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Nearest-neighbor distribution functions and mean separation for impenetrable particles in one to three dimensions

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Expressions for the hard-sphere nearest-neighbor probability distribution, P_{NN}, and the associated mean nearest-neighbor distance, $\langle r_{NN}\rangle$, in $D=1$ to 3 dimensions, which were recently derived by Torquato, Lu, and Rubinstein [Phys. Rev. A **41**, 2059 (1990)] are compared with earlier results of Reiss and Casberg [J. Chem. Phys. **61**, 1107 (1974)] and Macdonald [Mol. Phys. **44**, 1043 (1981)]. Full agreement is found for the $D=1$ results, where an exact solution can be found. But no such solution is possible for $D=2$ and 3. The equation of state, P_{NN}, and $\langle r_{NN}\rangle$ can all be calculated from knowledge of the central function G_D, a conditional probability depending on both density and distance, r, from a particle center. The consequences of several different approximations for G_D are explored for hard disks and spheres. In spite of the much more approximate G_D functions used by Macdonald compared to those of Torquato, differences in the resulting P_{NN} responses are relatively small even at high densities, and the differences in $\langle r_{NN}\rangle$ predictions, the quantities of primary experimental value, are entirely negligible. Although the original $D=2$ Torquato expression for P_{NN} was not properly normalized, a sign correction restores normalization and leads to close agreement with the earlier work. For $D=3$, numerical results show that simple approximation of G_3 by the contact value of the ordinary radial distribution function, a quantity independent of r, yields results for P_{NN} very close to those of Torquato, and the corresponding $\langle r_{NN}\rangle$ results are completely indistinguishable.

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I. INTRODUCTION AND BACKGROUND

In an interesting paper with a title similar to this work [1] and in several others [2,3], Torquato, Lu, and Rubinstein (denoted TLR hereafter) presented expressions for the nearest-neighbor distribution function, P_{NN} (termed H_P by these authors), for a liquid-phase system of homogeneous, impenetrable D-dimensional particles of "diameter" σ for $D=1$, 2, and 3 in the thermodynamic limit. In addition, TLR used these results to calculate the normalized mean nearest-neighbor distance, $R_{NN}\equiv\langle r_{NN}\rangle/\sigma$, for $D=1$, 2, and 3. Here, these results are corrected where necessary and are then compared to earlier expressions not cited by TLR for these important "hard-sphere" quantities. It should be noted that except for $D=1$, where the explicit TLR and earlier results agree, it is impossible to obtain an exact, analytic expression for P_{NN} [as a function of density, ρ, and distance r ($\geq\sigma$) from the center of a given particle], which can be used to calculate these dependences explicitly for arbitrary densities. Thus, for the $D=2$ and 3 situations discussed below, all results are necessarily approximate.

For conciseness, it is convenient to express results in terms of normalized density, ϕ (the packing fraction), and normalized distance $x\equiv r/\sigma$ (≥ 1). The reduced density ϕ is defined as ρV_D, where V_D is the volume of a particle of diameter σ and $\rho\equiv N/V$ is the number density. The maximum allowed value of ρ, ρ_0, is $\sqrt{2}\sigma^{-3}$ for $D=3$, the hexagonal-solid, close-packed value. The corresponding maximum value of ϕ, ϕ_c, is $\sqrt{2}\pi/6\simeq 0.74048$. In general,

$$\phi=\pi^{D/2}\rho(\sigma/2)^D/\Gamma(1+(D/2)) , \tag{1}$$

where Γ is the gamma function, and, for notational simplicity, an explicit D subscript has been omitted for ϕ and most other quantities defined below. Since conservation of probability requires that $P_{NN}(\rho,r)dr=P_{NN}(\phi,x)dx$, we shall follow TLR and deal hereafter with the dimensionless quantity $P_{NN}(\phi,x)$. Its nth moment may be written as

$$J(n,\phi)\equiv\int_1^\infty x^n P_{NN}(\phi,x)dx . \tag{2}$$

When $n=0$, proper normalization of a probability density requires $J(0,\phi)=1$. But when $n=1$, $J(1,\phi)\equiv R_{NN}(\phi)$, the normalized mean nearest-neighbor distance. It is thus clear that once an expression for P_{NN} is given, the corresponding R_{NN} follows immediately.

