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Correlation Functions for Diatomic Symmetric Molecules from the RISM Equation

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Using the solution of the RISM equation for diatomic symmetric molecules outlined in a previous paper, the site–site radial distribution function (RDF) is calculated and compared with the Monte Carlo results and the numerical RDF of Lowden and Chandler. The RDF calculated here and the numerical RDF of Lowden and Chandler agree well at intermediate and high densities. At low density, however, both have systematic errors. The agreement between the RDF calculated here and the Monte Carlo results suggests that a simplified formulation of the RISM solution may serve well as a reference system in a perturbation theory for diatomic fluids.

KEY WORDS: RISM equation; diatomic; correlation functions.

1. INTRODUCTION

In a recent paper,$^{(1)}$ it was shown that the RISM equation for diatomic symmetric molecules could be solved using a Weiner–Hopf factorization technique. This technique introduced a function $Q(r)$ which is related to the site–site total correlation function in the following way:

$$Q'(r) + \frac{1}{2L}\left[\,Q(r+L) - Q(r-L)\right] + \frac{\delta(r-L)}{4\pi\rho L}$$
$$= 2J'(r) - 4\pi\rho\int_0^\infty dt\; Q(t)J'(|r-t|) \tag{1.1}$$

$Q(r)$ is a known function, in terms of a set of parameters $\hat{Q}(-\lambda_n)$ for r greater than the hard sphere diameter R, and is given by

$$Q(r) = \frac{1}{\pi\rho}\sum_1^\infty \mathrm{Re}\left(\zeta_n e^{-i\lambda_n r}\right) \tag{1.2}$$

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where

$$\zeta_n = i/\hat{Q}(-\lambda_n)\hat{w}'(\lambda_n) \tag{1.3}$$

and λ_n is the solution of

$$\hat{w}(\lambda_n) = 1 + \frac{\sin\lambda_n L}{\lambda_n L} = 0 \tag{1.4}$$

As $Q(r)$ is zero for $r < 0$, $Q(r)$ remains only to be solved on the range $0 < r < R$.

In Ref. 1 it was shown that it is possible to solve Eq. (1.1) for all values of L in the range $0 < L \leqslant R$, which corresponds to all physically relevant cases or all possible diatomic intramolecular spacings. The solution obtained expresses $Q(r)$ in terms of the infinite set of parameters $\hat{Q}(-\lambda_n)$, so to obtain useful results it is necessary to truncate the infinite sum in Eq. (1.2). If this sum is truncated after N terms we obtain a system of N coupled algebraic equations to solve for the parameters $\hat{Q}(-\lambda_1), \ldots, \hat{Q}(-\lambda_N)$. These coupled algebraic equations are obtained by replacing k by $-\lambda_1, \ldots, -\lambda_N$ in

$$\hat{Q}(k) = 1 - 2\pi\rho\int_0^\infty dr\, e^{ikr}Q(r) \tag{1.5}$$

In the following section the solution is formulated exactly, that is, with infinite sums rather than truncated finite sums. The results presented here are for truncation of Eq. (1.2) after three terms. The consequences of this truncation are investigated and discussed.

The purpose of this paper is to compare the numerical site–site radial distribution functions of Lowden and Chandler$^{(2)}$ with those calculated here, and with the "exact" Monte Carlo results. The site–site radial distribution functions calculated using the method of Lowden and Chandler,$^{(2)}$ hereafter referred to as "Lowden's method," were obtained by determining the $c(r)$ for which the functional

$$I_{\text{RISM}} = 4\rho^2\hat{c}(0) - \frac{1}{(2\pi)^3}\int dk\{2\rho[1 + \hat{w}(k)]\hat{c}(k) + \ln(1 - 2\rho[1 + \hat{w}(k)]\hat{c}(k))\} \tag{1.6}$$

is minimal. The site–site direct correlation function $c(r)$ is represented as a sum of basis functions chosen to allow $c(r)$ to be discontinuous at $r = R$ and discontinuous in first derivative at $r = L$ and $R - L$. For the case considered here, that is $L = \frac{1}{2}R$, $c(r)$ was chosen to be a cubic polynomial on each of the two ranges, $0 < r < L$ and $L < r < R$, with the restriction that $c(r)$ be continuous at $r = L$.

