On the mean separation of particles of finite size in one to three dimensions

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Particles of finite size are assumed to move randomly in a gas or liquid, with their only interactions arising from their hard cores and excluded volume. The mean nearest neighbour separation of such particles is calculated exactly for one dimension ($n=1$, rods) and quite accurately for two and three dimensions ($n=2, 3$; hard discs and spheres). Results are exact for $n=2$ and 3 in the limit of zero density or for any density when the particles are points. For finite-size particles the results are extended to the close-packed limiting densities. For $n=2$ and 3, the present predictions differ very appreciably over the entire density range from those calculated by conventional approaches.

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1. INTRODUCTION

The problem of the average nearest-neighbour separation between particles, such as molecules, atoms, or ions, is one of considerable interest and is relevant to the lattice and hole theories of liquids. The situation to be considered is appropriate for gases and liquids where the particles can move randomly and are not constrained to a lattice. The only interaction between the particles is here taken to be that arising from a distance of closest approach, r_0, which is primarily steric for uncharged particles of finite size. For charged particles of the same sign, however, r_0 may exceed the steric value because of coulombic repulsion [1]. In three dimensions ($n=3$), we shall be dealing with the standard problem of the hard sphere gas with particles of diameter r_0, but we shall be concerned with densities, ρ, up to the close packed limit associated with r_0.

Although the assumption of particle–particle interactions arising only from r_0 is a stringent one, it nevertheless leads to more realistic results than do the conventional treatments of the mean nearest-neighbour separation, $\langle r \rangle$. These treatments [2, 3], which are often applied to electrolyte situations, generally ignore finite size effects completely, ignore the random aspect of particle motion in a liquid or gas, and assume, in order to obtain an expression for $\langle r \rangle$, that the particles are arranged on a fully occupied lattice whose primitive spacing is determined by the particle concentration. As we shall see, both random motion and finite size effects can make the $\langle r \rangle$ values calculated herein quite different from those predicted by the conventional approach.

We begin with the calculation of $\langle r \rangle$ for $n=1$, 2, and 3, and follow this with a comparison of random-situation predictions of $\langle r \rangle$ with those of the conventional approach.

2. CALCULATIONS FOR RANDOM ARRANGEMENTS

Although we shall be concerned with $n = 1$, 2, and 3 situations, i.e. hard rods, hard discs, and hard spheres, it is convenient to pose the problem for $n = 3$ and then discuss the necessary specialization for $n = 1$ and 2. The mean nearest neighbour separation is given by

$$\langle r \rangle \equiv \int_0^\infty \xi P(\xi)\, d\xi, \tag{1}$$

with

$$\int_0^\infty P(\xi)\, d\xi = 1. \tag{2}$$

Here $P(r)\, dr$ is the probability of finding the nearest neighbour of a particle, whose centre is at $r = 0$, in the spherical shell of thickness dr and inner radius r. Because in general $r_0 \neq 0$, $P(r)$ must be zero for $r < r_0$ and thus must involve the unit step function $U_0(r - r_0)$. Equation (2) is the usual normalization condition for a probability density.

Now $P(r)\, dr$ may be expressed as the product of three terms,

$$P(r)\, dr = P_{\mathrm{F}}(r) P_{\mathrm{N}}(r) U_0(r - r_0). \tag{3}$$

Here $P_{\mathrm{F}}(r)$ is the probability of finding a particle within the spherical shell of thickness dr and inner radius r and $P_{\mathrm{N}}(r)$ is the probability that the nearest neighbour does not lie in the spherical volume of radius r. Through the use of (2), we can express $P_{\mathrm{N}}(r)$ as

$$P_{\mathrm{N}}(r) = 1 - \int_0^r P(\xi)\, d\xi, \tag{4}$$

the same in form for $n = 1$, 2, and 3.

