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## Continuum percolation in dipolar fluids

Fernando Vericat†

Instituto de Física de Líquidos y Sistemas Biológicos (IFLYSIB), Universidad Nacional de La Plata, Casilla de Correo 565 (1900) La Plata, Argentina

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**Abstract.** We consider the analytical solution of the mean spherical approximation for the pair-connectedness function of a dipolar hard-sphere fluid. Based on this solution, we propose an exponential approach to the continuum percolation of dipolar fluids.

### 1. Introduction

The pair-connectedness function  $\rho^\dagger(\mathbf{1}, \mathbf{2})$  (Coniglio *et al* 1977) is a very suitable tool to describe molecular clustering in fluids. This is the probability density for two molecules, labelled 1 and 2, to be in the differential elements  $d\mathbf{1}$  and  $d\mathbf{2}$  around their coordinates specified by  $\mathbf{1}$  and  $\mathbf{2}$ , respectively, with both molecules belonging to the same cluster. We consider that two molecules of the fluid belong to the same cluster if they are either directly connected to each other or indirectly connected through a path of directly connected molecules. The concept of directly connected particles is eventually dependent on the particular definition of the model.

The connectedness correlation functions, although useful from a theoretical point of view, are not directly measurable. Actually, in percolation studies, one is more interested in the threshold percolation density  $\rho_c$ , which in fact is a measurable quantity. Theoretically, we interpret  $\rho_c$  as the critical density at which the molecules in the fluid are connected to such an extension as to constitute clusters of macroscopic size. At this point it is convenient to introduce the total pair-connectedness function given by  $h^\dagger(\mathbf{1}, \mathbf{2}) = (\rho/4\pi)^{-1}\rho^\dagger(\mathbf{1}, \mathbf{2}) - 1$  with  $\rho$  the number density. In terms of  $h^\dagger(\mathbf{1}, \mathbf{2})$ , the mean cluster size is defined as (where  $V =$  sample volume)

$$s(\rho) = 1 + \frac{\rho}{V} \int d\mathbf{1} d\mathbf{2} h^\dagger(\mathbf{1}, \mathbf{2}) \quad (1)$$

in close analogy with the compressibility equation. Therefore  $\rho_c$  satisfies

$$s(\rho_c) \rightarrow \infty. \quad (2)$$

In the last few years, the problem of obtaining the pair-connectedness functions for several models of atomic fluids has been addressed through the solution of integral equations (Chiew and Glandt 1983, Chiew *et al* 1985, Stell 1984, DeSimone *et al* 1986a, b). These models involve particles that interact among them via central forces.

† Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina.

In this work, we consider the percolation problem for a system with orientation-dependent interactions, namely a dipolar hard-sphere fluid, which is an ensemble of hard spheres of diameter  $\sigma$  with a central point dipole moment  $\mu$ . Two particles are taken as directly connected to each other if their centres are at distances shorter than a given value  $d$ .

We show how the pair-connectedness functions for this model can be obtained in analytical form using the mean spherical approximation (MSA) of Lebowitz and Percus (1966), conveniently adapted to connectivity.

The possibility of having an analytical solution emerges in a natural way from Wertheim's MSA solution (Wertheim 1971, Hansen and McDonald 1976) for the ordinary correlation functions of the dipolar hard-sphere fluid and from the work of DeSimone *et al* (1986a, b), where the analytical Percus–Yevick connectedness functions of extended hard spheres are reported for connectivity distances such that  $\sigma < d < 2\sigma$ .

As Wertheim has so elegantly shown, the solution of the MSA for the dipolar hard-sphere fluid reduces to the solution of three Percus–Yevick integral equations for three hypothetical hard-sphere fluids, one for each term in the invariant expansion of the dipole–dipole correlation functions. A similar separation can be achieved in solving the connectivity problem. Therefore, the problem becomes analytically tractable for connectivity distances that satisfy  $\sigma < d < 2\sigma$ .

However, the MSA expansion for the pair-connectedness function has the very undesirable property that its hard-sphere term is completely decoupled from the dipolar contributions. Therefore the mean cluster size in equation (1) does not depend at all on the dipolar interaction.

A related theory which still preserves the analyticity of the MSA is the exponential approximation (EXP) (Andersen and Chandler 1972). In this approximation, adapted to connectivity, the mean cluster size can be written as a function of the dipolar strength in terms of the generalised Bessel functions recently reported by Blum and Torruella (1988). The same is true for the connectedness version of the reference average Mayer function (RAM) theory (Smith 1974, Perram and White 1974) and the  $y$  expansion of Gubbins and Gray (1972). We briefly discuss these exponential expressions in connection with the percolation of dipolar fluids.

