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Parametric integral equation for radial distribution functions

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An integral equation is proposed whose solutions approximate the radial distribution functions of classical fluids whose single-type particles interact with pairwise radial forces. The equation contains a parameter which is adjustable to improve moderate- and high-density solutions. The equation is applied to the hard-sphere model of a fluid, solutions are obtained for four densities, and the pressure equation of state is expressed in terms of a 2×2 Padé approximant. A single value of the parameter yields pressures which are in excellent agreement with "exact" values.

I. INTRODUCTION

This report is a continuation of a previous paper dealing with the same subject.[1] In the interval of time that has elapsed, numerous Monte Carlo (MC) and molecular dynamics (MD) computations have been completed. With the availability of these numerous "exact" solutions for radial distribution functions, the time appears right to reexamine the possibilities of parametric integral equations. The basic ideas involved will be briefly reviewed here and a more complete discussion may be found in Ref. 1.

For systems of classical particles interacting through pairwise radial forces, thermodynamic equations of state may be obtained from a knowledge of the radial distribution function g. Two basic methods have been used to obtain g: (i) "exact" methods, including MC and MD, and (ii) integral equations, including the well-known Percus-Yevick (PY) and convolution-hypernetted chain (CHNC) equations.[2] The integral equations provide dependable results at low densities, but at intermediate and high densities large errors may occur. The "exact" methods provide dependable results at densities for which the integral equations yield large errors. The advantages of integral equations are shorter computer-time requirements and the possibility for inverting the problem, that is, determining the pair potential energy given an experimental g.

The PY and CHNC equations are equivalent to partial summations of terms from the density expansion for $ge^{\beta\phi}$. Both equations correctly sum the diagrams (used to represent integrals) through the first power in density but omit diagrams corresponding to higher-density coefficients. Although the CHNC summation includes all of the diagrams summed by PY plus an additional set, the PY equation often provides better results than CHNC, thus indicating that cancellation of omitted diagrams is important. Parametric integral equations also sum the diagrams correctly through the first power in density and in addition contain a parameter which appears in the higher-order terms. This parameter is fixed by some well-defined scheme in efforts to extend the range of validity for integral equations.

In this paper we propose a parametric integral equation, give the summation of terms through the second power in density for $ge^{\beta\phi}$, give the solutions for g for four densities of hard spheres, determine the pressure equation of state as a Padé approximant, and compare the results with the PY, CHNC, and exact values for pressure.

II. THE INTEGRAL EQUATION

There appear to be a large number of integral equations which yield the correct first two terms in the density expansion for $ge^{\beta\phi}$ and for which a parameter appears in higher-order terms. In an earlier paper[1] two such equations were considered and called (A) and (B). Here we introduce a third such integral equation and call it Eq. (C). The direct correlation function c is defined by

$$G(r) = c(r) + \bar{n} \int G(\vec{s})c(|\vec{s} - \vec{r}|)d\vec{s}, \tag{1}$$

where $\vec{r}$ and $\vec{s}$ represent position vectors,

$$G = g - 1, \tag{2}$$

$$\bar{n} = N/V, \tag{3}$$

and N is the number of particles in the volume V. Equation (C) makes the approximation

$$c = g - 1 - a^{-1}\ln(age^{\beta\phi} - a + 1), \tag{4}$$

$$\beta = (kT)^{-1}, \tag{5}$$

where ϕ is the pair potential energy, k is Boltzmann's constant, T is the absolute temperature, and a is an adjustable parameter. For $a = 1$, Eq. (C) reduces to the CHNC equation and as a approaches 0 one obtains the PY equation. In the calculations reported here, a is chosen to be a constant number, but more generally it could be considered to be a function of r and no difficulties arise in obtaining solutions to the integral equation. Figure 1 gives the density expansion for $ge^{\beta\phi}$ through the $\bar{n}^2$ term exactly, for PY, CHNC, and for (C). The diagrams involve integrals over Mayer f functions:

$$f(ij) = f(r_{ij}) = \exp[-\beta\phi(r_{ij})] - 1 . \tag{6}$$

A line between the circles i and j indicates the presence of the function $f(ij)$ in the integrand and integration is over the coordinates of the dark circles.