Consider now the $n = 1$ situation of hard rods of length r_0. Since it can be solved exactly, it gives some guidance for the $n = 2$ and 3 situations. Let there be a total number of N rods distributed in a total length L. Then the density is $\rho \equiv N/L$, and the maximum possible density is $\rho_0 = (L/r_0)/L = r_0^{-1}$. Now $P_{\mathrm{F}}(r)$ is just $2N\, dr/(L - Nr_0)$, where $(L - Nr_0)$ is the free or available length [4], corresponding to the free volume for $n = 3$. If we now divide through by L, we have

$$P_{\mathrm{F}}(r) = 2\rho\, dr/[1 - \rho r_0]. \tag{5}$$

Let us define the relative free 'volume' as $T \equiv (1 - \rho\omega)$ for any n. For $n = 1$, $\omega = r_0$ exactly, but no exact expression for $\omega(\rho)$ is known for $n = 2$ and 3. Here $\omega(\rho)$ is essentially the average 'volume' taken up by a particle for $n = 2$ or 3 when two or more are present. In the $n = 2$ and 3 cases, $\omega > V_n$, where V_n is the 'volume' of a single particle, because discs and spheres do not fit together exactly and some volume is thereby excluded. But since rods do fit together exactly in one dimension, (5) is exact, as is the resulting $P(r)$. The integral equation resulting from the substitution of (4) and (5) into (3) may be readily solved by the approach in [1] and yields

$$P(r) = [2\rho/(1 - \rho r_0)] \exp\,[(2\rho/(1 - \rho r_0))(r_0 - r)] \cdot U_0(r - r_0). \tag{6}$$

The resulting exact $\langle r \rangle$ for $n = 1$ is

$$\langle r \rangle = 0 \cdot 5(r_0 + \rho^{-1}), \tag{7}$$

which yields $\langle r \rangle = r_0$ when $\rho = \rho_0$ as it should.

The approach and solutions are similar for $n=2$ and 3. In these cases $P_Y(r)=2\pi(2)^{n-2}\,\rho r^{n-1}\,dr/T(\rho)$. The simplest choice for $T(\rho)$ is to take $\omega=0$ and thus ignore excluded volume effects. This was the course followed earlier [1] for the $n=2$ case. It is, of course, valid in the $\rho\to0$ limit but not otherwise. Here we have elected to use the results of Andrews [4] for $\omega(\rho)$ for $n=2$ and 3. Since the present random approach will be extended to the dense limit, $\rho\to\rho_0$, where ρ_0 is the close packed, ordered density, we need $T(\rho)$ over the entire range of ρ. Now $\rho_0\equiv(2/\sqrt{3})r_0^{-2}$ and $\sqrt{2}r_0^{-3}$ for $n=2$ and 3, respectively, corresponding to hexagonal close packing and face centred cubic close packing. Let
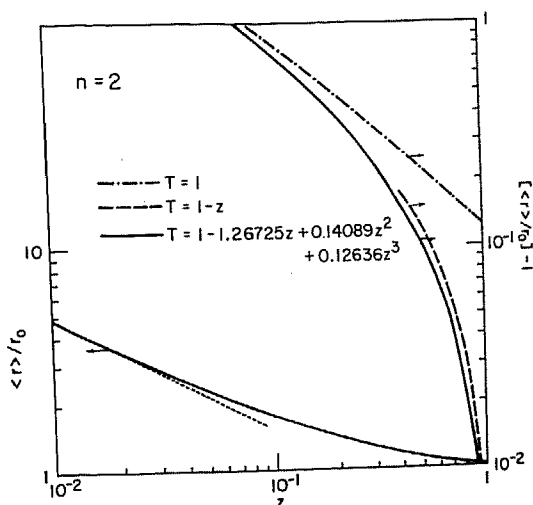

