partial}{\partial b} \int h_a(y)h_b(x-y)\,\mathrm{d}y \Big|_{b=a}, \quad (5.5)$$

$$A_2 = \frac{\partial}{\partial b} \iint h_a(y_1)h_b(x-y_2)\,\nu_2(y_1-y_2)\,\mathrm{d}y_1\mathrm{d}y_2 \Big|_{b=a}. \quad (5.6)$$

The coefficient A_1 can be immediately found differentiating (3.5) at $\xi = b$ and putting $b = a$ in the result:

$$\frac{\partial}{\partial b}(h_a * h_b)(r) \Big|_{b=a} = \pi a^2 \begin{cases} 2-\rho, & \text{if } 0 \le r \le 2a, \\ 0, & \text{if } r > 2a, \end{cases} \quad (5.7)$$

and hence

$$A_1 n = \frac{1}{2} S \begin{cases} 1-\rho/2, & \text{if } 0 \le r \le 2a, \\ 0, & \text{if } r > 2a. \end{cases} \quad (5.8)$$

The formula (5.8) means that

$$F^{\mathrm{sp}}(x) = \overline{F}^{\mathrm{sp}}(x) = \frac{1}{2} S \left(1 - \frac{r}{2a}\right) h_{2a}(x) + o(n),$$

which agrees with the result of Berryman [2], see also [14], found by means of different arguments.

To evaluate the coefficient A_2 from (5.6), we shall literally follow the reasoning of [7]. Consider to this end the triple convolution

$$\left(h_a * \frac{\partial}{\partial b} h_b * h_A\right)(r) \Big|_{b=a} = \left(\left(\varphi^{\mathrm{sp}}(t) h_{2a}\right) * h_A\right)(r), \quad (5.9)$$

where, according to (5.7),

$$\varphi^{\mathrm{sp}}(t) = \left(h_a * \frac{\partial}{\partial b} h_b\right)(r) \Big|_{b=a} = \pi a^2 (2-t), \quad t = r/a. \quad (5.10)$$

Similarly to [7], we treat $\varphi^{\mathrm{sp}}(t)$ as pertaining to an inhomogeneous and radially-symmetric ball whose density decreases along the radius according to (5.10). This inhomogeneous ball is then approximated, for a given division $0 = \xi_0 < \xi_1 < \ldots \xi_{N-1} <$

$\xi_N = 2a$ of the interval $(0, 2a)$, by a family of concentric spherical layers $\xi_i < r < \xi_{i+1}$, each one homogeneous and of density $\varphi^{\rm sp}(\xi_i)$. In the limit $\triangle\xi_i = \xi_i - \xi_{i-1} \to 0$ one finds

$$\begin{aligned}
&\Big(\big(\varphi^{\rm sp}(t)h_{2a}\big) * h_A\Big)(r) = \int_0^{2a} \varphi^{\rm sp}(\xi/a)\,\frac{\partial}{\partial\xi}\big(h_\xi * h_A\big)(r)\,{\rm d}\xi \\
&= \varphi^{\rm sp}(\xi/a)\big(h_\xi * h_A\big)(r)\,\Big|_{\xi=0}^{\xi=2a} - \frac{1}{a}\int_0^{2a}\big(h_\xi * h_A\big)(r)\frac{\partial}{\partial\xi}\varphi^{\rm sp}(\xi/a)\,{\rm d}\xi \qquad (5.11)\\
&= \pi a^2 \int_0^2 \big(h_\xi * h_A\big)(r)\,{\rm d}\mu = 4\pi a^2 V_a U_{\rm sp}(\rho;\tau),
\end{aligned}$$

since $\varphi^{\rm sp}(2) = 0$ and $h_\xi * h_A\,\Big|_{\xi=0} = 0$. In accordance with the notations (3.7), $\mu = \xi/a$ and $\tau = A/a \geq 2$. The evaluation of the function $U_{\rm sp}(\rho;\tau)$ is obvious, using (3.5) at $b = A$ in (5.11), and the final result reads

$$U_{\rm sp}(\rho;\tau) = \begin{cases} U_{\rm sp}^{(I)}(\rho;\tau), & \text{if } 0 \leq \rho \leq \tau - 2, \\ U_{\rm sp}^{(II)}(\rho;\tau), & \text{if } \tau - 2 \leq \rho \leq \tau, \\ U_{\rm sp}^{(III)}(\rho;\tau), & \text{if } \tau \leq \rho \leq \tau + 2\,, \\ 0, & \text{if } \rho > \tau + 2, \end{cases} \qquad (5.12)$$

where

$$\begin{aligned}
U_{\rm sp}^{(I)}(\rho;\tau) &= \frac{1}{4}\int_0^2 \mu^3 {\rm d}\mu = 1, \\
U_{\rm sp}^{(II)}(\rho;\tau) &= \frac{1}{4}\int_0^{\tau-\rho} \mu^3\, d\mu + \frac{1}{4}\int_{\tau-\rho}^2 \Psi(\rho;\tau,\mu)\,{\rm d}\mu, \qquad (5.13)\\
U_{\rm sp}^{(III)}(\rho;\tau) &= \frac{1}{4}\int_{\rho-\tau}^2 \Psi(\rho;\tau,\mu)\,{\rm d}\mu,
\end{aligned}$$

with $\Psi(\rho;\tau,\mu)$ defined in (3.6). The integrals in (5.13) can be analytically evaluated, but the only formulae that will be important for the sequel are

$$\begin{aligned}
&\left(h_a * \frac{\partial}{\partial b}\, h_b * h_{2a}\right)(r)\,\Bigg|_{b\,=\,a} = 4\pi a^2 V_a U_{\rm sp}(\rho;2), \\
&U_{\rm sp}(\rho;2) = \begin{cases} 1 - \dfrac{1}{4}\rho^2 + \dfrac{5}{160}\rho^3 + \dfrac{1}{160}\rho^4, & \text{if } 0 \leq \rho \leq 2, \\ \dfrac{(4-\rho)^3(\rho^2 + 7\rho - 4)}{160\rho}\,, & \text{if } 2 < \rho < 4, \\ 0, & \text{if } \rho \geq 4. \end{cases} \qquad (5.14)
\end{aligned}$$

