J. Phys. A: Math. Gen. 23 (1990) L103–L107. Printed in the UK

LETTER TO THE EDITOR

Nearest-neighbour distribution function for systems of interacting particles

S Torquato†, B Lu‡ and J Rubinstein§

† Departments of Mechanical and Aerospace Engineering and of Chemical Engineering, North Carolina State University, Raleigh, NC 27695-7910, USA
‡ Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, NC 27695-7910, USA
§ Department of Mathematics, Technion-Israel Institute of Technology, Haifa 32000, Israel

Received 17 August 1989

Abstract. One of the basic quantities characterising a system of interacting particles is the nearest-neighbour distribution function $H(r)$. We give a general expression for $H(r)$ for a distribution of D-dimensional spheres which interact with an arbitrary potential. Specific results for $H(r)$ are obtained, for the first time, for D-dimensional hard spheres with $D = 1$, 2 and 3. Our results for $D = 3$ are shown to be in excellent agreement with Monte Carlo computer-simulation data for a wide range of densities. From $H(r)$, one can determine other quantities of fundamental interest such as the mean nearest-neighbour distance and the random close-packing density.

In considering systems composed of many interacting particles, a key fundamental question to ask is: what is the effect of the nearest neighbour on some reference particle in the system? The answer to this query requires knowledge of the nearest-neighbour distribution function $H(r)$, i.e. the probability density associated with finding a nearest neighbour at some given distance r from the reference particle. From $H(r)$ one can determine other quantities of fundamental interest such as the mean nearest-neighbour distance and the random close-packing density. Knowing $H(r)$ is of importance in a host of problems in the physical and biological sciences, including liquids and amorphous solids [1–5], transport properties of suspensions and composite materials [6–8], stellar dynamics [9], and the structure of some cell membranes [10], to mention but a few examples. It should be emphasised that $H(r)$ is *different* from the well known radial distribution function. The latter quantity is proportional to the probability of finding any particle (not necessarily the nearest one) a distance r away from a central particle.

Hertz [11] apparently was the first to consider the evaluation of $H(r)$ for a system of 'point' particles, i.e. particles whose centres are randomly (Poisson) distributed. The D-dimensional generalisation of Hertz's [11] solution of $H(r)$ for Poisson distributed points, at number density ρ, is given by

$$H(r) = \rho \frac{\mathrm{d}v_D(r)}{\mathrm{d}r} \exp[-\rho v_D(r)] \tag{1}$$

where $v_D(r)$ is the volume of a D-dimensional sphere of radius r ($v_1(r) = 2r$, $v_2(r) = \pi r^2$, $v_3(r) = \frac{4}{3}\pi r^3$).

Interestingly, there is currently no theoretical formalism to obtain and compute $H(r)$ for distributions of *finite-sized* interacting particles at arbitrary density†. In this letter, we briefly describe such general results for D-dimensional spheres. We then specifically determine $H(r)$ and the mean nearest-neighbour distance for D-dimensional random arrays of impenetrable spheres of diameter σ as a function of density. (The rather lengthy derivation of all the theoretical results given here and the calculation of functions closely related to $H(r)$ will be described in detail elsewhere [13].) The case $D=1$ (hard rods) may serve as a useful model of various types of layered media [14]. The case $D=2$ (hard discs) is a reasonable model of fibre-reinforced materials [15], thin films [15], certain types of cell membranes [10], etc. The case $D=3$ (hard spheres) has probably the widest application as it can be used to model liquids [1, 2, 16], amorphous solids [2-5], suspensions [6], porous media [7, 8], particulate composites [17], powders [18], etc.

We have derived an exact analytical representation of $H(r)$ for homogeneous distributions of identical interacting D-dimensional spheres of diameter σ at number density ρ in terms of the so-called n-particle probability density functions $\rho_1, \rho_2, \ldots, \rho_n$. It is found [13] that

$$H(r)=\sum_{k=1}^{\infty}(-1)^{k+1}H^{(k)}(r) \tag{2}$$

where

$$H^{(k)}(r)=\frac{1}{k!}\frac{\partial}{\partial r}\int \rho_{k+1}(\boldsymbol{R}^{k+1})\prod_{i=2}^{k+1} m(|\boldsymbol{R}_1-\boldsymbol{R}_i|;\, r)\,\mathrm{d}\boldsymbol{R}_i \tag{3}$$

