

## Radial Distribution Function Calculated by the Monte-Carlo Method for a Hard Sphere Fluid\*†

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The radial distribution function of a fluid of rigid spheres has been calculated using IBM equipment by a Monte-Carlo method which is valid only at relatively low densities. Up to the highest densities studied, 20 percent of closest packing, the radial distribution function agrees within the precision of the method with the one calculated by the use of the superposition approximation in triplet space. Another Monte-Carlo approach was used at a higher density, 72.4 percent of closest packing, and the results agree with published computations.

### I.

KNOWLEDGE of the distribution of molecules relative to each other in a fluid permits the prediction of all the thermodynamic properties.<sup>1</sup> It has thus been the aim of a number of investigators<sup>2-4</sup> to evaluate this distribution function from the general principles of statistical mechanics for a given system of molecules. The mathematical problems involved in this procedure are made formidable by the multiple interactions which have to be taken into account as the density of the system becomes appreciable. Various mathematical approximations have therefore been introduced to make the equations tractable. For example, the free-volume theory simplifies the problem by letting a molecule interact with the average potential of its neighbors. The superposition approximation<sup>2</sup> does not smooth the interaction quite so drastically, since the potential of the average forces among three molecules is written as the sum of pair potentials of average force.

The error introduced by these mathematical approximations is difficult to estimate unless a more exact procedure is found. With modern computing facilities the Monte Carlo method becomes such a feasible procedure, although it has its own limitations.<sup>5,6</sup> For the hard-sphere fluid, however, the Monte-Carlo approach is quite straightforward. Since there are no fluctuations

in energy, all possible states of the system are weighted equally. As long as the calculation is done so that the statistics favor none of the possible states of the system more than any other, the distribution function can be obtained as exactly as desired. The accuracy is limited by the geometric size of the sample and the amount of statistical data accumulated.

### II.

The procedure adopted was as follows: A unit cube (volume,  $v=1$ ) was set up, and the coordinates of a center of a sphere inside that cube were specified by a "random" nine-decimal-digit number. The first three digits specified the  $x$  coordinate, the next three the  $y$  coordinate, and the last three the  $z$  coordinate of the particle. The sphere was given the diameter,  $d=(0.02)^{\frac{1}{2}}$ . Additional particles were then introduced into the unit cube at positions indicated by new "random" nine-digit numbers. These numbers were generated by successive squaring of the nine-digit numbers, using a middle group of nine digits as the next "random" number. A new particle was left in the box if it did not overlap with any particles already in place; otherwise it was rejected and a new particle was tried.

The box could contain 500 particles if they were closely packed, and approximately half of these would be at the surface. In order to ameliorate the inaccuracies due to the small sample volume, periodic boundary conditions were introduced; that is, on all sides of the cube identical cubes were also built up. This procedure avoids surface effects and is analogous to a cellular treatment of fluids in which the cells are quite large and the restriction of single occupancy is not imposed.

The IBM 604 electronic calculator was used to check whether a new particle overlapped any of the particles already in the box or their counterparts in the adjacent boxes. The machine calculated for a new particle the distance to each particle in the central box or to its reflection in the adjacent boxes, whichever was the closest. The operations involved then were to tabulate for a new particle having coordinates  $x$ ,  $y$ , and  $z$  the quantities  $\Delta x$ ,  $\Delta y$ , and  $\Delta z$ , where  $\Delta x$  stands for  $x-x_i$ ,  $x-x_i+1$ , or  $x-x_i-1$ , whichever has the smallest

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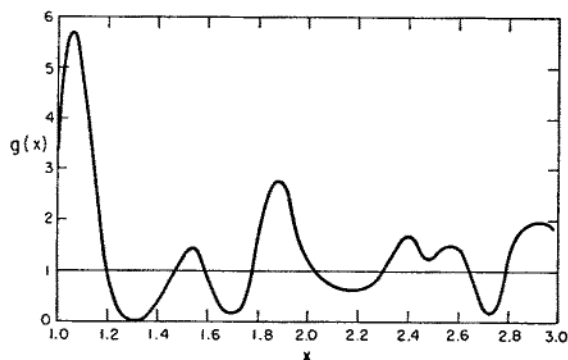


FIG. 1. The radial distribution function at a density corresponding to  $\lambda_0 = 12.86$ .

magnitude, and similarly for the quantities  $\Delta y$  and  $\Delta z$ . The minimum squared distance,  $(\Delta x^2 + \Delta y^2 + \Delta z^2)$ , to a particle located in the central box at  $x_i, y_i,$  and  $z_i$  was then calculated and compared to  $d^2 = 0.02$ . The new particle was rejected if  $(\Delta x^2 + \Delta y^2 + \Delta z^2)$  was less than 0.02 for any particle already in the box. By this procedure the IBM cards had printed on them the squared distances for any new member to all the old members. This tally of distances is the information needed to evaluate the distribution function.