Also, it turns out that

$$
\begin{aligned}
&\frac{\partial}{\partial\tau}\,U_{\mathrm{sp}}(\rho;\tau) = \frac{\tau}{\rho}\,G^{\mathrm{sp}}(\rho-\tau), \\
&G^{\mathrm{sp}}(t) = \begin{cases} f^{\mathrm{sp}}(t), & \text{if } -2 \le t \le 0, \\ f^{\mathrm{sp}}(-t), & \text{if } 0 \le t \le 2, \\ 0, & \text{if } |t| \ge 2, \end{cases} \\
&f^{\mathrm{sp}}(t) = \frac{1}{8}(2+t)^2\,(1-t).
\end{aligned} \tag{5.15}
$$

As a first application of the foregoing formulae, consider the well-stirred approximation, see (3.2). The coefficient A_2 from (5.6) then becomes

$$
A_2 n^2 = -n^2 \left(h_a * \frac{\partial}{\partial b}\,h_b * h_{2a} \right)(r)\,\bigg|_{b=a}
$$

and application of (5.4), (5.8) and (5.14) gives eventually

$$
\begin{aligned}
&F^{\mathrm{sp}}_{\mathrm{ws}}(r) = \eta_1 S + \overline{F}^{\mathrm{sp}}_{\mathrm{ws}}(r), \\
&\overline{F}^{\mathrm{sp}}_{\mathrm{ws}}(r) = S \begin{cases} \dfrac{1}{2} - \dfrac{\rho}{4} - \eta_1 \left[1 - \dfrac{1}{4}\rho^2 + \dfrac{5}{160}\rho^3 + \dfrac{1}{160}\rho^4 \right], & \text{if } 0 \le \rho \le 2, \\ \dfrac{(4-\rho)^3(4-7\rho-\rho^2)}{160\rho}\,\eta_1, & \text{if } 2 < \rho < 4, \\ 0, & \text{if } \rho \ge 4. \end{cases}
\end{aligned} \tag{5.16}
$$

In the general case the radial correlation function $g(r)$ is decomposed again as the sum (3.1), so that

$$
F^{\mathrm{sp}}(r) = F^{\mathrm{sp}}_{\mathrm{ws}}(r) + \widetilde{F}^{\mathrm{sp}}(r), \tag{5.17}
$$

with the well-stirred contribution, given in (5.16), and

$$
\widetilde{F}^{\mathrm{sp}}(r) = n^2 \frac{\partial}{\partial b} \iint h_a(y_1) h_b(x-y_2)\,\widetilde{g}(y_1-y_2)\,\mathrm{d}y_1 \mathrm{d}y_2 \,\bigg|_{b=a}. \tag{5.18}
$$

The evaluation of this integral follows the reasoning of Section 3. Namely, inserting (3.12) in the right-hand side of (5.18) yields

$$
\begin{aligned}
\widetilde{F}^{\mathrm{sp}}(r) &= n^2 \int_{2a}^{\infty} \widetilde{g}(A) \frac{\partial}{\partial A} \left(h_a * \frac{\partial h_b}{\partial b} * h_A \right)(r)\,\mathrm{d}A \,\bigg|_{b=a} \\
&= 4\pi a^2 n^2 V_a \int_2^{\infty} \widetilde{g}(\tau) \frac{\partial}{\partial\tau} U_{\mathrm{sp}}(\rho;\tau)\,\mathrm{d}\tau \\
&= \frac{\eta_1 S}{\rho} \int_{\max\{\rho-2,2\}}^{\rho+2} G^{\mathrm{sp}}(\rho-\tau)\,\tau\nu_2(\tau)\,\mathrm{d}\tau,
\end{aligned} \tag{5.19}
$$

as it follows from (2.16) and (5.15).

The formulae (5.16), (5.17), (5.15) and (5.19) provide the needed representation of the "surface-particle" correlation $F^{\rm sp}(r)$ for an arbitrary dispersion of nonoverlapping spheres. They imply, in particular, that indeed $F^{\rm sp}(0) = S/2$, as it was argued in the beginning of this Section, see (5.3). The correction to the total correlation function, $\widetilde{g}(r) = \nu_2(r)$, see (3.4), for the set of sphere centers features in the expression for $F^{\rm sp}(r)$ through a simple one-tuple integral in (5.19). It is noted that the obtained formula for $F^{\rm sp}(r)$ is fully similar to that of Markov and Willis [7], for the "particle-particle" correlation $F^{\rm pp}(r)$ defined in (2.6). (In the latter case, let us recall, the counterpart of the function $f^{\rm sp}(t)$ from (5.15) is $f(t) = f^{\rm pp}(t) = (2+t)^3(4-6t+t^2)$, see [7, eq. (33b)].)

Similarly to the previous Sections, the formula (5.19) allows us to evaluate the moments of $\overline{F}^{\rm sp}(x)$ on the semiaxis $(0,\infty)$ to be

$$\theta_k^{\rm sp} = \int_0^\infty \rho^k\, \overline{F}^{\rm sp}(\rho){\rm d}\rho = \theta_{k,\rm ws}^{\rm sp} + \widetilde{\theta}_k^{\rm sp}, \tag{5.20}$$