with

$$m(y;\, r)=\begin{cases}1 & y\leq r\\ 0 & y>r.\end{cases} \tag{4}$$

The quantity $\rho_n(\boldsymbol{R}_1, \ldots, \boldsymbol{R}_n)$ characterises the probability of finding a configuration of n spheres with centres at positions $\boldsymbol{R}^n \equiv \boldsymbol{R}_1, \ldots, \boldsymbol{R}_n$, respectively, and is given information for the statistical ensemble under consideration. For spatially uncorrelated centres (Posson distribution), ρ_n is trivially a constant equal to ρ^n and our expression leads to the simple formula (1). On the other hand, if the particles are mutually impenetrable, then the ρ_n are generally quite complicated [16].

For the case of hard rods ($D=1$), the ρ_n, for any n, are known exactly for equilibrium distributions [19]. Our relation for H then yields the exact dimensionless result

$$\sigma H(x)=\frac{2\eta}{1-\eta}\exp\left(\frac{-2\eta(x-1)}{1-\eta}\right) \qquad x>1 \tag{5}$$

where $x=r/\sigma$ is a scaled distance and $\eta=\rho v_1(\sigma/2)=\rho\sigma$ is a reduced density. For $x<1$, $H(x)=0$ in any dimension.

For the cases of $D=2$ and $D=3$, however, the two-particle probability density ρ_2 (or equivalently, the radial distribution function) is only known approximately for

† The nearest-neighbour distribution function $H(r)$ defined here should not be confused with the one defined by Reiss *et al* [12] in their scaled-particle theory. Whereas the former considers nearest neighbours around an actual inclusion centred at the origin, the latter considers nearest neighbours at a radial distance from the centre of a spherical cavity *empty* of sphere centres. The distinction between these two different types of nearest-neighbour distribution functions is fully detailed in [13].

arbitrary density, albeit accurately [16]; the higher-order $\rho_n (n \geq 3)$ are generally never known. This implies that an exact solution of $H(r)$ for $D=2$ and 3 under general conditions is out of the question. For $D=2$ and 3, therefore, we have devised schemes to approximately sum the series using statistical mechanical theory [13] and found

$$\sigma H(x) = \frac{4\eta(2x-\eta)}{(1-\eta)^2} \exp\left(\frac{-4\eta}{(1-\eta)^2}[(x^2-1)+\eta(x-1)]\right) \qquad x>1 \tag{6}$$

for hard discs ($D=2$), where $\eta = \rho v_2(\sigma/2)$, and

$$\sigma H(x) = 24\eta(ex^2+fx+g)\exp\{-\eta[8e(x^3-1)+12f(x^2-1)+24g(x-1)]\} \qquad x>1 \tag{7}$$

for hard spheres ($D=3$), where $\eta = \rho v_3(\sigma/2)$ and

$$e = \frac{1+\eta}{(1-\eta)^3} \qquad f = \frac{-\eta(3+\eta)}{2(1-\eta)^3} \qquad g = \frac{\eta^2}{2(1-\eta)^3}. \tag{8}$$

It should be emphasised that the relations (5), (6), and (7) for $D=1$, $D=2$, and $D=3$, respectively, are new, i.e. it is the first time that expressions for $H(r)$ valid for D-dimensional hard-sphere systems at arbitrary density have been given.

In figure 1 we plot $H(r)$ for distributions of D-dimensional impenetrable spheres at a sphere volume fraction $\phi = \eta = 0.2$. Of course, for $r < \sigma$, $H(r) = 0$ for any D. For r near σ, the effect of increasing the dimensionality is to increase $H(r)$, i.e. the likelihood of finding a nearest neighbour at such r increases with increasing D. Consistent with this behaviour is a decrease of $H(r)$ with increasing D for large r.

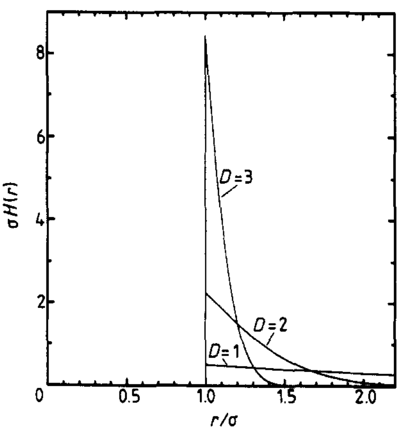

Figure 1. The dimensionless nearest-neighbour distribution function $\sigma H(r)$ for distributions of identical D-dimensional impenetrable spheres of diameter σ at a D-dimensional particle volume fraction $\phi = 0.2$. Results for $D = 1$, 2 and 3 are obtained from (5), (6) and (7), respectively. For impenetrable spheres, the D-dimensional volume fraction ϕ equals the D-dimensional reduced density $\eta = \rho v_D(\sigma/2)$, where $v_D(r)$ is the D-dimensional volume of a sphere of radius r described in the text and ρ is the particle number density.

