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1985 J. Phys. A: Math. Gen. 18 141

(http://iopscience.iop.org/0305-4470/18/1/025)

J. Phys. A: Math. Gen. **18** (1985) 141-148. Printed in Great Britain

Characterisation of the microstructure of distributions of rigid rods and discs in a matrix

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Received 29 June 1984

Abstract. The microstructure of two-phase disordered media can be characterised in terms of a set of n-point matrix probability functions S_n which give the probability of finding n points all in the matrix phase. We obtain, for the first time, an exact analytical expression for S_2 for a distribution of equi-sized rigid rods in a matrix at any density and for all values of its argument. We evaluate, also for the first time, S_2 for a distribution of equi-sized rigid discs in a matrix, for a wide range of densities. Using these results for S_2 and rigorous upper and lower bounds on S_3, one may obtain bounds on S_3 for distributions of rigid rods and discs. The one- and two-dimensional results obtained here are compared to the three-dimensional results of Torquato and Stell at certain particle volume fractions.

1. Introduction

We consider characterising the microstructure of those two-phase random media in which one of the phases consists of inclusions or particles distributed throughout a matrix phase (which may be fluid, solid, or void) according to some probability density function. In particular, the set of probabilities that have been termed n-point matrix probability functions S_n (Torquato and Stell 1982), which give the probability of simultaneously finding n points in the matrix phases are fundamental to the study of bulk properties of two-phase disordered media, such as the dielectric constant of suspensions, the diffusion coefficient and the permeability of porous media and the elastic moduli of composites (Brown 1955, Prager 1961, Weissberg and Prager 1962, Prager 1963, Beran 1968, McCoy 1970 and Milton 1982). However, because of a lack of reliable assessment of the two-point and three-point matrix functions for most useful models, progress in the prediction of bulk properties of disordered media continues to be hampered. The quantities S_2 and S_3 have recently been evaluated and approximated for three-dimensional two-phase systems of randomly centred spheres (Torquato and Stell 1983a), and rigid spheres (Torquato and Stell 1984). Corresponding computations in lower dimensions have not hitherto been carried out.

In this study, we consider obtaining S_2 and S_3 for distributions of equi-sized rigid rods and rigid discs in a matrix. A two-dimensional system of rigid discs is a useful model of a three-dimensional material of rigid, infinitely long, parallel circular cylinders in a matrix (e.g., fibre-reinforced material) (Hill 1963). A one-dimensional medium of rigid rods is a model of a three-dimensional two-phase system of infinite plane slabs

0305-4470/85/010141+08$02.25

parallel to each other. In one sense, investigations of the S_n for one-dimensional systems are of mathematical interest, since, in the context of predicting bulk properties of random media which depend upon the S_n, effective properties are known exactly (Beran 1968). Study of one-dimensional media, however, may help to illuminate our understanding of the S_n in the more complex cases of two and three dimensions, since, unlike the latter instances, we can often obtain exact, closed-form expressions for microstructural quantities associated with one-dimensional systems.

In the following section, we give expressions for the S_n in terms of n-particle distribution functions for rigid particles of any dimensionality. In § 3, we obtain, for the first time, an exact analytical expression for $S_2(r)$ for a distribution of rigid rods in a matrix at any density and for all r. In § 4, we evaluate, also for the first time, $S_2(r)$ for a distribution of rigid discs in a matrix, for a wide range of densities. Using the results of §§ 2, 3, and 4, one may obtain rigorous upper and lower bounds on S_3 for distributions of rigid rods and discs. Finally, we compare our one- and two-dimensional results to the three-dimensional results of Torquato and Stell (1984) at particular particle volume fractions.

2. Expressions for the S_n for rigid particles

For any statistically inhomogeneous two-phase random medium consisting of identical rigid particles (inclusions) dispersed throughout a matrix phase such that the location of each inclusion is fully specified by a position vector, Torquato and Stell (1982, 1983b) have found that the probability of simultaneously finding n points at $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n$, respectively, all in the matrix phase is given by

$$S_n(1, \ldots, n) = 1 + \sum_{s=1}^{n+1} \frac{(-1)^s}{s!} \int \ldots \int\int \rho_s(n+1, \ldots, n+s)$$
$$\times \prod_{j=n+1}^{n+s} \left(1 - \prod_{i=1}^{n} [1 - m(i,j)]\right) \mathrm{d}j. \tag{2.1}$$

