ON THE TWO-POINT CORRELATION FUNCTION
FOR DISPERSIONS OF NONOVERLAPPING SPHERES

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Random dispersions of spheres are useful and appropriate models for a wide
class of particulate random materials. They can be described in two equivalent
and alternative ways—either by the multipoint moments of the characteristic
function of the region, occupied by the spheres, or by the probability densities of
the spheres' centers. On the "two-point" level, a simple and convenient integral
formula is derived which interconnects the radial distribution function of the
spheres with the two-point correlation of the said characteristic function. As
one of the possible applications of the formula, the behaviour of the correlation
function near the origin is studied in more detail and related to the behaviour of
the radial distribution function at the "touching" separation of the spheres.

1. Introduction

The heterogeneous internal structure of almost all natural and man-made
materials requires that any adequate theory concerning their macroscopic
behaviour should start with modeling them as random media. This means,
let us recall very briefly,[1,2] that we should possess from the very beginning a
number of macroscopically identical samples, labeled by a certain ω, chosen
from a suitable sample space Ω. The sampling procedure depends on the
specific problem and, as a rule, is not of direct concern to us, and neither is
the measure on Ω, with respect to which ensemble averaging is defined in a
standard way. A random medium can then be characterized by means of the
probability distributions of its relevant physical properties, see, e.g,. Refs. 3
and 4.

Among random media, perhaps most important are the two-phase (or
binary) ones, an example of which are the porous bodies. Each realization

$\omega \in \Omega$, assumed to occupy the entire space $\mathbb{R}^3$, can be divided in this case into two nonintersecting parts, $\mathcal{K}_1$ and $\mathcal{K}_2$, containing the constituent '1' and '2', respectively. From a practical point of view, instead of dealing with probability distributions, it is more convenient to introduce, say, the random field

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

i.e., the characteristic function of the region occupied by the phase '1'. The statistical properties of the medium follow from the set of multipoint probabilities, or moments of I_1 (see, for instance, Refs. 1 to 4)

$$\eta_1 = \langle I_1(0) \rangle,$$

$$\eta_p(y_1, y_2, \ldots, y_{p-1}) = \langle I_1(0) I_1(y_1) I_1(y_2) \ldots I_1(y_{p-1}) \rangle, \quad p = 2, 3, \ldots, \tag{2}$$

where each $y_k \in \mathbb{R}^3$; η_1 is the volume fraction of the phase '1'. The angled brackets signify ensemble averaging. Such multipoint probabilities are symmetric in their arguments. One point could be taken at the origin, because of the statistical uniformity, assumed hereafter. The interpretation of the moments (2) is obvious—they give the probability for p points $0, y_1, \ldots, y_{p-1}$, thrown at random, to be found in the phase '1'. This interpretation provides a Buffon needle game to find experimentally the lower-order moments η_2 and η_3 for real two-phase media.[5]

Among the multipoint moments (2), the two-point moment $\langle I_1(0) I_1(x) \rangle$ shows up most often in various applications of random media. We shall only mention here flow through porous materials or diffusion-controlled reactions, where this moment plays a key role in evaluating or bounding the needed macroscopic quantities, see, e.g., Refs. 6, 7 and 8. Usually, instead of $\langle I_1(0) I_1(x) \rangle$ the so-called two-point correlation function, $\gamma_2(x)$, is introduced

$$\gamma_2(x) = \frac{\langle I_1'(0) I_1'(x) \rangle}{\langle I_1'^2(0) \rangle}, \quad \langle I_1'^2(0) \rangle = \eta_1(1 - \eta_1), \tag{3}$$

where $I_1'(x) = I_1(x) - \eta_1$ is the fluctuating part of the random field $I_1(x)$. Obviously, $\gamma_2(0) = 1$; if there is no long-range order in the dispersion, $\gamma_2(x) \to 0$ as $|x| \to \infty$. It is noted that

$$\langle I_1(0) I_1(x) \rangle = \eta_1 \Pr(x \mid 0), \quad \Pr(x \mid 0) = (1 - \eta_1) \gamma_2(x) + \eta_1, \tag{4}$$

with $\Pr(x \mid 0)$ standing for the conditional probability that x lies in the phase '1', provided the origin also lies in the same phase.

In turn, two-phase media of practical interest are often particulate, in the sense that one of the constituents, labeled '2' hereafter, is connected, playing the role of a matrix, within which well distinguishable inclusions of the other phase, labeled '1', are distributed at random. In many important cases it suffices to imagine the inclusions spherical and hence to model the material as a dispersion of nonoverlapping and identical spheres. Classical examples of media of this kind are supplied by the liquid-state theory, fluid suspensions of rigid particles, or solids reinforced or weakened by spherical inhomogeneities (pores, in particular). Due to the specific "point-wise" structure of such dispersions, they can alternatively be described statistically by means of

the multipoint probability densities $f_p(y_1, \ldots, y_p)$ that give the probability $dP = f_p(y_1, \ldots, y_p) \, dV_1 \ldots dV_p$ to find a sphere center in the vicinities dV_1, $\ldots$, dV_p of the points $y_1, \ldots, y_p$ respectively. Note that $f_1 = n$, where n is the number density of the spheres and $\eta_1 = nV_a$, $V_a = \frac{4}{3}\pi a^3$. Most often the two-point density $f_2(x) = f_2(0, x)$ is used and is traditionally expressed as

$$f_2(x) = n^2 g(x). \tag{5}$$

The function $g(x)$ in Eq. (5) is the well-known radial distribution function, whose theoretical and experimental investigation in liquid state theory has been a subject of many works, see, e.g., the book of Balescu.[9]

Hence, random dispersions of spheres can be described in two alternative and equivalent ways: either by means of the multipoint moments (2) or by the set of probability density functions f_p. In various applications it is necessary that these two kinds of descriptions be interconnected as simply as possible. Such is the case, for example, when the two- and three-point functions f_2 and f_3 are assumed known, and integrals involving the two- and three-point moments η_2 and η_2 should be evaluated in bounds on the effective properties of dispersions.[10] Similarly, in diffusion-controlled reaction models, one needs integrals involving the two-point moment η_2 for a known radial distribution function.[11] Here we shall discuss this interconnection for the simplest "two-point" level, and will finally propose (Section 5) an elementary formula that expresses $\gamma_2(x)$ as a simple one-tuple integral containing the radial distribution function. But first a general and well-known formula of this kind should be recalled (Section 2). In Section 3 the triple convolution $h_a * h_a * h_A$ of characteristic functions of spheres is found by means elementary geometrical reasoning. This allows explicit development of the correlation function $\gamma_2(r)$ for the simplest "well-stirred" sphere distribution. For general sphere statistics, the formula for $\gamma_2(r)$ splits into two parts: an explicit algebraic expression which applies for the "well-stirred" approximation, and a "correction" in the form of an integral, for an arbitrary radial distribution function. In the final Section 6, as an application of the obtained formula, the behaviour of the correlation function near the origin is studied in detail and interconnected with the behaviour of the radial distribution function at the "touching" separation of the spheres. In this way results of Kirste and Porod[12] and Frisch and Stillinger[13] are generalized. Other possible applications are briefly mentioned in the concluding Section.