$k = 0, 1, \ldots$ The well-stirred contribution $\theta_{k,\rm ws}^{\rm sp}$ can be found by means of an elementary integration, using (5.16). For the "corrections" $\theta_k^{\rm sp}$ we have

$$\begin{aligned} \widetilde{\theta}_k^{\rm sp} &= \eta_1 S \int_2^\infty H_k^{\rm sp}(\mu)\mu\nu_2(\mu){\rm d}\mu, \\ H_k^{\rm sp}(\mu) &= \int_{\mu-2}^{\mu} \rho^{k-1} f^{\rm sp}(\rho-\mu)\,{\rm d}\rho + \int_{\mu}^{\mu-2} \rho^{k-1} f^{\rm sp}(\mu-\rho)\,{\rm d}\rho, \end{aligned} \tag{5.21}$$

as it follows from (5.19) and (5.20). Recalling the form of $f^{\rm sp}(t)$ from (5.15), one easily finds, in particular, $H_1^{\rm sp}(\mu) = 1$, $H_2^{\rm sp}(\mu) = \mu$, etc., and hence, using (5.16),

$$\theta_1^{\rm sp} = S\eta_1 \left(\frac{5-26\eta_1}{15\eta_1} + m_1\right), \quad \theta_2^{\rm sp} = S\eta_1 \left(\frac{1-8\eta_1}{3\eta_1} + m_2\right), \quad \text{etc.}, \tag{5.22}$$

where m_k are the moments (3.18).

6. THE "SURFACE-SURFACE" CORRELATION

Due to (2.17), (2.15) and (2.2), we have in this case

$$\overline{F}^{\rm ss}(x) = \frac{\partial^2}{\partial b \partial c} \iint h_b(y_1) h_c(x-y_2)\, \langle \psi'(y_1)\psi'(y_2)\rangle\, {\rm d}y_1 {\rm d}y_2 \,\Big|_{b,c=a} = B_1 n + B_2 n^2, \tag{6.1}$$

where

$$B_1 = \frac{\partial^2}{\partial b \partial c} \int h_b(y) h_c(x-y)\,{\rm d}y \,\Big|_{b,c=a}, \tag{6.2}$$

$$B_2 = \frac{\partial^2}{\partial b \partial c} \iint h_b(y_1) h_c(x-y_2)\, \nu_2(y_1-y_2)\,{\rm d}y_1 {\rm d}y_2 \,\Big|_{b,c=a}. \tag{6.3}$$

The coefficient B_1 can be immediately found, evaluating the second mixed derivative $\partial^2/\partial\mu\partial\tau$ of the function Ψ, see (3.5), and putting $\mu = \tau = 1$ in the result:

$$B_1 = \frac{2\pi a}{\rho}\begin{cases}1, & \text{if } \rho \le 2,\\ 0, & \text{if } \rho > 2,\end{cases} \tag{6.4}$$

which means that in the dilute case

$$F^{\rm ss}(x) = \overline{F}^{\rm ss}(x) = \frac{S}{2r}h_{2a}(x) + o(n).$$

The latter agrees with the result of Berryman [2], see also [14], found by means of different arguments.

To calculate B_2, consider again the appropriate triple convolution, similar to (5.9):

$$\begin{aligned}\Big(\frac{\partial}{\partial b}\,h_b * \frac{\partial}{\partial c}\,h_c * h_A\Big)(r)\,\Big|_{b,c\,=\,a} &= \Big(\big(\varphi^{\rm ss}(\xi/a)h_{2a}\big) * h_A\Big)(r)\\ &= \varphi^{\rm ss}(\xi/a)\big(h_\xi * h_A\big)(r)\,\Big|_{\xi=0}^{\xi=2a} - \int_0^2 \big(h_\xi * h_A\big)(r)\frac{\mathrm{d}}{\mathrm{d}\mu}\varphi^{\rm ss}(\mu)\,\mathrm{d}\mu\\ &= \pi a\big(h_{2a} * h_A\big)(r) + 4\pi a V_a U_{\rm ss}(\rho;\tau),\end{aligned} \tag{6.5}$$

having used that

$$\varphi^{\rm ss}(t) = \left(\frac{\partial}{\partial b}\,h_b * \frac{\partial}{\partial c}\,h_c\right)(r)\,\Big|_{b,c\,=\,a} = \frac{2\pi a}{t}h_{2a}(t),$$

$t = r/a$, see (6.2) and (6.4). The function $U_{\rm ss}(\rho;\tau)$ in (6.5) has the same form as that of its “surface-particle" counterpart $U_{\rm sp}(\rho;\tau)$ in (5.12), with the functions

$$\begin{aligned}U_{\rm ss}^{(I)}(\rho;\tau) &= \frac{1}{2}\int_0^2 \mu d\mu = 1,\\ U_{\rm ss}^{(II)}(\rho;\tau) &= \frac{1}{2}\int_0^{\tau-\rho}\mu\,d\mu + \frac{1}{2}\int_{\tau-\rho}^2 \frac{1}{\mu^2}\,\Psi(\rho;\tau,\mu)\,d\mu,\\ U_{\rm ss}^{(III)}(\rho;\tau) &= \frac{1}{2}\int_{\rho-\tau}^2 \frac{1}{\mu^2}\,\Psi(\rho;\tau,\mu)\,d\mu,\end{aligned} \tag{6.6}$$

where $\Psi(\rho;\tau,\mu)$ is defined in (3.6). The integrals in (6.6) can be analytically evaluated, similarly to those in (5.13), but again the only formulae important for the sequel are, first,

$$\left(\frac{\partial}{\partial b}\,h_b * \frac{\partial}{\partial c}\,h_c * h_{2a}\right)(r)\,\Big|_{b,c\,=\,a} = \pi a\big(h_{2a} * h_{2a}\big)(r) + 4\pi a V_a U_{\rm ss}(\rho;2),$$

$$U_{\rm ss}(\rho;2) = \begin{cases}1 - \dfrac{1}{8}\rho^2 - \dfrac{1}{64}\rho^3, & \text{if } 0 \le \rho \le 2,\\ \dfrac{(4-\rho)^3(\rho+4)}{64\rho}, & \text{if } 2 < \rho < 4,\\ 0, & \text{if } \rho \ge 4.\end{cases} \tag{6.7}$$

