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COMMENT

## Exact pair-connectedness function of a one-dimensional hard rod fluid

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**Abstract.** Assuming that two molecules of a fluid are connected (i.e. belong to the same cluster) when their centres are closer than a given distance  $d$ , we present, in explicit form, the exact pair-connectedness function for a one-dimensional fluid of hard rods of length  $\sigma$  such that  $\sigma < d < 2\sigma$  and for densities which are compatible with the existence of a region of translational invariance in the system.

In order to study the continuum percolation problem in interacting systems, DeSimone *et al* (1986a, b) have recently applied the Percus-Yevick integral equation for connectivity in liquids (Chiew and Glandt 1983, Chiew *et al* 1985) to an extended hard sphere model. In the model the molecules of the fluid are hard spheres of diameter  $\sigma$ . Two molecules of such fluid are considered directly connected if their centres are at a distance shorter than a certain pre-established value  $d$ .

The percolation problem is to calculate the minimum particle density necessary to have a macroscopic physical cluster (Hill 1955). We must understand that two molecules of the fluid belong to the same cluster if they are either directly connected or indirectly connected through a path of directly connected intermediary molecules.

At first sight, the same system seems to be much less interesting when it is considered in one dimension. In fact, in this case, the molecules become simple impenetrable hard rods (of length  $\sigma$ ) moving on a line and the critical percolation density is, for  $\sigma < d < 2\sigma$ , trivially equal to  $\sigma^{-1}$ .

However, even from the percolation point of view, the interesting aspect of the one-dimensional version of the hard sphere model is that, as we show in this comment, the pair-connectedness function admits an exact analytical expression. This way we have at our disposal an exact result for the pair connectedness that can be used as a 'laboratory' in order to test several approximate theories which can eventually be applied to the more realistic case of hard spheres in three dimensions.

For a system of  $N$  hard rods of length  $\sigma$  whose positions  $x_i$  ( $i = 1, 2, \dots, N$ ) are constrained to the segment  $[0, L]$ , the ordinary pair distribution function  $\rho(x_1, x_2)$ , which is the probability of finding two particles in volume elements  $dx_1$  and  $dx_2$  around the positions  $x_1$  and  $x_2$  respectively, is given in the canonical ensemble by

$$\rho(x_1, x_2) = \frac{N!}{(N-2)!} \frac{1}{Z(L, N)} \int \dots \int dx_3 \dots dx_N \prod_{i < j}^N \exp[-u(x_i, x_j)/k_B T] \quad (1)$$

with  $Z(L, N)$  the configurational integral

$$Z(L, N) = \int \dots \int dx_1 dx_2 dx_3 \dots dx_N \prod_{i < j}^N \exp[-u(x_i, x_j)/k_B T]. \quad (2)$$

In these equations  $k_B$  is the Boltzmann constant,  $T$  the absolute temperature and  $u(x_i, x_j)$  the pair potential between particles  $i$  and  $j$  at positions  $x_i$  and  $x_j$  respectively. For hard rods of diameter  $\sigma$ , it is given by

$$u(x_i, x_j) = \begin{cases} \infty & |x_i - x_j| < \sigma \\ 0 & |x_i - x_j| > \sigma. \end{cases} \quad (3)$$

Following Hill (1955), the Boltzmann factors  $\exp[-u(x_i, x_j)/k_B T]$  can be separated into two parts

$$\exp[-u(x_i, x_j)/k_B T] = \exp[-u^*(x_i, x_j)/k_B T] + \exp[-u^+(x_i, x_j)/k_B T] \quad (4)$$

where the effective pair potentials between unbound ( $u^*$ ) and bound ( $u^+$ ) particles are respectively given by

$$u^*(x_i, x_j) = \begin{cases} \infty & |x_i - x_j| < d \\ u(x_i, x_j) & |x_i - x_j| > d \end{cases} \quad (5)$$

and

$$u^+(x_i, x_j) = \begin{cases} u(x_i, x_j) & |x_i - x_j| < d \\ \infty & |x_i - x_j| > d \end{cases} \quad (6)$$

with  $d$  the connectivity distance. Therefore  $\rho(x_1, x_2)$  can also be separated (Coniglio *et al* 1977)

$$\rho(x_1, x_2) = \rho^*(x_1, x_2) + \rho^+(x_1, x_2) \quad (7)$$

in such a way that  $\rho^+(x_1, x_2)$ , the pair-connectedness function, is the density probability that particles 1 and 2 are in the elements  $dx_1$  and  $dx_2$  around  $x_1$  and  $x_2$  respectively, both particles belonging to the same cluster. Consequently, the remaining term,  $\rho^*(x_1, x_2)$ , is the density probability that particles 1 and 2 are in  $dx_1$  and  $dx_2$  around  $x_1$  and  $x_2$  but they do not belong to the same cluster.