2. The Basic Formula

It is clear that the "two-point" information incorporated in the function $g(x)$ must suffice for the evaluation of the two-point correlation function $\gamma_2(x)$. A formula of this kind can be immediately derived in a formal and straightforward way, if one introduces after Stratonovich[14] the so-called random density field for the dispersion

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

where the random points $\{x_\alpha\}$ are the centers of the spheres, and $\delta(x)$ is the Dirac delta function. Recall that

$$\langle \psi(y) \rangle = n,$$

$$\langle \psi(y_1)\psi(y_2)\rangle = n\delta(y_1 - y_2) + n^2 g(y_1 - y_2), \tag{6}$$

etc., see Ref. 14. In turn, the random field $I_1(x)$, see Eq. (1), has a simple integral representation by means of the field $\psi(x)$, namely,

$$I_1(x) = \int h_a(x - y)\psi(y)\, dy, \quad I_1'(x) = \int h_a(x - y)\psi'(y)\, dy, \tag{7}$$

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.

The correlation function, due to Eqs. (3) to (7), is

$$\gamma_2(x) = \frac{1}{\eta_1(1 - \eta_1)}\int\int h_a(x - z_1)h_a(z_2)\langle\psi'(z_1)\psi'(z_2)\rangle\, dz_1\, dz_2$$

$$= \frac{1}{\eta_1(1 - \eta_1)}\Big\{n\int h_a(x-y)h_a(y)\, dy + n^2\int\int h_a(x-z_1)h_a(z_2)\nu_2(z_1-z_2)\, dz_1 dz_2\Big\}, \tag{8}$$

since $\langle I_1'^2(0)\rangle = \eta_1(1 - \eta_2)$ for the dispersion under study; in Eq. (8)

$$\nu_2(y) = g(y) - 1. \tag{9}$$

In the liquid state theory ν_2 is the so-called binary correlation function, see, e.g., Ref. 9, ch. 7.1.

Note that the formula (8) is well-known in the literature, in this or in equivalent forms. We have supplied here the above derivation in order to underline the usefulness of Stratonovich[14] formalism in the theory of random particulate media. (For further applications and development of this formalism for random solids, see, e.g., Ref. 15.)

Due to the importance and the key role played by the formula (8) in the theory of random dispersions, it is worth mentioning that it also can be derived by means of very simple and instructive arguments, without invoking the random density function and the related formalism of Stratonovich, see, e.g., Ref. 16, in which not only the two-point, but the multipoint correlations are discussed for both cases of overlapping and nonoverlapping dispersions of spheres.

Indeed, consider two points y_1, y_2 thrown at random in the dispersion. The average quantity $\langle I_1(y_1)I_1(y_2)\rangle$, we are interested in, represents just the probability that both points y_1, y_2 fall into a sphere. There are only two possibilities for such an event: either both y_1, y_2 fall into one and the same sphere, or they fall into different spheres. The probability of the former event is the product of n (the number density of the spheres) and the common volume of two spheres of radius a centered at y_1, y_2. The reason is that this common volume comprises the centers of all spheres of radius a which contain both y_1 and y_2. If the second possibility takes place, i.e., y_1 and y_2 fall into different spheres, then the centers z_1, z_2 of the latter should lie within spheres of radius a around each one the points y_1 and y_2. The probability of this event is an integral over these two spheres; the

integrand is the probability density for finding sphere centers at z_1 and z_2, i.e., $n^2 g(z_2 - z_1)$, see Eq. (5). Hence

$$\langle I_1(y_1) I_1(y_2) \rangle = n \int h_a(y_1 - y) h_a(y_2 - y)\, dy$$

$$+ n^2 \iint h_a(y_1 - z_1) h_a(y_2 - z_2) g(z_2 - z_1)\, dz_1 dz_2 \qquad (10)$$

which yields immediately Eq. (8), taking into account the definition of $\gamma_2(x)$, see Eqs. (3) and (4).

The first integral in Eq. (8) is just the convolution square $h_a * h_a$ of the characteristic function h_a of a sphere. Its analytical form is well-known since it represents geometrically, as already discussed, the volume of intersection of two equal spheres of radius a, whose centers are separated by r:

$$(h_a * h_a)(x) = V_a \begin{cases} 1 - \dfrac{3}{4}\dfrac{r}{a} + \dfrac{1}{16}\left(\dfrac{r}{a}\right)^3, & \text{if } r/a \le 2, \\ 0, & \text{if } r/a > 2; \quad r = |x|. \end{cases} \qquad (11)$$

The second integral in Eq. (8) is much more complicated however—it is six-tuple obviously. Our aim here is to reduce it to a simple one-tuple integral in the case when the distribution of the spheres is statistically isotropic, so that g becomes a function of $r = |x|$ only.

3. Evaluation of the Triple Convolution $h_a * h_a * h_A$

The key point in our analysis is the evaluation of the triple convolution $h_a * h_a * h_A$, where h_A denotes the characteristic function of a sphere of radius A located at the origin; hereafter we assume $A \ge 2a$, though the reasoning that follows is not limited by this assumption. Such a convolution, among others of similar kind, has been first found by McQuarrie[17] in a different context, by means of a method initiated by Katsura:[18] namely, application of the Fourier transform combined with some nontrivial formulae from Bessel function theory (Weber-Schafheitlin's discontinuous integral and its generalizations[19]). Here an elementary method with simple and clear geometrical interpretation will be employed. As a matter of fact, the method was used by one of the authors,[20] when evaluating a statistical parameter for a dispersion. The method also has the advantage that it can be easily applied when evaluating not only convolutions of characteristic functions, but of radially symmetric functions as well, as will be demonstrated elsewhere.

Note first that, due to Eq. (11),

$$h_a * h_a * h_A = V_a\Big(\varphi(t) h_{2a}(r)\Big) * h_A,$$

$$\varphi(t) = 1 - \frac{3}{4}t + \frac{1}{16}t^3, \quad t = r/a. \qquad (12)$$

Approximate $\varphi(t) h_{2a}(r)$ by the step-constant function

$$\varphi(t) h_{2a}(r) \approx \sum_{i=1}^{N-1} \varphi(\xi_i/a)[h_{\xi_i + \triangle \xi_i}(r) - h_{\xi_i}(r)], \qquad (13)$$

where $0 = \xi_0 < \xi_1 < \ldots \xi_{N-1} < \xi_N = 2a$, $\triangle\xi_i = \xi_i - \xi_{i-1}$, see Fig. 1.
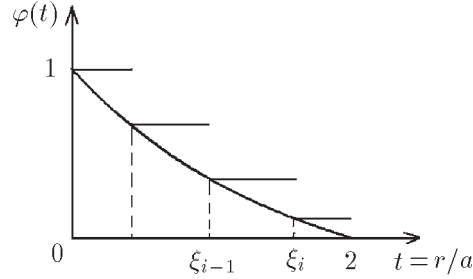

Fig. 1. Step-function approximation to $\varphi(t)$.