Figure 1. The normalized quantities $\langle r\rangle/r_0$ and $[\langle r\rangle/r_0]-1$ versus $z\equiv\rho/\rho_0$ for the hard disc situation and for several choices for the excluded 'volume' function $T(z)$.
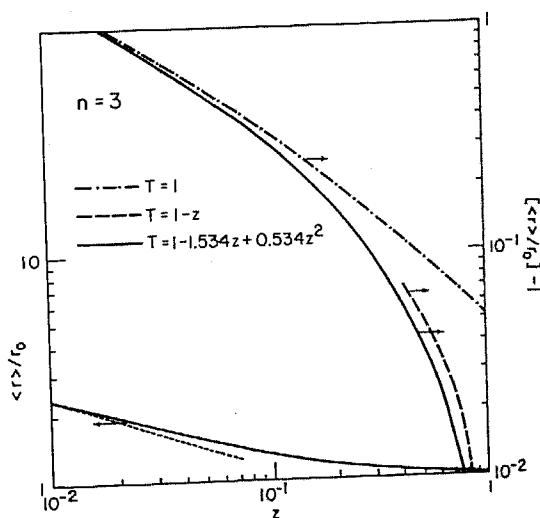

Figure 2. The normalized quantities $\langle r\rangle/r_0$ and $[\langle r\rangle/r_0]-1$ versus $z\equiv\rho/\rho_0$ for the hard sphere situation and for several choices for the excluded volume function $T(z)$.

$z \equiv \rho/\rho_0$; then $0 \leqslant z \leqslant 1$.   We may write $T \equiv 1 - \rho\omega = 1 - [\rho_0\omega(z)]z$.   Since there is no volume available to add another particle when $z = 1$, it is necessary for $z = 1$ that $\omega = \rho_0^{-1}$, and thus $T = 0$ in this limit.   Sensible formulas for $T(z)$ have been given by Andrews and are listed in figures 1 and 2.   They have led [4] to very good agreement between derived equations of state and molecular dynamics and Monte Carlo hard disc and hard sphere results for $n = 2$ and 3.   Slightly different expressions for $\omega(z)$ have been employed in later work [5], where a more precise definition of ω also appears.

For $n = 2$ and 3 let us introduce the new normalized variable

$$x \equiv 2\pi n^{-1}(n-1)r_0{}^n T^{-1} \rho \equiv x_m T^{-1} z, \tag{8}$$

where $T(z) \equiv 1 - [\rho_0\omega(z)]z$, and

$$x_m = \begin{cases} (4/3)^{1/2} \pi \cong 3{\cdot}6276, & n = 2 \\[2mm] (32)^{1/2} \pi/3 \cong 5{\cdot}9238, & n = 3. \end{cases} \tag{9}$$

Note that if $T(z) = 1$ for all z, x_m is the maximum possible value of x, that at close packing.   Otherwise the maximum value of x is infinity.   Results for $P(r)$ and $\langle r \rangle$ may now be expressed as

$$P(r) = n(x/r_0)(r/r_0)^{n-1} \exp\left[x\{1 - (r/r_0)^n\}\right] \times U_0(r - r_0), \tag{10}$$

and

$$\langle r \rangle/r_0 = x^{-1/n} \exp(x)\Gamma(1 + n^{-1}, x), \tag{11}$$

where $\Gamma(a, x)$ is the incomplete gamma function.   These results would be exact if the function $\omega(\rho)$ were exactly known, and they are, of course, exact in the $\rho \to 0$ limit and for $r_0 \equiv 0$ with any ρ.

Now as $x \to 0$, (11) reduces to $\langle r \rangle/r_0 \to x^{-1/n}\Gamma(1 + n^{-1})$, where $\Gamma(1 + n^{-1})$ is the complete gamma function.   Thus for $n = 2$, $\langle r \rangle/r_0 \to 0{\cdot}5\sqrt{(\pi/x)}$ and for $n \to 3$ it approaches $x^{-1/3}\Gamma(4/3)$, where $\Gamma(4/3) \cong 0{\cdot}89398$.   In the other extreme as $x \to \infty$, $\langle r \rangle/r_0 \to 1 + (nx)^{-1} + \dots$.