2. FORMULATION

Algebraically the simplest case to consider is when L (the intramolecular spacing) is half the hard sphere diameter R. $Q(r)$ then has only two different functional forms: one on the range $0 < r < L$ and the other on the range $L < r < R$. Also the hard sphere diameter can be scaled out of the problem by choosing R to be unity, so we have $R = 1$ and $L = \frac{1}{2}$.

It was shown in Ref. 1 that the right-hand side (RHS) of Eq. (1.1) can be written as

$$\mathrm{RHS} = \sum_{0}^{\infty} (a_n r + b_n) + \mathrm{Re}\left(\sum_{1}^{\infty} d_n e^{-i\lambda_n r} \right) \tag{2.1}$$

where

$$a_0 = 2 - 4\pi\rho \int_0^1 dt\ Q(t) \tag{2.2}$$

$$b_0 = 4\pi\rho \int_0^1 dt\, t Q(t) \tag{2.3}$$

and for $n \geqslant 1$

$$a_n = -4\mathrm{Re}\left(\frac{\zeta_n}{i\lambda_n} e^{-i\lambda_n} \right) \tag{2.4}$$

$$b_n = -4\mathrm{Re}\left[\frac{\zeta_n}{\lambda_n^2} (1 + i\lambda_n) e^{-i\lambda_n} \right] \tag{2.5}$$

$$d_n = -4\zeta_n \tilde{G}(i\lambda_n) \tag{2.6}$$

$$\tilde{G}(i\lambda_n) = \int_0^{\infty} dr\, r g(r) e^{-i\lambda_n r} \tag{2.7}$$

The numerical scheme used to solve the coupled algebraic equations (1.5) is based on iterating the parameters $\hat{Q}(-\lambda_n)$, or equivalently the parameters ζ_n. Therefore, in the algebra that follows we consider the parameters ζ_n ($n = 1, 2, 3, \ldots$) to be given, initially as a first guess and then as improvements on that first guess. Using Eq. (2.1) we can solve Eq. (1.1) for $Q(r)$ yielding

$$\begin{aligned} Q(r) = {} & \sum_{0}^{\infty} \left(-a_n r + \frac{a_n}{2} - b_n \right) + \mathrm{Re}\left(P_0 e^{-ir} \right) \\ & + \sum_{1}^{\infty} \mathrm{Re}\left\{ \left[\frac{\zeta_n e^{-i\lambda_n}}{\pi\rho} - d_n\left(i\lambda_n + e^{-i\lambda_n/2} \right) \right] \frac{e^{-i\lambda_n r}}{1 - \lambda_n^2} \right\} \\ & \text{for } 0 < r < \tfrac{1}{2} \end{aligned} \tag{2.8}$$

and

$$Q(r) = \sum_{0}^{\infty}\left(a_n r + \frac{a_n}{2} + b_n\right) + \operatorname{Re}\left(iP_0 e^{i/2} e^{-ir}\right)$$
$$+ \sum_{1}^{\infty} \operatorname{Re}\left\{\left[\frac{i\lambda_n e^{-i\lambda_n}}{1-\lambda_n^2}\,\frac{\zeta_n}{\pi\rho} + \left(\frac{1 - i\lambda_n e^{-i\lambda^n/2}}{1-\lambda_n^2}\right) d_n\right] e^{-i\lambda_n r}\right\}$$
$$\text{for } \tfrac{1}{2} < r < 1 \tag{2.9}$$

At this stage we have $Q(r)$ given in functional form but with unknowns a_0, b_0, P_0, and d_n still to be determined (note that a_0 and b_0 are real while both P_0 and d_n are complex).