Here we have introduced a shorthand notation in which we indicate only the labels associated with position. The quantity dj denotes the volume element d$\boldsymbol{r}_j$. The n-particle probability density $\rho_n(1, \ldots, n)$ characterises the probability of simultaneously finding a particle centred in volume element d1, another particle centred in d2, etc. Here $m(\boldsymbol{r})$ is a step function which is unity whenever $\boldsymbol{r}$ is inside the particle and zero otherwise. For rods, discs and spheres

$$m(r) = \theta(\sigma/2 - r), \tag{2.2}$$

where $r = |\boldsymbol{r}|$, $\theta(r)$ is the Heaviside step function, and where σ is the length in one dimension and the diameter in two or three dimensions.

In the case of statistically homogeneous media, the ρ_n and, hence, the S_n are translationally invariant and for such distributions it is convenient to define another distribution function, g_n, such that $\rho^n g_n \equiv \rho_n$ (where ρ is the density). For statistically homogeneous distributions of rigid rods, discs or spheres, Torquato and Stell (1983b) have shown that (2.1) simplifies for $n = 1$, 2 or 3 in such a way that

$$S_1 = 1 - \rho U_1 \tag{2.3}$$

$$S_2(1, 2) = 1 - \rho U_2(1, 2) + \rho^2 V(1, 2) \tag{2.4}$$

and

$$S_3=(1,2,3)=1-\rho U_3(1,2,3)+\rho^2[V(1,2)+V(1,3)+V(2,3) - W(1;2,3)-W(2;1,3)-W(3;1,2)]-\rho^3 X(1,2,3), \tag{2.5}$$

where

$$V(i,j)=\int \mathrm{d}3 \int \mathrm{d}4\; m(i,3)m(j,4)g_2(3,4) \tag{2.6}$$

$$W(i;j,k)=\int \mathrm{d}3 \int \mathrm{d}4\; m(i,3)m(j,4)m(k,4)g_2(3,4) \tag{2.7}$$

and

$$X(i,j,k)=\int \mathrm{d}3 \int \mathrm{d}4 \int \mathrm{d}5\; m(i,3)m(j,4)m(k,5)g_3(3,4,5). \tag{2.8}$$

Here $U_n(1,\dots,n)$ is a region of space which is the union of n particles. For example, $U_2(r)$ in one, two and three dimensions is given for $r\geq 0$ by

$$U_2(r)=2\sigma-(\sigma-r)\theta(\sigma-r) \tag{2.9}$$

$$U_2(r)=\tfrac{1}{2}\pi\sigma^2-\tfrac{1}{2}\sigma^2[\tfrac{1}{2}\pi-\sin^{-1} r\sigma^{-1}-r\sigma^{-1}(1-r^2\sigma^{-2})^{1/2}]\theta(\sigma-r) \tag{2.10}$$

and

$$U_2(r)=\tfrac{1}{3}\pi\sigma^3-\tfrac{1}{6}\pi\sigma^3[1-\tfrac{3}{2}r\sigma^{-1}+\tfrac{1}{2}r^3\sigma^{-3}]\theta(\sigma-r), \tag{2.11}$$

respectively.

Note that since the integrals V, W and X as given in (2.6), (2.7) and (2.8), respectively, involve either the 2-particle or 3-particle distribution functions, they depend upon all powers of ρ. In this article, we evaluate V and, thus, S_2 for all densities in one dimension and for a very wide range of ρ in two dimensions. We do not evaluate either W or X in this study, which implies that S_3, for arbitrary values of its arguments, is not exactly determined through order ρ^2 here. We can, however, apply rigorous upper and lower bounds on S_3 (Torquato and Stell 1984) which are given in terms of known quantities and S_2 (the function we determine in this paper), namely,

$$S_3(1,2,3)\geq \rho[I_2(1,2)+I_2(1,3)-I_3(1,2,3)-U_1]+S_2(2,3) \tag{2.12}$$

and

$$S_3(1,2,3)\leq 1-3S_1+S_2(1,2)+S_2(1,3)+S_2(2,3)-\rho I_3(1,2,3), \tag{2.13}$$

where

$$I_n(\mathcal{N})=\sum_{\mathcal{M}\subseteq\mathcal{N}}(-1)^{n-m+1}U_n(\mathcal{M}). \tag{2.14}$$