## 2. Mean spherical approximation (MSA) pair-connectedness function

We denote the coordinates of a given molecule, labelled  $i$ , by  $i \equiv (\bar{r}_i, \hat{\Omega}_i)$ , where  $\bar{r}_i$  is the position of the sphere centre and  $\hat{\Omega}_i$  gives the orientation of the point dipole.

All distances are expressed in units of the sphere diameter  $\sigma$ . Define  $\rho^* = \rho\sigma^3$ ,  $\alpha = d/\sigma$  and  $\mu^{*2} = \beta\mu^2/\sigma^3$  where  $\beta$  is the Boltzmann thermal factor.

The pair interaction between two such dipolar molecules is

$$\beta V(\mathbf{1}, \mathbf{2}) = \begin{cases} \infty & r_{12} < 1 \\ -(\mu^{*2}/r_{12}^3)[3(\hat{\Omega}_1 \cdot \hat{r}_{12})(\hat{\Omega}_2 \cdot \hat{r}_{12}) - (\hat{\Omega}_1 \cdot \hat{\Omega}_2)] & r_{12} > 1. \end{cases} \quad (3)$$

Here  $r_{12}$  is the magnitude and  $\hat{r}_{12}$  the direction of the vector of  $\bar{r}_{12} = \bar{r}_1 - \bar{r}_2$ .

Two pair potentials appropriate for connected and disconnected molecules, respectively, are naturally defined

$$V^\dagger(\mathbf{1}, \mathbf{2}) = \begin{cases} V(\mathbf{1}, \mathbf{2}) & r_{12} < \alpha \\ \infty & r_{12} > \alpha \end{cases} \quad (4)$$

$$V^*(\mathbf{1}, \mathbf{2}) = \begin{cases} \infty & r_{12} < \alpha \\ V(\mathbf{1}, \mathbf{2}) & r_{12} > \alpha \end{cases} \quad (5)$$

with  $V(\mathbf{1}, \mathbf{2})$  the 'true' potential given in equation (3).

Following Hill (1955), we can further separate the Boltzmann factor  $e(\mathbf{1}, \mathbf{2}) = \exp[-\beta V(\mathbf{1}, \mathbf{2})]$  as a sum of two terms

$$e(\mathbf{1}, \mathbf{2}) = e^\dagger(\mathbf{1}, \mathbf{2}) + e^*(\mathbf{1}, \mathbf{2}). \quad (6)$$

Here the Boltzmann factors  $e^\dagger(\mathbf{1}, \mathbf{2})$  and  $e^*(\mathbf{1}, \mathbf{2})$  are proportional to the probabilities of finding particles 1 and 2 in the elements  $d\mathbf{1}$  and  $d\mathbf{2}$  when they are directly connected and disconnected, respectively

$$e^\dagger(\mathbf{1}, \mathbf{2}) = \exp[-\beta V^\dagger(\mathbf{1}, \mathbf{2})] \quad (7)$$

$$e^*(\mathbf{1}, \mathbf{2}) = \exp[-\beta V^*(\mathbf{1}, \mathbf{2})]. \quad (8)$$

Since  $e(\mathbf{1}, \mathbf{2})$  is the statistical weight in the configuration integrals, any pair of statistical functions can be separated as  $e(\mathbf{1}, \mathbf{2})$  in equation (6). Thus, the total and the direct correlation functions are written

$$h(\mathbf{1}, \mathbf{2}) = h^\dagger(\mathbf{1}, \mathbf{2}) + h^*(\mathbf{1}, \mathbf{2}) \quad (9)$$

$$c(\mathbf{1}, \mathbf{2}) = c^\dagger(\mathbf{1}, \mathbf{2}) + c^*(\mathbf{1}, \mathbf{2}). \quad (10)$$

We focus on the total connectedness function. The MSA equation for  $h^\dagger(\mathbf{1}, \mathbf{2})$  reads

$$h^\dagger(\mathbf{1}, \mathbf{2}) = c^\dagger(\mathbf{1}, \mathbf{2}) + (\rho^*/4\pi) \int d\mathbf{3} h^\dagger(\mathbf{1}, \mathbf{3}) c^\dagger(\mathbf{3}, \mathbf{2}) \quad (11)$$

$$h^\dagger(\mathbf{1}, \mathbf{2}) = g(\mathbf{1}, \mathbf{2}) \quad r < \alpha \quad (12)$$

$$c^\dagger(\mathbf{1}, \mathbf{2}) = 0 \quad r > \alpha. \quad (13)$$

Here  $g(\mathbf{1}, \mathbf{2}) = h(\mathbf{1}, \mathbf{2}) + 1$ ,  $h(\mathbf{1}, \mathbf{2})$  being the total correlation function for the dipolar hard-sphere fluid.