Figures 1 and 2 show the dependence of $\langle r \rangle/r_0$ and $[\langle r \rangle/r_0] - 1$ on z for $n = 2$ and 3 and several choices of $T(z)$.   The dotted lines show the approach to limiting $z \to 0$ behaviour.   The quantity $\langle r \rangle/r_0$ has been plotted only for the third form of T, that derived by Andrews for the fluid region of the equation of state, $z \gtrsim 0{\cdot}67$ for $n = 3$.   When spheres begin to cooperate and establish regions of close packed order, at $z \gtrsim 0{\cdot}74$, the material begins to approach a hard sphere crystal rather than a liquid or gas.   Andrews has suggested that a reasonable choice for $\omega(\rho)$ is ρ_0^{-1} in this region, leading to $T = 1 - z$.   In order to allow comparison of differences in $\langle r \rangle/r_0$ arising from different $T(z)$ choices, the figures include curves for $[\langle r \rangle/r_0] - 1$ for the three T expressions of interest.   As far as $\langle r \rangle/r_0$ is concerned, it clearly makes little difference whether the second or third form of T is used.   But the $T = 1$ results, where free volume corrections are ignored, lead to $x = x_m$ at $\rho = \rho_0$, rather than to $x = \infty$ at this limiting density. The values of $\langle r \rangle/r_0$ obtained for $x = x_m$ are about $1{\cdot}124$ and $1{\cdot}051$ for $n = 2$ and 3, respectively, results which are significantly different from the correct value of unity.   To use the present results properly one should switch from the third to the second form of T as one passes from the fluid phase to the crystalline one. But since $\langle r \rangle/r_0$ is so close to unity by either approach when $0{\cdot}7 \gtrsim z \leqslant 1$, there is no practical reason to do so as far as calculation of $\langle r \rangle/r_0$ is concerned.

3. Comparison with conventional approaches

Since the conventional methods of calculation of $\langle r \rangle$ do not take explicit account of the finite size of particles [2, 3], we cannot normalize with r_0 and must compare $\langle r \rangle$ predictions directly. For the low density limit it is convenient to introduce the function

$$F_n \equiv [\rho^{1/n}\langle r \rangle]_{\rho \to 0}, \tag{12}$$

which becomes, on using (11),

$$F_n = [2\pi\{(n-1)/n\}]^{-1/n}\,\Gamma(1+n^{-1}). \tag{13}$$

Table 1 shows $n = 2$ and 3 results for F_n for the several choices of interest. Note that the particle diameter r_0 plays no role in the $\rho \to 0$ limit where the particles are far apart. The F_2 random results for $n = 2$ has been given previously [1]. The table shows a difference between conventional and random results of about a factor of two. Such a large difference suggests that the present, very nearly correct, result should always be preferred to those of the conventional approaches. Not only is this the case for $\rho \to 0$, but because the present random-situation approach takes r_0 explicitly into account, the present formulas should be preferable for all ρ, up to $\rho = \rho_0$.

Finally, it is of interest to compare directly a few $\langle r \rangle$ values calculated from the various approaches already discussed. Table 2 shows a few such values for uncharged particles and $n = 2$ for three choices of ρ. Again we see large differences between conventional and random predictions. For the lowest ρ, the

Table 1. Values of the function $F_n \equiv [\rho^{1/n}\langle r \rangle]_{\rho \to 0}$ for several arrangements in two ($n = 2$) and three ($n = 3$) dimensions.

n	Arrangement	F_n
2	Square array	1
	Hexagonal array	$(4/3)^{1/4} \cong 1.075$
	Random	0.5
3	Simple cubic array	1
	Face centred cubic array	$2^{1/6} \cong 1.123$
	Random	0.554

Table 2. Calculated values of $\langle r \rangle$ for $n = 2$ for three values of ρ and several situations.