Second, it turns out that

$$
\begin{aligned}
&\frac{\partial}{\partial\tau}\,U_{\rm ss}(\rho;\tau)=\frac{3\tau}{16\rho}\,G_0^{\rm ss}(\rho-\tau),\\
&G_0^{\rm ss}(t)=\begin{cases} f_0^{\rm ss}(t), & \text{if } -2\le t\le 0,\\ f_0^{\rm ss}(-t), & \text{if } 0\le t\le 2,\\ 0, & \text{if } |t|\ge 2,\end{cases}\\
&f_0^{\rm ss}(t)=(2+t)^2.
\end{aligned}
\tag{6.8}
$$

In the well-stirred case, as it follows from (3.5), (6.1), (6.3), (6.4) and (6.7),

$$
\overline{F}^{\rm ss}_{\rm ws}(x)=\frac{S^2}{12\eta_1}\left\{\frac{2}{\rho}\,h_{2a}(x)-\eta_1\left[\frac{1}{16}(\rho-4)^2(\rho+8)h_{4a}(x)+4U_{\rm ss}(\rho;2)\right]\right\}. \tag{6.9}
$$

In the general case $g(r)$ is once again decomposed into the form (3.1), so that

$$
\overline{F}^{\rm ss}(r)=\overline{F}^{\rm ss}_{\rm ws}(r)+\widetilde{F}^{\rm ss}(r), \tag{6.10}
$$

with the well-stirred part, $\overline{F}^{\rm ss}_{\rm ws}(r)$, given in (6.7), and

$$
\begin{aligned}
\widetilde{F}^{\rm ss}(r)&=n^2\int_{2a}^{\infty}\widetilde{g}(A)\frac{\partial}{\partial A}\left(\frac{\partial h_b}{\partial b}*\frac{\partial h_c}{\partial c}*h_A\right)(r)\,{\rm d}A\,\bigg|_{b,c=a}\\
&=\int_2^{\infty}\widetilde{g}(\tau)\frac{\partial}{\partial\tau}\Big\{\pi a(h_{2a}*h_A)(r)+4\pi aV_aU_{\rm ss}(\rho;\tau)\,{\rm d}\tau\Big\}\\
&=\frac{1}{16\rho}S^2\int_{\max\{\rho-2,2\}}^{\rho+2}\left[4-(\rho-\tau)^2+G_0^{\rm ss}(\rho-\tau)\right]\tau\widetilde{g}(\tau)\,{\rm d}\tau,
\end{aligned}
\tag{6.11}
$$

as it follows from (2.16), (3.5), (3.6) and (6.8), $\tau=A/a$. Taking into account (6.8), we can recast (6.11) into the following final form:

$$
\widetilde{F}^{\rm ss}(r)=\frac{S^2}{\rho}\int_{\max\{\rho-2,2\}}^{\rho+2}G^{\rm ss}(\rho-\tau)\,\tau\nu_2(\tau)\,{\rm d}\tau, \tag{6.12}
$$

where the function $G^{\rm ss}$ has the same form as $G_0^{\rm ss}$ in (6.8), but with the function $f_0^{\rm ss}(t)$ replaced by

$$
f^{\rm ss}(t)=\frac{1}{4}(2+t). \tag{6.13}
$$

For the moments of $\overline{F}^{\rm sp}(x)$ on the semiaxis $(0,\infty)$ we have, similarly to the previous sections,

$$
\begin{aligned}
\theta_k^{\rm ss} &= \int_0^\infty \rho^k\, \overline{F}^{\rm ss}(r) {\rm d}\rho = \theta_{k,{\rm ws}}^{\rm ss} + \widetilde{\theta}_k^{\rm ss}, \quad k = 0, 1, \ldots, \\
\widetilde{\theta}_k^{\rm ss} &= S^2 \int_2^\infty H_k^{\rm ss}(\mu) \mu \widetilde{g}(\mu) {\rm d}\mu, \\
H_k^{\rm ss}(\mu) &= \frac{1}{4} \left\{ \int_{\mu-2}^{\mu} \rho^{k-1} (2 + \rho - \mu)\, {\rm d}\rho + \int_{\mu}^{\mu-2} \rho^{k-1} (2 + \mu - \rho)\, {\rm d}\rho \right\}, \\
H_1^{\rm sp}(\mu) &= 1, \quad H_2^{\rm sp}(\mu) = \mu, \quad \text{etc.}
\end{aligned} \tag{6.14}
$$

The well-stirred contribution, $\theta_{k,{\rm ws}}^{\rm ss}$, can be elementary found by means of (6.9). In particular,

$$
\theta_1^{\rm ss} = S^2 \left(\frac{1 - 5\eta_1}{3\eta_1} + m_1 \right), \quad \theta_2^{\rm ss} = S^2 \left(\frac{1 - 8\eta_1}{3\eta_1} + m_2 \right), \tag{6.15}
$$

where m_k are the moments (3.18).

7. DIRECT EVALUATION OF THE FIRST TWO MOMENTS OF THE CORRELATION FUNCTIONS

In the application to be dealt with below (Section 8), the first moments like $\theta_1^{\,\mathrm{pp}}$, θ_1^{ps}, etc., will be of central importance. They were evaluated in the preceding sections as consequences of the appropriate integral representations of the two-point correlations through the radial distribution functions. There exists, however, a simpler and more direct method, based on the interconnections (2.9) and (2.18). The method works equally well in the 2-D case, when the derivation of the counterparts of the above integral representations for the two-point correlations should be considerably more complicated. (The reason is that the common surface of two circles in the plane is not already a rational function of the distance between the circle's centers and their radii, in contrast with the 3-D simple function (3.6) that gives the common volume of two balls.)

Integrate $(2.9)_2$ over the whole $\mathbb{R}^3$ and introduce (3.1) in the result:

$$\int \overline{F}^{\mathrm{pc}}(x)\,\mathrm{d}x = 4\pi a^3\theta_2^{\mathrm{pc}} = nV_a + n^2V_a(-V_{2a} + 4\pi a^3 m_2),$$

having used the definition of m_2, see (3.18). Since $V_{2a} = 8V_a$ and $nV_a = \eta_1$, the already known formula for θ_2^{pc} immediately follows, cf. (3.19).

