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1984 J. Phys. A: Math. Gen. 17 L855

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## LETTER TO THE EDITOR

### Exact equation for the pair-connectedness function

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Received 2 August 1984

**Abstract.** An exact integral equation for the pair-connectedness function  $g^\ddagger(12)$  is derived on the basis of the author's earlier exact equation for the pair-distribution function  $g(12)$ . The new equation gives rise to a sequence of approximations for  $g^\ddagger(12)$ , starting with the Percus–Yevick approximation. Significant aspects of the first two approximations are noted, as is the relevance of the blocking function  $g - g^\ddagger$  for ionic and chemically associating particles.

The pair connectedness function  $g^\ddagger(12)$  has come to be recognised as a quantity of basic importance in treating percolation, clustering, and gelation (Coniglio *et al* 1977a, b, Chiew and Glandt 1983), with a role analogous to that of the pair-distribution function  $g(12)$  in the treatment of condensing fluids. We derive here a formally exact integral equation for  $g^\ddagger$ , based on our earlier equation for  $g$ , which permits the systematic introduction of a sequence of increasingly refined approximations for  $g^\ddagger$ , beginning with an equation induced by the Percus–Yevick (PY) approximation for  $g$  that has already been found useful in this context (Chiew and Glandt 1983). Our equation for the next approximation is given and applied to the prototypal system of randomly centred spheres. We note that for this system the equation is solvable with high accuracy by analytic methods. For the same system we discuss the significance of the remarkable correspondence between  $g^\ddagger$  at density  $\rho$  and  $g$  continued analytically to density  $-\rho$  in the PY approximation. We also note the significance of our general equation as a new formalism for obtaining the atom–atom or ion–ion correlation functions of chemically or ionically associating species.

Let the quantity  $\rho_2^\ddagger(12) d\mathbf{r}_1 d\mathbf{r}_2$  be the probability of finding a particle in  $d\mathbf{r}_1$  at  $\mathbf{r}_1$  and another particle, of the same cluster, in  $d\mathbf{r}_2$  at  $\mathbf{r}_2$ . Then  $\rho_2^\ddagger(12) = \rho_1(1)\rho_1(2)g^\ddagger(12)$  where  $\rho_1(1)$  is the one-particle probability density of the system. In a uniform system, which we treat here for simplicity,  $\rho_1(1)$  is the expected number density  $\rho$ . Without the cluster condition, the above statements define the two-particle distributions  $\rho_2(12)$  and  $g(12)$ . We begin by summarising our earlier integral equation for  $g(12)$  for a system at temperature  $T$  with  $\beta = -kT$ , where  $k$  is the Boltzmann constant with pair potential  $\phi(12)$ . Letting  $e = \exp(-\beta\phi(12))$ , we have  $f = e - 1$ ,  $h = g - 1$ . Denoting the convolution  $\int a(13)b(23)r_3$  as  $a \bullet b$ , we have the Ornstein–Zernike equation

$$h = c + \rho c \bullet h \quad (1)$$

and the closure

$$c = f[g - c] + m \quad m = ed \quad (2)$$

where  $d(12)$  has infinite-series representations, both as a functional of  $f$  and  $\rho$  (an ' $f$ -bond,  $\rho$ -circle' representation) and of  $h$  and  $\rho$ . We shall begin with the former here. Letting  $d_2[ff] = f \bullet f$  and  $d_5[fffff] = \int f(13)f(14)f(34)f(23)f(24) d\mathbf{r}_3 d\mathbf{r}_4$  we can write to lowest order in  $\rho$

$$d/\rho^2 = \frac{1}{2}d_2^2[ff] + \frac{1}{2}d_5[fffff]. \quad (3)$$

The first 'series-union' approximation (SU1) of Stell (1963) is defined by setting  $m = 0$  whereas the original approximation of Percus and Yevick (1958) is equivalent to setting  $d = 0$ . The two approximations coincide except in the case of hard-core potentials, where  $m = 0$  is the weaker statement since  $m = ed$ ; the stronger  $d = 0$  inside the core region forces one to identify  $-c$  inside the core with the cavity function  $y$ , where  $g = ey$ . (In general  $-c$  is very poorly approximated by  $y$  inside the core region.) Similarly, higher SU approximations require the use of (3) only outside the core region rather than for all  $\mathbf{r}_{12}$ , since they involve  $d$  only through  $m = ed$ . Because the core values of  $y$  will not be an issue in the work here, however, it will be unnecessary to make a distinction between the SU1 and PY approximation in the development below.