In other words, the inhomogeneous ball of radius $2a$, whose density varies radially according to the law $\varphi = \varphi(t)$, is replaced by a family of concentric spherical layers $\xi_i \leq r < \xi_{i+1}$, each one homogeneous and of density $\varphi(\xi_i)$, $i = 0, \ldots, N-1$. Then

$$(\varphi(t)h_{2a}) * h_A \approx \sum_{i=1}^{N-1} \varphi(\xi_i/a) \left[h_{\xi_i + \triangle\xi_i} * h_A - h_{\xi_i} * h_A \right]$$

$$= \sum_{i=1}^{N-1} \varphi(\xi_i/a) \frac{h_{\xi_i + \triangle\xi_i} * h_A - h_{\xi_i} * h_A}{\triangle\xi_i} \triangle\xi_i,$$

which, in the limit $\triangle\xi_i \to 0$, yields

$$\Big((\varphi(t)h_{2a}) * h_A \Big)(r) = \int_0^{2a} \varphi(\xi/a) \frac{d}{d\xi}(h_\xi * h_A)(r)\, d\xi$$

$$= \varphi(\xi/a)(h_\xi * h_A)(r) \Big|_{\xi=0}^{\xi=2a} - \frac{1}{a} \int_0^{2a} \varphi'(\xi/a)(h_\xi * h_A)(r)\, d\xi. \qquad (14)$$

But $(h_\xi * h_A)(\xi) = 0$ at $\xi = 0$, i.e., $r = 0$; also, in our case $\varphi(2) = 0$, see Eq. (12), so that the nonintegral term in Eq. (14) vanishes:

$$\Big((\varphi(t)h_{2a}) * h_A \Big)(r) = - \int_0^2 \varphi'(\mu)(h_\xi * h_A)(r)\, d\mu$$

$$= \frac{3}{16} \int_0^2 (4 - \mu^2)\Big(h_\xi * h_A \Big)(r)\, d\mu = V_a F(\rho; \tau), \qquad (15)$$

having used the expression (12) for $\varphi(t)$; hereafter $\rho = r/a$, $\tau = A/a \geq 2$ and $\mu = \xi/a \in [0, 2]$ are nondimensional.

To evaluate $F(\rho; \tau)$, recall the known formula for the convolution $h_\xi * h_A$, i.e., for the common volume of two spheres of radii ξ and A, which we shall write as follows

$$(h_\xi * h_A)(\rho) = V_a \begin{cases} \mu^3, & \text{if } 0 \le \rho \le \tau - \mu, \\ \Psi(\rho; \tau, \mu), & \text{if } \tau - \mu \le \rho \le \tau + \mu, \\ 0, & \text{if } \rho > \tau + \mu, \end{cases} \qquad (16)$$

where

$$\Psi(\rho; \tau, \mu) = \frac{1}{16\rho} (\tau + \mu - \rho)^2 [\rho^2 + 2(\tau + \mu)\rho - 3(\tau - \mu)^2]. \qquad (17)$$
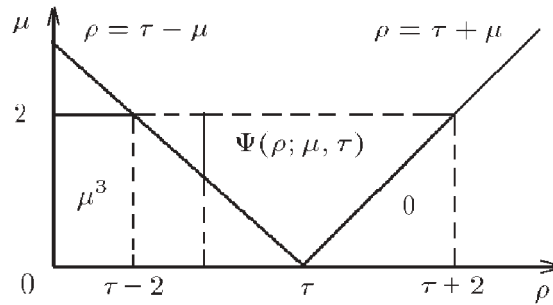

Fig. 2. The range of integration in Eq. (15).

The integration domain for the integral (15), with the convolution $h_\xi * h_A$ given in Eqs. (16) and (17), is shown in Fig. 2. The integration is elementary and the final result reads

$$F(\rho; \tau) = \begin{cases} F^{(I)}(\rho; \tau), & \text{if } 0 \le \rho \le \tau - 2, \\ F^{(II)}(\rho; \tau), & \text{if } \tau - 2 \le \rho \le \tau, \\ F^{(III)}(\rho; \tau), & \text{if } \tau \le \rho \le \tau + 2 , \\ 0, & \text{if } \rho > \tau + 2, \end{cases} \qquad (18)$$

where

$$F^{(I)}(\rho; \tau) = \frac{3}{16} \int_0^2 (4 - \mu^2)\mu^3 \, d\mu = 1, \qquad (19\text{a})$$

$$F^{(II)}(\rho; \tau) = \frac{3}{16} \int_0^{\tau - \rho} (4 - \mu^2)\, \mu^3 \, d\mu + \frac{3}{16} \int_{\tau - \rho}^2 (4 - \mu^2)\, \Psi(\rho; \tau, \mu) \, d\mu$$

$$= \frac{1}{2240\rho} \left\{ -576 + 1120\rho - 672\rho^2 + 140\rho^4 + 42\rho^5 - \rho^7 \right.$$

$$+ 21(\rho + 2)^3 (\rho^2 - 6\rho + 4)\tau^2 - 70\rho (\rho - 4)(\rho + 2)^2\tau^3$$

$$+ 105(\rho + 2)(\rho^2 - 2\rho - 2)\tau^4 + 84(2 - \rho^2)\tau^5 + 35\rho\tau^6 - 6\tau^7\Big\}, \quad (19b)$$

$$F^{(III)}(\rho; \tau) = \frac{3}{16}\int_{\rho - \tau}^{2}(4 - \mu^2)\,\Psi(\rho; \tau, \mu)\,d\mu = \frac{1}{2240\rho}(2 + \tau - \rho)^4$$

$$\times \Big\{(\rho - 2)(\rho^2 + 10\rho + 18) + 4(\rho^2 + 10\rho + 18)\tau - (48 + 11\rho)\tau^2 + 6\tau^3\Big\}. \quad (19c)$$

Hence

$$(h_a * h_a * h_A)(r) = F(\rho; \tau)V_a^2, \quad \rho = r/a, \quad (20)$$

with the function $F(\rho; \tau)$ given explicitly in Eqs. (18) and (19).

