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# ON THE ANALYSIS OF THE BINARY CORRELATION FUNCTION IN A TWO-PHASE SYSTEM

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Simple geometrical considerations are used to obtain an equation for a binary correlation function in the system of rigid spheres of equal radii. A self-consistent method of introducing an effective volume assigned to a single particle, makes possible the determination of the binary correlation function for the systems with a low and a moderate volume concentration of the particles. In the limiting case of low volume concentrations, the equation for the binary function becomes indentical with the known linearized Kirkwood [1, 2] superposition approximation equation. Following [3], it is assumed that the initial particle distribution is realized in such a manner that the positions of their centers are assigned one after the other, and the center of each new particle can be found with equal probability in any geometrically accessible part of the region occupied by the suspension.

Experimental data concerning the relative distribution of spheres in a liquid of the same density following a vigorous shaking of the mixture, are given in [4]. The binary correlation function obtained in this paper by statistical treatment of a large number of measurements of the relative distances between the sphere centers indicates the presence of a short range order in the particle distribution. A decisive part is played here by the geometrical effect related to the impermeability of the spheres which results in their layer-type distribution in the neighborhood of the specified particle irrespective of the character of the hydrodynamic interaction.

Study of the spatial distribution of a monodisperse system of spherical particles falling through a liquid at a volume concentration of 0.025 and the Reynolds number for a separate particle equal to 0.6, have shown that [5] the probability of finding particles within a certain volume has an approximately binomial character. This indicates that all positions of the center of a single particle are equally probable within a geometrically accessible region and implies that the hydrodynamic forces acting between the particles do not have a decisive influence on the form of the binary correlation function. For the particles in a viscous fluid of comparable density, a small region corresponding to the interparticle distances comparable to the particle diameter, constitutes an exception.

**1. Correlation functions.** Let us consider a system containing a very large number $N_\infty$ of identical particles (spheres of radius $a$) located in a volume $V_\infty$. We use, as the characteristic parameters of this system, the number $n = N_\infty / V_\infty$ of the sphere centers per unit volume and the volume concentration of the particles $c = {}^4/_3\pi a^3 n$. In a system consisting of a large number of chaotically distributed spheres, the positions of their centers can only be determined with a certain probability. Let $dW_1(\mathbf{x})$ and $dW_2(\mathbf{x}_1, \mathbf{x}_2)$ denote respectively the probability of finding the center of an arbitrary

particle in the neighborhood of the point $\mathbf{x}$, and the probability of finding the centers of two, arbitrarily selected particles in the neighborhood of the points $\mathbf{x}_1$ and $\mathbf{x}_2$. Let, in addition, $dW_1(\mathbf{x}_1; \mathbf{x}_2)$ denote the probability of discovering the center of a specified particle in the neighborhood of $\mathbf{x}_1$ when the center of another particle is fixed at the point $\mathbf{x}_2$. We introduce the dimensionless correlation functions $f_1(\mathbf{x})$, $f_2(\mathbf{x}_1, \mathbf{x}_2)$ and $f_1(\mathbf{x}_1; \mathbf{x}_2)$ by means of the following formulas:

$$\begin{aligned} dW_1(\mathbf{x}) &= V_\infty^{-1} f_1(\mathbf{x})\, d\mathbf{x} \\ dW_2(\mathbf{x}_1, \mathbf{x}_2) &= V_\infty^{-2} f_2(\mathbf{x}_1, \mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \\ dW_1(\mathbf{x}_1; \mathbf{x}_2) &= V_\infty^{-1} f_1(\mathbf{x}_1; \mathbf{x}_2) d\mathbf{x}_1 \\ f_2(\mathbf{x}_1, \mathbf{x}_2) &= f_1(\mathbf{x}_2) f_1(\mathbf{x}_1; \mathbf{x}_2) \end{aligned} \tag{1.1}$$

where the last equation follows from the theorem on multiplication of probabilities.

