A heuristic radial distribution function for hard disks

S. Bravo Yuste and A. Santos
Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain

(Received 8 February 1993; accepted 22 April 1993)

We propose a model radial distribution function for hard disks that is interpolated between the Percus–Yevick distribution functions for hard rods and hard spheres. The model contains a mixing parameter and two scaling parameters, which are determined by imposing self-consistency with an extension to $d=2$ of the Carnahan–Starling equation of state. Comparison with computer simulation is carried out.

I. INTRODUCTION

In order to gain insight into the structure and thermodynamic properties of fluids, nontrivial analytic approximations are very useful. For that purpose, hard-core fluids can be taken as prototype systems. Furthermore, fluids of hard spheres in d dimensions are interesting as models to test approximate theories and as reference systems in perturbation methods.[1] Consequently, an important problem in equilibrium statistical mechanics is the derivation of the radial distribution (RDF) $g^{(d)}(r)$ for d-dimensional hard-sphere fluids. This function contains all the relevant physical information about the system. In particular, the equation of state can be obtained through the virial route,

$$\frac{p}{\rho k_B T}=1+2^{d-1}\eta g^{(d)}(1^+;\eta), \tag{1}$$

or through the compressibility route,

$$k_B T\left(\frac{\partial \rho}{\partial p}\right)_T=1+d2^d\eta\int_0^\infty dr\, r^{d-1}[g^{(d)}(r;\eta)-1]. \tag{2}$$

In the above equations, k_B is the Boltzmann constant, p is the pressure, T is the temperature, ρ is the number density, and $\eta\equiv\rho v_d$, $v_d=(\pi/4)^{d/2}/\Gamma(1+d/2)$ being the volume of a d-dimensional sphere of unit diameter. In the low density limit, a convenient representation of the RDF is provided by the virial expansion

$$g^{(d)}(r;\eta)=g_0^{(d)}(r)+g_1^{(d)}(r)\eta+O(\eta^2), \tag{3}$$

where

$$g_0^{(d)}(r)=\Theta(r-1), \tag{4}$$

$$g_1^{(d)}(r)=\Theta(r-1)\int d^{(d)}\vec{r}'\,\Theta(r')\Theta(|\vec{r}-\vec{r}'|), \tag{5}$$

Θ being the Heaviside step function. The integral in (5) represents the common volume of two d-dimensional spheres of unit radius whose centers are a distance r apart. For $d=1$, 2, 3 one has

$$g_1^{(1)}(r)=\Theta(r-1)\Theta(2-r)(2-r), \tag{6}$$

$$g_1^{(2)}(r)=\Theta(r-1)\Theta(2-r)\,\frac{8}{\pi}\left[\arccos\left(\frac{r}{2}\right)-\frac{r}{4}\sqrt{4-r^2}\right], \tag{7}$$

$$g_1^{(3)}(r)=\Theta(r-1)\Theta(2-r)(8-6r+\tfrac{1}{2}r^3). \tag{8}$$

At moderate or high densities, the virial expansion is not useful. To predict the RDF in that case one must resort to approximate theories, which generally yield equations of state that depend on the route followed. A successful approximation is given by the Percus–Yevick (PY) integral equation.[1] The PY approximation for hard spheres consists of solving the Orstein–Zernike equation,[1] that relates the RDF $g^{(d)}(r)$ and the direct correlation function (DCF) $c^{(d)}(r)$, subject to the conditions $g^{(d)}(r)=0$ for $r<1$ and $c^{(d)}(r)=0$ for $r>1$. While the first condition is an exact property of the hard-sphere RDF, the second condition holds in the PY approximation only. The PY equation is exactly solvable for hard molecules in odd dimensions.[2] In particular, it becomes exact for hard rods ($d=1$). For hard spheres ($d=3$), the exact solution of the so-called generalized mean-spherical approximation represents an improvement over the PY solution.[3,4] For the purpose of this paper, we quote the following results:

$$g_{\rm PY}^{(d)}(1^+;\eta)=\begin{cases}\dfrac{1}{1-\eta}, & d=1,\\[2mm] \dfrac{1+\frac{1}{2}\eta}{(1-\eta)^2}, & d=3,\end{cases} \tag{9}$$

$$H_{\rm PY}^{(d)}(\eta)=\begin{cases}-\frac{1}{2}+\frac{2}{3}\eta-\frac{1}{4}\eta^2, & d=1,\\[2mm] -\dfrac{\eta^2-2\eta+10}{20(2\eta+1)}, & d=3,\end{cases} \tag{10}$$

where in Eq. (10) we have introduced the function

$$H^{(d)}(\eta)=\int_0^\infty dr\, r[g^{(d)}(r;\eta)-1], \tag{11}$$

that will be used in the sequel.