Following earlier work [4], it is possible to write a single general expression for P_{NN} for $D=1$, 2, and 3 in terms of the functions

$$F(\phi,x)\equiv D2^D\phi x^{D-1}G_D(\phi,x) \tag{3}$$

and

$$I(\phi,x)\equiv\int_1^x F(\phi,y)dy . \tag{4}$$

Then,

$$P_{NN}(\phi,x)=F(\phi,x)\exp[-I(\phi,x)] . \tag{5}$$

It follows that an expression for P_{NN} may be found given any plausible form for the basic function $G_D(\phi,x)$, which itself need be defined only for $x\geq 1$ in the present situation. But it is worth reiterating that for $D>1$ no exact expressions for $G_D(\phi,x)$ are known. From the form of the

Eq. (5) result, P_{NN} is clearly normalized.

The first general expression for the nearest-neighbor distribution function seems to be that given in a 1974 paper by Reiss and Casberg [5] for $D=3$, although a simple form of it with $G_2=1$ appeared in 1967 [6]. The Reiss-Casberg expression is consistent with Eqs. (3)–(5) but no explicit form was given for $G_3(\phi,x)$ [or $G_2(\phi,x)$], there denoted as G and termed the central function of scaled particle theory [7]. Although TLR [1,2] claimed to be the first to present explicit results for P_{NN} in one to three dimensions, they did not refer to the Reiss-Casberg work and were unaware of earlier work [4] where explicit results for P_{NN} appeared and where closed-form expressions for R_{NN} for all three values of D were derived. Although TLR gave no general expression for P_{NN}, their individual results for $D=1$, 2, and 3 are consistent with Eq. (5). Reference [4] was itself carried out without knowledge of the Reiss-Casberg treatment but led to a result of the form of Eq. (5) with an exact expression for $G_1(\phi,x)$ and approximate ones for $G_2(\phi,x)$ and $G_3(\phi,x)$.

II. THE CENTRAL FUNCTION $G_D(\phi,x)$

TLR [1] termed $G_3(\phi,x)$ (denoted by them as $G_V=G_P$ for $x\geq 1$) a conditional pair distribution function and defined it as "the radial distribution function for a special binary mixture of spheres, namely, one for a single test particle of radius $r-\sigma/2$ (i.e., test particles at infinite dilution) and an actual inclusion of diameter σ at contact, i.e., when such particles are separated by the distance r." The definition of G_3 given earlier by Reiss and Casberg [5] is essentially equivalent. The function corresponding to the present $F(\phi,r)dr$ was defined by TLR [1] as the probability that, given a sphere of radius r encompassing any particle centered at some arbitrary position but empty of particle centers, particle centers are contained in the spherical shell of radius r and thickness dr surrounding the central particle. The corresponding arbitrary-D probability introduced in Ref. [4], $P_Y(r)dr$, was defined as the probability of finding a particle within the spherical shell of thickness dr and inner radius r (measured from a particle center). In this definition, the conditional character of the probability, incorporated by Reiss and Casberg and TLR, does not appear. This approximation was addressed by Kenkel, Simons, and Hermans [8] using a Monte Carlo simulation, and the conclusion was reached that the neglect of conditionality was of consequence only for very small, finite systems.

There are three general equations [5,7,9–11] which must be satisfied by an accurate expression for $G_D(\phi,x)$. The first requires that

$$G_D(\phi,1)=g_r(\phi,1)\,, \tag{6}$$

where $g_r(\phi,1)$ is the contact value of the ordinary D-dimensional radial distribution function. Now define the pressure equation of state as $Z(\phi)\equiv P/\rho kT$, where P is the pressure of the system and k and T have their usual meanings. Then the two remaining equations are

$$Z(\phi)=1+2^{D-1}\phi g_r(\phi,1) \tag{7}$$

and

$$G_D(\phi,\infty)=Z(\phi)\,. \tag{8}$$

For the $D=1$ situation, matters are particularly simple; then the relations $G_1(\phi,x)=g_r(\phi,x)=(1-\phi)^{-1}$ are exact and independent of $x(\geq 1)$ [5,10]. In addition, for $D=1$ $F(\phi,x)=2\phi/(1-\phi)$ with $\phi=\rho\sigma$ [4]. In the earlier work [4], approximate expressions for G_2 and G_3 were based on extrapolation of these $D=1$ relations to higher dimensions. They made use of expressions of Andrews [12,13] for the available relative free volume of a particle, and thus the formulas for G_D with $D=2$ and 3 involved no x dependence and should become less adequate as D increases.

