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AN ACCURATE ALGORITHM FOR THE COMPUTATION OF THE RADIAL DISTRIBUTION FUNCTIONS OF HARD SPHERES

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ABSTRACT
Perram, J.W. and Rasmussen, J., An accurate algorithm for the computation of the radial distribution functions of hard spheres.

We present a new algorithm for the calculation of the radial distribution functions of hard spheres in the Percus-Yevick approximation. This algorithm represents the radial distribution function as a piecewise Taylor series. The algorithm allows the generation of hard sphere correlation functions numerically accurate to machine precision.

1. INTRODUCTION

The properties of hard spheres play a fundamental role in many perturbation theories of fluids (Weeks and Chandler, 1970, Weeks et al, 1971) and fluid mixtures (Lee and Levesque, 1973). One of the crucial ingredients in all such perturbation theories are the radial distribution function g(r) for the underlying equivalent hard sphere system. This is also the ingredient whose numerical implementation poses the most difficulties.

One of the most fruitful approaches to this problem has been to make use of the fundamental paper of Baxter (Baxter, 1968a) on the Wiener-Hopf method for the solution of the Percus-Yevick equation (Percus and Yevick, 1958). It is thus appropriate that one of the authors (JWP) was privileged to be a visitor at the University of Vienna in the fall of 1973 when Professor Kohler and he realized the important potential for application of this work in the perturbation theory of fluids. This work led to a successful numerical method for the generation of the soft-sphere PY distribution functions (Kohler et al, 1975), as well as hard sphere correlation functions (Perram, 1975).

Since that time, Professor Kohler and collaborators have made extensive application of these algorithms and their extension to mixtures (Baxter, 1968b) to obtain what are generally regarded as the best perturbation theories currently available for computing the properties of simple molecular fluids (see for example, Kohler et al, 1979, Fischer, 1980, Fischer and Lago, 1983,).

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These algorithms have their limitations however. This is because the free energies obtained in the application of perturbation theories need to be numerically differentiated with respect to temperature and density to obtain the equation of state and the internal energy function, and, in the case of mixtures, differenced to obtain excess properties. These processes make severe computational demands on the algorithms used to compute the correlation functions. For example, it has recently been demonstrated (Fischer and Lago, 1983, Perram et al, 1988) that the apparent failure of the obvious extension of the WCA theory to mixtures (Lee and Levesque, 1973) was due to numerical difficulties concerned with the generation of the radial distribution functions.

In a recent article (Perram et al 1988), a new algorithm was employed for the computation of the radial distribution functions of assemblies of hard spheres and their binary mixtures which enables the generation of these functions essentially without numerical error. In this paper, we present the details of these algorithms for the mono-disperse case. The extension to polydisperse systems is a much more complex issue and is much too complicated and technical to be published here (Rasmussen, 1987, Rasmussen and Perram 1988).

2. PIECEWISE POLYNOMIAL APPROXIMATIONS FOR THE RADIAL DISTRIBUTION FUNCTION

Our starting point is the Baxter form (Baxter 1968a) of the equation for the total correlation function $h(r) = g(r) - 1$ for hard spheres of diameter R present with number density ρ, namely

$$rh(r) = -Q'(r) + 2\pi\rho \int_0^R Q(t)\ (r-t)h(|r-t|)dt \tag{2.1}$$

where the function $Q(r)$ is known and is given by

$$\begin{aligned} Q(r) &= (a/2)(r^2 - R^2) + bR(r - R),\ 0 \le r < R \\ &= 0,\ r \ge R \end{aligned} \tag{2.2}$$

with

$$a = (1 + 2\eta)/(1 - \eta)^2 \tag{2.3}$$

$$b = -(3/2)\eta/(1 - \eta)^2 \tag{2.4}$$

Further progress is expedited if we define the function $\theta(r)$ by

$$\theta^{(0)}(r) = rh(|r|) \tag{2.5}$$

so that equation (2.1) has the form

$$\theta^{(0)}(r) = -Q'(r) + 2\pi\rho \int_0^R Q(t)\, \theta^{(0)}(r-t)\, dt \tag{2.6}$$