For a system of hard disks ($d=2$), the PY approximation is in good agreement with computer simulation results,[1,5] but must be solved numerically at each density η. Recently, Leutheusser[6] and Baus and Colot[7] have proposed analytic forms for the DCF of hard disks, containing a number (3 and 1, respectively) of density-dependent parameters that must be obtained numerically. In both cases, excellent agreements with the DCF obtained from the numerical solution of the PY equation are found. It must be emphasized that the DCF contains as much information

 0021-9606/93/99(3)/2020/4/$6.00

about the structure of the fluid as the RDF. In fact, both functions can be obtained from measurements of the structure factor in neutron or x-ray diffraction experiments. On the other hand, the RDF is the quantity that is directly determined in computer simulations and also has a more transparent interpretation as a correlation function.[1] In order to get the RDF from the approaches in Refs. 6 and 7, a double integral must be numerically evaluated. Furthermore, the ansatzs in Refs. 6 and 7 borrow from the PY approximation the property $c^{(2)}(r)=0$ for $r>1$. Consequently, they cannot lead to the exact property $g^{(2)}(r)=0$ for $r<1$.

The aim of this paper to propose, by following heuristic arguments, a simple approximation that directly provides a meaningful RDF for hard disks. The approximation is based on the naîve assumption that the structure and spatial correlations of a hard-disk fluid share some features with those of a hard-rod ($d=1$) and a hard-sphere ($d=3$) fluids. Thus, one might expect the properties of hard disks to lie between the properties of hard rods and those of hard spheres.

II. MODEL RADIAL DISTRIBUTION FUNCTION

We construct a model of hard disks in which the RDF is given by

$$g^{(2)}(r;\eta)=\alpha(\eta)g_{\rm PY}^{(1)}(r;\lambda^{(1)}(\eta)\eta)+[1-\alpha(\eta)]\times g_{\rm PY}^{(3)}(r;\lambda^{(3)}(\eta)\eta). \tag{12}$$

The parameter $\alpha(\eta)$ mixes the PY RDF's for hard rods and for hard spheres. The parameters $\lambda^{(1)}(\eta)$ and $\lambda^{(3)}(\eta)$ scale the density of the reference systems. On the other hand, the distance r is not modified. The density expansion of Eq. (12) is given by Eq. (3) with

$$g_1^{(2)}(r)=\alpha_0\lambda_0^{(1)}g_1^{(1)}(r)+(1-\alpha_0)\lambda_0^{(3)}g_1^{(3)}(r), \tag{13}$$

where α_0, $\lambda_0^{(1)}$, and $\lambda_0^{(3)}$ are the limits when $\eta\to 0$ of $\alpha(\eta)$, $\lambda^{(1)}(\eta)$ and $\lambda^{(3)}(\eta)$, respectively. The fact that Eq. (13) does not agree with the exact expression (7) is a consequence of the simplicity of the model. Also, it must be noted that the exact RDF $g_{\rm PY}^{(1)}$ has a discontinuity in its nth order derivative at $r=n+1$, $n=1, 2, 3,\ldots$. Consequently, these singularities are transferred to our model RDF $g^{(2)}$.