Wertheim's solution of  $h(\mathbf{1}, \mathbf{2})$  in the MSA (Wertheim 1971) is expanded in terms of the following three rotational invariants (we use Blum's (1978) notation):

$$\Phi^{000}(\mathbf{1}, \mathbf{2}) = 1$$

$$\Phi^{110}(\mathbf{1}, \mathbf{2}) = -3^{1/2}(\hat{\Omega}_1 \cdot \hat{\Omega}_2) \quad (14)$$

$$\Phi^{112}(\mathbf{1}, \mathbf{2}) = (3/10)^{1/2} [3(\hat{\Omega}_1 \cdot \hat{r})(\hat{\Omega}_2 \cdot \hat{r}) - (\hat{\Omega}_1 \cdot \hat{\Omega}_2)].$$

Therefore  $h^\dagger(\mathbf{1}, \mathbf{2})$  and  $c^\dagger(\mathbf{1}, \mathbf{2})$  have a similar invariant expansion

$$f^\dagger(\mathbf{1}, \mathbf{2}) = f^{\dagger 000}(r)\Phi^{000}(\mathbf{1}, \mathbf{2}) + f^{\dagger 110}(r)\Phi^{110}(\mathbf{1}, \mathbf{2}) + f^{\dagger 112}(r)\Phi^{112}(\mathbf{1}, \mathbf{2}) \quad (15)$$

with  $f^\dagger \equiv h^\dagger$  or  $c^\dagger$ .

The connectedness Ornstein-Zernike (OZ) equation (11), decouples into three independent equations. To this end, we first go to  $k$ -space using ( $\bar{F} \equiv \bar{H}$  or  $\bar{C}$ )

$$\bar{F}_\chi^{\dagger m}(k) = \sum_{l=0}^{2m} (-1)^\chi \begin{pmatrix} m & m & l \\ \chi & -\chi & 0 \end{pmatrix} 4\pi i^l \int_0^r dr r^2 j_l(kr) f^{\dagger mml}(r) \quad (16)$$

where  $(m, \chi) = (0, 0)$ ,  $(1, 0)$  and  $(1, 1)$ ,  $j_l(x)$  is the spherical Bessel function of order  $l$

and we use the notation and conventions of Edmonds (1957) for the 3- $j$  symbols. We have (Blum and Torruella 1972)

$$\tilde{H}_\chi^{+m}(k) = \tilde{C}_\chi^{+m}(k) + \rho^* \tilde{H}_\chi^{+m}(k) \tilde{C}_\chi^{+m}(k). \quad (17)$$

These equations are transformed back to real space by means of

$$f_\chi^{+m}(r) = (-1)^x 4\pi(2\pi)^{-3/2} \int_0^\infty dk k^2 j_l(kr) \tilde{F}_\chi^{+m}(k) \quad (18)$$

and

$$\tilde{f}_\chi^{+m}(r) = (-1)^x f_\chi^{+m}(r) / K_\chi^m. \quad (19)$$

Here  $K_0^0 = 1$ , while  $K_0^1 (= -2K_1^1)$  satisfies Wertheim's equation

$$q(2\xi) - q(-\xi) = (4\pi/3)\rho^* \mu^{*2} \quad (20)$$

with  $\xi = K_0^1 \rho^* / 12$  and  $q(x) = (1 + 2x)^2 / (1 - x)^4$ .

Therefore we obtain

$$\bar{h}_\chi^{+m}(r) = \bar{c}_\chi^{+m}(r) + \rho_\chi^m \int dt \bar{h}_\chi^{+m}(|r-t|) \bar{c}_\chi^{+m}(t) \quad (21)$$

with  $\rho_\chi^m = K_\chi^m \rho^*$ .

The original ( $f^{+mm'l}$ ) and the auxiliary functions ( $\tilde{f}_\chi^{+m}$ ) are related by Blum (1978)

$$\tilde{f}_0^{+0}(r) = f^{+000}(r)$$

$$\tilde{f}_0^{+1}(r) = -(1/3)^{1/2} f^{+110}(r) + (2/15)^{1/2} \left( f^{+112}(r) - 3 \int_r^\infty dt f^{+112}(t)/t \right) \quad (22)$$

$$\tilde{f}_1^{+1}(r) = (1/3)^{1/2} f^{+110}(r) + (1/30)^{1/2} \left( f^{+112}(r) - 3 \int_r^\infty dt f^{+112}(t)/t \right).$$