Evaluating eq. (2.6) at the points $R^{\pm}$ just to the right and left of R and subtracting the results, we obtain

$$\Delta_1^{(0)}(r) = \theta^{(0)}(R^+) - \theta^{(0)}(R^-)$$

$$= Q'(R) \tag{2.7}$$

which since the function $\theta^{(0)}(r)$ has the known form $-r$ for $r < R$, determines the contact value $\theta^{(0)}(R^+)$. We may also differentiate equation (2.6) with respect to r and integrate by parts to obtain

$$\theta^{(1)}(r) = -Q''(r) + 2\pi\rho Q(0)\theta^{(0)}(r) + 2\pi\rho \int_0^R Q'(t)\, \theta^{(0)}(r-t)\, dt \tag{2.8}$$

Again, by subtracting the results of evaluating eq. (2.8) at the points $R^{\pm}$ and subtracting the results, we obtain

$$\Delta_1^{(1)}(R) = \theta^{(1)}(R^+) - \theta^{(1)}(R^-)$$

$$= Q''(R) + 2\pi\rho Q(0)\Delta_1^{(0)}(R) \tag{2.9}$$

which enables us to compute the value of $\theta^{(1)}(R^+)$. Repeating the operation of differentiation with respect to r and integration by parts on equation (2.8), we obtain

$$\theta^{(2)}(r) = 2\pi\rho Q(0)\theta^{(1)}(r) + 2\pi\rho Q'(0)\theta^{(0)}(r) - 2\pi\rho Q'(R)\theta^{(0)}(r-R)$$

$$+ 2\pi\rho \int_0^R Q''(t)\, \theta^{(0)}(r-t)\, dt \tag{2.10}$$

and repeating the differencing operation at $R^{\pm}$, we obtain

$$\Delta_1^{(2)}(R) = \theta^{(2)}(R^+) - \theta^{(2)}(R^-)$$

$$= 2\pi\rho Q(0)\Delta_1^{(1)}(R) + 2\pi\rho Q'(0)\Delta_1^{(0)}(R) \tag{2.11}$$

from which the value of $\theta^{(2)}(R^+)$ may be calculated.

If we now repeat the differentiation with respect to r and integration by parts on equation (2.10), the integral vanishes and we obtain

$$\theta^{(3)}(r) = 2\pi\rho Q(0)\theta^{(2)}(r) + 2\pi\rho Q'(0)\theta^{(1)}(r) + 2\pi\rho Q''(0)\theta^{(0)}(r)$$

$$- 2\pi\rho Q'(R)\theta^{(1)}(r-R) - 2\pi\rho Q''(R)\theta^{(0)}(r-R) \qquad (2.12)$$

The right hand side of eq. (2.12) may be evaluated directly at R^+ to obtain

$$\theta^{(3)}(R^+) = 2\pi\rho Q(0)\theta^{(2)}(R^+) + 2\pi\rho Q'(0)\theta^{(1)}(R^+) + 2\pi\rho Q''(0)\theta^{(0)}(R^+)$$

$$- 2\pi\rho Q'(R)\theta^{(1)}(0^+) - 2\pi\rho Q''(R)\theta^{(0)}(0^+) \qquad (2.13)$$

We may now differentiate equation (2.12) with respect to r as many times as we please to obtain

$$\theta^{(n)}(r) = 2\pi\rho Q(0)\theta^{(n-1)}(r) + 2\pi\rho Q'(0)\theta^{(n-2)}(r) + 2\pi\rho Q''(0)\theta^{(n-3)}(r)$$

$$- 2\pi\rho Q'(R)\theta^{(n-2)}(r-R) - 2\pi\rho Q''(R)\theta^{(n-3)}(r-R),\ n = 3,.. \qquad (2.14)$$

which enables us to determine the values of the third and higher derivatives of $\theta(r)$ at the point R^+.

These derivatives may be used to construct a N-term Taylor series approximation to the function $\theta(r)$ as

$$\theta^{(0)}(r) = \sum_{n=0}^{N} [\theta^{(n)}(R^+)/n!](r - R)^n \qquad (2.15)$$

There are convenient methods available (Press et al, 1987) for the rapid and accurate evaluation of such expressions.