In order to close the construction of the model, we still have to determine α, $\lambda^{(1)}$ and $\lambda^{(3)}$. We first impose the condition that $g^{(2)}(1^+;\eta)$ be equal to a prescribed function $G(\eta)$, with independence of the choice of the mixing parameter $\alpha(\eta)$. Consequently,

$$\lambda^{(1)}(\eta)=\frac{G(\eta)-1}{\eta G(\eta)}, \tag{14}$$

$$\lambda^{(3)}(\eta)=\frac{4G(\eta)+1-\sqrt{24G(\eta)+1}}{4\eta G(\eta)}, \tag{15}$$

where use has been made of Eq. (9). The second step consists of requiring that $H^{(2)}(\eta)$, defined by Eq. (11), be given by a prescribed function $H(\eta)$. This condition yields the parameter α:

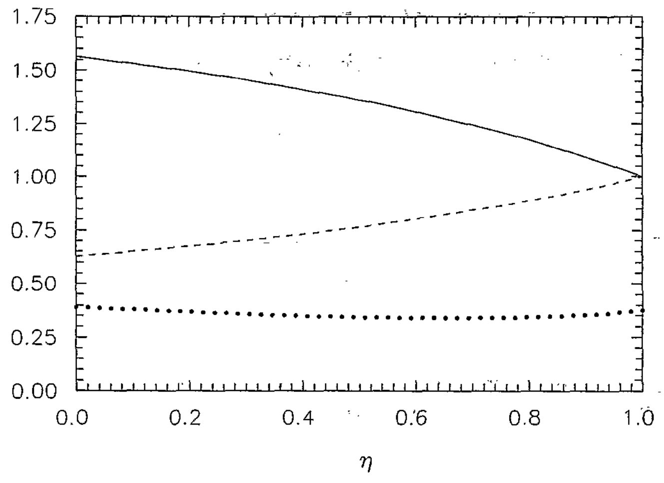

FIG. 1. Density dependence of the mixing parameter α (dotted line) and the scaling parameters $\lambda^{(1)}$ (solid line) and $\lambda^{(3)}$ (dashed line).

$$\alpha(\eta)=\frac{H(\eta)-H_{\rm PY}^{(3)}(\lambda^{(3)}(\eta)\eta)}{H_{\rm PY}^{(1)}(\lambda^{(1)}(\eta)\eta)-H_{\rm PY}^{(3)}(\lambda^{(3)}(\eta)\eta)}, \tag{16}$$

where $H_{\rm PY}^{(1)}$ and $H_{\rm PY}^{(3)}$ are given by Eq. (10).

Equations (14)–(16) give the three parameters of our model in terms of the prescribed functions G and H. These two functions are related to the virial and compressibility routes, respectively, to the equation of state. Self-consistency between both routes leads then to the following relationship:

$$H(\eta)=-\frac{1}{4}\frac{2G(\eta)+\eta G'(\eta)}{1+4\eta G(\eta)+2\eta^2G'(\eta)}, \tag{17}$$

where $G'(\eta)\equiv dG/d\eta$. Thus only $G(\eta)$ needs to be proposed. We choose the criterion of reproducing the equation of state for hard disks recently proposed[8] as an extension of the Carnahan–Starling equation of state for hard spheres.[9] Such an equation of state reads

$$\frac{p}{\rho k_BT}=\frac{1+(1-2a)\eta^2}{(1-\eta)^2}, \tag{18}$$

where $a\equiv 2\sqrt{3}/\pi-2/3\simeq 0.436$. Insertion of Eq. (18) into Eq. (1) yields

$$G(\eta)=\frac{1-a\eta}{(1-\eta)^2}. \tag{19}$$

Therefore, Eq. (17) becomes

$$H(\eta)=-\frac{1}{4}\frac{2-3a\eta+a\eta^2}{1+\eta+3(1-2a)\eta^2-(1-2a)\eta^3}. \tag{20}$$

Equations (14)–(16), (19), and (20) close the definition of our model (12). The parameters $\lambda^{(1)}$, $\lambda^{(3)}$ and α are plotted in Fig. 1. Although the whole interval $0\leqslant\eta\leqslant 1$ is considered, it must be pointed out that the largest meaningful density corresponds to the first-order fluid–solid transition,[1,10] i.e., $\eta_F\simeq 0.69$. For hard spheres, $\eta_F\simeq 0.49$.[1] Hence, one could estimate $\lambda^{(1)}\simeq 1/0.69=1.45$, $\lambda^{(3)}$