III. CONSEQUENCES AND COMPARISONS OF DIFFERENT G_D CHOICES

Although $G_D(\phi,x)$ is indeed the central function of the present area since knowledge of it allows one to calculate P_{NN}, R_{NN}, and the equation of state, this centrality should not be overemphasized. Both $G_D(\phi,x)$ and P_{NN} are primarily important because they lead to quantities of experimental interest such as R_{NN} and the associated equation of state. But passing from knowledge of these latter quantities down to expressions for P_{NN} and G_D is an inverse problem and usually is quite ill posed. Thus, even if an exact expression for $R_{NN}(\phi)$ or $Z(\phi)$ were known, it would not allow one to write an exact one for $G_D(\phi,x)$. It should not, therefore, be very surprising to find that appreciable differences between alternate choices for $G_D(\phi,x)$ may lead to negligible differences in the associated R_{NN} functions.

Here we shall consider the consequences at the P_{NN} and R_{NN} levels of several such $G_D(\phi,x)$ choices. Ever since the scaled particle theory of Reiss, Frisch, Lebowitz, and Helfand [7,10], it has been conventional to approximate $G_2(\phi,x)$ and $G_3(\phi,x)$ by means of a truncated series in x^{-1} (or r^{-1}), such as

$$G_{Dj}(\phi,x)\simeq a_j(\phi)+b_j(\phi)x^{-1}+c_j(\phi)x^{-2}\,, \tag{9}$$

where the index j will be used below to distinguish different choices.

For $D=2$, where the maximum hcp value of ϕ is $\pi/(2/\sqrt{3})$, we shall compare the original Ref. [4] predictions with those of TLR. Then, $a_1(\phi)=1/[1-1.397\,34\phi+0.171\,30\phi^2+0.169\,47\phi^3]$, $b_1(\phi)=0$, and $c_1(\phi)=0$ from Ref. [4]. The TLR result, taken directly from scaled particle theory [10] and satisfying Eqs. (6), (7), and (8), has $a_2(\phi)=[1-\phi]^{-2}$, $b_2(\phi)=-(\phi/2)a_2(\phi)$, and $c_2(\phi)=0$. A comparison of the resulting $P_{NN}(0.5,x)$ results is shown in Fig. 1. Unfortunately, there is an incorrect sign in TLR's Eqs. (5.13), (5.14), and (6.7), resulting in incorrect formulas for P_{NN} and R_{NN} and in inaccurate curves in the TLR Figs. 5, 10, and 11. In the present Fig. 1, the TLR curve was calculated from their original expression and the CTLR one from the corrected formula. We see that there are only small deviations between the JRM (Ref. [4]) and CTLR curves here, even though the JRM $G_2(\phi,x)$ expression has no x dependence. Further, differences are even smaller for smaller ϕ values. Comparison of R_{NN} predictions will be presented

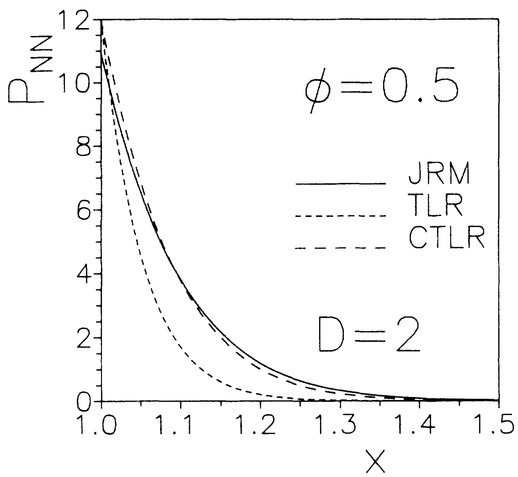

FIG. 1. The normalized nearest-neighbor particle distribution function $P_{NN}(\phi,x)$ vs $x\equiv r/\sigma$ for a system of hard disks of diameter σ for a value of the dimensionless density variable, ϕ, of 0.5. Here JRM designates results following from the analysis of Ref. [4]; TLR, those of Refs. [1,2]; and CTLR, a corrected version of the TLR results (see text).

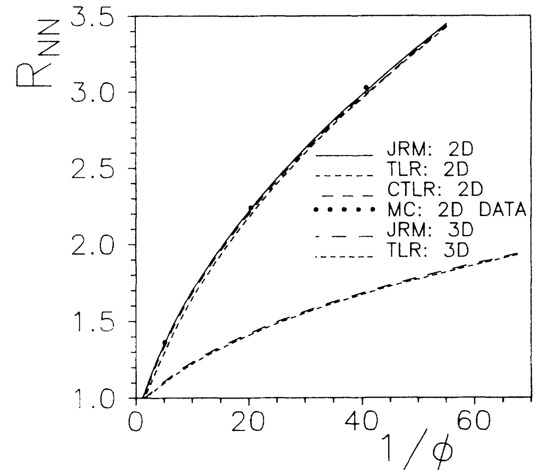

FIG. 2. The normalized mean nearest-neighbor distance $R_{NN}(\phi)$ vs $1/\phi$ for a variety of 2D and 3D choices for the central function $G_D(\phi,x)$. The points identified as MC are Monte Carlo values taken from Ref. [8].

later.

