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On the distribution of the nearest neighbor

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(Received 23 September 1985; accepted for publication 19 December 1985)

The classical derivation of the distance distribution function of the nearest neighbor is discussed, and its limitations outlined. A new derivation, more general, is presented and applied to a random distribution of particles in a sphere.

I. INTRODUCTION

The approximation to consider, only, the interaction between a particle and its nearest neighbor is sometimes made in many-particle systems. For example, this has been done in electronic energy transfer[1,2] and stellar dynamics.[3] Using the distance distribution function of the nearest neighbor (DFN) the mean distance between the particles can also be obtained (Appendix A).

The classical DFN[4] is valid whenever two conditions are fulfilled: (i) uniform distribution of the particles and (ii) mean distance between particles much smaller than the dimensions of the volume containing the particles.

A case where the first condition is not met is that of a liquid: its molecules are crowded, and therefore the volume occupied by each molecule must be taken into account. Besides this *excluded volume effect*, a *short range order* exists. Both effects are mathematically expressed by the well-known radial distribution function, $g(r)$.[5] This function is defined as the ratio of the actual number density (number of particles per unit volume) at distance r from the particle, $n(r)$, to the bulk number density, n,

$$g(r)=n(r)/n. \tag{1}$$

Two typical cases are shown in Fig. 1: in Fig. 1(a) the radial distribution function of a monoatomic liquid and in Fig. 1(b) the radial distribution of a dilute monoatomic gas. In both cases r is the center-to-center distance. The probability of two molecules having a very small separation is low because of the repulsive forces ("excluded volume"). Several progressively decreasing peaks occur in $g(r)$ of the liquid, reflecting a sort of multilayer disposition of the molecules around the central molecule. Only for large distances is the distribution uniform, with $g(r)=1$.

In order to have a mean distance between particles similar to the dimensions of the vessel, it is clear that the particles can only be a few, say, less than one thousand. But this is really a very small number. Does it have any physical meaning? The answer is yes, and systems with this peculiarity are not unknown. They may be called compartmentalized systems. Examples are gases in porous media and molecules dissolved in micelles. In both cases a large number of molecules is distributed by an equally large number of compartments. In this way, each compartment contains only a few molecules.

It is the purpose of this paper to derive DFN's for the two above-mentioned cases, where the classical DFN is not valid. For the sake of completeness, we start with the derivation of the classical DFN.

II. CLASSICAL DISTRIBUTION

Consider a large volume V, containing N particles, $N\gg 1$. The number density is then $n=N/V$. Let $w(r)$ be the sought-for distribution function of the nearest neighbor. If we choose a particle at random, and define a sphere of radius r centered in that particle, and if the particles are uniformly distributed, the probability for a particle to occur inside the sphere is simply v/V, where $v=4\pi r^3/3$.

Since the particles are considered dimensionless, they can occur in any number (up to N) interior to r. Then the probability of having K particles in the sphere (plus the central particle) is given by the binomial law

$$p(K)=\binom{N}{K}\left(\frac{v}{V}\right)^K\left(1-\frac{v}{V}\right)^{N-K}. \tag{2}$$

The probability that no particles occur interior to r is of course $P(0)$, but is also equal to one minus the probability that the nearest neighbor occurs between zero and r, that is,

$$1-\int_o^r w(r)dr=\left(1-\frac{v}{V}\right)^N. \tag{3}$$

By taking the limit $N\rightarrow\infty$, while fixing $n=N/V$, we get

$$1-\int_o^r w(r)dr=\exp\left(-\frac{4\pi r^3 n}{3}\right) \tag{4}$$

thus

$$w(r)=4\pi r^2 n\exp(-4\pi r^3 n/3). \tag{5}$$

Now it is clear that the derivation of the classical DFN involves two assumptions, as referred in the introduction: (i) uniform distribution of particles, that is, dimensionless and noninteracting entities and (ii) infinite volume, valid