In (2.14), $\mathcal{N}$ is a set of position labels, n and m are, respectively, the number of labels in $\mathcal{N}$ and $\mathcal{M}$, and the sum is over all subsets of $\mathcal{N}$. Clearly, I_n is the region of space which is the intersection of n particles. Comparing the upper and lower bounds to the exact relation (2.5), we see that (2.12) and (2.13) are exact through order ρ. An analytical expression for U_3 in one dimension is trivial to obtain and in two dimensions has been given by Rowlinson (1964). Both the lower bound (2.12) and the upper bound (2.13) take on the exact value of S_1 (Prager 1961) when all three points with positions 1, 2 and 3 coincide. Moreover, the lower bound (2.12) takes on the exact value of $S_2(i,j)$ (Prager 1961) when the points with positions j and k coincide for all $i \neq j$($i = 1$, 2 or 3) except when points with positions 2 and 3 coincide. Using the results of this article, therefore, one may obtain rigorous upper and lower bounds on S_3 for distributions of rigid rods and discs in a matrix which are exact under the conditions stated above.

Before closing this section, we comment on the integrals W, equation (2.7), and X, equation (2.8), which are the remaining non-trivial quantities which contribute to S_3. Although W is a non-trivial integral, it most likely can be obtained analytically in one dimension and can be evaluated numerically in higher dimensions. The integral X, however, requires knowledge of the 3-particle distribution function, which in one dimension is known analytically (Salsburg *et al* 1953) and in higher dimensions is not known analytically. In two and three dimensions one must resort to analytical approximations for g_3 such as the superposition approximation (Hansen and McDonald 1976).

3. Evaluation of S_2 in one dimension

Here we obtain an exact analytical expression for S_2 for a statistically isotropic distribution of rigid rods in a matrix at arbitrary values of density. Since U_2 in one dimension is given by (2.9), we need only evaluate the double-convolution integral V as given by (2.6). In one dimension the 2-particle distribution function for an equilibrium distribution of rigid rods of length σ is known analytically (Zernike and Prins 1927) and is given by

$$\rho g_2(r) = \sum_{k=1}^{\infty} h_k(r), \tag{3.1}$$

where

$$h_k(r) = \theta(r - k\sigma)\frac{(r-k\sigma)^{k-1}}{a^k(k-1)!}\exp[-(r-k\sigma)/a], \tag{3.2}$$

with

$$a = (1-\eta)\sigma/\eta \quad \text{and} \quad \eta = \rho\sigma. \tag{3.3}$$

Direct integration of (2.6) using (2.2) and (3.1) yields

$$\rho V(r) = \begin{cases} r - a[1-\exp(-r/a)], & 0 \leqslant r \leqslant \sigma \\ \sigma - a[1-\exp(-r/a)] + (r-\sigma)\exp[-(r-\sigma)/a], & \sigma \leqslant r \leqslant 2\sigma \\ \sigma - a + \sigma A(r) - 2\sigma B(r) + \sigma C(r), & j\sigma \leqslant r \leqslant (j+1)\sigma, \quad j \geqslant 2 \end{cases} \tag{3.4}$$

where

$$A(r) = \sum_{k=1}^{j+1} \frac{\exp\{-[r-(k-1)\sigma]/a\}}{a^{k-1}} \sum_{s=1}^{k} \frac{sa^s}{(k-s)!}[r-(k-1)\sigma]^{k-s} \tag{3.5}$$

$$B(r) = \sum_{k=1}^{j} \frac{\exp\{-[r-k\sigma]/a\}}{a^{k-1}} \sum_{s=1}^{k} \frac{sa^s}{(k-s)!}[r-k\sigma]^{k-s} \tag{3.6}$$

and

$$C(r)=\sum_{k=1}^{j-1}\frac{\exp\{-[r-(k+1)\sigma]/a\}}{a^{k-1}}\sum_{s=1}^{k}\frac{sa^{s}}{(k-s)!}[r-(k+1)\sigma]^{k-s}. \tag{3.7}$$