Note that the function $F(\rho; \tau)$ and its first three derivatives $\dfrac{d^{(k)}F(\rho; \tau)}{d\rho^{(k)}}$, $k = 1, 2, 3$, are continuous for all $\rho \in (0, \infty)$; the fourth derivative $\dfrac{d^{(4)}F(\rho; \tau)}{d\rho^{(4)}}$ has, however, jumps at the points $\rho = \tau - 2$, τ, $\tau + 2$, so that $F(\rho; \tau) \in C^3([0, \infty))$ only with respect to ρ.

In the particular case $A = 2a$, i.e., $\tau = 2$, the formulae (18) and (19) simplify, yielding

$$(h_a * h_a * h_{2a})(r) = F^{2a}(\rho)V_a^2, \quad \rho = r/a, \quad (21)$$

$$F^{2a}(\rho) = F(\rho; 2) = \begin{cases} 1 - \dfrac{3}{16}\rho^3 + \dfrac{9}{160}\rho^4 - \dfrac{\rho^6}{2240}, & \text{if } 0 \le \rho \le 2, \\[3mm] \dfrac{(\rho - 4)^4(-36 + 34\rho + 16\rho^2 + \rho^3)}{2240\rho}, & \text{if } 2 \le \rho \le 4, \\[3mm] 0, & \text{if } \rho > 4. \end{cases} \quad (22)$$

4. The Two-Point Correlation of a "Well-stirred" Dispersion

Consider the simplest case of a "well-stirred" dispersion of nonoverlapping spheres for which the radial distribution function is simply $g(r) = 1$, if $r \ge 2a$, and vanishes otherwise. This means that as far as the two-point statistics is concerned, the spheres are only forbidden to overlap; otherwise their location is statistically independent. This assumption, despite its obvious crudeness, is very often adopted when modeling random dispersions, due to its extreme simplicity.

For a well-stirred dispersion the binary correlation (9) becomes $\nu_2(r) = -h_{2a}(r)$, so that

$$\gamma(r) = \gamma_2^{\text{ws}}(r) = \frac{1}{1 - \eta_1}\Big\{(h_a * h_a)(r)/V_a - \eta_1(h_a * h_a * h_{2a})(r)/V_a^2\Big\}.$$
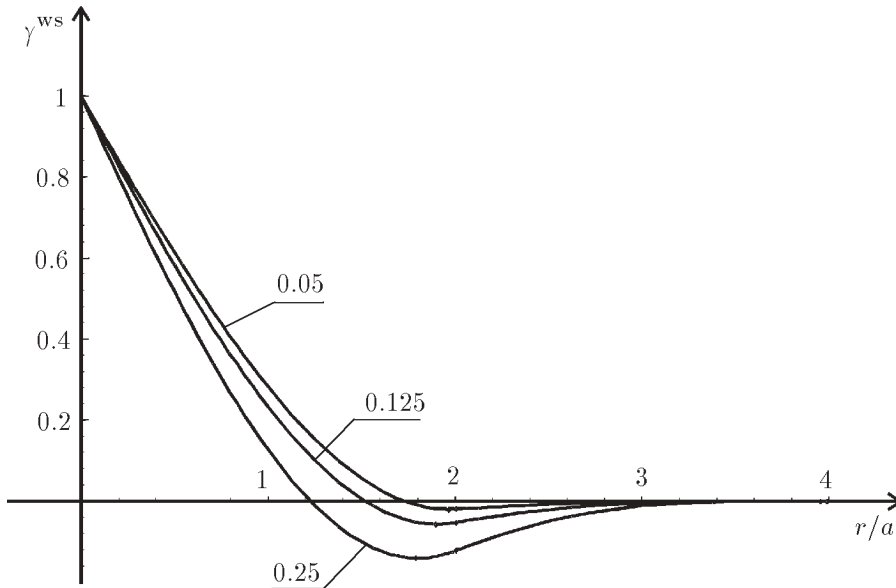
Fig. 3. The two-point correlation function for a well-stirred dispersion
for sphere fractions $\eta_1 = 0.05$, 0.125 and 0.25.

Using Eqs. (11) and (22) gives

$$\gamma_2^{\text{ws}}(r) = \begin{cases} 1 - \dfrac{3\rho}{4(1 - \eta_1)} + \dfrac{(1 + 3\eta_1)\rho^3}{16(1 - \eta_1)} - \dfrac{9\eta_1\rho^4}{160(1 - \eta_1)} \\[2mm] \quad + \dfrac{\eta_1\rho^6}{2240(1 - \eta_1)}, & \text{if } 0 \le \rho \le 2, \\[4mm] \dfrac{\eta_1}{1 - \eta_1} \dfrac{(\rho - 4)^4 (36 - 34\,\rho - 16\,\rho^2 - \rho^3)}{2240\rho}, & \text{if } 2 \le \rho \le 4, \\[4mm] 0, & \text{if } \rho \ge 4. \end{cases} \tag{23}$$

The two-point correlation $\gamma_2^{\text{ws}}(r)$ is always negative for $2 \le \rho < 4$. It is shown in Fig. 3 for sphere volume fractions $\eta_1 = 0.05$, 0.125 and 0.25.

The formula (23) was first given in an equivalent form by Torquato and Stell,[21] who used the triple convolution (22) as evaluated by McQuarrie.[17] Independently, (23) was also derived, in a concise and purely geometrical way, by Berryman[22] in his analysis of variational bounds on permittivity of random aggregates of spheres.

Note that the formula (23) allows the evaluation of the statistical param-

eter, proportional to the Laplace transform of $r\gamma_2^{\mathrm{ws}}(r)$

$$i_2(p) = p^2 \int_0^\infty r e^{-pr} \gamma_2^{\mathrm{ws}}(r)\, dr, \quad p \in (0, \infty), \tag{24}$$

which appears in variational bounds on the effective absorption coefficient for a dispersion (see, e.g., Ref. 23), namely

$$i_2(p) = \frac{A(pa) - \eta_1 B(pa)}{1 - \eta_1}, \quad A(pa) = 1 - 3\frac{1 + pa}{(pa)^3} e^{-pa}(pa \cosh pa - \sinh pa),$$

$$B(pa) = 1 - \frac{9(1 + 2pa)(pa \cosh pa - \sinh pa)^2}{(pa)^6} e^{-2pa}. \tag{25}$$

The formula (25) can be derived directly from the definition of $i_2(p)$ without using the explicit form (23) for $\gamma_2^{\mathrm{ws}}(r)$, as done in Ref. 24. In turn Eq. (23) can be restored by inverting the Laplace transform $i_2(p)$, as given in Eq. (25). Note that an appropriate analysis of the asymptotic behaviour of the parameter $i_2(p)$ as $p \to \infty$ also allows one to find the analytical form (23) of $\gamma_2^{\mathrm{ws}}(r)$ in a certain (but unspecified) vicinity of the origin, see Ref. 25 for details.