Following Hill (1955) we decompose  $e(12)$  into a sum of Boltzmann factors  $e^\dagger(12) = \exp(-\beta\phi^\dagger(12))$  and  $e^*(12) = \exp(-\beta\phi^*(12))$  where  $\phi^\dagger$  and  $\phi^*$  are the pair potentials associated with bound and unbound pairs of particles, resp:  $e = e^\dagger + e^*$ . Then

$$f = f^\dagger + f^* \quad (4)$$

where  $f^\dagger = e^\dagger$ ,  $f^* = e^* - 1$ . All the functions  $h$ ,  $g$ ,  $c$ ,  $m$ , and  $d$  have  $f$ -bond,  $\rho$ -circle expansions; if we re-express these as  $f^\dagger$ -bond,  $f^*$ -bond,  $\rho$ -circle expansions induced by (4) then in these expansions the sum of all terms such that there is at least one  $f^\dagger$ -bond path between the two circles labelled 1 and 2 (root points) defines the connectedness functions  $h^\dagger$ ,  $g^\dagger$ ,  $c^\dagger$ ,  $m^\dagger$ ,  $d^\dagger$ , resp., and the remaining sums define the blocking functions  $h^*$ ,  $g^*$ ,  $c^*$ ,  $m^*$ ,  $d^*$ . We have  $h^\dagger = g^\dagger$ ,  $h^* = g^* - 1$ , and (1) and (2) give rise to the equivalent set of equations

$$h^\dagger = c^\dagger + \rho c^\dagger \bullet h^\dagger \quad (5)$$

$$h^* = c^* + \rho c^\dagger \bullet h^* + \rho c^* \bullet h^\dagger + \rho c^* \bullet h^* \quad (6)$$

$$c^* = f^*[g^* - c^*] + m^* \quad (7)$$

$$m^* = e^*d^* \quad (8)$$

$$c^\dagger = f[g^\dagger - c^\dagger] + f^\dagger[g^* - c^*] + m^\dagger \quad (9)$$

$$m^\dagger = e^\dagger d^\dagger + e^\dagger d^* + e^* d^\dagger \quad (10)$$

where to lowest order in  $\rho$ ,

$$d^\dagger/\rho^2 = \frac{1}{2}d_2^2[f^\dagger f^\dagger] + 2d_2[f^\dagger f^\dagger]d_2[f^\dagger f^*] + d_2[f^\dagger f^\dagger]d_2[f^* f^*] + d_5[f^\dagger f^* f^\dagger f^* f^\dagger] \\ + \frac{1}{2}d_5[f^\dagger f^\dagger f^\dagger f^\dagger] + d_5[f^\dagger f^\dagger f^\dagger f^*] + d_5[f^\dagger f^* f^\dagger f^*] \quad (11)$$

with  $d$  given by (3) and

$$d^* = d - d^\dagger. \quad (12)$$

The PY approximation  $d = 0$  in (1)–(3) induces the approximation in (5)–(12) in which  $d^\dagger = d^* = 0$ . Our next-order approximation is given by (5)–(12). (The generalisations to mixtures, non-uniform systems, and systems with intrinsic  $n$ -body potential terms,  $n \geq 3$ , are all immediate.)

Before treating a specific Hamiltonian we make the general observation that if  $\phi^\ddagger$  is an association potential that binds two atoms or ions into a molecule, then the blocking function  $g^*$  is exactly that part of the full particle-particle  $g$  that corresponds to the probability that two particles are *not* bound and so refers to the probability of finding one particle (e.g., ion or atom) at some point and another particle (e.g., ion or atom) that is *not* part of the same cluster (e.g., molecule) at another point. Since  $g^*$  carries precisely the same information as the function often called the atom-atom or site-site distribution function in earlier formalisms (see, e.g., Chandler and Pratt 1976), our equations represent a new method for treating such functions.