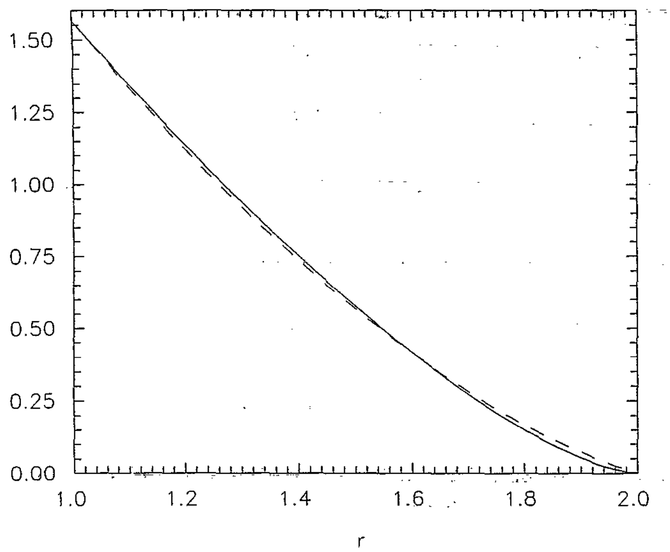

FIG. 2. Comparison between the exact (solid line) and the model (dashed line) virial coefficient $g_1^{(2)}(r)$.

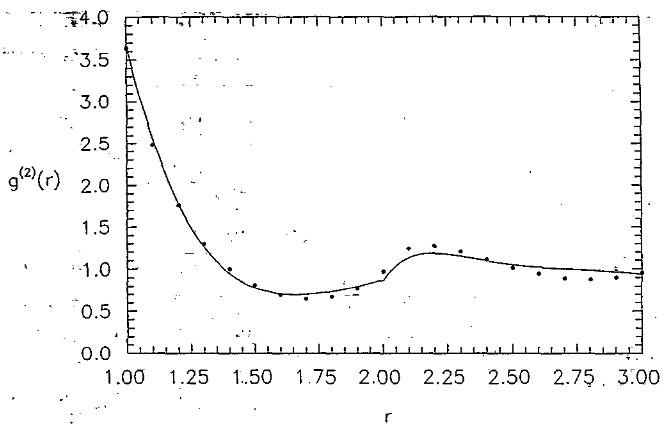

FIG. 4. Comparison between the model radial distribution function (solid line) and Monte Carlo simulation data from Ref. 5 (dots) at a reduced density $\eta=0.544$.

$\simeq 0.49/0.69=0.71$. These values are not far from those shown in Fig. 1 for $\eta\simeq 0.69$. It is also noticeable in Fig. 1 the fact that the mixing parameter α hardly depends on η. In the limit $\eta\to 0$, we have $\lambda_0^{(1)}=2-a\simeq 1.564$, $\lambda_0^{(3)}=(2/5)(2-a)\simeq 0.626$, $\alpha_0=(357a-114)/68(2-a)\simeq 0.392$. Insertion of these values into Eq. (13) gives the approximate function $g_1^{(2)}(r)$ of the model. This function is compared with the exact one, Eq. (7), in Fig. 2. In spite of its simplicity, the approximate $g_1^{(2)}(r)$ reproduces quite well the behavior of the exact function.

The model RDF $g^{(2)}(r;\eta)$ is compared with computer simulation results[5,11] in Figs. 3–5. Figure 3 shows a remarkable agreement for a moderate density ($\eta=0.363$). For high densities, the RDF exhibits a more complicated structure and the agreement worsens. Nevertheless, Figs. 4 and 5 indicate that the model is still reasonable up to the second peak. From that point on, our simple interpolation model is not able to reproduce the details of long-range correlations anticipating the fluid–solid phase transition. The kink at $r=2$ is a remnant of that of a system of hard rods.