Therefore, the closures of equation (21) are ( $\delta_{nm} =$  Kronecker delta)

$$\bar{h}_\chi^{+m}(r) = \bar{g}_\chi^m(r) - \delta_{1m} \quad r < \alpha \quad (23)$$

$$\bar{c}_\chi^{+m}(r) = 0 \quad r > \alpha. \quad (24)$$

The function  $\bar{g}_\chi^m(r)$  is the Percus-Yevick correlation function (Percus and Yevick 1958) for a system of hard spheres of diameter 1 and density  $\rho_\chi^m$ :  $\bar{g}_\chi^m(r) = g^{(PY)}(r; \rho_\chi^m)$ . If  $1 < \alpha < 2$ , then we just need to know  $g^{(PY)}(r; \rho_\chi^m)$  in the interval  $1 < r < 2$  (for  $r < 1$  it is identically zero). In the interval  $1 < r < 2$ ,  $g^{(PY)}(r; \rho_\chi^m)$  is given in terms of  $\eta = \pi\rho_\chi^m/6$  by (Thiele 1963, Wertheim 1963)

$$rg^{(PY)}(r; \rho_\chi^m) = \sum_{j=0}^2 A_j \exp[z_j(r-1)] \quad (25)$$

where

$$A_j = Q(z_j)/P'(z_j) \quad (26)$$

with

$$Q(s) = (a_3s^2 - a_0s)/12\eta \quad (27)$$

$P'(s)$  the derivative of the polynomial

$$P(s) = s^3 + a_2s^2 + a_1s + a_0 \quad (28)$$

and  $z_j$  ( $j = 0, 1, 2$ ) the three roots of the algebraic equation  $P(s) = 0$ . In these equations,

$$\begin{aligned} a_0 &= -12\eta a & a_2 &= 12\eta(a/2 + b) \\ a_1 &= -12\eta b & a_3 &= 12\eta(a + b) \end{aligned} \quad (29)$$

with

$$a = (1 + 2\eta)/(1 - \eta)^2 \quad b = -3\eta/2(1 - \eta)^2. \quad (30)$$

The problem of finding the pair-connectedness functions (equation (15)) has been reduced to solving the integral equation given by equations (21), (23) and (24). In the Appendix, we outline its solution following Baxter's factorisation technique (Baxter 1968).

The mean cluster size is obtained by inserting the invariant expansion (15) for the total connectedness function into equation (1). We have

$$s(\rho) = 1 + 4\pi\rho \int_0^\infty dr r^2 h^{*000}(r). \quad (31)$$

Since equation (21) for  $h_0^{*0}(r)$  decouples completely from the corresponding equations for  $h_0^{*1}(r)$  and  $\bar{h}_1^{*1}(r)$ , we see that  $h^{*000}(r)$  is the pair-connectedness function for extended hard sphere (DeSimone *et al* 1986a, b) and it does not depend on the dipole strength. Therefore, the critical density obtained from equation (2) is the same as for simple hard spheres. In short, the MSA critical density does not take into account the dipoles.

The conclusion is that the MSA by itself is not useful for describing the percolation threshold of dipolar, and in general multipolar, fluids. However, the MSA is susceptible to extensions where this disadvantage is overcome. In the next section, we explore some of these possible extensions.

### 3. Exponential approaches to percolation

The shortcomings of the MSA for describing the structure of dipolar fluids are well known. Nowadays, several theories which improve the MSA correlation functions are available. Integral equations, such as the linearised (LHNC) are quadratic (QHNC) hypernetted-chain approximation (Patey 1977, 1978), as well as some perturbation theories, have been demonstrated to be superior to the MSA for dipolar fluids. Within these last theories, we mention the exponential (EXP) approximation of Andersen and Chandler (1972), the perturbation theory of Gubbins and Gray (1972) and the reference average Mayer function theory (RAM) (Smith 1974, Perram and White 1974).

All these approximations (except the LHNC) are non-linear. Therefore, the angular average of the total correlation function of a dipolar fluid is coupled to the remaining harmonic projections and depends on the dipole strength. As a consequence, the

compressibility, which is proportional to the angular average, also depends on the dipole moment of the molecules. Thus, they are good candidates to improve also the connectedness MSA because they take into account the effect of the dipole–dipole interaction over the mean cluster size.

In the application of the perturbation theories to dipolar hard spheres, the complete pair potential (equation (3)) is split

$$V(\mathbf{1}, \mathbf{2}) = V_0(\mathbf{1}, \mathbf{2}) + \omega(\mathbf{1}, \mathbf{2}) \quad (32)$$

with

$$V_0(r) = V^{000}(r) = \begin{cases} \infty & r < 1 \\ 0 & r > 1 \end{cases} \quad (33)$$

(the reference pair potential) and

$$\beta\omega(\mathbf{1}, \mathbf{2}) = \beta V^{112}(r)\Phi^{112}(\mathbf{1}, \mathbf{2}) = -(10/3)^{1/2}(\mu^*2/r^3)\Phi^{112}(\mathbf{1}, \mathbf{2}) \quad (34)$$

the dipolar interaction, which is taken as the perturbation.