It remains to discuss the radius of convergence of this series. This may be ascertained by reference to equation (2.12) which is a third order inhomogeneous linear differential equation with constant coefficients for the function $\theta(r)$. The solution is continuous (and hence the Taylor series convergent) in any region in which the last two inhomogenous terms are continuous. This is the case if $0 \le r - R < R$, so that the series (2.15) converges uniformly to $\theta(r)$ for $R \le r < 2R$.

Because of the uniform convergence, the equation (2.15) may be differentiated twice to obtain

$$\theta^{(1)}(r) = \sum_{n=1}^{N} [\theta^{(n)}(R^+)/(n-1)!](r - R)^{n-1} \tag{2.16}$$

$$\theta^{(2)}(r) = \sum_{n=2}^{N} [\theta^{(n)}(R^+)/(n-2)!](r - R)^{n-2} \tag{2.17}$$

from which we may evaluate the quantities $\theta^{(1)}(2R^-)$, $\theta^{(2)}(2R^-)$.

The form of equation (2.6) indicates that the function $\theta^{(0)}(r)$ is continuous for $r > R$ and the form of equation (2.8) indicates that this is also the case for the function $\theta^{(1)}(r)$. However, the form of eqs (2.10, 2.11) indicates that the function $\theta^{(2)}(r)$ possesses a jump discontinuity at the point $r = 2R$. At this juncture, we need to generalize the notation for the functions $\theta^{(n)}(r)$ to take into account the piecewise continuity. Let us denote by $\theta_m^{(n)}(r)$ the form of the function $rh(r)$ in the region $mR \le r < (m+1)R$.

To extend the expansion (2.15) into the region $2R \le r < 3R$, we use equations (2.6, 2.8, 2.10) to obtain

$$\Delta_2^{(0)}(2R) = \theta_2^{(0)}(2R^+) - \theta_1^{(0)}(2R^-) = 0 \tag{2.18}$$

$$\Delta_2^{(1)}(2R) = \theta_2^{(1)}(2R^+) - \theta_1^{(1)}(2R^-) = 0 \tag{2.19}$$

and

$$\Delta_2^{(2)}(2R) = \theta_2^{(2)}(2R^+) - \theta_1^{(2)}(2R^-) = - 2\pi\rho Q'(R)\Delta_1^{(0)}(R) \tag{2.20}$$

from which the function $\theta_2^{(0)}(2R^+)$ and its first two derivatives $\theta_2^{(1)}(2R^+)$, $\theta_2^{(2)}(2R^+)$ may be computed at the point $2R^+$. We may now evaluate the remaining derivatives $\theta_2^{(n)}(2R^+)$ using the expression (2.14) to obtain

$$\theta_2^{(n)}(2R^+) = 2\pi\rho Q(0)\theta_2^{(n-1)}(2R^+) + 2\pi\rho Q'(0)\theta_2^{(n-2)}(2R^+) + 2\pi\rho Q''(0)\theta_2^{(n-3)}(2R^+)$$

$$- 2\pi\rho Q'(R)\theta_1^{(n-2)}(R^+) - 2\pi\rho Q''(R)\theta_1^{(n-3)}(R^+), \quad n = 3,.. \tag{2.21}$$

to obtain the Taylor series approximation

$$\theta_2^{(0)}(r) = \sum_{n=0}^{N} [\theta_2^{(n)}(2R^+)/n!](r - 2R)^n \tag{2.22}$$

which converges uniformly to the function $rh(r)$ for $2R \le r < 3R$. As before, we may use eq. (2.22) and its once and twice differentiated forms to obtain the necessary values at the points $3R^-$, viz

$$\theta_2^{(0)}(3R^-) = \sum_{n=0}^{N} [\theta_2^{(n)}(2R^+)/n!]\ R^n \tag{2.23}$$

$$\theta_2^{(1)}(3R^-) = \sum_{n=1}^{N} [\theta_2^{(n)}(2R^+)/(n-1)!]\ R^n \tag{2.24}$$

$$\theta_2^{(2)}(3R^-) = \sum_{n=2}^{N} [\theta_2^{(n)}(2R^+)/(n-2)!]\ R^n \tag{2.25}$$

needed to extend the algorithm into the region $3R \le r < 4R$. As the form of the algorithm in this and all subsequent regions is identical, we complete this section by giving the general form. Assuming that we have constructed the Taylor series in the region $mR \le r < (m+1)R$, we compute in turn