In what follows, we shall concern ourselves with a spatially homogeneous system, and this is found at a sufficient distance from the boundary surfaces of the volume $V_\infty$. In this case all positions of a particle are equally probable and from (1.1) we have

$$f_1(\mathbf{x}) = 1, \quad f_1(\mathbf{x}_1; \mathbf{x}_2) = f_2(\mathbf{x}_1, \mathbf{x}_2)$$

Moreover, in this case the distribution of the spheres near the specified sphere will be spherically symmetrical in the mean. For this reason the function $f_2(\mathbf{x}_1, \mathbf{x}_2)$ will depend on a single argument, namely the distance between the centers of the particles in question, so that

$$f_2(\mathbf{x}_1, \mathbf{x}_2) = g(r), \quad r = |\mathbf{x}_1 - \mathbf{x}_2|$$

Thus in the case of a spatially homogeneous system the function $g(r)$ is not only a binary correlation function, but also a conditional correlation function. The mean number of the sphere centers which can be found in a spherical layer $(r, r + dr)$ is:

$$dN(r) = 4\pi r^2 n g(r) dr \tag{1.2}$$

The above formula will be used in processing experiments dealing with the distribution of spherical particles in a liquid [4].

**2. Effective volume of a sphere in the system.** Let us denote by $w_-(r_1, r_2; r_{12})$ the volume of a region formed by intersection of a sphere of radius $r_1$ with another sphere of radius $r_2 \leqslant r_1$ when the distance separating the two centers is $r_{12}$ $(r_1 \leqslant r_{12} \leqslant r_1 + r_2)$. We denote by $w_+(r_1, r_2; r_{12})$ the volume of the part of the sphere of radius $r_2$ which lies outside the sphere of radius $r_1 \geqslant r_2$, with the distance between the sphere centers equal to $r_1 - r_2 \leqslant r_{12} \leqslant r_1$ (see Fig. 1). Let us write the functions $w_-$ and $w_+$ in explicit form

$$\begin{aligned} w_-(r_1, r_2; r_{12}) &= \pi [r_1^3 T_-(\theta) + r_2^3 T_-(\theta')] \\ w_+(r_1, r_2, r_{12}) &= \begin{cases} \pi [r_2^3 T_+(\theta') - r_1^3 T_-(\theta)], & \cos\theta' \leqslant 0 \\ {}^4/_3 \pi r_2^3 - \pi [r_1^3 T_-(\theta) + r_2^3 T_-(\theta')], & \cos\theta' > 0 \end{cases} \\ 3T_\pm(\theta) &= 2 \pm 3\cos\theta \mp \cos^3\theta \\ \cos\theta &= \frac{r_1^2 + r_{12}^2 - r_2^2}{2 r_1 r_{12}}, \quad \cos\theta' = \frac{r_{12}^2 + r_2^2 - r_1^2}{2 r_2 r_{12}} \end{aligned} \tag{2.1}$$

where the angles $0$ and $\theta'$ are shown in the figure.

The functions $w_+$ and $w_-$ have the following obvious properties:

$$w_+(r_1, r_2;\ r_1) + w_-(r_1, r_2;\ r_1) = {}^4/_3\pi r_2^3 \qquad (2.2)$$
$$w_-(r_1, r_2;\ r_1 + r_2) = w_+(r_1, r_2;\ r_1 - r_2) = 0$$

Despite the fact that the functions $w_+$ and $w_-$ are defined in different regions, we have the following formal relation:

$$\frac{\partial w_-}{\partial r_1} = -\frac{\partial w_+}{\partial r_1} = 2\pi r_1^2(1 - \cos\theta) \qquad (2.3)$$

Let us introduce the concept of effective volume and effective radius into the system of chaotically moving spheres. Let $v_c = {}^4/_3\pi a^3$ be the specific volume of a particle. We define the effective volume of a particle in the system as the increase in the volume of the region inaccessible to the centers of other particles of the same size when the number of particles in the system is increased by one.

First we consider the case of very small volume concentrations. We choose one of the particles of the ensemble as a sample particle and surround it with a sphere $S_d$ of radius $2a$ concentric with the sample particle. The part of the space bounded by the sphere $S_d$ is "inaccessible" to the centers of the remaining particles. As far as these centers are concerned, the sample particle has effective radius of $2a$ and effective volume of $8v_c$.