There are two continuity conditions which $Q(r)$ must satisfy. Firstly that $Q(r)$ be continuous at the hard core diameter

$$Q(1^+) = Q(1^-) \tag{2.10}$$

and secondly that $Q(r)$ have the required jump discontinuity,

$$Q(\tfrac{1}{2}^-) = Q(\tfrac{1}{2}^+) + 1/2\pi\rho \tag{2.11}$$

Along with Eqs. (2.2) and (2.3), Eqs. (2.10) and (2.11) can be used to eliminate the unknowns a_0, b_0, and P_0. The algebra is tedious but straightforward and therefore omitted. It should be noted, however, that it is not possible to solve these four equations simultaneously when

$$(1 - 5\pi\rho)(1 + \sin\tfrac{1}{2}) + 8\pi\rho\cos\tfrac{1}{2} = 0 \tag{2.12}$$

This corresponds to a density

$$\rho = \frac{1}{\pi}\cdot\frac{1 + \sin\frac{1}{2}}{5(1 + \sin\frac{1}{2}) - 8\cos\frac{1}{2}} \doteqdot 1.25 \tag{2.13}$$

As a similarity in topology between the RISM approximation and the Percus–Yevick approximation has been suggested,$^{(3)}$ a term of this form is expected. The Percus–Yevick theory for hard spheres contains a term $(1 - \frac{1}{6}\pi\rho R^3)^{-2}$ which gives a maximum density of $6/\pi R^3$. This maximum density is unphysical as it corresponds to deforming the hard sphere particles so that they occupy the whole volume of the fluid (i.e., a specific volume of unity). The RISM maximum density is likewise unphysical and corresponds almost exactly to a specific volume of unity for the case we are considering.

It now remains only to eliminate the parameters d_n, and this can be achieved using the method outlined in Ref. 1, that is,

$$d_n = \frac{-2\zeta_n \tilde{\sigma}(i\lambda_n)}{\hat{Q}(-\lambda_n)} \tag{2.14}$$

where

$$\tilde{\sigma}(s) = \int_R^\infty dr \exp(-sr)\left\{ \sum_{n=0}^{\infty} (a_n r + b_n) + \mathrm{Re}\left[\sum_{n=1}^{\infty} d_n \exp(-i\lambda_n r)\right]\right\}$$
$$- \int_R^{R+L} dr \exp(-sr)\left\{ Q'(r) + \frac{1}{2L}\left[Q(r+L) - Q(r-L)\right]\right\} \tag{2.15}$$

Again the algebra is tedious and therefore omitted. Substituting Eqs. (2.8) and (2.9) into Eq. (1.5) gives an infinite set of algebraic equations of the form

$$\hat{Q}(-\lambda_n) = f[\hat{Q}(-\lambda_1), \ldots] \tag{2.16}$$

to solve for the parameters $\hat{Q}(-\lambda_n)$. Clearly in order to obtain useful results from this analytic solution the infinite set of equations must be truncated.

3. NUMERICAL METHOD

Truncating all the summations in the previous section after $n = N$ (or $m = N$) gives N coupled algebraic equations to solve for $\hat{Q}(-\lambda_1)$, $\hat{Q}(-\lambda_2), \ldots, \hat{Q}(-\lambda_N)$ of the form

$$\hat{Q}(-\lambda_n) = f[\hat{Q}(-\lambda_1), \ldots, \hat{Q}(-\lambda_N)] \tag{3.1}$$

The iteration procedure chosen must, in effect, find the fixed points of this equation. In Ref. 1 it was shown that as $|k| \to \infty$, $\hat{Q}(k) \to 1$, so $\hat{Q}(-\lambda_n) = 1$ for all n can be chosen as a first guess. It is found that the fixed points of Eq. (3.1) are stable, so the following simple iteration procedure works very well when $N = 2$ and 3.