Substitution of (2.9) and (3.4) into (2.4) yields S_2 for an equilibrium distribution of rigid rods at arbitrary ρ. In one dimension the particle volume fraction $\eta=\rho\sigma=1-S_1$ may take on values between zero and the close packing value of unity. When $\eta=1$ we find that $S_2(r)=0$ for all r, as expected. This feature is not exhibited in higher dimensions since the closepacking η in two or three dimensions is less that unity and therefore implies that $S_2(r)$ can never be equal to zero for all r in these instances. We plot in figure 1 $S_2(r)$ as a function of r, as computed from the result of this section, at η values of 0.2, 0.3 and 0.8, where σ is taken to be unity. The two-point matrix probability function for rigid particles, in any dimension, is a damped-oscillatory function which oscillates about its long-range value of $S_1^2=(1-\eta)^2$ and tends to s_1 as $r\to 0$. In the one-dimensional case, the correlation length, defined to be the distance at which the quantity $(S_2(r)-S_1^2)$ becomes negligible, is seen to increase as η increases up to $\eta\approx 0.95$. For values of η greater than about 0.95 but less than or equal to unity, the correlation length decreases as η increases, vanishing completely when $\eta=1$ for reasons mentioned above. Note that the first derivative at $r=1$, the location of the first and absolute minimum, is discontinuous in one dimension. The location of the first minimum is independent of η in this instance. As we shall see, neither of the last two statements holds for higher dimensions.

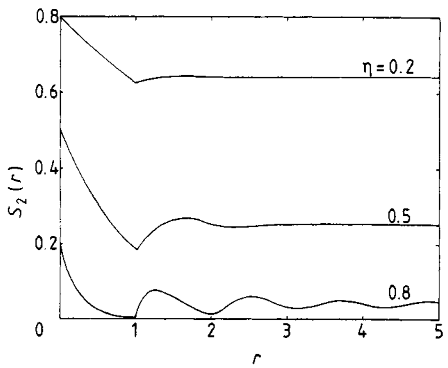

Figure 1. The two-point matrix probability function $S_2(r)$ as a function of r for an equilibrium distribution of rigid rods in a matrix at $\eta=0.2$, 0.5 and 0.8.

4. Evaluation of S_2 in two dimensions

In this section, we evaluate $V(r)$ and, thus, $S_2(r)$ for a statistically isotropic distribution of rigid discs in a matrix over a wide range of densities. The evaluation of the double-convolution integral V in two dimensions is considerably more difficult than the corresponding calculation in one or three dimensions. For an equilibrium distribution of rigid rods we obtained, in § 3, an exact analytical expression for $V(r)$ and $S_2(r)$ using an analytical expression for $g_2(r)$. For an equilibrium distribution of rigid spheres Torquato and Stell (1984) used the Verlet–Weis (Verlet and Weis 1972) semi-empirical modification of the Percus-Yevick (Percus and Yevick 1958) radial distribution function to compute $S_2(r)$ for all ρ corresponding to the disordered state. The Ornstein-Zernike (OZ) equation in three dimensions yields an analytical result in the Percus -Yevick approximation.

In two dimensions, however, the OZ equation can not be solved analytically in any approximation and therefore solutions of it must be obtained numerically. Lado (1968) has solved the OZ equation in the Percus-Yevick approximation using numerical Fourier transforms for distributions of rigid discs.

We define the two-dimensional Fourier transform $\tilde{F}(k)$ of a circularly symmetric function $F(r)$ by

$$\tilde{F}(k) \equiv 2\pi \int_0^\infty \mathrm{d}r\, rF(r)J_0(kr), \tag{4.1}$$

where $J_0(x)$ is the zeroth-order Bessel function of the first kind and k is the wavenumber. The inverse Fourier transform of $\tilde{F}(k)$ is given by

$$F(r) = \frac{1}{2\pi} \int_0^\infty \mathrm{d}k\, k\tilde{F}(k)J_0(kr). \tag{4.2}$$

Equations (4.1) and (4.2) are Hankel transforms.

Since (2.6) is a double-convolution integral, we have upon taking the Fourier transform of (2.6) and inverting

$$V(r) = \left(\frac{\pi\sigma^2}{4}\right)^2 + \frac{1}{2\pi} \int_0^\infty \mathrm{d}k\, k\tilde{m}^2(k)\tilde{h}(k)J_0(kr), \tag{4.3}$$

where

$$\tilde{m}(k) = \frac{\pi\sigma}{k} J_1\left(\frac{k\sigma}{2}\right) \tag{4.4}$$

and $\tilde{h}(k)$ is the Fourier transform of the total correlation function $h(r) \equiv g_2(r) - 1$. Given $\tilde{h}(k)$, the evaluation of $V(r)$ has been reduced to a one-dimensional quadrature. We evaluate (4.3) using the numerical Fourier-transform technique given by Lado (1971) and employing the Percus-Yevick $\tilde{h}(k)$. The rules for the numerical integration are similar to the trapezoidal rule, but with the intervals determined by the zeros of the orthogonal basis functions. Evaluation of (4.3) in conjunction with (2.10) enables us to compute the Percus-Yevick S_2 from (2.4) for a wide range of densities.