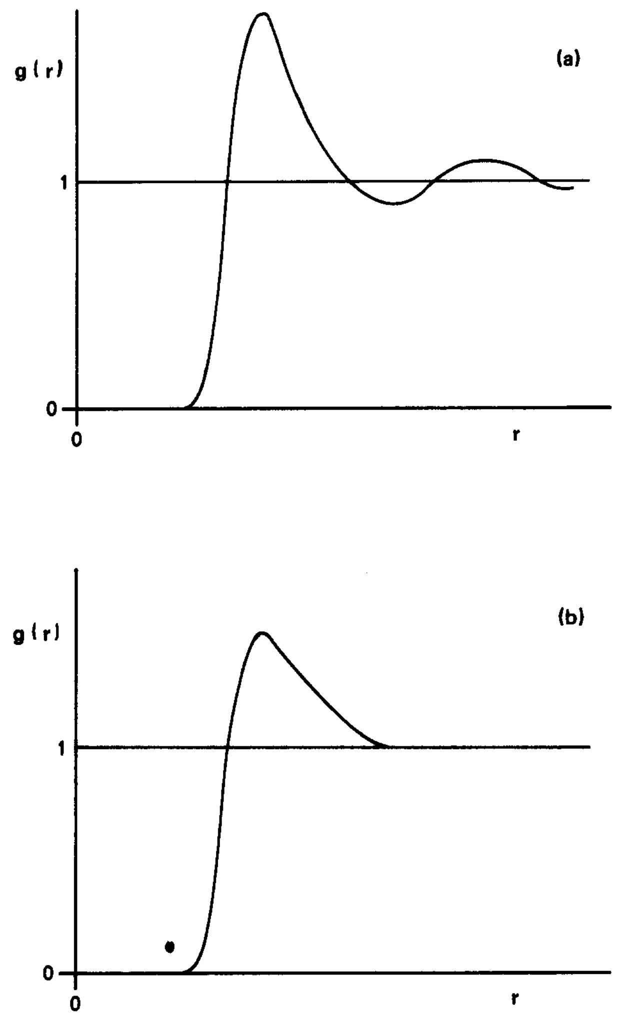

Fig. 1. Radial distribution function for a liquid (a) and a dilute gas (b).

for finite volume systems if the number of particles is not very small, roughly $N > 1000$.

III. NONUNIFORM DISTRIBUTION OF PARTICLES

The probability for a particle to be inside the sphere is the ratio of the number of particles it contains to the total number of particles, which leads to v/V for a uniform distribution. The number of particles that exist in a spherical layer of thickness dr at a distance r is $4\pi r^2 n g(r) dr$, therefore the number of particles interior to r is $\int_0^r 4\pi r^2 n g(r) dr$. Substituting v/V in Eq. (3) by this expression multiplied by $1/N$, we get, instead of (5),

$$w(r) = 4\pi r^2 n g(r) \exp\left(- \int_o^r 4\pi r^2 n g(r) dr \right). \qquad (6)$$

This equation is still based on the assumption that the particles are independently distributed outside the sphere. Therefore, it will not hold when the bulk density is high. However, in such a case $w(r) \sim \delta(r-d)$, where d is the distance of closest approach.

IV. SMALL NUMBER OF PARTICLES

Quite another approach is required to obtain the DFN when the number of particles is small. The starting point is the distance distribution function for the isolated pair, $w_1(r)$, which we assume to be known. We further assume a uniform distribution of the particles. In a three-particle system there are two pairs comprising the same particle. The relative distances in these pairs are random variables, R_1 and R_2. The random variable minimum distance (nearest-neighbor distance), $R(2)$, is then

$$R(2) = \min \{R_1, R_2\} \qquad (7)$$

or, explicitly,

$$R(2) = (R_1 + R_2 - |R_1 - R_2|)/2. \qquad (8)$$

Both R_1 and R_2 are distributed according to w_1. At this point, we are faced with the problem of finding the probability density function of a random variable $[R(2)]$ that is a known function of other random variables with known distribution functions, and this is a standard procedure in probability theory.[6] The region of integration is shown in Fig. 2, for a hypothetical case where $a < r < b$.

The cumulative distribution function of the nearest neighbor, $F_2(r)$, is then given by

$$F_2(r) = \int_a^b \int_a^r w_1(r_2) w_1(r_1) dr_1 dr_2 + \int_a^r \int_r^b w_1(r_2) w_1(r_1) dr_1 dr_2. \qquad (9)$$

Hence

$$F_2(r) = F_1(r) + [1 - F_1(r)] F_1(r) \qquad (10)$$

and, since by definition

$$w_2(r) = \frac{dF_2}{dr}, \qquad (11)$$

Eq. (11) becomes

$$w_2(r) = 2 w_1(r) \int_r^b w_1(r) dr. \qquad (12)$$

The generalization to a number N of pairs is straightforward if one considers that, for example,

$$R(3) = \min \{R_1, R_2, R_3\} = \min\{R_1, \min\{R_2, R_3\}\} = \min\{R_1, R(2)\}. \qquad (13)$$

Hence, in general, we can write

$$R(N) = \min \{R_1, R(N-1)\} \qquad (14)$$

and then Eq. (9) becomes

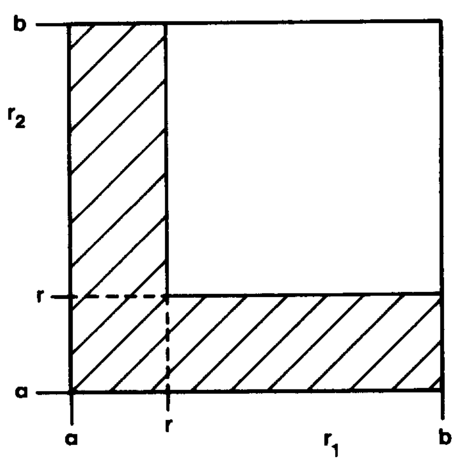

Fig. 2. Region of integration for the calculation of the DFN. The hatched portion corresponds to $\min \{r_1, r_2\} < r$.

$$F_N(r) = \int_a^b \int_a^r w_{N-1}(r) w_1(r_1) dr_1\, dr + \int_a^r \int_r^b w_{N-1}(r) w_1(r_1) dr_1\, dr \quad (15)$$

or

$$F_N(r) = F_1(r) + [1 - F_1(r)] F_{N-1}(r). \quad (16)$$

The solution of (16) is easily obtained as

$$F_N(r) = 1 - [1 - F_1(r)]^N. \quad (17)$$

Thus

$$w_N(r) = N w_1(r) \left(\int_r^b w_1(r) dr \right)^{N-1}. \quad (18)$$

This equation is, of course, applicable to any distribution of particles, even if not three-dimensional.