		$\langle r \rangle$ (Å) ρ (cm^{-2})		
Arrangement	r_0 (Å)	5×10^{12}	5×10^{13}	5×10^{14}
Square	—	44.72	14.14	4.47
Hexagonal	—	48.06	15.20	4.81
Random	0	22.36	7.07	2.24
Random	1	22.39	7.15	2.45
Random	3	22.60	7.68	3.49
Random	4.25	22.81	8.18	4.37

distance of closest approach, r_0, makes little difference because the particles are generally much farther apart than this distance. This is certainly no longer the case for $\rho = 5 \times 10^{14}$ cm^{-2}. The quantity z is about 0·043 for $r_0 = 1$ Å and increases to about 0·782 for $r_0 = 4\cdot25$ Å when $\rho = 5 \times 10^{14}$ cm^{-2}. The 4·25 Å value has been picked here because it has been employed in recent Monte Carlo simulations of the diffuse double layer [6]. Some discussion of the approach to hexagonal close packing for charged particles has been given elsewhere [7].

Table 3. Calculated values of $\langle r \rangle$ for $n = 3$ for three different molarity situations.

M Arrangement	r_0 (Å)	0·1 (neutral) $6\cdot02 \times 10^{19}$	1 (neutral) $6\cdot02 \times 10^{20}$	1 (charged) $1\cdot2 \times 10^{21}$
		$\langle r \rangle$ (Å) ρ (cm^{-3})		
Simple cubic	—	25·51	11·84	9·40
Face centered cubic	—	28·64	13·29	10·55
Random	0	14·13	6·56	5·21
Random	1	14·14	6·57	5·23
Random	3	14·21	6·83	5·59
Random	4·25	14·32	7·20	6·07

Finally, table 3 shows similar results for $n = 3$. Here we use the molarity, M, in mol l^{-1} to establish values of ρ for consideration. We have $\rho = 10^{-3} \epsilon M N_A$, where N_A is Avogadro's number, and ϵ is unity for uncharged particles and two for a z–z-valent binary electrolyte. Again one sees appreciable differences between conventional and random calculation results. Only for $M \gtrsim 1$ does a non-zero r_0 make much difference. The relative density z is about $8\cdot5 \times 10^{-4}$ for $r_0 = 1$ Å and $\rho \cong 1\cdot2 \times 10^{21}$ cm^{-3} and about 0·065 for $r_0 = 4\cdot25$ Å and the same ρ value. We thus consider looser packed systems here in three dimensions than we did for the $n = 2$ results of table 2. Although the conventional approach has been applied up to $M = 10$ or more [3], it is quite clear that for such high concentrations one must not ignore the packing density limitations set by r_0. Since $z \cong 0\cdot065$ for the situation leading to $\langle r_3 \rangle \cong 6\cdot07$ Å in table 3, it is likely that the predictions of fluid random packing are still adequate here, although $r_0 = 4\cdot25$ Å would probably need to be interpreted as a coulombic hard core rather than the smaller steric hard core [7] in this charged particle case.

The present approach is most pertinent for uncharged particles and is, of course, less applicable for charged particles because of its neglect of Coulomb interactions. Nevertheless, a few possibilities for charged systems are worth mentioning. First, the theory should become more and more applicable for such systems as the charge density decreases, the particles are farther and farther apart on the average, and Coulomb interactions become less and less important. Second, for regions where the particles are mostly of the same sign, as in a space charge region, one might apply the present results for $n = 2$ or 3, as appropriate, with r_0 an effective coulombic radius possibly dependent on charge density. Finally, for a bulk electrolyte region of overall charge neutrality containing charges of both signs, one might apply the present theory to the ion pairs present

[8, 9], neutral entities whose concentration would be calculated by conventional ion-pairing theory. It would be simplest to take r_0 as the effective diameter of the ion pair, and the theory should then yield an estimate of the mean nearest-neighbour distance for such pairs. In most cases of practical interest, the low-density limiting form of the theory would be quite adequate.

Note added in proof.—Recent work of F. C. Andrews and H. M. Ellerby, (1981, *J. chem. Phys.*, **75**, 3542), applies probability distributions equivalent to those herein to the problem of deriving an equation of state for liquids. Excellent agreement with Monte Carlo and molecular dynamics results is obtained.

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