1. Choose a first guess for $\hat{Q}(-\lambda_n)$ for $n = 1, N$ [i.e., $\hat{Q}(-\lambda_n) = 1$].
2. Calculate $\zeta_n, a_n, b_n, a_0, b_0, P_0, d_n$. These coefficients specify $Q(r)$ over its whole range.
3. Calculate the Fourier transform $\hat{Q}(-\lambda_n)$.
4. Replace old $\hat{Q}(-\lambda_n)$ by new $\hat{Q}(-\lambda_n)$ and return to step 2. Repeat this procedure until the old $\hat{Q}(-\lambda_n)$ equal the new $\hat{Q}(-\lambda_n)$.

The convergence of this iteration scheme is very rapid. For all densities considered $\rho = 0.01$ to 0.7 the coefficients calculated at step 2 are accurate to seven significant figures after only three iterations; each iteration requiring approximately 5 sec of ICL 1100 computer time.

The existence of such a stable fixed point is most interesting as other problems in statistical mechanics of fluids (for example, the solution of the Ornstein–Zernike equation for hard spheres with Yukawa closure) require the solution of a similar set of coupled algebraic equations.(7)

4. SITE–SITE RADIAL DISTRIBUTION FUNCTION

The numerical method of Perram[(4)] can be used to generate the site–site radial distribution function $g(r)$. Returning to Eq. (1.1) it can be shown that the left-hand side (LHS) is zero for $r > 3/2$ and for $1 < r < 3/2$

$$\begin{aligned} \mathrm{LHS} = & -\sum_0^\infty (a_n r + b_n) - \mathrm{Re}\left(ie^i P_0 e^{-ir}\right) \\ & -\sum_1^\infty \mathrm{Rr}\left\{\left[d_n\left(\frac{1 - i\lambda_n e^{-i\lambda_n/2}}{1-\lambda_n^2}\right)e^{i\lambda_n}\right.\right. \\ & \left.\left. +\frac{\zeta_n}{\pi\rho}\left(\frac{i\lambda_n - e^{i\lambda_n/2}}{1-\lambda_n^2}\right)\right]e^{-i\lambda_n r}\right\} \end{aligned} \tag{4.1}$$

The right-hand side of Eq. (1.1) can be shown to be

$$\begin{aligned} \mathrm{RHS} = & -2rg(r) + \sum_0^\infty (a_n r + b_n) + \sum_1^\infty \mathrm{Re}\left(d_n e^{-i\lambda_n r}\right) \\ & + 4\pi\rho \int_0^r dt\ Q(t)(r-t)g(r-t) \qquad \text{for } r > R \end{aligned} \tag{4.2}$$

Combining Eqs. (4.1) and (4.2), the site–site radial distribution function is given by

$$\begin{aligned} g(r) = & \sum_0^\infty \left(a_n + \frac{b_n}{r}\right) + \frac{1}{2r}\sum_1^\infty \mathrm{Re}\left\{\left[d_n\left(1 + \frac{1 - i\lambda_n e^{-i\lambda_n/2}}{1-\lambda_n^2} e^{i\lambda_n}\right)\right.\right. \\ & \left.\left. + \frac{\zeta_n}{\pi\rho}\left(\frac{i\lambda_n}{1-\lambda_n^2} - e^{i\lambda_n/2}\right)\right]e^{-i\lambda_n r}\right\} + \frac{1}{2r}\mathrm{Re}\left(ie^i P_0 e^{-ir}\right) \\ & + \frac{4\pi\rho}{2r}\int_1^r dt\ Q(r-t)tg(t) \qquad \text{for } 1 < r < 3/2 \end{aligned} \tag{4.3}$$

and

$$\begin{aligned} g(r) = & \frac{1}{2}\sum_0^\infty \left(a_n + \frac{b_n}{r}\right) + \frac{1}{2r}\sum_1^\infty \mathrm{Re}\left(d_n e^{-i\lambda_n r}\right) \\ & + \frac{4\pi\rho}{2r}\int_1^r dt\ Q(r-t)tg(t) \qquad \text{for } r > 3/2. \end{aligned} \tag{4.4}$$

The continuity of $g(r)$ at $r = 3/2$ is assured by the condition that $Q(r)$ be continuous at $r = 1$.