As more and more particles were placed in the box the rejection rate increased very rapidly. A total of 98 particles was put in the box, which corresponds to a  $\lambda_0 = (4\pi N d^3)/v$  of 3.460 (20 percent of closest packing), in order to compare the distribution function with one that had been obtained at the same density with the use of the superposition approximation. However, it proved impractical to go to any appreciably higher density by this method since the acceptance rate for the last few particles was about one in ten.

A box prepared in this way represents a small sample of an actual system. Rather than dealing with a bigger box so that statistical errors are reduced, it proved more economical to prepare an assembly of such boxes, although the effect of the periodic boundary condition is more serious and the distribution function becomes less accurate at large separations. Eleven boxes were prepared and the distribution function calculated from them. The squared distances were listed in order of increasing magnitude and the distribution function,  $g(R)$ , calculated by noting the number,  $\Delta n$ , of these distances in each interval  $\Delta R$  of distance:

$$g(R) = \frac{\Delta n}{\frac{N(N-1)}{2} 4\pi R^2 \Delta R},$$

where  $N$  is the total number of particles in the box and  $R$  is the distance separating any representative pair of molecules. Changing to a scale of distance,  $x$ , in which the spheres have a diameter of unity,  $R$  must be replaced by  $R = (0.02)^{1/2} x$ .

Table I gives a comparison of the radial distribution function obtained in this way and the one obtained by solving the integral equation.<sup>3</sup> It can be seen that within statistical errors the two are the same. Since the integral equation depends on the approximation of superposition in triplet space but the Monte-Carlo method does not, it is apparent that within the precision of the present study this assumption is valid at the density,  $\lambda_0 = 3.460$ , studied and at all lower ones. It should be pointed out, however, that at this density the number of triplets whose centers at a given time are close together is quite small.

### III.

At higher densities a different procedure must be adopted. The one that was used is identical to the method already described in the literature.<sup>5,6</sup> A unit

TABLE I. Comparison of the radial distribution functions.

| $x$  | $g^a(x)$ | $g^b(x)$ | $[g^a(x)]/[g^b(x)] - 1$ | Std. Dev. <sup>c</sup> |
|------|----------|----------|-------------------------|------------------------|
| 1.04 | 1.399    | 1.374    | 0.018                   | 0.052                  |
| 1.12 | 1.313    | 1.286    | 0.021                   | 0.051                  |
| 1.20 | 1.242    | 1.098    | 0.131                   | 0.049                  |
| 1.28 | 1.181    | 1.142    | 0.035                   | 0.048                  |
| 1.36 | 1.129    | 1.200    | -0.059                  | 0.047                  |
| 1.44 | 1.083    | 1.108    | -0.023                  | 0.046                  |
| 1.52 | 1.049    | 1.058    | -0.008                  | 0.045                  |
| 1.60 | 1.018    | 1.006    | 0.012                   | 0.044                  |
| 1.68 | 0.996    | 1.057    | -0.058                  | 0.043                  |
| 1.76 | 0.981    | 1.013    | -0.032                  | 0.042                  |
| 1.84 | 0.974    | 0.993    | -0.019                  | 0.041                  |
| 1.92 | 0.972    | 0.990    | -0.018                  | 0.041                  |
| 2.00 | 0.980    | 0.994    | -0.014                  | 0.040                  |
| 2.08 | 0.989    | 0.922    | 0.072                   | 0.040                  |
| 2.16 | 0.995    | 0.968    | 0.027                   | 0.039                  |
| 2.24 | 1.000    | 1.013    | -0.013                  | 0.038                  |
| 2.32 | 1.002    | 1.021    | -0.018                  | 0.038                  |
| 2.40 | 1.003    | 1.028    | -0.024                  | 0.037                  |
| 2.48 | 1.004    | 1.013    | -0.009                  | 0.036                  |
| 2.56 | 1.003    | 0.981    | 0.022                   | 0.036                  |

<sup>a</sup> From solution of integral equation.

<sup>b</sup> From Monte-Carlo method.