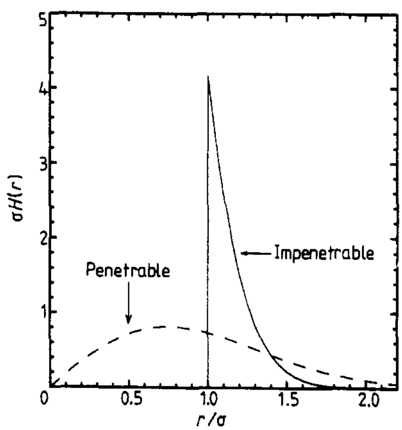

Figure 2. The dimensionless nearest-neighbour distribution function $\sigma H(r)$ for penetrable discs (Poisson distributed 'point' particles) and impenetrable discs of diameter σ as calculated from (1) and (6), respectively, at a particle area fraction $\phi = 0.3$. For D-dimensional penetrable spheres, the sphere volume fraction $\phi = 1 - \exp(-\eta)$. Exclusion-volume effects associated with the hard cores considerably change the behaviour of $h(r)$ relative to the idealised case of point particles. $H(r)$ behaves qualitatively the same for these models in any dimension.

What is the effect of impenetrability of the spheres on $H(r)$? In figure 2 we compare Hertz's result (1) for Poisson distributed centres in two-dimensional space with our new result (6) for two-dimensional impenetrable discs at a disc area fraction $\phi = 0.2$. Note that exclusion-volume effects associated with hard cores lead to a nearest-neighbour distribution function which is strikingly different to the corresponding quantity for spatially uncorrelated discs. For $r < \sigma$, unlike hard discs, $H(r) \neq 0$ for penetrable discs since their centres can come arbitrarily close to one another. For large r, $H(r)$ for penetrable discs is larger than $H(r)$ for impenetrable discs since in the former system one is more likely to find larger 'void' regions surrounding the central particle as the result of interparticle overlap. The behaviour of $H(r)$ for these models for any D is qualitatively the same.

Monte Carlo computer simulations in three dimensions have been carried out by Torquato and Lee [20] to obtain, among other quantities, $H(r)$. A standard Metropolis [16] algorithm was employed to generate 200–6000 different realisations of 500 impenetrable spheres in a cubical cell with periodic boundary conditions. Figure 3 compares the simulation results with our relation (4) for $\phi = 0.2$ and $\phi = 0.5$. The agreement is seen to be excellent. In fact, one finds relatively good agreement up to $\phi = 0.6$, which is very close to the random close-packing volume fraction ϕ_c, estimated to range from 0.62–0.66 [2, 4]. In conclusion, this verifies the accuracy of the three-dimensional expression (7) (as well as the two-dimensional expression which is based on a similar approximation scheme) up to densities near the close-packing value (see discussion below).

Another important measure is the 'mean nearest-neighbour distance' l defined as

$$l = \int_0^\infty rH(r)\,\mathrm{d}r. \tag{9}$$

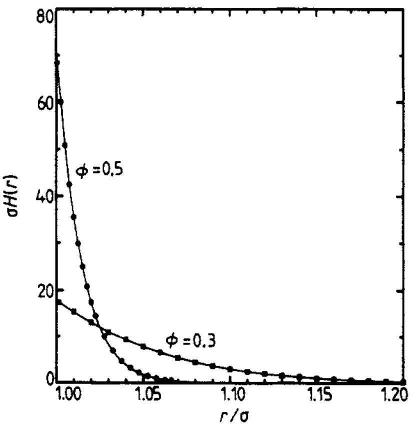

Figure 3. The dimensionless nearest-neighbour distribution function $\sigma H(r)$ for three-dimensional hard spheres of diameter σ at values of the sphere volume fraction $\phi = \eta = 0.3$ and 0.5. Full curves are computed from relation (7) and circles and squares are Monte Carlo computer-simulation data. Observe the excellent agreement of the theory with the simulation data. For r near σ, $H(r)$ increases with increasing ϕ, as expected. for large r, $H(r)$ decreases with increasing ϕ for similar reasons.