The contact value of the site–site radial distribution function $g(1^+)$ can be obtained from Eq. (4.3) by simply setting $r = 1$, but when the infinite sum is truncated, $g(1^+) \sim \rho^{-1}$ as ρ approaches zero. We shall return to this difficulty when comparing the various radial distribution functions.

5. MONTE CARLO SIMULATION

The site–site radial distribution function for the RISM molecules considered here, was determined using the Monte Carlo method.(5) The calculation was done for 144 molecules in a cubic box, with periodic boundary conditions applied to the center of mass of the molecule. Each move consisted of moving a RISM molecule at random both translationally and rotationally. The rotational movement was made using a three-dimensional rotation matrix for which the three angles were chosen at random. The bound on each move was chosen in order to ensure an acceptance rate of 30%–70%.

Initially the molecules were arranged in a cubic lattice with all intramolecular bonds parallel. In general 10^5 moves were allowed for the lattice to "melt" (5×10^5 for density 0.6) and the site–site radial distribution function averaged over the next 10^6 moves.

6. RESULTS AND DISCUSSION

The site–site radial distribution functions reported here are those using three poles (3P) of Eq. (1.2) (that is truncating all infinite sums in Section 2 after $n = 3$). The site–site radial distribution functions calculated using Lowden's programs(6) agree well with those calculated using 3 poles, particularly at high densities. This can readily be seen in Figs. 1–3. These figures have been drawn with the intention of accentuating rather than diminishing the differences between the various site–site radial distribution functions. At a density of 0.6 the two radial distribution functions coincide almost exactly, so only the 3P one has been drawn. As the density is lowered the differences between the two radial distribution functions increase in a systematic way. The contact value $g(1^+)$ of the 3P radial distribution function is lower than Lowden's and its shoulder height $g(1.5)$ is higher. However, at both places, contact and shoulder (and indeed generally), the 3P radial distribution function shows better agreement with the Monte Carlo results than Lowden's. A comparison of the 3P and Monte Carlo (MC) radial distribution functions shows that the 3P results have higher contact values (except at $\rho = 0.6$) and lower shoulder values. Also the long-range oscillations are out of phase. The differences between 3P and MC radial distribution functions are very similar to the differences between Percus–Yevick and Monte Carlo radial distribution functions for hard spheres, especially from the shoulder outwards. This is further evidence of the Percus–Yevick-like structure of the RISM approximation.

As mentioned earlier the contact value of the radial distribution function contains a zero density divergence, when Eq. (1.2) is truncated after a finite number of terms. If for example, no poles are included the divergence remains as $P_0 \rightarrow \rho^{-1}$. This divergence has dire consequences for

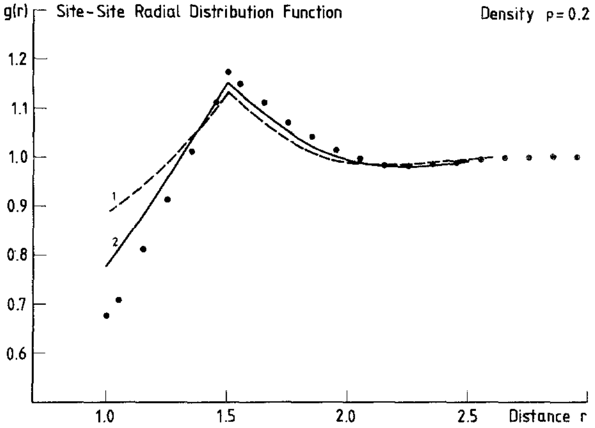

Fig. 1. Site–site radial distribution function $g(r)$ at a density of 0.2. Curve 1 is from Lowden's program. Curve 2 is the 3P. ● are the Monte Carlo values.