Increasing the volume concentration leads to an overlap of the neighboring spheres $S_d$. At moderate volume concentrations the overlaps will mainly involve pairs of spheres, i.e. the overlaps involving three or more particles will be, on average, few. Estimates carried out for a model of cubic distribution of spheres show that the assumption of the binary character of the sphere overlap holds for the concentrations up to $c \approx 0.2$.

The overlapping of spheres $S_d$ reduces the volume of the inaccessible regions computed for a single particle as compared with $8v_c$, although the radius of the inaccessible region surrounding the separate particles remains equal to $2a$. Since the spheres $S_d$ constructed for the sample sphere and its neighbor have a common part, the volume $8v_c$ is reduced by an amount equal to half the volume of the common part, i.e. by the quantity ${}^1/_2 w_-(2a,\ 2a;\ r_{12})$. The average number of the particle centers at the distance $(r_{12},\ r_{12} + dr_{12})$ from the center of the sample particle is equal, in accordance with (1.2), to $4\pi r_{12}^2 n g(r_{12}) dr_{12}$, and the effective volume of a particle in the system is therefore

$$v_0 = 8v_c - 2\pi n \int_{2a}^{4a} r_{12}^2 g(r_{12})\, w_-(2a, 2a; r_{12})\, dr_{12} \qquad (2.4)$$

The formula (2.4) defines the effective volume in the case of moderate concentrations.

At high concentrations of particles the effective volume of a sphere at a distance $r$ from the sample sphere should depend on a three-particle correlation function which can be expressed in terms of the binary correlation function only at low volume concentrations.

Making use of the earlier assumption of homogeneity and spherical symmetry

(in the mean) of the system, we can write the effective radius of the particle in the form

$$r_0 = (^3/_4 v_0 / \pi)^{1/3} \tag{2.5}$$

where $v_0$ and $r_0$ denote the mean statistical characteristics of the system of spheres, and depend only on the volume concentration $c$.

**3. Equation of the binary correlation function.** Let us choose and fix a center of an arbitrary (sample) sphere belonging to the system in question. We draw a sphere of radius $r$ concentric with the sample sphere. According to (1.2) the determination of the function $g(r)$ requires the knowledge of the average number $N(r)$ of the sphere centers lying within the sphere of radius $r$. Let $v = V_\infty / N_\infty$ denote the mean volume of a single particle in the system. This is clearly equal to the mean free volume per center, of an arbitrary particle in the system.

We introduce $V(r) = v\,N(r)$ as mean free volume per $N(r)$ particle centers. Then the relation (1.2) assumes the form

$$g(r) = \frac{1}{4\pi r^2}\frac{dV(r)}{dr} \tag{3.1}$$

When $r/a \to \infty$, then clearly $V(r) \to {}^4/_3\pi r^3$. If however $r \sim a$, then the influence of the neighboring spheres the centers of which are distributed within the layer from $r$ to $r + dr$, manifests itself by reducing the free volume within the sphere of radius $r$ by the amount

$$V_-(r) = 4\pi n \int_r^{r+r_0} r_{12}^2 g(r_{12})\, w_-(r, r_0; r_{12})\, dr_{12}$$

Spheres with the centers within the layer $(r - r_0, r)$ reduce the free volume outside the sphere of radius $r$ by the amount

$$V_+(r) = 4\pi n \int_{r-r_0}^{r} r_{12}^2 g(r_{12})\, w_+(r, r_0; r_{12})\, dr_{12}$$

When $r - r_0 < 2a$, the lower limit of integration in the expression above must be replaced by $2a$. This is because two impermeable spheres cannot approach each other closer than the distance of $2a$ between their centers. We can however leave the formula unchanged by setting $g(r) \equiv 0$ when $r < 2a$. Thus at $r \geqslant 2a$ we have

$$V(r) = {}^4/_3\pi r^3 - v_0 + V_+(r) - V_-(r)$$

Relation (3.1) and the properties (2.2) and (2.3) of the functions $w_+$ and $w_-$ together yield the following equation for the binary correlation function:

$$(1 - nv_0)\, g(r) = 1 - 2\pi n \int_{r-r_0}^{r+r_0} r_{12}^2 (1 - \cos\theta)\, g(r_{12})\, dr_{12}, \quad r \geqslant 2a \tag{3.2}$$