The EXP pair correlation function is (Andersen and Chandler 1972)

$$g(\mathbf{1}, \mathbf{2}) = g_0(r) \exp[C(\mathbf{1}, \mathbf{2})]. \quad (35)$$

Here,  $g_0(r) = g^{000}(r)$  denotes the reference pair correlation function and  $C(\mathbf{1}, \mathbf{2})$  is the renormalised potential, sum of generalised chains whose bonds are  $h^{000}(r)$  and  $\beta\omega(\mathbf{1}, \mathbf{2})$  functions. The renormalised potential can be expressed in terms of the MSA solution:

$$C(\mathbf{1}, \mathbf{2}) = h_{\text{MSA}}(\mathbf{1}, \mathbf{2}) - h_{\text{MSA}}^{000}(r) = h_{\text{MSA}}^{110}(r)\Phi^{110}(\mathbf{1}, \mathbf{2}) + h_{\text{MSA}}^{112}(r)\Phi^{112}(\mathbf{1}, \mathbf{2}). \quad (36)$$

From equation (35), we see that the connectedness part of the total correlation function is

$$h^\dagger(\mathbf{1}, \mathbf{2}) = g^\dagger(\mathbf{1}, \mathbf{2}) = g_0^\dagger(r) \exp[C(\mathbf{1}, \mathbf{2})] + g_0^*(r) \{\exp[C(\mathbf{1}, \mathbf{2})]\}^\dagger. \quad (37)$$

Here,  $\{\exp[C(\mathbf{1}, \mathbf{2})]\}^\dagger$  denotes the subset of diagrams of  $\exp[C(\mathbf{1}, \mathbf{2})]$  whose root points 1 and 2 belong to the same cluster. We make the further approximation

$$\{\exp[C(\mathbf{1}, \mathbf{2})]\}^\dagger \simeq \exp[C^\dagger(\mathbf{1}, \mathbf{2})] \quad (38)$$

with  $C^\dagger(\mathbf{1}, \mathbf{2})$  the connectedness part of  $C(\mathbf{1}, \mathbf{2})$ :

$$C^\dagger(\mathbf{1}, \mathbf{2}) = h_{\text{MSA}}^{+110}(r)\Phi^{110}(\mathbf{1}, \mathbf{2}) + h_{\text{MSA}}^{+112}(r)\Phi^{112}(\mathbf{1}, \mathbf{2}). \quad (39)$$

Here  $h^{+110}(r)$  and  $h^{+112}(r)$  are the (110) and (112) radial coefficients in the invariant expansion (15) of the MSA total connectedness function  $h^\dagger(\mathbf{1}, \mathbf{2})$ .

The approximation (38) implies discarding all the diagrams of  $\{\exp[C(\mathbf{1}, \mathbf{2})]\}^\dagger$  which are not products of diagrams of  $C^\dagger(\mathbf{1}, \mathbf{2})$ . Then (37) yields

$$h^\dagger(\mathbf{1}, \mathbf{2}) = g_{\text{MSA}}^{+000}(r) \exp[C(\mathbf{1}, \mathbf{2})] + [g_{\text{MSA}}^{000}(r) - g_{\text{MSA}}^{+000}(r)] \exp[C^\dagger(\mathbf{1}, \mathbf{2})] \quad (40)$$

with  $C(\mathbf{1}, \mathbf{2})$  and  $C^\dagger(\mathbf{1}, \mathbf{2})$  given by equations (36) and (39), respectively.

The substitution of  $h^\dagger(\mathbf{1}, \mathbf{2})$  in (1) for equation (40) gives the mean cluster size. Then, from equation (2), the critical percolation density can be obtained.

The integrations involved are greatly simplified if the invariant expansion for the exponential of tensorial expressions, recently reported by Blum and Torruella (1988), is used. Instead of expanding the renormalised potentials  $C(\mathbf{1}, \mathbf{2})$  and  $C^\dagger(\mathbf{1}, \mathbf{2})$  in the

invariant representation (equations (39) and (36)), it is convenient to expand them in the irreducible representation (Blum 1978, Blum and Torruella 1988). We have

$$C^+(\mathbf{1}, \mathbf{2}) = \tilde{h}^{+0}(r)\Phi_0^{11}(\mathbf{1}, \mathbf{2}) + \tilde{h}^{+1}(r)[\Phi_1^{11}(\mathbf{1}, \mathbf{2}) + \Phi_{-1}^{11}(\mathbf{1}, \mathbf{2})] \quad (41)$$

and an analogous expression for  $C(\mathbf{1}, \mathbf{2})$ .