For $D=3$, where TLR based their best results on the Carnahan-Starling equation of state, we shall consider four approximations for $G_3(\phi,x)$, progressing from least appropriate to most appropriate. These four are (1) the original formula from Ref. [4] (2) the Carnahan-Starling $g_r(\phi,1)$ function (3) the TLR expression, and (4) an improved version of (3). Then $a_1(\phi)=1/[1-\frac{29}{14}\phi+0.9736\phi^2]$, $b_1(\phi)=0$, and $c_1(\phi)=0$; $a_2(\phi)=(1-\phi/2)/(1-\phi)^3$, $b_2(\phi)=0$, and $c_2(\phi)=0$; $a_3(\phi)\equiv(1+\phi)/(1-\phi)^3$; $b_3(\phi)\equiv-\phi(3+\phi)/\{2(1-\phi)^3\}$, $c_3(\phi)\equiv\phi^2/\{2(1-\phi)^3\}$; and $a_4(\phi)\equiv(1+\phi+\phi^2-\phi^3)/(1-\phi)^3$, $b_4(\phi)\equiv-3\phi(1+\phi)/\{2(1-\phi)^3\}$, and $c_4(\phi)\equiv\phi^2(1+2\phi)/\{2(1-\phi)^3\}$.

First, it is clear that the $G_3(\phi,x)$ expression of Ref. [4] does not satisfy Eqs. (6), (7), and (8) for the Carnahan-Starling equation of state. For the second choice, where $g_r(\phi,1)=a_2(\phi)$, Eq. (8) is not satisfied since there is still no x dependence present. But now the initial value of P_{NN}, $P_{NN}(\phi,1)=F(\phi,1)$, is correct. The TLR choice also does not satisfy the Eq. (8) condition even though the equivalent of this relation appears in their work. The fourth choice rectifies this problem so that the resulting $G_3(\phi,x)$ satisfies all three of the necessary equations. Note, however, that the result is still approximate, both because of imperfection in the Carnahan-Starling equation and because of truncation of the series in x^{-1}.

But what differences do these various choices make? First, differences at the P_{NN} level are reduced by the normalization condition, one that ensures exact agreement between any two resulting P_{NN}'s for at least one x value. Second, detailed comparison of these four choices [14,15] shows that much of the necessary x dependence arises from the x^{D-1} term of Eq. (3) and that the x dependence of $G_D(\phi,x)$ plays a lesser role. Such a comparison indicates that the difference in the TLR and improved TLR P_{NN}'s is wholly negligible. The difference between the JRM and TLR choices is not negligible, however, and a plot similar to that of Fig. 1, again for $\phi=0.5$, shows somewhat more overall discrepancy between the P_{NN} values than that apparent in the $D=2$ results. Finally, comparison of the second and third choices results in P_{NN} curves which are very nearly indistinguishable over the range of x of importance. Thus, even at this level, for most situations it will be sufficiently accurate to use $g_r(\phi,1)$ in place of $G_D(\phi,x)$. Note that $\phi=0.5$ is at the upper end of the fluid branch of the assembly of particles (freezing point at $\sim$0.49); different treatments [16,17] would be needed for larger ϕ values; and agreement will be even closer for smaller ones.

The R_{NN} predictions following from the various $D=2$ and 3 choices discussed above are shown in Fig. 2. Because R_{NN} involves another level of integration, one would expect even smaller differences between R_{NN}'s than P_{NN}'s, as is indeed evident in the figure. These results also properly apply only for ϕ values below the freezing point. The $D=2$ Monte Carlo points in the figure are from Ref. [8]. The figure shows that the very small differences between the JRM predictions of [4] and those of TLR are of negligible importance at the R_{NN} level, the level of the analysis of most practical value. For $D=2$, there is very good agreement between the Monte Carlo points and the JRM and CTLR ones, except at the lowest densities. Even the TLR curve, based on a P_{NN} expression which is not properly normalized, is quite close to the more accurate results. For $D=3$, curves for the G_3 choice numbers 2 and 4 have been omitted since they are indistinguishable from the TLR (choice 3) curve.

The original aim of Ref. [4] was to obtain accurate expressions for R_{NN}. The present comparisons show that this aim was indeed attained in spite of the severe approximations present in the G_2 and G_3 choices. Finally, the present work demonstrates that the use of the contact value of the ordinary radial distribution function as an approximation for G_D will generally lead to good approximations for P_{NN} and to excellent ones for R_{NN}.

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