where $\cos\theta$ is given by the formula (2.1). Let us introduce the notation

$$\tau_0 = \left(\frac{r_0}{a}\right)^3, \quad \xi = \frac{2a}{r_0}, \quad x = \frac{r}{r_0}$$
$$y = \frac{r_{12}}{r_0}, \quad \lambda = \frac{3c\tau_0}{1 - c\tau_0}$$

and consider, instead of $g(x)$, a new unknown function $\varphi(x) = x[g(x) - 1]$. From (3.2) follows

$$\varphi(x) = \frac{\lambda}{4}\int_{x-1}^{x+1} \varphi(y)\,[(x-y)^2 - 1]\,dy, \quad x \geqslant \xi \tag{3.3}$$

$$\varphi(x) = -x, \quad 0 < x < \xi$$

For the low concentrations we obviously have $\xi = 1$ and Eq. (3.3) becomes the linearized equation of superposition approximation known in the theory of liquids and obtained earlier in [1, 2] using the methods of statistical mechanics. The solution of (3.3) has the following form with the accuracy of up to and including the terms of order $c$:

$$\varphi(x) = \begin{cases} cx\,(8 - 6x + {}^1/_2 x^3), & 1 < x < 2 \\ 0, & x > 2 \end{cases}$$

In the region of moderate concentrations however, Eq. (3.3) differs from the linearized equation of [1, 2] in, that in the present paper the region $0 < r < 2a$ where $g(r) \equiv 0$, does not correspond to the region $0 < x < 1$ where $x$ is a dimensionless variable. The difference is apparently connected with the introduction of the effective radius of interaction between the particles which depends on the binary correlation function.

**4. Computation of the binary correlation function.** Following [1], we extend Eq. (3.3) to the whole of the real axis putting $\varphi(-x) = \varphi(x)$ for $x < 0$ and introducing the inhomogeneity function $\psi(x) = \psi(-x)$ unknown for the time being and vanishing at $|x| \geqslant \xi$:

$$\varphi(x) = \psi(x) + \frac{\lambda}{4}\int_{-\infty}^{\infty} K(x-y)\,\varphi(y)\,dy, \quad -\infty < x < \infty \tag{4.1}$$

$$\psi(x) = 0, \quad |x| \geqslant \xi$$

$$K(x) = \begin{cases} x^2 - 1, & |x| < 1 \\ 0, & |x| \geqslant 1 \end{cases}$$

The function $\psi(x)$ is found from the condition: $\varphi(x) = -|x|$ when $|x| < \xi$. Since $K(x)$ and $\psi(x)$ are both finite and $\varphi(x)$ can be assumed, from the physical arguments, to belong to class $L_2(-\infty, \infty)$, a solution of (4.1) unique in $L_2(-\infty, \infty)$ can be constructed using the following formulas [6]:

$$\varphi(x) = \psi(x) + \int_{-\xi}^{\xi} l(x-y)\,\psi(y)\,dy \tag{4.2}$$

$$l(x) = -\frac{\lambda}{2\pi}\int_{-\infty}^{\infty} \frac{L(i\omega)\,e^{-i\omega x}}{1 + \lambda L(i\omega)}\,d\omega$$

$$L(z) = -\frac{1}{4}\int_{-\infty}^{\infty} K(x)\,e^{zx}\,dx = \frac{1}{z^3}(z\,\mathrm{ch}\,z - \mathrm{sh}\,z)$$

Let us first consider Eq. (4.2) on the interval $|x| \leqslant \xi$ (where $\varphi(x) = -|x|$). We can find the function $\psi(x)$ by solving the equation

$$\psi(x) = -|x| - \int_{-\xi}^{\xi} l(x-y)\,\psi(y)\,dy, \quad |x| < \xi \tag{4.3}$$

Further, using (4.2) we can construct $\varphi(x)$ for $x \geqslant \xi$

$$\varphi(x) = \int_{-\xi}^{\xi} l(x-y)\,\psi(y)\,dy \tag{4.4}$$

To find the functions $\psi(x)$ and $\varphi(x)$ from (4.3) and (4.4), we must know $l(x)$ at $|x| \leqslant \xi$. Knowing the zeros of the function $M(z) = 1 + \lambda L(z)$, we can use the theorem of residues to transform the integral defining $l(x)$ in (4.2) to the form suitable for numerical methods.