The formula (23) makes possible the analytic evaluation of the moments of $\gamma_2^{\mathrm{ws}}(r)$ on the semiaxis $(0, \infty)$, that is the quantities

$$\theta_k^{\mathrm{ws}} = \int_0^\infty r^k \gamma_2^{\mathrm{ws}}(r)\, dr = a^{k+1} \int_0^\infty \rho^k \gamma_2^{\mathrm{ws}}(\rho)\, d\rho = a^{k+1} \frac{T_k - \eta_1 S_k}{1 - \eta_1},$$

$$T_k = \frac{1}{V_a} \int_0^\infty \rho^k (h_a * h_a)(\rho)\, d\rho = \frac{3 \cdot 2^{k+1}}{(k+1)(k+2)(k+4)}, \quad k \geq 0,$$

$$S_0 = \frac{18\,(9 - 8\ln 2)}{35} \approx 1.77676,$$

$$S_k = \int_0^\infty \rho^k F^{2a}(\rho)\, d\rho = \frac{9 \cdot 2^{k+4}(k + 8 + (k-1)\,2^{k+3})}{k(k+1)(k+2)(k+4)(k+5)(k+7)}, \tag{26}$$

$k = 1, 2, \ldots$. In particular,

$$\theta_1^{\mathrm{ws}} = \frac{2 - 9\eta_1}{5(1 - \eta_1)}\, a^2, \quad \theta_2^{\mathrm{ws}} = \frac{1 - 8\eta_1}{3(1 - \eta_1)}\, a^3. \tag{27}$$

Note that for any statistically homogeneous and isotropic random medium the moment θ_2 should be nonnegative, as pointed out, e.g., in Ref. 4. (As a matter of fact, this is a consequence of the well-known positive-definiteness of the two-point correlation function $\gamma_2(x)$ for any statistically homogeneous medium.[4]) Hence from Eq. (27) it follows that the well-stirred approximation is realistic only at $\eta_1 \leq 1/8$—something first conjectured by Willis,[26] who noticed that a certain well-known approximate scheme of the mechanics of

composites in the context of wave propagation yields unrealistic predictions for this approximation, if $\eta_1 > 1/8$.

It is to be remarked that the well-stirred distribution is the roughest zeroth-order virial approximation for the radial distribution function in the liquid-state theory. As such, it has never been of any interest in this theory, where much more realistic and refined approximations have been extensively studied, say, the Percus-Yevick or Verlet-Weis ones, see, e.g., any basic book on the subject, such as that of Balescu.[9] This explains why the above critical value of sphere fraction, though elementary, has never been noted in the liquid-state theory. On the other hand, in the literature on homogenization of heterogeneous media, and of random dispersions in particular, people focused on predicting the overall properties for a given sphere statistics, very often choosing the well-stirred distribution for the sake of simplicity. At the same time no attention was paid, as a rule, to the elementary necessary conditions (like positive-definiteness of the two-point correlation and, in particular, of θ_2, which can obviously be checked through an elementary integration, using Eq. (23)). This may elucidate the reason why the critical values of applicability for the well-stirred case were only conjectured by Willis[26] in the study of certain approximate homogenization schemes, and not found using the obvious arguments, concerning, say, positive-definiteness of the appropriate correlation.

Fig. 3 illustrates geometrically the reason why the well-stirred approximation fails at $\eta_1 > 1/8$. Indeed, as already pointed out, the correlation $\gamma_2^{\mathrm{ws}}(r)$ becomes negative in the region $(r_0, 4a)$, for a certain $r_0 \in (0, 2a)$. Moreover, the higher the sphere fraction η_1 becomes, the deeper below the abscissa axis the function $\gamma_2^{\mathrm{ws}}(r)$ "dives." On the other hand θ_2, i.e., the integral $\int_0^\infty r^2 \gamma_2^{\mathrm{ws}}(r)\, dr$ should be nonnegative which is violated at $\eta_1 > 1/8$, since $\gamma_2^{\mathrm{ws}}(r)$ "dives" in this case too deep and the well-stirred approximation "suffocates" as a result, cf. Fig. 3.

5. The General Case

Represent the radial distribution function $g(r)$ ($r = |y|$) in the form

$$g(r) = 1 - h_{2a}(y) + \widetilde{g}(y), \tag{28}$$

where $\widetilde{g}(y)$ vanishes for $|y| < 2a$ and $\widetilde{g}(y) \to 0$ at $y \to \infty$. Obviously $\widetilde{g}(y) = 0$ corresponds to the well-stirred case. The binary correlation is then

$$\nu_2(y) = g(y) - 1 = -h_{2a}(y) + \widetilde{g}(y), \tag{28}$$

so that $\widetilde{g}(y)$ coincides with $\nu_2(y)$ at $|y| \geq 2a$. The two-point correlation (8) has in turn the form

$$\gamma_2(r) = \gamma_2^{\mathrm{ws}}(r) + \widetilde{\gamma}_2(r); \tag{29}$$

here $\gamma_2^{\mathrm{ws}}(r)$ is the correlation (23), corresponding to the well-stirred case, and

$$\widetilde{\gamma}_2(r) = \frac{\eta_1}{1 - \eta_1} \frac{1}{V_a^2} \iint h_a(x - z_1) h_a(z_2) \widetilde{g}(z_1 - z_2)\, dz_1 dz_2. \tag{30}$$

The evaluation of the integral in Eq. (30) is based on the formula

$$\widetilde{g}(y) = \int_{2a}^\infty \widetilde{g}(\xi) \frac{d}{d\xi} h_\xi(y)\, d\xi, \tag{31}$$

whose derivation follows the reasoning of Section 3. Indeed, approximate $\widetilde{g}(r)$, $r \geq 2a$, by the step-constant functions of the type, shown in Fig. 1:

$$\widetilde{g}(r) \approx \sum_{i=1}^{N} \widetilde{g}(\xi_i)[h_{\xi_i + \triangle\xi_i}(r) - h_{\xi_i}(r)],$$

where $2a = \xi_0 < \xi_1 < \ldots < \xi_N$, $\triangle\xi_i = \xi_i - \xi_{i-1}$. Divide each term in the right side by $\triangle\xi_i$ and multiply by $\triangle\xi_i$; Eq. (31) is generated in the limit $\triangle\xi_i \to 0$.

Insert Eq. (31) into Eq. (29) and write the result as

$$\widetilde{\gamma}_2(r) = \frac{\eta_1}{1 - \eta_1} \frac{1}{V_a^2} \int_{2a}^{\infty} \nu_2(\xi) \frac{d}{d\xi} \left\{ \int\int h_a(x - z_1)h_a(z_2)h_\xi(z_1 - z_2) \, dz_1 dz_2 \right\} d\xi,$$

having replaced $\widetilde{g}(\xi)$ by the binary correlation $\nu_2(\xi)$, because the integration in Eq. (31) is over the region $\xi \geq 2a$ in which $\widetilde{g}(\xi)$ and $\nu_2(\xi)$ coincide, see Eq. (28).