$$\theta_m^{(0)}([m+1]R^-) = \sum_{n=0}^{N} [\theta_m^{(n)}(mR^+)/n!]\ R^n \tag{2.26}$$

$$\theta_m^{(1)}([m+1]R^-) = \sum_{n=1}^{N} [\theta_m^{(n)}(mR^+)/(n-1)!]\ R^n \tag{2.27}$$

$$\theta_m^{(2)}([m+1]R^-) = \sum_{n=2}^{N} [\theta_m^{(n)}(mR^+)/(n-2)!]\ R^n \tag{2.28}$$

$$\theta_m^{(n)}([m+1]R^+) = \theta_m^{(n)}([m+1]R^-),\ n = 1,2,3 \tag{2.29}$$

$$\theta_{m+1}^{(n)}([m+1]R^+) = 2\pi\rho\Big[Q(0)\theta_{m+1}^{(n-1)}([m+1]R^+) + Q'(0)\theta_{m+1}^{(n-2)}([m+1]R^+) + Q''(0)\theta_{m+1}^{(n-3)}([m+1]R^+) - Q'(R)\theta_m^{(n-2)}(mR^+) - Q''(R)\theta_m^{(n-3)}(mR^+)\Big], \tag{2.30}$$

For this to be a useful algorithm, it needs to be not only convergent, which we have discussed above, but also stable. For recurrence relations as complicated as the ones above, this is a very difficult matter to prove. We can however present two pieces of numerical evidence that the algorithm is indeed stable. Firstly, we have computed the function $rh(r)$ for $r \le 50R$, to which point it shows no sign of instability. Moreover, when this function is multiplied by r and integrated, the correct value of the inverse compressibility is obtained. Secondly, we have shown that Perram's (1975) earlier algorithm using the trapezoidal rule converges towards values predicted by the new algorithm with the correct order.

3. PRACTICAL IMPLEMENTATION OF THE PIECEWISE TAYLOR SERIES ALGORITHM

The algorithm outlined above can be readily implemented in any suitable high level language or other computational tool. This is in contrast to its generalization to mixtures which is extremely difficult to implement in a language not capable of recursion (ie Fortran). We have implemented the algorithm in the languages Fortran 77 and Pascal. To produce the figure below showing a sequence of radial distribution functions at various values of the packing fraction η, we have used the commercially available spreadsheet package SuperCalc4.

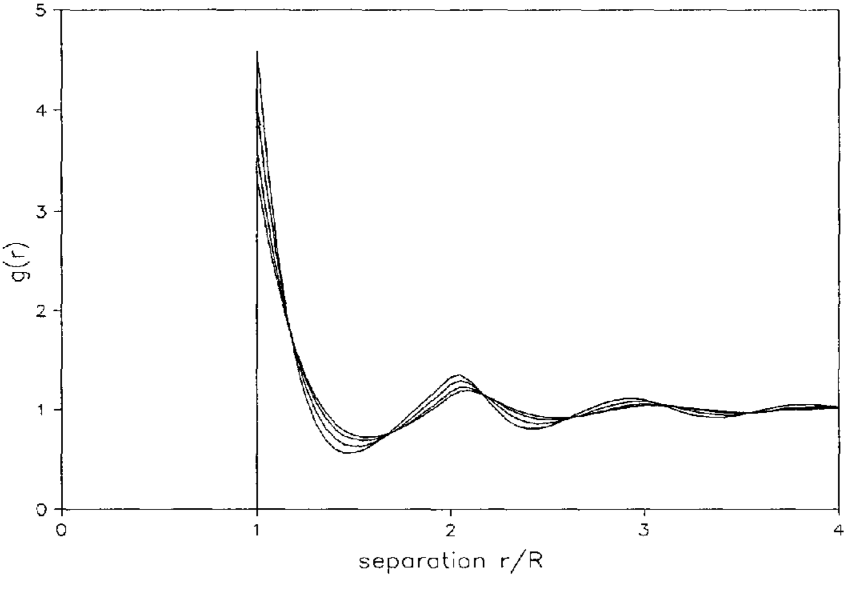

Fig. 1. Showing the radial distribution functions g(r) at various values of the packing fraction η. The curves have been computed using 20 terms in the piecewise Taylor series.

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