The function $M(z)$ is an analytic and entire function. Its zeros obviously coincide with the roots of the equation

$$z^3 = \lambda(\operatorname{sh} z - z \operatorname{ch} z) \tag{4.5}$$

It should be noted that if $z_n$ is a root of (4.5), so are $\bar{z}_n$, $-z_n$ and $-\bar{z}_n$ (the upper bar denotes a complex conjugate). The right-hand side of (4.5) contains a transcendental entire function, and the left-hand side contains a polynomial. The generalization of the Picard's Theorem implies that such an equation has, for all $\lambda$ except perhaps one, infinitely many roots such that $|z_n| \to \infty$ as $n \to \infty$ [7]. The authors of [1] computed, for some values of $\lambda$, the roots $z_1$ and $z_2$ of (4.5) with the smallest moluli. The asymptotic behavior of the roots $z_n$ as $n \to \infty$ can be established for all $\lambda$ by considering Eq. (4.5) in which only the terms with largest moduli remain

$$z_n = \pm \ln \frac{8\pi^2 n^2}{\lambda} \pm 2\pi i n + O\left(\frac{\ln n}{n}\right), \quad n \to \infty$$

The Jordan Lemma can be used to compute $l(x)$

$$l(x) = -\sum_{n=1}^{\infty} \frac{\exp(-z_n x)}{M'(z_n)}, \quad x > 0 \tag{4.6}$$

$$(M'(z) = dM(z)/dz)$$

The series in (4.6) extends over those $z_n$ for which $\operatorname{Re} z_n > 0$. Another expression for $l(x)$ can be obtained by writing the function $L(z)$ in the form

$$L(z) = \frac{z-1}{z^3} e^z + \frac{z+1}{z^3} e^{-z}$$

and separating the integral defining $l(x)$ into two integrals. Applying the Jordan Lemma and theory of residues to each of these integrals yields the following results:

$$l(x) = \frac{3\lambda}{4(\lambda+3)}\left(x^2 - \frac{15+6\lambda}{15+5\lambda}\right) - \tag{4.7}$$

$$\lambda \sum_{n=1}^{\infty} \frac{1+z_n}{z_n^3} \frac{\exp(-z_n)}{M'(z_n)} \operatorname{ch}(z_n x), \quad |x| < 1$$

The sum in the formula (4.7) is distributed, just as in (4.6), over the $z_n$ which have $\mathrm{Re}\, z_n > 0$. The expression (4.7) was given in [1] in a somewhat distorted form.

The analysis carried out in [1] shows that the formula (4.6) in which the series is replaced by just first two terms corresponding to $z_1$ and $\bar{z}_1$, approximates $l(x)$ sufficiently well when $x \geqslant 1$, and a two-term formula (4.7) where the series is again replaced by the first two terms approximates $l(x)$ sufficiently well when $|x| < 1$. In the present paper the function $l(x)$ was taken, for the numerical computations, as two-term formulas on the intervals $x < 1$ and $x \geqslant 1$. Having found $l(x)$, the authors determined $\psi(x)$ for $|x| < \xi$ using (4.3) which was transformed into a system of linear algebraic equations by replacing the integral term by its Simpson Rule equivalent. Relation (4.4) was then used to obtain the required function $g(x) = 1 + \varphi(x)/x$. The problem of unique determination of $g(x)$ for various values of $c$ is self-consistent, since the effective radius $r_0$ and parameter $\xi$ entering (4.4) and (4.5) both depend on the function $g(x)$. Determination of the relations $\tau_0 = \tau_0(c)$ and $r_0 = r_0(c)$ and construction of the binary correlation function were carried out by iterative method using the formulas (2.4) and (2.5). Below we give the resulting relation $\tau_0(c)$:

| c | 0.04 | 0.06 | 0.08 | 0.10 | 0.12 | 0.14 | 0.16 | 0.18 | 0.20 |
|---|---|---|---|---|---|---|---|---|---|
| $\tau_0$ | 7.28 | 6.89 | 6.47 | 6.03 | 5.56 | 5.07 | 4.59 | 3.72 | 3.15 |

We see that the dimensionless effective volume $\tau_0$ decreases monotonously, as was expected, with increasing volume concentration. We note that the formula (2.4) cannot be used for the concentrations which are almost maximum, since in this case the contribution of the triple and higher order overlaps of the spheres $S_d$, which is not accounted for in (2.4), becomes considerable.