The integral in the braces is just the triple convolution $h_a * h_a * h_\xi$, $\xi \geq 2a$, evaluated in Sec. 2. According to Eq. (20),

$$\widetilde{\gamma}_2(r) = \frac{\eta_1}{1 - \eta_1} \int_{2a}^{\infty} \nu_2(\xi) \frac{d}{d\xi} F(\rho; \xi/a) \, d\xi = \frac{\eta_1}{1 - \eta_1} \int_{2}^{\infty} \nu_2(\tau) \frac{d}{d\tau} F(\rho; \tau) \, d\tau, \tag{32}$$

$\rho = r/a$, $\tau = \xi/a \geq 2$. In turn, the derivative $\dfrac{d}{d\tau}F(\rho; \tau)$ has a simple and concise representation:

$$\frac{d}{d\tau}F(\rho; \tau) = \frac{3\tau}{160\rho} G(\rho - \tau),$$

with the function

$$G(t) = \begin{cases} f(t), & \text{if } -2 \leq t \leq 0, \\ f(-t), & \text{if } 0 \leq t \leq 2, \\ 0, & \text{if } |t| \geq 2, \end{cases} \tag{33a}$$

where

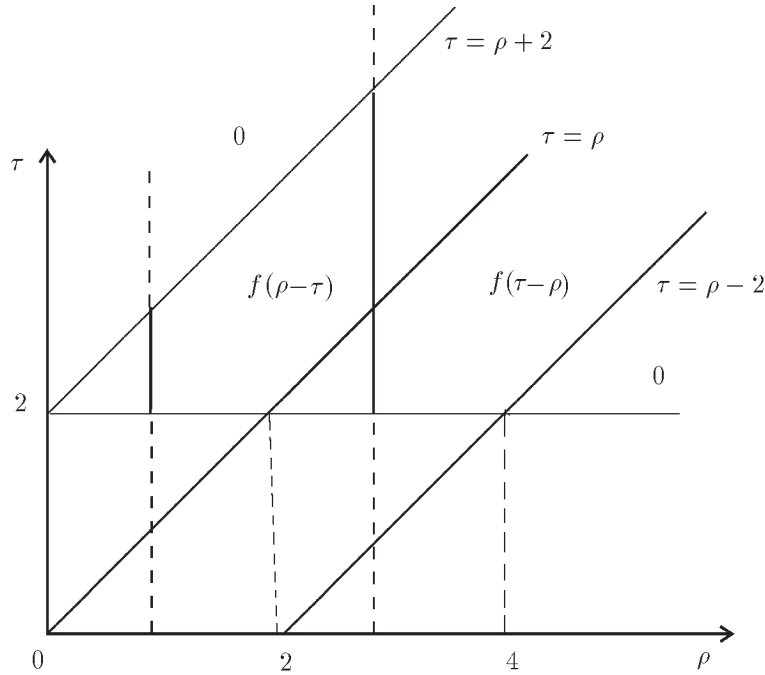$$f(t) = (2 + t)^3 \, (4 - 6t + t^2). \tag{33b}$$

Fig. 4. The range of integration in Eq. (32).

The integration domains for the integral (32) with the appropriate values of the kernel $G(t)$, according to Eq. (33), are shown in Fig. 4. Hence,

$$\rho\widetilde{\gamma}_2(r) = \frac{3\eta_1}{160(1 - \eta_1)} \int_{\max\{\rho-2,2\}}^{\rho+2} G(\rho - \tau)\tau\nu_2(\tau)\,d\tau, \qquad (34)$$

i.e.,

$$\rho\widetilde{\gamma}_2(r) = \frac{3\eta_1}{160(1 - \eta_1)}$$

$$\times \begin{cases} \displaystyle\int_2^{\rho+2} f(\rho - \tau)\tau\nu_2(\tau)\,d\tau, & \text{if } 0 \le \rho \le 2, \\[2mm] \displaystyle\int_2^{\rho+2} f(\rho - \tau)\tau\nu_2(\tau)\,d\tau + \int_2^{\rho} f(\tau - \rho)\tau\nu_2(\tau)\,d\tau, & \text{if } 2 \le \rho \le 4, \\[2mm] \displaystyle\int_{\rho-2}^{\rho} f(\tau - \rho)\tau\nu_2(\tau)\,d\tau + \int_{\rho}^{\rho+2} f(\rho - \tau)\tau\nu_2(\tau)\,d\tau, & \text{if } \rho \ge 4. \end{cases} \quad (35)$$

The formula (35), together with Eqs. (23) and (29), is our central result which accomplishes the needed representation of the two-point correlation as a simple one-tuple integral containing the radial distribution function of a statistically isotropic dispersion of nonoverlapping spheres.

6. The Behaviour of the Two-Point Correlation for $r \le 2a$

As a nontrivial application of the formula (35) consider in more detail the behaviour of the two-point correlation $\gamma_2(r)$ in the vicinity of the origin $r = 0$. This behaviour is important, because it can be simply associated with that of the so-called scattering curve for the dispersion in the long wave-length limit. (Recall that the scattering curve is directly connected to the Fourier transform of $\gamma_2(r)$, see Ref. 9 for details.) Hence experimental data concerning the leading terms in this long wave-length limit allow determination of the coefficients of the correlation $\gamma_2(r)$ in its Taylor expansion at $r = 0$. The latter coefficients, in turn, provide nontrivial information for the radial distribution function, as first pointed out in Refs. 12 and 13.

Indeed, in the vicinity of the origin $r = 0$ and, more precisely, for $r \leq 2a$, Eq. (35) implies

$$\rho\widetilde{\gamma}_2(r) = \frac{3\eta_1}{160(1-\eta_1)} \int_0^{\rho} P(\rho, u)\, \nu_2(u+2)\, du, \quad u = r/a - 2, \qquad (36)$$

with the polynomial

$$P(\rho, u) = (\rho - u)^3(u+2)\,[(\rho - u)^2 - 10\,(\rho - u) + 20], \qquad (37)$$

since $\nu_2(\tau) = 0$ at $\tau < 2$.