We shall now specialise to a prototypical connectivity problem, that of a system of randomly centred spheres of diameter  $R$ . Here  $\phi = 0$  so  $f = h = c = d = m = 0$ ,  $e = g = 1$ , and  $f^\ddagger = -f^*$ ,  $h^\ddagger = -h^*$ ,  $c^\ddagger = -c^*$ , etc. We choose connectedness to be defined by overlap, so

$$e^\ddagger = \begin{cases} 1 & \text{for } r < R \\ 0 & \text{for } r > R. \end{cases} \quad (13)$$

Then

$$e^* = \begin{cases} 0 & \text{for } r < R \\ 1 & \text{for } r > R. \end{cases} \quad (14)$$

Hence  $\phi^*$ , the blocking potential, is just the hard-sphere potential. Equations (5)–(12) now simplify drastically. They become

$$\begin{aligned} h^\ddagger &= c^\ddagger + \rho c^\ddagger \bullet h^\ddagger \\ c^\ddagger &= d^\ddagger & \text{for } r > R & \quad h^\ddagger = 1 & \text{for } r < R \end{aligned} \quad (16)$$

and

$$\begin{aligned} h^* &= c^* - \rho c^* \bullet h^* \\ c^* &= d^* & \text{for } r > R & \quad h^* = -1 & \text{for } r < R \end{aligned} \quad (17)$$

where  $d^\ddagger$  of (11) to  $O(\rho^2)$  is given by

$$d^\ddagger / \rho^2 = -\frac{1}{2} d_2^2 [f^* f^*] + d_s [f^* f^* f^* f^*] \quad (18)$$

with  $f^*$  the hard-sphere Mayer  $f$ -function and  $d^* = -d^\ddagger$ .

In the PY approximation,  $d^\ddagger = d^* = 0$  in (16) and (17). Moreover, it is worth noting that for athermal Boltzmann factors such as those given by the expression  $e = 1$  and (13) and (14), the PY approximation coincides with the mean spherical (MS) approximation (Lebowitz and Percus 1966). For a hard-sphere potential the PY/MS approximation becomes, from (1) and (2)

$$\begin{aligned} h &= c + \rho c \bullet h \\ c &= 0 & \text{for } r > R & \quad h = -1 & \text{for } r < R. \end{aligned} \quad (19)$$

Comparing (16) and (17) with  $d^\ddagger = d^*$  to (19) we see that in the PY/MS approximation

$$\begin{aligned} h^\ddagger \text{ and } c^\ddagger \text{ at } \rho & \text{ are } -h \text{ and } -c \text{ at } -\rho, \\ h^* \text{ and } c^* \text{ at } \rho & \text{ are } h \text{ and } c \text{ at } -\rho. \end{aligned} \quad (20)$$

Hence there is a precise correspondence in this approximation between the singularities of the connectivity structure for randomly centred spheres at  $\rho$  and those of the thermal

structure for hard spheres at corresponding  $-\rho$ . This correspondence presumably becomes exact in appropriate infinite species and mean field limits as well as in the PY/MS approximation. Klein (1984) has already encountered this correspondence in a mean-field approximation in the context of his  $q$ -species continuous Potts Model (Klein 1982) which reduces to the randomly centred sphere model in the  $q \rightarrow 1$  limit. It is lost in our next approximation, since  $d^+$  is not  $-d$  at  $-\rho$ .

When  $d^+ = 0$  equation (16) has an analytic solution, as it would for  $d^+$  that can be expressed as a linear combination of Yukawa functions (Høye *et al* 1976). The  $d^+$  given by (18) is in fact well approximated by a single Yukawa term; we intend to report in due course a comparison between its predictions using such a term and those of the best available series and computer-simulation studies. When the function  $d$  is expressed in terms of  $h$  and  $\rho$ , it has an ' $h$ -bond,  $\rho$ -circle' representation that, to lowest order in  $\rho$  can also be expressed as in (3), but with all  $f$ 's there replaced by  $g$ 's. The approximation so generated is less easily handled than (3), but may also prove useful in the study of pair connectedness.

The author gratefully acknowledges the financial support of the National Science Foundation.

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