Figure 1 shows the graphs of $g(r)$ for various values of $c$. An increase in the volume concentration is accompanied by the increase in the amplitude and decrease in the damping of the oscillations. This implies that at moderate volume concentrations of the particles any correlation between the positions of their centers practically vanishes at the distance equal to several radii of the particles. At sufficiently large distances from the center of the sample particle all positions at which the center of the given particle can be found, become equally probable. The dashed line in the Fig. 1 depicts the results of the computation of a correlation function obtained in [2] for $c = 0.144$. It can be assumed that at small and moderate concentrations the results of this paper are in satisfactory agreement with the results obtained earlier.

In the statistical mechanics the function $g(r)$ is used to construct an equation of state for a gas composed of rigid spheres, and the equation has the form

$$p/(nkT) = 1 + 4cg(2a) \tag{4.8}$$

where $p$ is pressure, $T$ is temperature and $k$ is the Boltzmann's constant. The following virial expansion of the equation of state in powers of the volume concentration is given in [8]:

$$p/(nkT) = 1 + 4c + 10c^2 + 18.36c^3 + (29.44 \pm 1.28)c^4 + \ldots \tag{4.9}$$

Below we give the results of computing the quantity $p / (nkT)$ according to (4.8) and (4.9):

| c | 0.04 | 0.06 | 0.08 | 0.10 | 0.12 | 0.14 | 0.16 | 0.18 | 0.20 |
|---|---|---|---|---|---|---|---|---|---|
| (4.8) | 1.18 | 1.28 | 1.40 | 1.54 | 1.71 | 1.89 | 2.06 | 2.23 | 2.41 |
| (4.9) | 1.18 | 1.27 | 1.38 | 1.52 | 1.66 | 1.82 | 1.99 | 2.18 | 2.39 |

which show good agreement (within 2 - 3%) with the virial expansion (4.9).

In conclusion, we consider the problem of the asymptotics of the function $\varphi(x)$ when $x \gg 1$. This requires, according to the formula (4.4), the knowledge of the behavior of $l(x)$ when $x \gg 1$. The modulus of the general term of (4.6) can be shown, using the asymptotics of the roots $z_n$ derived above, to have the following form at large $n$ :

$$\left| \frac{\exp(-z_n x)}{M'(z_n)} \right| \sim \left( \frac{\lambda}{8\pi^2} \right)^x \frac{1}{n^{2x}}$$

and this proves that $l(x)$, and therefore also $\varphi(x)$, decrease exponentially as $x \to \infty$ provided that $\lambda < 8\pi^2$.

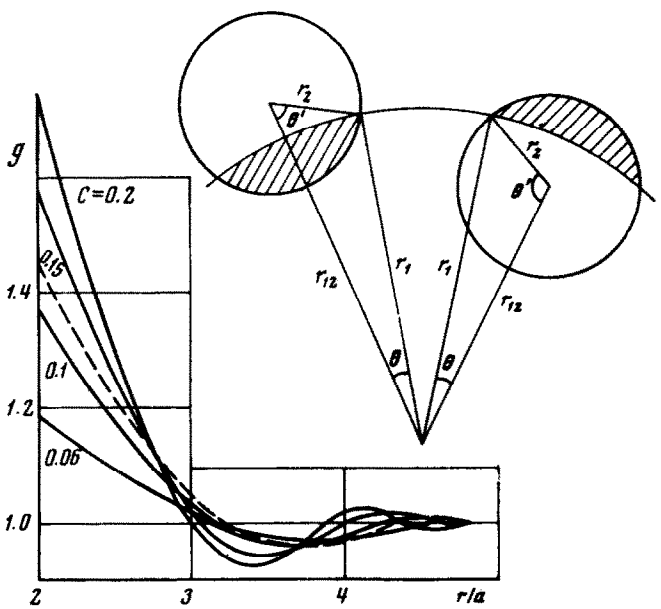


Fig. 1

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