Hence, as seen from Eq. (36), knowledge of the radial distribution function $g(r)$ in the interval $(2a, 2a + r_0)$ defines the values of the two-point correlation in the interval $(0, r_0)$. Moreover, let us assume that $g(r)$ is analytic in the vicinity $(2a, 2a + r_0)$ of $2a$, so that

$$\nu_2(2 + u) = \sum_{k=0}^{\infty} \frac{a^k \nu_2^{(k)}(2a)}{k!} \left(\frac{r}{a} - 2\right)^k = \sum_{k=0}^{\infty} \frac{(2a)^k \nu_2^{(k)}(2a)}{k!}(s - 1)^k$$

$$= g_0 + g_1(s-1) + g_2(s-1)^2 + \cdots, \quad s \geq 1, \quad s = \frac{r}{2a}, \qquad (38)$$

the series converging for $0 \leq u \leq u_0$, $u_0 = r_0/a - 2 \leq 2$. In Eq. (38),

$$g_k = \frac{1}{k!}(2a)^k \nu_2^{(k)}(2a). \qquad (39)$$

The series expansion in powers of $s - 1$ with the notations g_0, g_1, etc., for its coefficients was introduced by Frisch and Stillinger.[13]

From Eq. (36) it follows that once $g(r)$ is analytic in the interval $(2a, 2a + r_0)$, the function $\widetilde{\gamma}_2(r)$ is analytic in $(0, r_0)$, and

$$\widetilde{\gamma}_2(r) = \sum_{k=0}^{\infty} \frac{a^k \widetilde{\gamma}_2^{(k)}(0)}{k!} \left(\frac{r}{a}\right)^k$$

$$= \frac{3\eta_1}{160(1-\eta_1)} \sum_{k=0}^{\infty} \frac{a^k \nu_2^{(k)}(2a)}{k!} \frac{1}{\rho} \int_0^{\rho} u^k P(\rho, u)\, du, \quad \rho = r/a. \qquad (40)$$

The integral in Eq. (40) is elementary, see Eq. (37), and the final result reads

$$\widetilde{\gamma}_2(r) = \sum_{k=0}^{\infty} \frac{a^k \widetilde{\gamma}_2^{(k)}(0)}{k!} \left(\frac{r}{a}\right)^k = \frac{9\eta_1}{4(1-\eta_1)}\rho^3$$

$$\times \sum_{k=0}^{\infty} \frac{k! g_k}{2^k} \rho^k \left[\frac{2}{(k+4)!} + \frac{k-3}{(k+5)!}\rho - \frac{2k}{(k+6)!}\rho^2 + \frac{k+1}{(k+7)!}\rho^3\right]. \quad (41)$$

Hence the behaviour of $\widetilde{\gamma}_2(r)$ and thus of the correlation $\gamma_2(r)$ in a certain vicinity of the origin $r = 0$ is uniquely defined by the behaviour of $g(r)$ in a certain vicinity of the "touching" distance $r = 2a$. In other words, as it follows from Eqs. (40), (29) and (23), the derivatives $\gamma_2^{(k)}(0)$ are uniquely and simply expressible in terms of the derivatives $g^{(k)}(2a)$ of the radial distribution function or, equivalently, by means of the derivatives $\nu_2^{(k)}(2a)$ of the binary correlation (since $\nu_2^{(k)}(2a) = g^{(k)}(2a)$, $k \geq 1$, and $\nu_2(2a) = g(2a) - 1$, see Eq. (9)).

Indeed, Eq. (41) yields first of all

$$\widetilde{\gamma}_2^{(k)}(0) = 0, \quad k = 0, 1, 2,$$

which means, when combined with Eqs. (29) and (23), that

$$\gamma_2'(0) = -\frac{3}{4(1-\eta_1)a}, \quad \gamma_2''(0) = 0, \quad (42)$$

independently of the sphere statistics, i.e., of the radial distribution function $g(r)$.

The first of Eqs. (42) is an obvious consequence of Debye's formula[27]

$$\frac{S}{V} = -4\eta_1(1-\eta_1)\gamma_2'(0), \quad (43)$$

which connects the specific surface S/V (i.e., that of the phase boundary S in the small volume V) with the derivative $\gamma_2'(0)$ of the two-point correlation, see also Stoyan *et al.*.[28] Indeed, the assumption of nonoverlapping yields $S/V = 4\pi a^2 n$, where n is the number density of the spheres in the dispersion. But $n = \eta_1/V_a$, $V_a = 4\pi a^3/3$, and therefore $S/V = 3a/\eta_1$, which, when inserted into (42), gives the same value of $\gamma_2'(0)$ as in Eqs. (43). Thus for any dispersion of *nonoverlapping* spheres $\gamma_2'(0)$ is not sensitive to the sphere statistics depending, at a fixed radius a, on the sphere fraction η_1 only. A stronger and more curious fact is embodied in the second relation of Eqs. (42), namely, the vanishing at the origin of the second derivative of the correlation function for such a dispersion whatever the sphere statistics may be. As argued by Markov,[25] the assumed spherical shape of the particles is not important here; the fact that $\gamma_2''(0) = 0$ is essentially connected with the assumption of nonoverlapping and, in particular, with the prohibition for

particles to touch each other. Indeed, consider a statistically isotropic dispersion of particles of fixed shape, whose location and orientation are both random but not interconnected statistically; the particles should not overlap whatever their orientations at fixed locations. An averaging with respect to orientation first (which is possible, due to the statistical independence of the latter), leads just to a dispersion of nonoverlapping spheres. (Each one is obtained through rotation of the particle, centered at the same location; the rotation represents simply the averaging with respect to all possible orientations of the particle.) Note that the fact that $\gamma_2''(0) = 0$ for a dispersion of nonoverlapping particles was first noticed by Kirste and Porod[12] using different and more complicated geometrical arguments; they also assumed that there are no corner points on the particle's surfaces. The results of Kirste and Porod were rederived and extended by Frisch and Stillinger,[13] who expanded directly $\gamma_2(r)$ at $r = 0$ starting, as a matter of fact, with its integral representation (8). In these references it also was shown that if the particles were allowed to touch each other, $\gamma_2''(0)$ would be a nonzero constant, proportional to the mean number of contact points.

As far as the higher derivatives of the two-point correlation are concerned, Eq. (41) yields

$$\widetilde{\gamma}_2^{(3)}(0) = \frac{9\eta_1}{8(1 - \eta_1)a^3}\, \nu_2(2a), \quad \widetilde{\gamma}_2^{(4)}(0) = \frac{9\eta_1}{20(1 - \eta_1)a^4}[2a\, \nu_2'(2a) - 3\nu_2(2a)],$$

$$\widetilde{\gamma}_2^{(5)}(0) = \frac{3\eta_1}{4(1 - \eta_1)a^5}[a^2\nu_2''(2a) - a\nu_2'(2a)], \quad \text{etc.,} \tag{44a}$$

and, in general,

$$\widetilde{\gamma}_2^{(k)}(0) = \frac{9\eta_1}{4(k + 1)(1 - \eta_1)a^k} \left\{ 2a^3\, \nu_2^{(k-3)}(2a) + a^4(k - 7)\, \nu_2^{(k-4)}(2a) \right.$$

$$\left. - 2a^5\,(k - 5)\nu_2^{\,(k-5)}(2a) + (k - 5)a^5\, \nu_2^{(k-6)}(2a) \right\}, \tag{44b}$$