Integrate next $(2.9)_3$ over $\mathbb{R}^3$:

$$\int \overline{F}^{\mathrm{pp}}(x)\,\mathrm{d}x = V_a\int \overline{F}^{\mathrm{pc}}(x)\,\mathrm{d}x, \quad \text{i.e.} \quad \theta_2^{\mathrm{pp}} = V_a\theta_2^{\mathrm{pc}},$$

or

$$\theta_2^{\mathrm{pp}} = \eta_1^2\left(\frac{1-8\eta_1}{3\eta_1} + m_2\right) \tag{7.1}$$

— a formula derived in [7] by means of the appropriate integral representation of $F^{\,\mathrm{pp}}(x)$ through the radial distribution function.

The reasoning is fully similar in 2-D; only the volume $V_a = \frac{4}{3}\pi a^3$ is replaced by the surface $S_a = \pi a^2$, $\eta_1 = nS_a$ and $S_{2a} = 4S_a$, which yields

$$\begin{aligned} &\int \overline{F}^{\mathrm{pc}}(x)\,\mathrm{d}x = 2\pi a^2\int \rho\overline{F}^{\mathrm{pc}}(x)\,\mathrm{d}\rho = 2\pi a^2\theta_1^{\mathrm{pc}}, \qquad \theta_1^{\mathrm{pp}} = S_a\theta_1^{\mathrm{pc}},\\ &\theta_1^{\mathrm{pc}} = n\left(\frac{1-4\eta_1}{2} + \eta_1 m_1\right), \quad \theta_1^{\mathrm{pp}} = \eta_1^2\left(\frac{1-4\eta_1}{2\eta_1} + m_1\right) \quad \text{in 2-D.} \end{aligned} \tag{7.2}$$

Note that the correlation function $F^{\,\mathrm{pp}}(x)$ should be positive definite for any realistic random constitution, see, e.g. [17]. This implies, in particular, that in the 3-D case $\theta_2^{\,\mathrm{pp}} > 0$, because θ_2^{pp} is proportional to the value of the Fourier transform of $F^{\,\mathrm{pp}}(x)$ at the origin; similarly, $\theta_1^{\mathrm{pp}} > 0$ in 2-D. From (7.1) and (7.2) it follows then that the well-stirred approximation (3.2) (for which $m_1 = m_2 = 0$) is admissible only if $\eta_1 < 1/8$ in 3-D and $\eta_1 < 1/4$ in 2-D (more generally, if $\eta_1 < 1/2^d$ in a d-dimensional space). Both these critical 3-D and 2-D values have been conjectured by Willis [19] who noticed that the quasi-crystalline approximation in the wave propagation problem in random dispersions fails if η_1 is bigger. A rigorous justification of this conjecture in 3-D was proposed, e.g., in [5] and [7].

For the interfacial correlation, the formulae (2.18) are to be employed in a similar manner. Namely, integrating $(2.18)_1$ over $\mathbb{R}^3$, together with (3.1), gives

$$\begin{aligned} 4\pi a^3\theta_2^{\rm sc} &= n\frac{\partial}{\partial b}\left(\tfrac{4}{3}\pi b^3\right)\Big|_{b=a} + n^2\int\frac{\partial}{\partial b}\left(\tfrac{4}{3}\pi b^3\right)\Big|_{b=a}\nu_2(y)\,\mathrm{d}y \\ &= 4\pi a^2 n + 4\pi a^2 n^2(-8V_a + 4\pi a^3 m_2), \end{aligned} \tag{7.3}$$

and it remains to notice that $n/a = nS/(3\eta_1)$ in order to reproduce the formula for $\theta_2^{\rm sc}$, cf. (4.10).

Integrate next $(2.18)_2$ over $\mathbb{R}^3$:

$$\int \overline{F}^{\rm sp}(x)\,\mathrm{d}x = V_a\int\overline{F}^{\rm sc}(x)\,\mathrm{d}x, \quad \text{i.e.} \quad \theta_2^{\rm sp} = V_a\theta_2^{\rm sc}, \tag{7.4}$$

cf. (5.22). Finally, from $(2.18)_2$ it follows

$$\int \overline{F}^{\rm ss}(x)\,\mathrm{d}x = 4\pi a^2\int\overline{F}^{\rm sc}(x)\,\mathrm{d}x, \quad \text{i.e.} \quad \theta_2^{\rm ss} = \frac{S}{n}\theta_2^{\rm sc} = \frac{S}{\eta_1}\theta_2^{\rm sp},$$

cf. (7.4) and (6.15).

The 2-D counterparts of the above moments are immediately derived. The counterpart of (7.3) now reads

$$\begin{aligned} 2\pi a^2\theta_1^{\rm sc} &= n\frac{\partial}{\partial b}\left(\pi b^2\right)\Big|_{b=a} + n^2\int\frac{\partial}{\partial b}\left(\pi b^2\right)\Big|_{b=a}\nu_2(y)\,\mathrm{d}y \\ &= 2\pi a n + 2\pi a n^2(-4S_a + 2\pi a^2 m_1), \end{aligned}$$

so that

$$\theta_1^{\rm sc} = nL\left(\frac{1-4\eta_1}{2\eta_1} + m_1\right) \quad \text{in 2-D}, \tag{7.5}$$

where $L = 2\pi a n$ is the "specific length" — the 2-D counterpart of the specific surface $S = 4\pi a^2 n$ in the dispersion; we have also noted that $1/a = L/(2\eta_1)$ in this case. In turn,

$$\theta_1^{\rm sp} = S_a\theta_1^{\rm sc} = L\eta_1\left(\frac{1-4\eta_1}{2\eta_1} + m_1\right), \quad \theta_1^{\rm ss} = \frac{L}{n}\theta_1^{\rm sc} = L^2\left(\frac{1-4\eta_1}{2\eta_1} + m_1\right) \quad \text{in 2-D}. \tag{7.6}$$