In figure 2 we plot $S_2(r)$ as a function of r for such a distribution of rigid discs of unit diameter at $\eta = 0.2$, 0.4 and 0.6, where $\eta = \rho\pi\sigma^2/4 = 1 - S_1$. In table 1 we tabulate $S_2(r)$ for rigid discs at various values of r and at η values between and including 0.1 and 0.7 in increments of 0.1. The particle volume fraction of 0.7 is slightly higher than the rigid-disc phase transition ($\eta \approx 0.69$) at which rigid-disc ordering is expected on the basis of computer-simulation studies (Wood 1968) and therefore corresponds to a metastable disordered (i.e., glassy) state for which the close-packing η is about 0.82 (Berryman 1983).

Figures 3 and 4 compare S_2 in one and two dimensions at $\eta = 0.1$ and $\eta = 0.5$, respectively, as computed from this study, to the corresponding three-dimensional cases obtained by Torquato and Stell (1984). The two-point matrix probability function for rigid discs and for rigid spheres are qualitatively similar to one another. Unlike the one-dimensional case, the first derivative at the first minimum in either two or

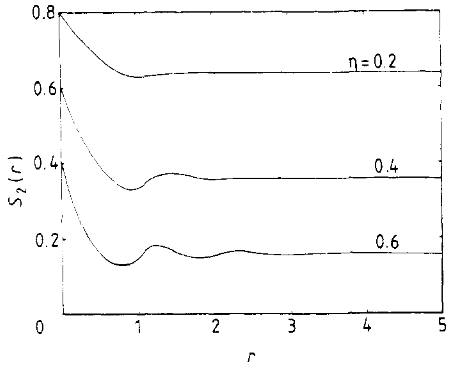

Figure 2. The two-point matrix probability function $S_2(r)$ as a function of r for a distribution of rigid discs in a matrix, in the Percus-Yevick approximation, at $\eta = 0.2$, 0.4 and 0.6.

Table 1. $S_2(r)$ as a function of r for a distribution of rigid discs in a matrix at $\eta = 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 in the Percus-Yevick approximation.

	$S(r)$						
r	$\eta = 0.1$	0.2	0.3	0.4	0.5	0.6	0.7
0.000	0.9000	0.8000	0.7000	0.6000	0.5000	0.4000	0.3000
0.256	0.8680	0.7369	0.6071	0.4796	0.3557	0.2383	0.1330
0.498	0.8408	0.6856	0.5361	0.3952	0.2673	0.1587	0.0777
0.759	0.8174	0.6442	0.4838	0.3411	0.2215	0.1305	0.0695
1.00	0.8063	0.6278	0.4689	0.3342	0.2273	0.1486	0.0920
1.24	0.8085	0.6366	0.4876	0.3636	0.2635	0.1811	0.1078
1.50	0.8098	0.6408	0.4905	0.3686	0.2598	0.1636	0.0829
1.76	0.8102	0.6411	0.4923	0.3613	0.2462	0.1497	0.0807
2.01	0.8101	0.6402	0.4893	0.3565	0.2433	0.1551	0.0936
2.25	0.8100	0.6398	0.4890	0.3583	0.2505	0.1668	0.0988
2.51		0.6399	0.4899	0.3610	0.2535	0.1631	0.0855
2.75		0.6400	0.4903	0.3610	0.2506	0.1564	0.0845
3.01			0.4902	0.3599	0.2482	0.1573	0.0929
3.25			0.4900	0.3595	0.2493	0.1622	0.0946
3.51				0.3599	0.2509	0.1620	0.0871
3.75				0.3602	0.2506	0.1588	0.0869
4.00				0.3601	0.2497	0.1584	0.0918
4.26				0.3600	0.2496	0.1606	0.0925
4.50					0.2501	0.1611	0.0884
4.76					0.2503	0.1597	0.0882
5.00					0.2500	0.1592	0.0912
5.26						0.1601	0.0914
5.50						0.1606	0.0890
5.76						0.1600	0.0889
6.01							0.0907

three dimensions is continuous. In the latter two cases, moreover, the location of the first minimum r_m monotonically decreases from its low-density limit of $r_m = 1$ (see figure 3) as η increases. For arbitrary η in the range $0 \leq \eta \leq 0.62$ (where 0.62 corresponds to the approximate random close-packing η value in three dimensions), we have $r_{m3} \leq r_{m2} \leq r_{m1}$, where r_{mi} is the location of the first minimum in i dimensions.