The solution of the equation involves an iterative procedure and is essentially that of Broyles.[3] A digital computer is programmed as outlined in Fig. 2. A function S is defined as

$$S = G - c , \tag{7}$$

and its Fourier transform as

$$\tilde{S}(k) = (2\pi)^{-3} \int\int\int S(\vec{r}) e^{i\vec{k}\cdot\vec{r}} d\vec{r} . \tag{8}$$

In terms of S we obtain

$$g = e^{-\beta\phi}(a^{-1}e^{aS} - a^{-1} + 1) , \tag{9}$$

$$c = e^{-\beta\phi}(a^{-1}e^{aS} - a^{-1} + 1) - 1 - S . \tag{10}$$

Taking the Fourier transform of both sides of Eq. (1) and combining the result with Eq. (7), one obtains

$$\tilde{S} = \frac{(2\pi)^3 \bar{n}\tilde{c}^2}{1 - (2\pi)^3 \bar{n}\tilde{c}} . \tag{11}$$

In the numerical solution outlined in Fig. 2, mixing and extrapolation procedures are also sometimes used.[3]

III. APPLICATION TO HARD SPHERES

We use the same notation and variables for the hard-sphere model as before.[1] The Mayer function is given by

$$f(r) = -1 , \quad r < d \tag{12}$$

$$f(r) = 0 , \quad r > d \tag{13}$$

where d is the diameter of the hard sphere. Taking d as our unit of length we define

$$x = r/d , \tag{14}$$

$$\bar{n}^* = \bar{n} d^3 . \tag{15}$$

The pressure p is given by

$$P^* = p\beta/\bar{n} = 1 - \frac{2\pi\bar{n}\beta}{3} \int_0^\infty \frac{d\phi(r)}{dr} g(r) r^3 dr , \tag{16}$$

which becomes for hard spheres

$$P^* = 1 + \tfrac{1}{3}[2\pi\bar{n}^* g(x=1)] . \tag{17}$$

To determine the parameter a, it was our intention to select a to give agreement in P^* between "exact" results and the integral equation at high density. Since the form of the equation ensures good results at low densities, the question remained whether or not the results would be good at densities between. The exact, PY, and CHNC values of P^* published by Lado[4] (L) were helpful in determining the parameter a. Since the PY and CHNC values bracketed the exact values, and since $a = 0$ for PY and $a = 1$ for CHNC, it was felt that as a starting point for determining a I would try

$$a = (P^*_E - P^*_{\text{PY}})/(P^*_{\text{CHNC}} - P^*_{\text{PY}}) . \tag{18}$$

An examination of Lado's Table I suggested that one take $a = 0.27$. The results obtained with this value of a agreed with the exact results within the

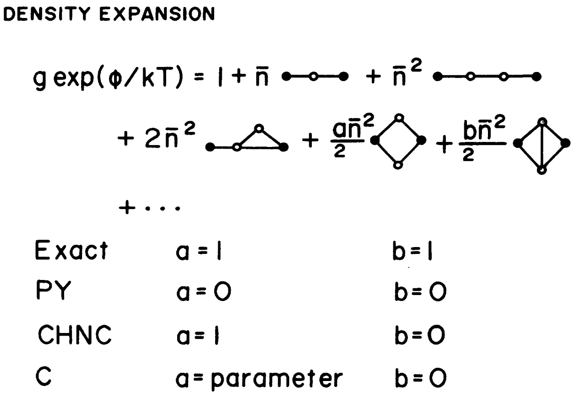

FIG. 1. Density expansion for the radial distribution function through the $\bar{n}^{*2}$ term. The integral equation approximations of PY, CHNC, and (C) are shown.

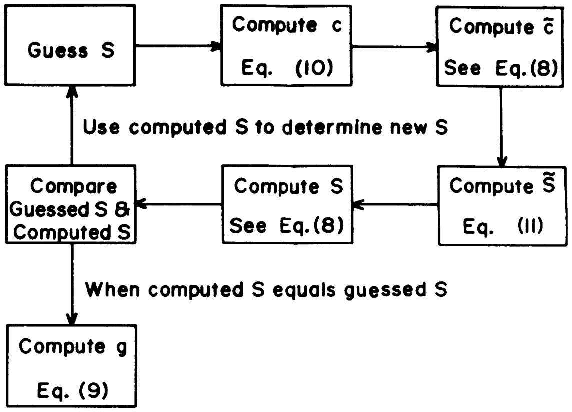

FIG. 2. Flow diagram for the numerical solution of the integral equation (C).

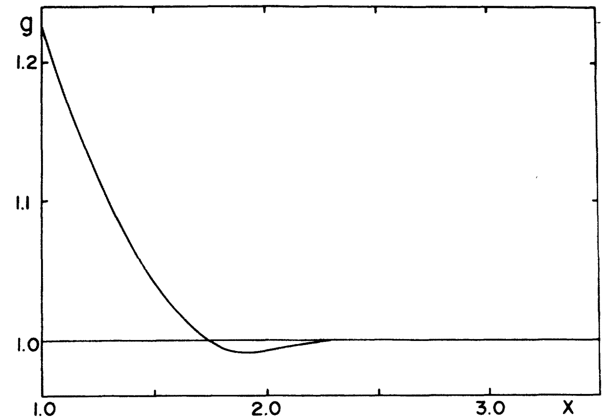

FIG. 3. Radial distribution function for a system of hard spheres at density $\bar{n}^*=0.15$ as computed from integral equation (C).

accuracy of our numerical solutions and so no additional adjusting of the parameter was needed.