To find in 3-D the moments $\theta_1^{\rm pc}$, $\theta_1^{\rm pp}$, etc., multiply first the formula $(2.9)_2$ by $G(x) = 1/(4\pi|x|)$ and integrate the result over $\mathbb{R}^3$:

$$\begin{aligned} a^2\theta_1^{\rm pc} &= \int G(x)\overline{F}^{\rm pc}(x)\,\mathrm{d}x = n\int G(x)h_a(x)\,\mathrm{d}x + n^2\int\varphi_a(y)\nu_2(y)\,\mathrm{d}y \\ &= n\frac{a^2}{2} - n^2\int\varphi_a(y)h_{2a}(y)\,\mathrm{d}y + n^2\int_{|y|\geq 2a}\varphi_a(y)\nu_2(y)\,\mathrm{d}y, \end{aligned}$$

where

$$\varphi_a(x) = (G * h_a)(x) = \begin{cases} (3a^2 - r^2)/6, & \text{if } r < a, \\ a^3/(3r), & \text{if } r \geq a, \end{cases} \tag{7.7}$$

is the well-known harmonic potential of a sphere of radius a. Elementary integration, using (7.7), reproduces the formula for θ_1^{pc}, cf. (3.19).

In turn, multiply $(2.18)_3$ by $G(x)$ and integrate over $\mathbb{R}^3$:

$$a^2\theta_1^{\mathrm{pp}} = \int G(x)\overline{F}^{\mathrm{pp}}(x)\,\mathrm{d}x = \int \varphi_a(y)\overline{F}^{\mathrm{pc}}(y)\,\mathrm{d}y. \tag{7.8}$$

But, as it follows from (7.7),

$$\varphi_a(x) = V_a G(x) + \left[\frac{1}{6}(3a^2 - r^2) - \frac{V_a}{4\pi r}\right] h_a(x), \tag{7.9}$$

which is introduced into (7.8):

$$a^2\theta_1^{\mathrm{pp}} = a^2 V_a \theta_1^{\mathrm{pc}} + \int \left[\frac{1}{6}(3a^2 - r^2) - \frac{V_a}{4\pi r}\right] h_a(x)\,\mathrm{d}x.$$

It remains to notice that $\overline{F}^{\mathrm{pc}}(x) = n\eta_2$ if $|x| \leq a$, as it follows from (3.8), (3.9) and (3.11), so that the integral in the last formula equals $-a^2\eta_1/10$ and therefore

$$\theta_1^{\mathrm{pp}} = V_a\theta_1^{\mathrm{pc}} - \frac{\eta_1}{10} = \eta_1^2\left(\frac{2 - 9\eta_1}{5\eta_1} + m_1\right) \tag{7.10}$$

— a result, also derived in [7] by means of the appropriate integral representation of $F^{\mathrm{pp}}(x)$.

For the interfacial correlation we have, first of all,

$$\begin{aligned} a^2\theta_1^{\mathrm{sc}} &= \int G(x)\overline{F}^{\mathrm{sc}}(x)\,\mathrm{d}x \\ &= n\int G(x)\frac{\partial}{\partial b}\,h_b(x)\,\Big|_{b=a}\,\mathrm{d}x + n^2\int \frac{\partial}{\partial b}\,\varphi_b(y)\,\Big|_{b=a}\,\nu_2(y)\,\mathrm{d}y, \end{aligned} \tag{7.11}$$

see $(2.18)_1$. Using (7.7) and (3.1) reproduces the formula (4.10) for θ_1^{sc} after simple integration. In turn, from $(2.18)_2$ it follows

$$a^2\theta_1^{\mathrm{sp}} = \int G(x)\overline{F}^{\mathrm{sp}}(x)\,\mathrm{d}x = \int \varphi(y)\overline{F}^{\mathrm{sc}}(y)\,\mathrm{d}y.$$

Inserting here (7.9) elementary yields the already known formula for θ_1^{sp}, cf. (5.22).

Finally, from $(2.18)_3$ one has

$$\begin{aligned} a^2\theta_1^{\mathrm{ss}} &= \int G(x)\overline{F}^{\mathrm{ss}}(x)\,\mathrm{d}x = \int \frac{\partial}{\partial b}\,\varphi_b(y)\,\Big|_{b=a}\,\overline{F}^{\mathrm{sc}}(y)\,\mathrm{d}y \\ &= 4\pi a^2\int G(x)\overline{F}^{\mathrm{sc}}(x)\,\mathrm{d}x + \int a\left(1 - \frac{a}{r}\right)\overline{F}^{\mathrm{sc}}(x)h_a(x)\,\mathrm{d}x, \end{aligned}$$

having used that

$$\left.\frac{\partial\varphi_b(x)}{\partial b}\right|_{b=a} = 4\pi a^2 G(x) + a\left(1-\frac{a}{r}\right)h_a(x), \tag{7.12}$$

which follows from (7.9). But $\overline{F}^{\rm sc}(x) = n\delta(r-a) - nS$, as it is seen from (4.1), (4.2) and (4.6), and the known formula (6.15) for $\theta_1^{\rm ss}$ shows up once again.