The irreducible angular functions are given in terms of the generalised spherical harmonics  $D_{\chi}^m(\hat{\Omega})$  (Edmonds 1957) by

$$\Phi_{\chi}^{mn}(\mathbf{1}, \mathbf{2}) = [(2m+1)(2n+1)]^{1/2} D_{0\chi}^m(\hat{\Omega}_1) D_{0\chi}^n(\hat{\Omega}_2). \quad (42)$$

The radial coefficients in equation (41) are related to the radial coefficients in the invariant expansion (39) according to

$$\begin{aligned} \tilde{h}^{+0}(r) &= (1/3)^{1/2} h_{\text{MSA}}^{+110}(r) - (2/15)^{1/2} h_{\text{MSA}}^{+112}(r) \\ \tilde{h}^{+1}(r) &= -(1/3)^{1/2} h_{\text{MSA}}^{+110}(r) - (1/30)^{1/2} h_{\text{MSA}}^{+112}(r). \end{aligned} \quad (43)$$

Similar relations are defined for the projections of  $C(\mathbf{1}, \mathbf{2})$ .

According to Blum and Torruella (1988), the exponential  $\exp[C^+(\mathbf{1}, \mathbf{2})]$  is expanded

$$\exp[C^+(\mathbf{1}, \mathbf{2})] = \sum_{m n \chi} i_{\chi}^{mn} \{ \tilde{h}_{\text{MSA}}^{+0}(r); \tilde{h}_{\text{MSA}}^{+1}(r) \} \Phi_{\chi}^{mn}(\mathbf{1}, \mathbf{2}). \quad (44)$$

The indices take the values  $(m, n, \chi) = (0, 0, 0), (1, 1, 0), (1, 1, 1)$  and  $(1, 1, -1)$ . We have explicitly indicated that the generalised Bessel functions  $i_{\chi}^{mn}$  are functionals of the irreducible functions  $\tilde{h}_{\text{MSA}}^{+0}(r)$  and  $\tilde{h}_{\text{MSA}}^{+1}(r)$ . The corresponding expression for  $\exp[C(\mathbf{1}, \mathbf{2})]$  is obtained by eliminating all daggers in equation (44).

When expression (40) for  $h^+(\mathbf{1}, \mathbf{2})$ , with the exponentials given by their irreducible expansions (44), is substituted in formula (1), we can see that the only terms of the irreducible expansions that contribute to the mean cluster size are those in which  $(m, n, \chi) = (0, 0, 0)$ .

The mean cluster size reads

$$s(\rho) = 1 + 4\pi\rho \int_1^{\infty} dr r^2 (h^+(\mathbf{1}, \mathbf{2}))^{000} \quad (45)$$

with

$$\begin{aligned} (h^+(\mathbf{1}, \mathbf{2}))^{000} &= g_{\text{MSA}}^{+000}(r) i_0^{00} \{ \tilde{h}_{\text{MSA}}^0(r); \tilde{h}_{\text{MSA}}^1(r) \} \\ &+ [g_{\text{MSA}}^{000}(r) - g_{\text{MSA}}^{+000}(r)] i_0^{00} \{ \tilde{h}_{\text{MSA}}^{+0}(r); \tilde{h}_{\text{MSA}}^{+1}(r) \}. \end{aligned} \quad (46)$$

In this case, the generalised Bessel functions take a simple form (Blum and Torruella 1988)

$$i_0^{00} \{ f^0(r); f^1(r) \} = \frac{1}{2} \int_{-1}^1 dz i_0(3\{[f^1(r)]^2 - z^2[f^0(r)]^2 - z^2[f^1(r)]^2\}^{1/2}). \quad (47)$$

Here,  $i_0(x) = \sinh(x)/x$  is the spherical modified Bessel function of zero order.

Other perturbation theories can be worked in the same way. For example, the first-order  $y$  expansion of Gubbins and Gray (1972)

$$g(\mathbf{1}, \mathbf{2}) = g_0(r) \exp[-\beta\omega(\mathbf{1}, \mathbf{2})] \quad (48)$$

where  $g_0(r)$  denotes the pair correlation function for the reference potential in equation (32). We can use  $g_0(r) = g_{\text{MSA}}^{000}(r)$ .



The connectedness pair correlation is

$$g^+(\mathbf{1}, \mathbf{2}) = g_{\text{MSA}}^{+000}(r) \exp[-\beta\omega(\mathbf{1}, \mathbf{2})] + [g_{\text{MSA}}^{000}(r) - g_{\text{MSA}}^{+000}(r)] \exp[-\beta\omega^+(\mathbf{1}, \mathbf{2})] \quad (49)$$

with  $\omega^+(\mathbf{1}, \mathbf{2})$  the perturbative part of the connectedness pair potential (4).