Computer solutions to the integral equation were obtained for values of $\bar{n}^*$ of 0.15, 0.35, 0.55, and 0.75. The results for g are given in Figs. 3–6. Previous calculations[5] have shown that an excellent interpolation formula for P^* is given by

$$P^*=1+\tfrac{1}{3}(2\pi n^*)\left(\frac{1+A_1\bar{n}^*+A_2\bar{n}^{*2}}{1+A_3\bar{n}^*+A_4\bar{n}^{*2}}\right) . \tag{19}$$

By writing four equations using the four values of $\bar{n}^*$ listed above and the corresponding values of P^*, the values of the A's can be determined. The result thus obtained gives for the integral Eq. (C) pressure equation of state

$$P^*=1+\tfrac{1}{3}(2\pi\bar{n}^*)\left(\frac{1+0.4680\bar{n}^*+0.2890\bar{n}^{*2}}{1-0.8394\bar{n}^*+0.09833\bar{n}^{*2}}\right) . \tag{20}$$

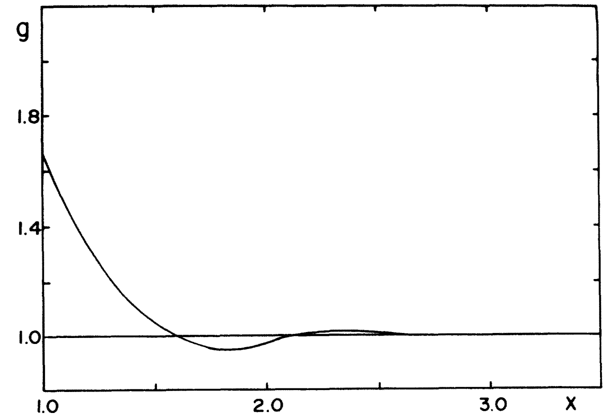

FIG. 4. Radial distribution function for a system of hard spheres at density $\bar{n}^*=0.35$ as computed from integral equation (C).

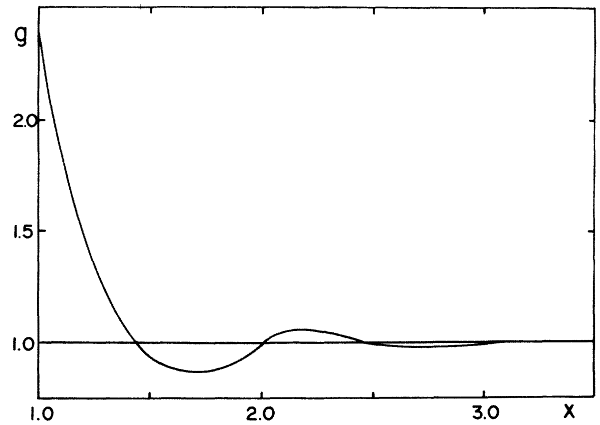

FIG. 5. Radial distribution function for a system of hard spheres at density $\bar{n}^*=0.55$ as computed from integral equation (C).

A comparison of results (using the values published by Lado) is given in Table I. Figure 7 is a graph of g as a function of x for a density of $\bar{n}^*=0.80$. Compared, for values of x near 1, are the radial distribution functions as reported by Lado[4] and as obtained from Eq. (C). The agreement between the three methods is seen to be quite good and the differences are probably not much larger than uncertainties in the numerical solutions. At lower densities and larger values of x, the differences in g can be expected to be even smaller. The differences between the radial distribution functions are too small to be shown to good advantage in Figs. 3–6.

IV. CONCLUSIONS

A parametric integral equation has been shown to produce excellent results for a single value of

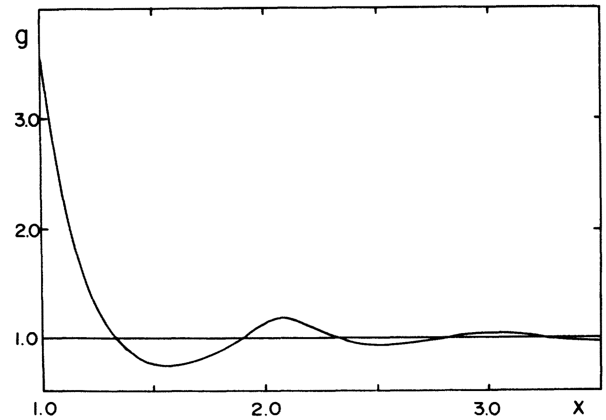

FIG. 6. Radial distribution function for a system of hard spheres at density $\bar{n}^*=0.75$ as computed from integral equation (C).