8. THE DOI-TALBOT-WILLIS BOUND

As a first and simplest application of the integral representations of the various kinds of two-point correlations, derived in Sections 2 to 6, consider a dispersion of ideal and nonoverlapping spherical sinks (the phase '1'), immersed into an unbounded matrix. The governing equations of this well-known problem read

$$\Delta c(x) + K = 0, \quad x \in \mathcal{K}_2, \quad \left. c(x)\right|_{\partial\mathcal{K}_2} = 0. \tag{8.1}$$

This equation describes the steady-state behaviour of a species (defects), generated at the rate K within the matrix phase '2', occupying the region $\mathcal{K}_2$, and absorbed by the sinks (the "trapping" phase '2') in the region $\mathcal{K}_1 = \mathbb{R}^3 \backslash \mathcal{K}_2$. Then the creation of defects is *exactly* compensated by their removal from the sinks, so that in the steady-state limit under study

$$k^{*2}\,\langle c(x)\rangle = K(1-\eta_1). \tag{8.2}$$

The rate constant k^{*2} is just the effective absorption coefficient (the sink strength) of the medium. Its evaluation and bounding for special kinds of random constitution and, above all, for random dispersion of spheres, have been the subject of numerous works, starting with classical studies of Smoluchowski (1916), see, e.g. [4, 3, 12, 9, 16] *et al.* (Note that we have added the factor $1-\eta_1$ in (8.2), due to the fact that in the case under study, defects are created *only* within the phase '2' (the sink-free region), see Richards and Torquato [8] for a discussion.)

We shall confine the analysis to variational bounding of the sink strength k^{*2}, taking into account the foregoing two-point statistical characteristics. Recall to this end the variational principle of Rubinstein and Torquato [9].

Let $\mathcal{A}$ be the class of smooth and statistically homogeneous trial fields such that

$$\mathcal{A} = \Big\{ u(x) \;\Big|\; \Delta u(x) + K = 0, x \in \mathcal{K}_2 \Big\}. \tag{8.3}$$

Then

$$k^{*2} \geq \frac{K^2(1-\eta_1)}{\langle I_2(x)|\nabla u(x)|^2\rangle}\,. \tag{8.4}$$

The equality sign in (8.4) is achieved if $u(x) = c(x)$ is the actual field that solves the problem (8.1).

Since $\left\langle I_2(x)|\nabla u(x)|^2\right\rangle \leq \left\langle|\nabla u(x)|^2\right\rangle$, another bound immediately follows from (8.4), namely,

$$k^{*2} \geq \frac{K^2(1-\eta_1)}{\langle|\nabla u(x)|^2\rangle}\,, \tag{8.5}$$

see [9]. Though weaker than (8.4), the evaluation of the bound (8.5) is simpler, because it obviously employs smaller amount of statistical information about the medium's constitution.

Following Doi [3] and Rubinstein and Torquato [9], consider the trial fields

$$u(x) = K\int G(x-y)\left[I_2(y) - \xi|\nabla I_1(y)|\right]\mathrm{d}y, \tag{8.6}$$

where $G(x) = 1/(4\pi|x|)$. Since $\Delta G_0(x) + \delta(x) = 0$, it is easily seen that $\Delta u(x) = K$ if $x \in \mathcal{K}_2$, and therefore the fields $u(x)$ in (8.6) are admissible. The constant ξ is uniquely defined from the condition that the integrand in (8.6) should possess zero mean value:

$$\langle I_2(y)\rangle - \xi\,\langle|\nabla I_2(y)\rangle = \eta_2 - \xi S = 0, \quad \text{i.e.} \quad \xi = \xi_0 = \eta_2/S. \tag{8.7}$$

For this choice of ξ, the trial field (8.6) becomes

$$u(x) = -K\int G(x-y)\left[I_1'(y) + \xi_0\big(|\nabla I_1(y)| - S\big)\right)\mathrm{d}y,$$

and hence

$$\left\langle|\nabla u(x)|^2\right\rangle = K^2\left(\theta_1^{\mathrm{pp}} + 2\xi_0\theta_1^{\mathrm{sp}} + \xi_0^2\theta_1^{\mathrm{ss}}\right),$$

after an obvious integration by parts. Using (8.7), (8.5) and the formulae for the appropriate moments (7.10), (5.22) and (6.15) leads eventually to the bound

$$k^{*2}a^2 \geq \frac{3\eta_1(1-\eta_1)}{1 - 5\eta_1 - \eta_1^2/5 + 3\eta_1 m_1}, \tag{8.8}$$

which coincides with the bound derived by Talbot and Willis [12] by means of an ingenious variational procedure of Hashin-Shtrikman's type, see [6] for more details and discussion. The fact that the original Doi's result, for a dispersion of nonoverlapping spheres, can be recast in the elegant Talbot and Willis' form (8.8) was noticed by Talbot (unpublished manuscript) and, independently, by Beasley and Torquato [1], who apparently were not aware of the paper [12]. Due to all these reasons it seems proper to call (8.8) Doi-Talbot-Willis bound. Another variational procedure that leads to (8.8) has been recently proposed by the author [6].

9. CONCLUDING REMARKS

In the present paper we have represented all two-point correlation functions (2.9) and (2.18) for a random dispersion of nonoverlapping spheres, as single integrals containing the binary correlation function $\nu_2(r)$ for the random set of sphere's centers. The reasoning of the recent paper [7], where only the “particle-particle" correlation has been treated in detail, has served as a basis of the analysis. The representations for all two-point correlations have one and the same structure, which can be summarized in the following formulae:

$$\begin{aligned} F^{\rm cor}(\rho) =& F^{\rm cor}_{\infty} + \overline{F}^{\rm cor}(\rho), \quad \lim_{\rho\to\infty} \overline{F}^{\rm cor}(\rho) = 0, \\ F^{\rm cor}(\rho) =& F^{\rm cor}_{\rm ws} + \widetilde{F}^{\rm cor}(\rho), \\ \widetilde{F}^{\rm cor}(\rho) =& F^{\rm cor}_{\infty} \int_{\max\{\rho-\beta,2\}}^{\rho+\beta} G^{\rm cor}(\rho-\tau)\, \tau \nu_2(\tau)\, {\rm d}\tau, \end{aligned} \tag{9.1}$$

where

$$G^{\rm cor}(t) = \begin{cases} f^{\rm cor}(t), & \text{if } -\beta \le t \le 0, \\ f^{\rm cor}(-t), & \text{if } 0 \le t \le \beta, \\ 0, & \text{if } |t| \ge \beta. \end{cases} \tag{9.2}$$