In order to proceed with the calculation of  $\rho^+(x_1, x_2)$ , we note that, independently of the model and of the dimension, in general, we can obtain  $\rho^+(1, 2)$  by first setting (4) into (1) (adapted to the corresponding dimensionality) and effecting the indicated products. We see that  $\rho(1, 2)$  is expanded as a sum of  $2^{N(N-1)/2}$  terms which are all the possible arrangements of the Boltzmann factors  $e^* = \exp(-u^*/k_B T)$  and  $e^+ = \exp(-u^+/k_B T)$  evaluated between the  $N(N-1)/2$  possible pairs of particles. According to its definition,  $\rho^+(1, 2)$  is then built by selecting among all these summands those such that they have at least one 'physical' path of  $e^+$  bonds between particles 1 and 2. It is evident that, except for the one that contains only  $e^+$  bonds, all the other summands so chosen contain a mixture of  $e^+$  and  $e^*$  factors and the evaluation of  $\rho^+(1, 2)$  by this route is, in general, a very difficult if not impossible task.

However in our one-dimensional system of hard rods, things simplify remarkably if, in addition, we restrict ourselves to the consideration of the case in which  $\sigma < d < 2\sigma$ .

In this case, a simple analysis shows that particles 1 and 2, with  $x_1 < x_2$ , belong to the same cluster if, independently of what happens in the external intervals  $[0, x_1]$  and  $[x_2, L]$ , all the particles which are in the interval  $[x_1, x_2]$  form a chain of  $e^+$ -bonded nearest neighbours.

Let us assume with Leff and Coopersmith (1967) a partition such that there are  $N_1$  particles in  $[0, x_1]$ ,  $N_2$  particles in  $[x_1, x_2]$  and  $N_3$  particles in  $[x_2, L]$ . Since the factors  $e^+$  are zero for particle separations larger than  $d$ , we see that among the  $2^{M_2(M_2-1)/2}$  (with  $M_2 = N_2 + 2$ ) possible diagrams in the interval  $[x_1, x_2]$ , the only one

that persists is one in which the  $M_2 - 1$  factors between nearest neighbours are  $e^+$  bonds, while the remaining  $M_2(M_2 - 1)/2 - (M_2 - 1)$  factors are  $e^*$  bonds. These last factors are, according to (5) and (3), all equal to one because they link pairs of particles separated by distances larger than  $d$ .

As a result, the problem of evaluating the contribution to  $\rho^+(x_1, x_2)$  from the  $N_2$  particles in the interval  $[x_1, x_2]$  becomes equivalent to calculating the configurational partition function  $Z_2^+(x_2 - x_1, N_2)$  for a system of  $N_2$  molecules in a volume  $x_2 - x_1$  with two extra particles fixed at  $x_1$  and  $x_2$ , respectively, and such that the particles of this subsystem interact only to first neighbours through the effective bound-pair potential  $u^+$  given by (6).

The complete pair connectedness function is then evaluated by considering that the contribution due to the  $N_1$  particles of the interval  $[0, x_1]$  (the  $N_3$  particles of the interval  $[x_2, L]$ ) agree with the configurational partition function  $Z_1(x_1, N_1)$  ( $Z_1(L - x_2, N_3)$ ) for a system of  $N_1$  (of  $N_3$ ) particles in a volume  $x_1$  (a volume  $L - x_2$ ) and an extra particle fixed at  $x_1$  (at  $x_2$ ) and such that the particles of this subsystem interact to first neighbours through the complete pair interaction  $u$  given by (3). We write

$$\rho^+(x_1, x_2) = \frac{1}{Z(L, N)} \sum'_{\{N_i\}} \frac{N!}{N_1! N_2! N_3!} Z_1(x_1, N_1) Z_2^+(x_2 - x_1, N_2) Z_1(L - x_2, N_3) \quad (8)$$

where  $Z(L, N)$  is the configurational partition function for the whole system as given by (2) with  $u(x_i, x_j)$  defined in (3). The primed summation denotes that  $N_i \in \{0, N\}$  ( $i = 1, 2, 3$ ) with the condition  $\sum_{i=1}^3 N_i = N - 2$ .