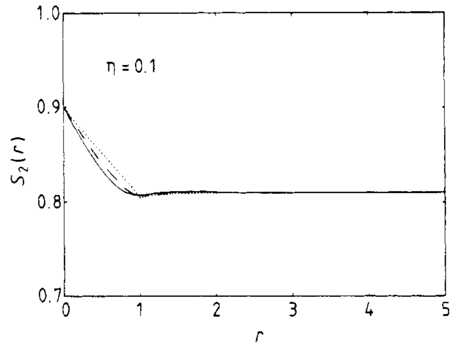

Figure 3. The two-point matrix probability function $S_2(r)$ as a function of r for distribution of rigid rods (····) and discs (---) in a matrix at $\eta = 0.1$, as calculated from this study, compared to the corresponding result of Torquato and Stell (1984) for rigid spheres (——) in a matrix.

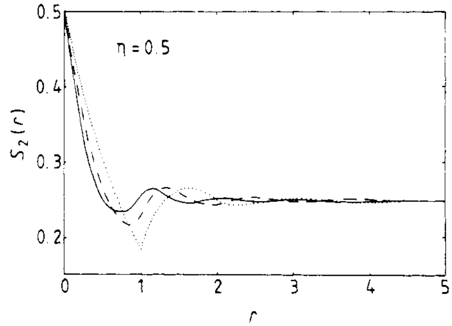

Figure 4. The two-point matrix probability function $S_2(r)$ as a function of r for distributions of rigid rods (····) and discs (---) in a matrix at $\eta = 0.5$, as calculated from this study, compared to the corresponding result of Torquato and Stell (1984) for rigid spheres (——) in a matrix.

The smallest value of r_{m3}, which occurs at $\eta = 0.62$, is about 0.6 (Torquato and Stell 1984). In contrast to the case of rigid rods the correlation length for rigid discs and spheres, increases as η increases for all realisable values of η.

Acknowledgments

ST is indebted to Professor George Stell for introducing him to the general problem of characterising the microstructure of multiphase disordered media.

We wish to acknowledge the support of the National Science Foundation under Grants CPE-8211966 and CHE-8402144.

References

Beran M 1968 *Statistical Continuum Theories* (New York: Wiley)
Berryman J G 1983 *Phys. Rev.* A **27** 1053
Brown W F 1955 *J. Chem. Phys.* **23** 1514
Hansen J P and McDonald I R 1976 *Theory of Simple Liquids* (New York: Academic)
Hill R 1963 *J. Mech. Phys. Solids* **11** 127
Lado F 1968 *J. Chem. Phys.* **49** 3092
—— 1971 *J. Comp. Phys.* **8** 417
McCoy J J 1970 *Recent Advances in Engineering* **5** (New York: Gordon and Breach)
Milton G W 1982 *J. Mech. Phys. Solids* **30** 177
Percus J K and Yevick G J 1958 *Phys. Rev.* **110** 1
Prager S 1961 *Phys. Fluids* **4** 1477
—— 1963 *Physica* 29 **129**
Rowlinson J S 1964 *Mol. Phys.* 7 593
Salsburg Z W, Zwanzig R W and Kirkwood J G 1953 *J. Chem. Phys.* **21** 1098
Torquato S and Stell G 1982 *J. Chem. Phys.* **77** 2071
—— 1983a *J. Chem. Phys.* **79** 1505
—— 1983b *J. Chem. Phys.* **78** 3262
—— 1984 *J. Chem. Phys.* submitted for publication
Verlet L and Weis J J 1972 *Phys. Rev.* A **5** 939
Weissberg H L and Prager S 1962 *Phys. Fluids* **5** 1390
Wood W W 1968 *J. Chem. Phys.* **48** 415
Zernike F and Prins J A 1927 *Z. Phys.* **41** 184