In (9.1) and (9.2), $F^{\rm cor}_{\infty}$ is the long-range value of the appropriate correlation, $\overline{F}^{\rm cor}(\rho)$ — its part that decays at infinity; $F^{\rm cor}_{\rm ws}$ is the contribution to the latter, generated by the well-stirred part (3.2) of the radial distribution function $g(r)$ for the set of sphere’s centers, and $\widetilde{F}^{\rm cor}(\rho)$ is due to the “deviation" $\widetilde{g}(r)$ of $g(r)$ from the well-stirred one, cf. (3.1) (recall that $\widetilde{g}(r) = \nu_2(r)$ if $r \ge 2a$, see (3.4)). The parameter β takes the values 1 or 2, depending on the kind of correlation under study. We note also that

$$G^{\rm cor}(t) = f^{\rm cor}(t), \quad \text{if} \quad |t| \le \beta,$$

provided $f^{\rm cor}(t)$ is even, which is the case with “particle-center" and “surface-center" correlations (for which $\beta = 1$), see (3.13) and (4.6).

For the sake of completeness, the function $f^{\rm cor}(t)$ for the “particle-particle" correlation $\overline{F}^{\rm pp}(x)$ is also given, see [7]. In this case, the well-stirred contribution reads

$$\overline{F}^{\rm pp}_{\rm ws}(r) = \begin{cases} 1 - \dfrac{3\rho}{4(1-\eta_1)} + \dfrac{(1+3\eta_1)\rho^3}{16(1-\eta_1)} - \dfrac{9\eta_1\rho^4}{160(1-\eta_1)} \\ \quad + \dfrac{\eta_1\rho^6}{2240(1-\eta_1)}, & \text{if } 0 \le \rho \le 2, \\ \dfrac{\eta_1}{1-\eta_1}\, \dfrac{(\rho-4)^4\,(36 - 34\,\rho - 16\,\rho^2 - \rho^3)}{2240\rho}, & \text{if } 2 \le \rho \le 4, \\ 0, & \text{if } \rho \ge 4, \end{cases} \tag{9.3}$$

see once again [7] for details and references.

Another set of useful formulae, derived in the paper, concerns the moments

$$\theta^{\rm cor}_k = \int_0^{\infty} \rho^k\, \overline{F}^{\rm cor}(\rho)\, {\rm d}\rho, \quad k = 1, 2, \ldots, \tag{9.4}$$

of the two-point correlations (2.9) and (2.18). For an arbitrary k, they can be evaluated by means of the representations (9.1), summarized in Table 1, and thus interconnected to the

TABLE 1. Notations, parameters and functions in the integral representations (9.1) of the various two-point correlations

Correlation	Notation	$F_\infty^{\rm cor}$	$\overline{F}_{\rm ws}^{\rm cor}(r)$	$f^{\rm cor}(t)$	β
center-center	$F^{\rm cc}$	n^2	$n\delta(x) - n^2 h_{2a}(x)$	–	–
particle-center	$F^{\rm pc}$	$n\eta_1$	Eq. (3.9)	$\frac{3}{4}(1-t^2)$	1
surface-center	$F^{\rm sc}$	nS	Eq. (4.4)	$\frac{1}{2}$	1
particle-particle	$F^{\rm pp}$	η_1^2	Eq. (9.3)	$\frac{3}{160}(2+t)^3(4-6t+t^2)$	2
surface-particle	$F^{\rm sp}$	$\eta_1 S$	Eq. (5.16)	$\frac{1}{8}(2+t)^2\,(1-t)$	2
surface-surface	$F^{\rm ss}$	S^2	Eq. (6.9)	$\frac{1}{4}(2+t)$	2

appropriate moments (3.18) of the binary correlation. In the cases $k=1$ and $k=2$, which seem to be most interesting for applications, evaluation of (9.4) does not need however the aforementioned representations, but can be done directly, using, as a matter of fact, just their definitions. This was illustrated in Section 7. The results, concerning $\theta_2^{\rm cor}$ (in 3-D) and $\theta_1^{\rm cor}$ (in 2-D), can be concisely summarized in the simple formulae

$$
\begin{aligned}
\theta_2^{\rm cor} &= F_\infty^{\rm cor}\left(\frac{1-8\eta_1}{3\eta_1} + m_2\right) \quad \text{in 3-D,} \\
\theta_1^{\rm cor} &= F_\infty^{\rm cor}\left(\frac{1-4\eta_1}{2\eta_1} + m_1\right) \quad \text{in 2-D,}
\end{aligned}
\tag{9.5}
$$

where $F_\infty^{\rm cor}$ are the long-range values of the appropriate correlation, see Table 1 and Eqs. (7.1), (7.2), (3.19), (4.10), (6.15), (7.5) and (7.6).

In 3-D the moments $\theta_1^{\rm cor}$ have a form, similar to (9.5):

$$\theta_1^{\rm cor} = F_\infty^{\rm cor}\left(T_1^{\rm cor}(\eta_1) + m_1\right), \tag{9.6}$$

but now the functions $T_1^{\rm cor}(\eta_1)$ are specific for different correlations. They are listed in Table 2, in which the foregoing formulae (3.19), (4.10), (6.15) and (7.10) are simply put together.

TABLE 2. The functions $T_1^{\rm cor}(\eta_1)$ in Eq. (9.6) for the various two-point correlations

Correlation	F^{pc}	F^{sc}	F^{pp}	F^{sp}	F^{ss}
$T_1^{\mathrm{cor}}(\eta_1)$	$\dfrac{5-19\eta_1}{10\eta_1}$	$\dfrac{1-11\eta_1/2}{3\eta_1}$	$\dfrac{2-9\eta_1}{5\eta_1}$	$\dfrac{5-26\eta_1}{15\eta_1}$	$\dfrac{1-5\eta_1}{3\eta_1}$

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