The Boltzmann factors  $\exp[-\beta\omega^+(\mathbf{1}, \mathbf{2})]$  and  $\exp[-\beta\omega(\mathbf{1}, \mathbf{2})]$  have irreducible expansions similar to equation (44). The generalised Bessel functions are now functionals of

$$\begin{aligned} \tilde{\omega}^{+0}(r) &= \begin{cases} \tilde{\omega}^0(r) & r < \alpha \\ \infty & r > \alpha \end{cases} \\ \tilde{\omega}^{+1}(r) &= \begin{cases} \tilde{\omega}^1(r) & r < \alpha \\ \infty & r > \alpha \end{cases} \end{aligned} \quad (50)$$

and

$$\begin{aligned} \beta\tilde{\omega}^0(r) &= -(2/3)^{1/2} \mu^*{}^2 / r^3 \\ \beta\tilde{\omega}^1(r) &= -(1/3)^{1/2} \mu^*{}^2 / r^3. \end{aligned} \quad (51)$$

The final expression for the mean cluster size is formally given by equations (45) and (46) but with  $\beta\tilde{\omega}^0$ ,  $\beta\tilde{\omega}^1$ ,  $\beta\tilde{\omega}^{+0}$  and  $\beta\tilde{\omega}^{+1}$  instead of  $\tilde{h}_{\text{MSA}}^0$ ,  $\tilde{h}_{\text{MSA}}^1$ ,  $\tilde{h}_{\text{MSA}}^{+0}$  and  $\tilde{h}_{\text{MSA}}^{+1}$ , respectively. Also, the integral involving  $\exp(-\beta\omega^+)$  has  $\alpha$ , instead of  $\infty$ , as upper limit.

#### 4. Concluding remarks

We have outlined the solution of the MSA for the pair connectedness function of a dipolar hard-sphere fluid in which two molecules are considered as directly connected when the mutual separation is shorter than a given distance  $d$ .

Assuming that the pair connectedness functions have an invariant expansion similar to that proposed by Wertheim for the ordinary pair correlation functions in a dipolar fluid, then the connectedness MSA integral equation decouples into three independent connectedness Percus–Yevick (or MSA) integral equations for extended hard spheres of the same diameter and at Wertheim's 'densities'.

As we show in the Appendix, the connectedness Percus–Yevick (or MSA) equation for hard spheres transforms into a system of two coupled fourth-order, linear, non-homogeneous equations with the proper boundary conditions. This system is solvable using the regular techniques for differential equations (e.g. D'Alembert substitution).

The MSA connectedness correlation functions give a mean cluster size which completely ignores the dipole strength. The reason for this is that the angular average of  $h^+(\mathbf{1}, \mathbf{2})$  equals the (0, 0, 0) projection  $h^{+000}(r)$  and that the integral equation for  $h^{+000}(r)$  is simply the equation for neutral hard spheres.

Perturbative approximations, such as the EXP approximation of Andersen and Chandler or the first-order  $y$  expansion of Gubbins and Gray, instead, have an angular average which mixes the different projections of the MSA connectedness correlation functions, giving a mean cluster size which does depend on the dipole strength. These or similar approaches should be a simple route in order to study, at least at a qualitative level of accuracy, the dependence of the dipole–dipole interactions on the critical percolation density in continuous systems.

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### Appendix

In this Appendix, we outline the steps we need to solve, in analytical form, the integral equation defined by equations (21), (23) and (24). To this end we use Baxter's factorisation technique (Baxter 1968). The analytical solution exists for connectivity distances  $d$  such that  $1 < d < 2$ .

As we have discussed in the text, for each of the three sets of indices  $(m, \chi) = (0, 0)$ ,  $(1, 0)$  and  $(1, 1)$ , equations (21), (23) and (24) define an integral equation for  $\bar{h}_\chi^{+m}(r)$  in  $r < \alpha$  and  $\bar{c}_\chi^{+m}(r)$  in  $r > \alpha$ . In order to simplify the notation, in what follows, we will omit the indices  $m$  and  $\chi$ , except in the Kronecker delta.

Using Baxter's factorisation, equation (21) is rewritten

$$r\bar{h}^+(r) = -q'(r) + 12\eta \int_0^\alpha dt (r-t)\bar{h}^+(|r-t|)q(t) \quad (r > 0) \quad (\text{A1})$$

with  $q'(r) = dq(r)/dr$ .

If the function  $q(r)$  is known, then (A1) is a Fredholm-type integral equation from which  $\bar{h}^+(r)$  can be obtained for  $r > \alpha$ . In particular Perram's method (Perram 1975) is a very suitable route for solving it in numerical form.