III. DISCUSSION

In summary, we have proposed a simple model directly giving the RDF for a system of hard disks. It is based upon the heuristic argument that the spatial correlations of hard disks lie between those of hard rods and hard spheres. Thus, the RDF or hard disk is modeled as an interpolation between the (exact) RDF of hard rods and the (PY) RDF of hard spheres. The model introduces a mixing parameter and two density scaling parameters. On the other hand, no distance scaling is introduced. The three parameters are explicitly determined by requiring the virial and the com-

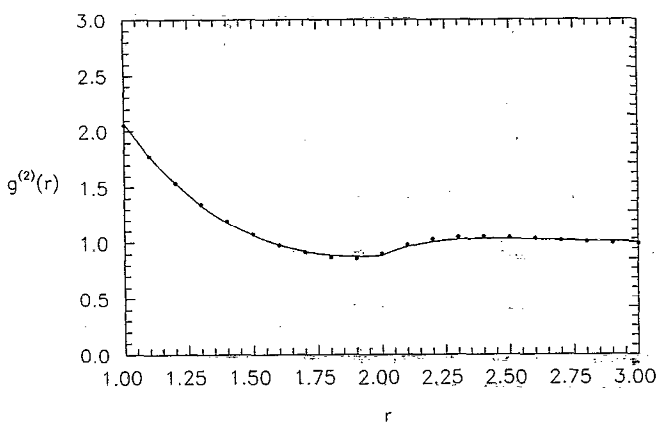

FIG. 3. Comparison between the model radial distribution function (solid line) and Monte Carlo simulation data from Ref. 5 (dots) at a reduced density $\eta=0.363$.

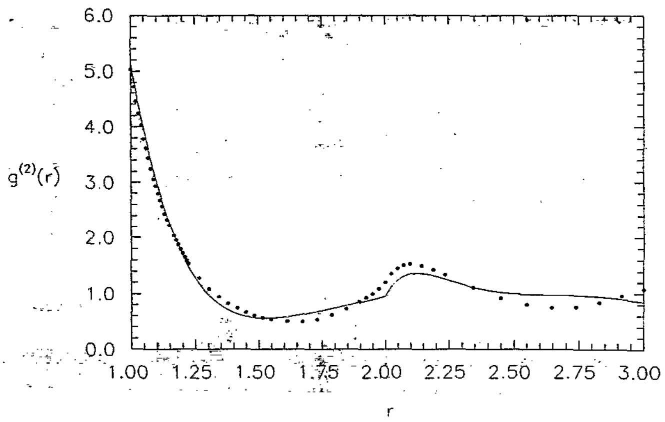

FIG. 5. Comparison between the model radial distribution function (solid line) and Monte Carlo simulation data from Ref. 11 (dots) at a reduced density $\eta=0.623$.

presibility routes to the equations of state to agree self-consistently with the one proposed in Ref. 8. Despite the absence of empirical fitting parameters, the resulting RDF shows an agreement with Monte Carlo data much better than one might expect on the basis of its crudeness. The discrepancies are important only for distances larger than the location of the second peak and at densities close to the fluid–solid transition. We must emphasize that our ansatz is not intended to compete with the accuracy obtained from the numerical solution of the PY equation. The latter correctly gives the virial coefficient (7) but has an intrinsic thermodynamic inconsistency between Eqs. (1) and (2). We think that the approach adopted here represents a step toward the goal of constructing analytic expressions for the RDF of hard disks that can compete successfully with numerical solutions of integral equations, such as the PY equation.

ACKNOWLEDGMENTS

This research has been partially supported by the Dirección General de Investigación Científica y Técnica (Spain) through Grant No. PB91-0316.

[1] J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).
[2] E. Leutheusser, Physica A **127**, 667 (1984).
[3] D. Henderson and L. Blum, Mol. Phys. **32**, 1627 (1976).
[4] S. Bravo Yuste and A. Santos, Phys. Rev. A **43**, 5418 (1991).
[5] D. G. Chae, F. H. Ree, and T. Ree, J. Chem. Phys. **50**, 1581 (1976).
[6] E. Leutheusser, J. Chem. Phys. **84**, 1050 (1986).
[7] M. Baus and J.-L. Colot, J. Phys. C **19**, L643 (1986).
[8] Y. Song, E. Mason, and R. M. Stratt, J. Phys. Chem. **93**, 6916 (1989).
[9] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).
[10] M. A. A. da Silva, A. Caliri, and B. J. Mokross, Phys. Rev. Lett. **58**, 2312 (1987).
[11] W. W. Wood, J. Chem. Phys. **52**, 729 (1970).