TABLE I. Pressure equations of state for hard spheres. Shown are values of P^* as computed by the MC method (Exact), Lado's integral equation (L), this integral equation (C), the Percus-Yevick integral equation (PY), and the convolution-hypernetted chain integral equation (CHNC).

$\bar{n}^*$	Exact	L	(C)	PY	CHNC
0.1	1.240	1.240	1.240	1.239	1.241
0.2	1.554	1.553	1.554	1.550	1.566
0.3	1.968	1.966	1.968	1.954	2.01
0.4	2.52	2.51	2.52	2.48	2.64
0.5	3.27	3.25	3.26	3.17	3.53
0.6	4.29	4.24	4.27	4.09	4.81
0.7	5.71	5.61	5.68	5.32	6.69
0.8	7.73	7.51	7.68	7.00	9.49
0.9	10.66	10.24	10.6	9.33	13.7
1.0	15.0	14.2	15.2	12.6	20.5

the parameter in the case of hard spheres. This suggests that MC and MD techniques might well be combined with parametric integral equations to take advantage of the accuracy of the exact methods and the reduced computer requirements of the integral equation. That is, high-density exact solutions can provide values of the parameters in integral equations which can then be used to complete the study of the system. The parameter a can be chosen to be a function of r although in this study it was felt that a single number for a was adequate. Perhaps in future studies it will be advisable to make use of this additional flexibility in a.

There are many possible parametric integral equations similar to Eq. (C). There are also many possible methods for determining the value, or values, of the parameter. For example, Hiroike[6] has pointed out that approximations introduced in obtaining integral equations may produce inconsistencies so that the energy equation[7] is not satisfied. Hence one might adjust the parameter to satisfy the energy equation. Rowlinson[8] proposed a parametric integral equation and obtained a power series in density for the parameter by requiring consistency in the pressure as computed by the virial equation of the canonical ensemble and by the compressibility equation of the grand canonical ensemble. Carley and Lado[1] studied two parametric integral equations and in one case chose the parameter to give the correct fourth virial coefficient and in the other case to improve the third term in the density expansion for $ge^{\beta\phi}$. Lado[4] studied the hard-sphere system and obtained his parameter according to the pressure-consistency equation (as did Rowlinson); however, he obtained his parameter through an iterative procedure involving the numerical solutions of the integral equations. This list is not exhaustive of the methods which have or might be used to determine the parameter. Since there are several possible parametric integral equations and several possible techniques of determining the parameters, there are an enormous number of combinations which could be studied.

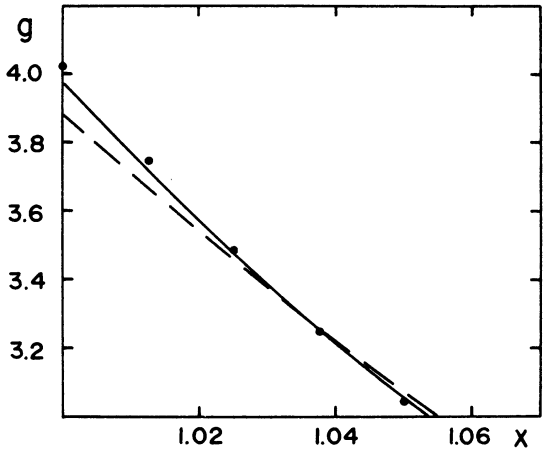

FIG. 7. Radial distribution function for a system of hard spheres at density $\bar{n}^*=0.80$ as computed by MC (dotted line) (. . .), Lado's equation (dashed line) (- -), and Eq. (C) (solid line) (—).

It has not been the purpose of this paper to suggest that this is necessarily the best possible equation. Past experience with integral equations has shown that an approximation which is excellent under one set of conditions is not necessarily good under all conditions. An advantage of the method of determining the parameter using pressures from MC results is the great simplicity. An obvious disadvantage is that exact results may not be available and MC and MD calculations require large computer facilities and time. The parameter, in this case a, most generally is a function of density, temperature, and separation distance. That is, for a given temperature and density there exists some $a(x)$ which will give the exact radial distribution function. In this study we found that a constant value for a provided good results for a system of hard spheres. However, in other cases, such as for a Lennard-Jones potential, it may be necessary to sacrifice the simplicity of a constant value for a to obtain more accurate results. Finally, it would appear to be useful to carry out many additional studies of parametric integral equations using various techniques to determine the parameters.

ACKNOWLEDGMENT

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