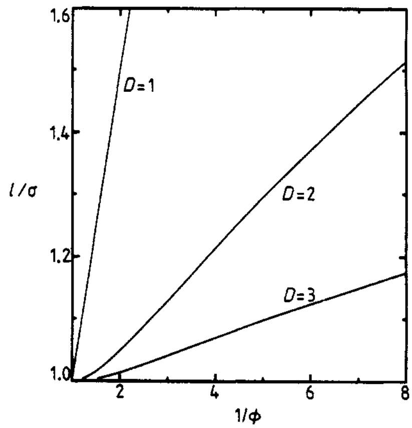

Figure 4. The dimensionless mean nearest-neighbour distance l/σ as a function of the inverse volume fraction ϕ^{-1} for distributions of D-dimensional impenetrable spheres with $D = 1$, 2 and 3.

An operational definition for the random close-packing volume fraction ϕ_c, a quantity of great fundamental interest [2-5], then follows, i.e. the volume fraction at which $l=\sigma$. We have computed (9) for D-dimensional hard spheres using the exact formula (5) and the approximate relations (6) and (7) as a function of the D-dimensional inverse volume fraction ϕ^{-1}. These results are summarised in figure 4. As expected, at fixed ϕ, l increases with increasing D. Unlike our exact one-dimensional result which correctly predicts $\phi_c = 1$, our two-dimensional and three-dimensional results for l cannot correctly predict the 'critical' point ϕ_c. This is not surprising considering the difficulty of predicting ϕ_c for $D=2$ and 3 (heretofore this problem has defined an exact analytical solution) and because our approximations are 'mean field' in nature and hence cannot accurately predict critical points [5]. Our plots of l/σ as a function of ϕ^{-1} are approximately linear over the entire range of ϕ, except for the near vicinity of ϕ_c. Interestingly, extrapolation of these two-dimensional and three-dimensional data (using the linear range) to the limit $l/\sigma = 1$, yields values of ϕ_c which fall within the respective estimated ranges [4] (for $D=2$, $\phi_c = 0.82 \pm 0.02$). Such linear extrapolations, however, are somewhat arbitrary. In future work we shall study methods for improving our approximations (6) and (7) in the near-critical region.

ST and BL gratefully acknowledge the support of the Office of Basic Energy Sciences, US Department of Energy, under Grant no DE-FG05-86ER 13842.

References

[1] Bernal J D 1964 *Proc. R. Soc.* A **280** 299
[2] Finney J L 1970 *Proc. R. Soc.* A **319** 479
[3] Zallen R 1983 *The Physics of Amorphous Solids* (New York: Wiley)
[4] Berryman J G 1983 *Phys. Rev.* A **27** 1053
[5] Song Y, Stratt R M and Mason E A 1988 *J. Chem. Phys.* **88** 1126
[6] Keller J B, Rubenfeld L A and Molyneux J E 1967 *J. Fluid Mech.* **30** 97
[7] Rubinstein J and Torquato S 1989 *J. Fluid Mech.* **206** 25
[8] Rubinstein J and Torquato S 1988 *J. Chem. Phys.* **88** 6372
[9] Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1
[10] Cornell B A, Middlehurst J and Parker N S 1981 *J. Colloid Interface Sci.* **81** 280
[11] Hertz P 1909 *Math. Ann.* **67** 387
[12] Reiss H, Frisch H L and Lebowitz J L 1959 *J. Chem. Phys.* **31** 369
[13] Torquato S, Lu B and Rubinstein J 1990 *Phys. Rev.* A in press
[14] Torquato S and Lado F 1985 *J. Phys. A: Math. Gen.* **18** 141
[15] Torquato S and Lado F 1988 *Proc. R. Soc.* A **417** 59
[16] Hansen J P and McDonald I R 1976 *Theory of Simple Liquids* (London: Academic)
[17] Torquato S and Lado F 1986 *Phys. Rev.* B **33** 6428
[18] Shahinpoor M 1980 *Powder Technol.* **25** 163
[19] Salsburg Z W, Zwanzig R W and Kirkwood J G 1953 *J. Chem. Phys.* **21** 1098
[20] Torquato S and Lee S B *Preprint*