The Baxter function  $q(r)$  is zero for  $r \geq \alpha$ . In order to determine it for  $0 < r < \alpha$ , we divide the interval  $(0, \alpha)$  into three sub-intervals,  $(0, \alpha - 1)$ ,  $(\alpha - 1, 1)$  and  $(1, \alpha)$ , and write

$$q(r) = \begin{cases} q_1(r) & 0 < r < \alpha - 1 \\ q_2(r) & \alpha - 1 < r < 1 \\ q_3(r) & 1 < r < \alpha. \end{cases} \quad (\text{A2})$$

For  $r < \alpha$ , equation (A1) can be written (using equation (23))

$$rg^{(\text{PY})}(r) = (\bar{a}r + \bar{b})\delta_{1m} - q'(r) + 12\eta \int_0^\alpha dt (r-t)g^{(\text{PY})}(|r-t|)q(t) \quad (\text{A3})$$

with

$$\bar{a} = 1 - 12\eta \int_0^\alpha dt q(t) \quad \bar{b} = 12\eta \int_0^\alpha dt tq(t). \quad (\text{A4})$$

Therefore for  $\alpha - 1 < r < 1$ , we have

$$q(r) = q_2(r) = (\bar{a}r^2/2 + \bar{b}r)\delta_{1m} + \bar{c} \quad (\text{A5})$$

while for  $0 < r < \alpha - 1$  equation (A3) can be written in two alternative forms

$$q_1'(r) = (\bar{a}r + \bar{b})\delta_{1m} - 12\eta \int_{r+1}^{\alpha} dt (t-r)g^{(\text{PY})}(t-r)q_3(t-1) \quad (\text{A6})$$

$$q_3'(r) = -(r+1)g^{(\text{PY})}(r+1) + (\bar{a}r + \bar{b})\delta_{1m} + 12\eta \times \int_0^r dt (r+1-t)g^{(\text{PY})}(r+1-t)q_1(t). \quad (\text{A7})$$

By repeatedly differentiating equations (A6) and (A7), we obtain

$$q_1^{\text{iv}}(r) - a_2q_1'''(r) + a_1q_1''(r) - a_0q_1'(r) - a_0q_3'(r) - a_3q_3''(r) = (-a_0\bar{a}r + a_1\bar{a} - a_0\bar{b})\delta_{1m} \quad (\text{A8})$$

$$q_3^{\text{iv}}(r) + a_2q_3'''(r) + a_1q_3''(r) + a_0q_3'(r) + a_0q_1'(r) - a_3q_1''(r) = (a_0\bar{a}r + a_1\bar{a} + a_0\bar{a} + a_0\bar{b})\delta_{1m}. \quad (\text{A9})$$

For  $m = 0$ ,  $\delta_{1m} = 0$  and we have the system of linear homogeneous equations considered by DeSimone *et al* (1986a) for the connectedness of extended hard spheres. For  $m = 1$ , we are left with a system of two coupled, fourth-order, linear, non-homogeneous differential equations. It transforms by using D'Alembert substitution into a system of six first-order, linear differential equations.

In order to determine  $q_2(r)$ ,  $q_1(r)$  and  $q_3(r)$  completely from equations (A5), (A8) and (A9) (or from the resulting system of six equations), we need nine boundary conditions (one for  $\bar{c}$ ), apart from the conditions (A4) for  $\bar{a}$  and  $\bar{b}$ . They are

$$\begin{aligned} q_3(\alpha - 1) &= 0 \\ q_1(\alpha - 1) &= q_2(\alpha - 1)\delta_{1m} = [\bar{a}(\alpha - 1)^2/2 + \bar{b} + \bar{c}]\delta_{1m} \\ q_3(0) &= q_2(1)\delta_{1m} = (\bar{a}/2 + \bar{b} + \bar{c})\delta_{1m} \\ q_1'(\alpha - 1) &= [\bar{a}(\alpha - 1) + \bar{b}]\delta_{1m} \\ q_3'(0) &= -H(0) + (\bar{a} + \bar{b})\delta_{1m} \\ q_1''(\alpha - 1) &= a_3q_3(\alpha - 1) + \bar{a}\delta_{1m} \\ q_3''(0) &= -H'(0) + a_3q_1(0) + \bar{a}\delta_{1m} \\ q_1'''(\alpha - 1) &= [a_0 - a_2(a_0 + a_1)]q_3(\alpha - 1) + a_3q_3'(\alpha - 1) \\ q_3'''(0) &= -H''(0) - [a_0 - a_2(a_0 + a_1)]q_1(0) + a_3q_1'(0). \end{aligned} \quad (\text{A10})$$

In these equations we have used

$$H(r) = (r+1)g^{(\text{PY})}(r+1). \quad (\text{A11})$$

Thus,

$$\begin{aligned}
 H(0) &= (a + b) = (1 + \eta/2)/(1 - \eta)^2 \\
 H'(0) &= a - 12\eta(a/2 + b)(a + b) = -(5\eta^2 + 5\eta - 1)/(1 - \eta)^3 \quad (\text{A12}) \\
 H''(0) &= \eta(21\eta^2 + 12\eta - 6)/(1 - \eta)^4.
 \end{aligned}$$

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