The partition functions  $Z(L, N)$ ,  $Z_1(x_1, N_1)$ ,  $Z_2^+(x_2 - x_1, N_2)$  and  $Z_1(L - x_2, N_3)$  can be evaluated as shown in appendix B of the work of Leff and Coopersmith (1967). We obtain

$$Z(L, N) = [L - (N - 1)\sigma]^N \theta[L - (N - 1)\sigma] \quad (9a)$$

$$Z_1(x_1, N_1) = [x_1 - N_1\sigma]^{N_1} \theta[x_1 - N_1\sigma] \quad (9b)$$

$$Z_1(L - x_2, N_3) = [(L - x_2) - N_3\sigma]^{N_3} \theta[(L - x_2) - N_3\sigma] \quad (9c)$$

and

$$\begin{aligned} Z_2^+(x_2 - x_1, N_2) &= \sum_{r=0}^{N_2+1} \binom{N_2+1}{r} (-1)^{N_2+1-r} [(x_2 - x_1) - (N_2 + 1)d + r(d - \sigma)]^{N_2} \\ &\quad \times \theta[(x_2 - x_1) - (N_2 + 1)d + r(d - \sigma)] \end{aligned} \quad (9d)$$

where  $\theta$  is the Heaviside step function.

Equation (8), with the  $Z$  given by (9), is, as it stands, an exact expression for the pair connectedness function of a system with arbitrary  $L$  and  $N$ , and with  $\sigma < d < 2\sigma$ . In particular we are interested in the thermodynamic limit ( $L \rightarrow \infty$ ,  $N \rightarrow \infty$ ,  $N/L = \rho = \text{constant}$ ). Then, in a similar way to that by which Flicker (1968) obtains the ordinary correlation function  $\rho(x_1, x_2)$  for a hard rod fluid, we find, for number densities less than half the close packing fraction and after some manipulations, that (8) and (9) yield in the thermodynamic limit

$$\begin{aligned} \rho^+(x_2, x_1) &= \frac{\rho^2}{1 - \rho\sigma} \sum_{N_2=0}^{\infty} \frac{\delta^{N_2} \exp[-\delta(y - N_2)]}{N_2!} \sum_{r=0}^{N_2+1} \binom{N_2+1}{r} (-1)^{N_2+1-r} \\ &\quad \times [y - N_2 - (N_2 + 1 - r)(\alpha - 1)]^{N_2} \theta[y - N_2 - (N_2 + 1 - r)(\alpha - 1)] \end{aligned} \quad (10)$$

with

$$\delta = \rho\sigma/(1 - \rho\sigma) \quad (11)$$

$$\alpha = d/\sigma \quad (12)$$

and

$$y = (x_2 - x_1 - \sigma)/\sigma. \quad (13)$$

The condition  $\rho < (2\sigma)^{-1}$  ensures the existence of an infinite region of translational invariance in the thermodynamic limit (Leff and Coopersmith 1967). Unfortunately, the particular character of the one-dimensional hard rod fluid causes, as we mentioned, that (10) is not useful in describing the region of main interest in percolation studies, namely the proximities of the critical percolation density.

Actually, as we have mentioned above, the usefulness of (10) must be found from the point of view of the availability of an exact result which can serve as an experiment in order to test several approximate theories to be used in more realistic cases. Such a test can still give an idea about the goodness of the approximations involved in those theories, even if the system density is not near to the critical percolation density.

Finally, we would like to point out that in order to calculate  $\rho^+(x_1, x_2)$  for connectivity distances which verify  $(n-1)\sigma < d < n\sigma$  with  $n = 3, 4, \dots$  etc., it is necessary to replace  $Z_2^+(x_2 - x_1, N_3)$  in (8) by the configurational partition function for a system of  $N_2$  particles in the volume  $x_2 - x_1$  with two extra particles fixed at  $x_1$  and  $x_2$  and such that the particles of this subsystem interact, through the effective bound interaction  $u^+$  given by (3), to second, third, etc, neighbours respectively.

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