V. AN EXAMPLE: PARTICLES IN A SPHERE

The distribution of the isolated pair, $w_1(x)$, with $x = r/R_s$, where R_s is the radius of sphere, is (Appendix B)

$$w_1(x) = (3x^2/16)(x-2)^2(x+4). \quad (19)$$

Using Eq. (18) we get

$$w_N(x) = (3Nx^2/16)(x-2)^2(x+4) \times (-x^6/32 + 9x^4/16 - x^3 + 1)^{N-1}. \quad (20)$$

When N is very large ($x \ll 1$, see Fig. 3)

$$w_N(x) = 3Nx^2 \exp(-Nx^3) \quad (21)$$

precisely the classical DFN, compare Eq. (5).

APPENDIX A

By definition the mean distance between particles D is

$$D = \int_0^\infty r w(r) dr, \quad (A1)$$

where $w(r)$ is the distance distribution function of the nearest neighbor. With the classical function we get

$$D = \Gamma(4/3)(3/4\pi)^{1/3} n^{-1/3} = 0.5540\, n^{-1/3}. \quad (A2)$$

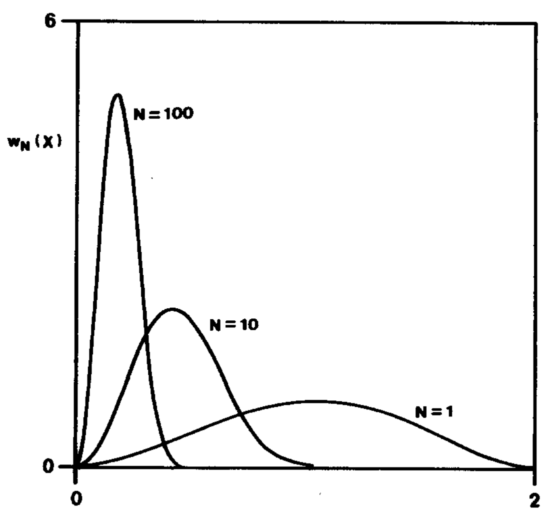

Fig. 3. Distribution function of the nearest neighbor for $N+1$ particles randomly distributed in a sphere.

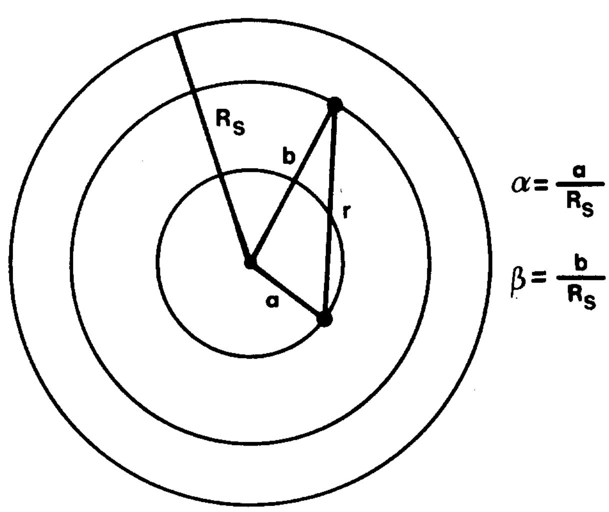

Fig. 4. Distribution of two particles on two spherical surfaces of radii a and b, interior to a sphere of radius R_s.

For example a perfect gas at 1 atm and 298 K has $D = 2$ nm and a solution of concentration 10^{-5} mol/dm^3 has $D = 30$ nm.

Note that the assumption of a cubic arrangement yields $D = n^{-1/3}$, in error by 81%.

APPENDIX B

In order to derive the distance distribution function of a pair of particles randomly distributed in a sphere we proceed by the following steps.

(1) Let the two particles be at first distributed at random on two spherical surfaces of radii a and b (one particle per surface), as shown in Fig. 4. It is not difficult to obtain the distance distribution function as

$$w_1(x) = x/2\alpha\beta, \quad (B1)$$

where $x = r/R_s$, $\alpha = a/R_s$, and $\beta = b/R_s$.

(2) Randomizing[7] the parameter β with the distribution function $3\beta^2$, one of the particles becomes uniformly distributed inside the sphere, while the other keeps its radial location α. The distribution function, obtained from (B1), is

$$w_1(x) = \begin{cases} 3x^2, & \text{if } x < 1 - \alpha \\ (3x/4\alpha)[1 - (x-\alpha)^2], & \text{otherwise.} \end{cases} \quad (B2)$$

(3) Finally, randomizing the parameter α with the distribution function $3\alpha^2$, both particles are now distributed at random in the sphere and we get

$$w_1(x) = (3x^2/16)(x-2)^2(x+4). \quad (B3)$$

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