<sup>c</sup> Statistical standard deviation from the average in the quantity  $[g^a(x)]/[g^b(x)] - 1$ . See H. Margenau and G. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1943), p. 422.

cube was employed containing 80 spheres of diameter  $d = (14/256)^{1/3}$ , initially in a hexagonal arrangement. After two "runs" the orderliness of the initial arrangement seemed to be washed out. A "run" consists of an attempted random displacement of each sphere in the box. Figure 1 is a graph of the distribution function obtained from a total of 7 runs of which the first two were not counted. Periodic boundary conditions were applied as previously. The general features of the graph agree with the published distribution functions obtained by this method.<sup>6</sup> The most notable fact is that at these higher densities the peak of the distribution function does not occur at the point of contact of the spheres. At the density investigated, 72.4 percent of closest packing, corresponding to a value of

$\lambda_0 = 12.86$ , a comparison with the distribution function from the solution of the integral equation is not possible, since that method breaks down.<sup>3</sup>

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## Spherical Interface. II. Molecular Theory\*

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The statistical mechanical theory of plane and spherical interfaces is developed on the basis of the virial theorem and the Gibbsian mechanical and thermodynamic definitions of surface tension. The expressions for the relevant thermodynamic functions in terms of molecular variables are employed in a discussion of the curvature dependence of surface tension which leads to an asymptotic expansion of the grand partition function in terms of the geometrical parameters that characterize the interface and thus provide a criterion for the range of validity of macroscopic concepts.

### I.

IT is the purpose of this paper to discuss the detailed molecular theory of surface tension whose chief results were anticipated in our earlier extension of the phenomenological treatment.<sup>1</sup> The calculations of superficial phenomena which will be presented are carried out on the basis of both the thermodynamic and mechanical definitions of surface tension. The appropriate techniques employed with these alternative definitions lead to the requisite identical results. A brief discussion of plane interfaces precedes the treatment of the spherical interface.

For the purpose of this discussion it will be convenient to place a Gibbs<sup>2</sup> dividing surface in the spherical transition zone separating the liquid phase  $\alpha$  from the vapor phase  $\beta$ . It is the function of this dividing surface to divide the total volume into a volume  $V_\alpha$  containing the liquid phase and a volume  $V_\beta$  containing the vapor phase. With this convention the thermodynamic definition of surface tension may then be based on the fundamental equation for the reversible change in Helmholtz free energy  $A$  of a small segment of the two phase system which is characterized by the area  $s$  and the curvature  $c$  of the dividing surface

$$d\left(\frac{A}{T}\right) = Ed\left(\frac{1}{T}\right) - \frac{p_\alpha}{T}dV_\alpha - \frac{p_\beta}{T}dV_\beta + \frac{\mu}{T}dN + \frac{\gamma}{T}ds + \frac{C}{T}dc, \quad (1)$$

where  $E$  and  $N$  are the energy and number of moles of

the segment of the one component system,  $T$  and  $\mu$  are its temperature and chemical potential,  $\gamma$  is the generalized surface tension, and  $C$  is the Gibbs curvature term. The pressure  $p_\alpha$  existing in the interior of the bulk phase  $\alpha$  is determined by the pressure  $p_\beta$  of the bulk phase  $\beta$  by the condition of uniformity of the chemical potential  $\mu$  in the two phases. In order to give explicit recognition to the open nature of the two phase system and to facilitate the physical interpretation of the theory which is presented in Sec. IV it is convenient to introduce the invariant function  $\Omega$  defined by the equation

$$\Omega = A - N\mu = \gamma s^{(F.E.)} - p_\alpha V_\alpha - p_\beta V_\beta. \quad (2)$$

It is of interest to remark that in applications of the preceding relation to liquids it is generally assumed that the surface tension  $\gamma$  may be set equal to the surface free energy  $\gamma^{(F.E.)}$ . However, an examination of interfaces with unequal principal curvatures  $c_1$  and  $c_2$  shows that this identification is only strictly valid when it is assumed that the stress ellipsoid is asymptotically one of revolution about the normal to the surface. Since in the present investigation this restriction is satisfied, the equivalence of  $\gamma$  and  $\gamma^{(F.E.)}$ , which constitutes the basic assumption in the derivation of the generalized<sup>1</sup> adsorption equation for spherical interfaces, is to be considered rigorous and it is possible to transform Eq. (1) to the form

$$d\left(\frac{\Omega}{T}\right) = Ed\left(\frac{1}{T}\right) - \frac{p_\alpha}{T}dV_\alpha - \frac{p_\beta}{T}dV_\beta - Nd\left(\frac{\mu}{T}\right) + \frac{\gamma}{T}ds + \frac{C}{T}dc, \quad (3)$$

$$\Omega = \gamma s - p_\alpha V_\alpha - p_\beta V_\beta. \quad (3')$$

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