for $k \geq 6$. In terms of the coefficients g_k, see (38), the relations (44) become

$$\widetilde{\gamma}_2'''(0) = \frac{9g_0\eta_1}{8(1 - \eta_1)a^3}, \quad \widetilde{\gamma}_2^{(4)}(0) = \frac{9(g_1 - 3g_0)\eta_1}{20(1 - \eta_1)a^4},$$

$$\widetilde{\gamma}_2^{(5)}(0) = \frac{3(g_2 - g_1)\eta_1}{8(1 - \eta_1)a^5}, \quad \widetilde{\gamma}_2^{(6)}(0) = \frac{9(3g_3 - g_2 - 2g_1 + g_0)\eta_1}{56(1 - \eta_1)a^6},$$

$$\gamma_2^{(k)}(0) = \widetilde{\gamma}_2^{(k)}(0) = \frac{9\eta_1}{2^{k-2}(k + 1)(1 - \eta_1)a^k}\left((k - 3)!\, g_{k-3} \right.$$

$$\left. + (k - 7)(k - 4)!\, g_{k-4} - 4(k - 5)(k - 5)!\, g_{k-5} + 4(k - 5)!\, g_{k-6} \right), \quad k \geq 7. \tag{45}$$

Note that indeed $\gamma_2^{(k)}(0) = \widetilde{\gamma}_2^{(k)}(0)$ for $k \geq 7$, since $\gamma_2^{\text{ws}}(r)$ is a polynomial of sixth degree in a vicinity of the origin, see Eqs. (23) and (29).

The formulae (44) were derived independently by Markov[25] using an asymptotic analysis of the statistical parameter $i_2(p)$ for arbitrary sphere statistics, see Eq. (24), in the limit $p \to \infty$.

The foregoing formulae (23), (29) and (45) imply, in particular, that

$$\widetilde{\gamma}_2(r) = 1 - \frac{3\rho}{4(1 - \eta_1)} + \frac{(1 + 3\eta_1 + 3\eta_1 g_0)}{16(1 - \eta_1)}\rho^3 - \frac{9\eta_1 - 3(g_1 - g_0)\eta_1}{160(1 - \eta_1)}\rho^4 + o(\rho^4).$$

$$(46)$$

It is remarked finally that the value of $\widetilde{\gamma}_2'''(0)$ in Eq. (45) coincides with that of Kirste and Porod[12] (for spherical particles) and of Frisch and Stillinger.[13] However, the value of $\gamma_2^{(4)}(0)$, as given by Frisch and Stillinger, contains an obvious misprint, since it does not reproduce correctly the ρ^4-coefficient in the well-stirred case, i.e., at $g_0 = g_1 = 0$, see Eq. (23).

Concluding Remarks

The formula (35) represents the central result of this study. It is a novel and useful relation which allows a straightforward and elementary evaluation of the two-point correlation $\gamma_2(r)$ for a dispersion whose radial distribution function is known.

Many applications of the the formula (35) for random dispersions can be envisaged. In Section 6 it allowed, for example, to elucidate the reason why and how the behaviour of $\gamma_2(r)$ at the origin is interconnected to that of the radial function at the "touching" distance $2a$, thus generalizing results of Refs. 12 and 13.

Another important implication of (35) is the possibility to evaluate explicitly the moments of $\gamma_2(r)$ on the semiaxis $(0, \infty)$, defined in the first line of Eq. (26). Obviously,

$$\theta_k = \theta_k^{\text{ws}} + \widetilde{\theta}_k, \qquad (47)$$

where θ_k^{ws} are the appropriate moments, corresponding to the well-stirred approximation, see Eq. (26), and

$$\widetilde{\theta}_k = \int_0^\infty r^k \widetilde{\gamma}_2(r)\, dr \qquad (48)$$

is the correction, due to the binary correlation $\nu_2(r)$. It is to be noted that the first moment θ_1 appears, e.g., in the variational estimates on the trapping (sink) constant and Darcy's permeability of a random dispersion.[11,6,22] The same moment θ_1 showed up very recently[29] as a quantity of central importance when rigorously estimating the size of the representative volume elements of elastic solids, reinforced with spherical inclusions. To evaluate θ_1 in this Ref. 29, Drugan and Willis have applied the formula (35), inserting it into (48) at $k = 1$, changed the order of integration and grouped the terms appropriately. Their method is applicable, however, for arbitrary k, yielding

$$\widetilde{\theta}_k = a^{k+1}\frac{\eta_1}{1 - \eta_1}\int_2^\infty H_k(\tau)\,\tau\nu_2(\tau)\, d\tau,$$

$$H_k(\tau) = \frac{3}{160} \left\{ \int_{\tau-2}^{\tau} f(\rho - \tau)\, \rho^{k-1}\, d\rho + \int_{\tau}^{\tau+2} f(\tau - \rho)\, \rho^{k-1}\, d\rho \right\}. \qquad (49)$$

With the function $f(t)$, given in Eq. (34b), the functions $H_k(\tau)$ in (49) are polynomials of τ, whose explicit evaluation is elementary. For example,

$$H_1(\tau) = 1, \quad H_2(\tau) = \tau, \quad H_3(\tau) = \frac{2}{5} + \tau^2, \quad H_4(\tau) = \frac{6}{5}\tau + \tau^3, \qquad (50)$$

etc. This means that the moments $\widetilde{\theta}_k$ are simply connected to the moments of the binary correlation, i.e., the quantities

$$m_l = \int_2^{\infty} \tau^l \nu_2(\tau)\, d\tau, \quad l = 0, 1, \dots .$$

In particular, the first two of the relations (50) yield

$$\widetilde{\theta}_1 = a^2 \frac{\eta_1}{1 - \eta_1}\, m_1, \quad \widetilde{\theta}_2 = a^3 \frac{\eta_1}{1 - \eta_1}\, m_2. \qquad (51)$$

Without going into detail, we shall only mention that for the Percus-Yevick distribution, widely used and explored in the liquid-state theory, the moments m_l can be easily found by means of the simple algebraic expression[30,9] for the Laplace transform of the function $rg(r)$. In this way Drugan and Willis[29] have obtained an extremely simple expression for the needed moment θ_1 in the Percus-Yevick case. At the same time the radial distribution function $g(r)$ itself is extremely cumbersome for this distribution.

Let us point out at last that the basic ideas of the above proposed approach can also be applied in studying the so-called "surface-void" and "void-void" correlations in a random dispersion, thus opening the possibility of representing them as simple one-tuple integrals of the type (35), involving again the radial distribution function. We can only recall here that these correlations are very important in the above mentioned theories of diffusion-controlled reactions and permeability of dispersions. A detailed study, however, goes beyond the scope of the present paper.

Acknowledgment

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