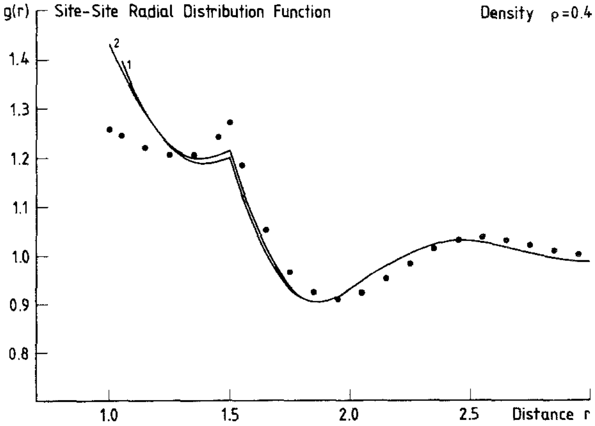

Fig. 2. Site–site radial distribution function $g(r)$ at a density of 0.4.

low-density radial distribution functions. However, it is clear from Fig. 1 that at a density of 0.2 no problems have emerged. In Fig. 4 we plot the contact value $g(1^+)$ as a function of density ρ and it can be seen that for densities less than 0.04 the contact value is negative and hence clearly unphysical. Below a density of 0.1 all radial distribution functions generated using this method would be of doubtful accuracy. At a density of 0.2

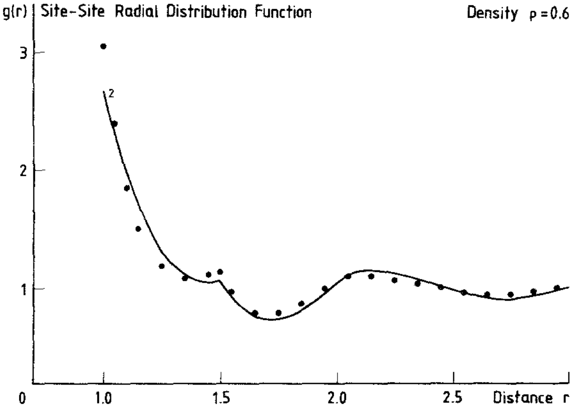

Fig. 3. Site–site radial distribution function $g(r)$ at a density of 0.6.

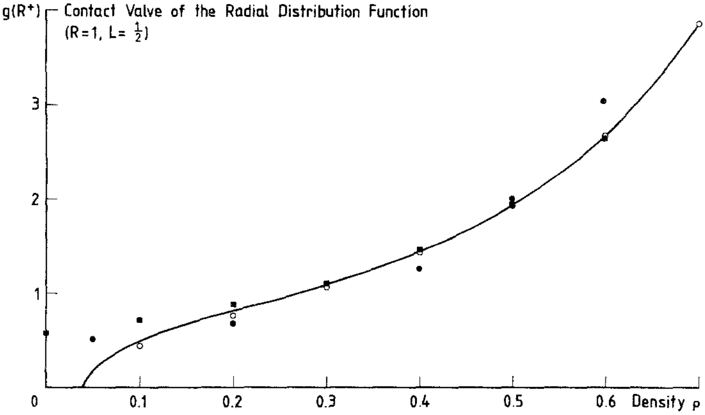

Fig. 4. Contact value of the radial distribution function $g(R^+)$. Solid curve is using no poles. ○ is $3P$. ■ is from Lowden's program. ● are the MC values.

the radial distribution functions appear quite reasonable, as can be seen in the following table.

	Contact value $g(1^+)$ at $\rho = 0.2$
Lowden	0.887
No poles	0.801
2 poles	0.780
3 poles	0.777
Monte Carlo	0.675

These results suggest that, at this density, the contact value obtained using Lowden's methods is poor. The contact value obtained using our method is in increasingly better agreement with the MC value as the number of poles increases.

7. SUMMARY

From a practical point of view the calculation of radial distribution functions using the formulation of Section 2 is only feasible for the case considered (i.e., $L = \frac{1}{2} R$). Changing the value of L requires the complete reformulation of Section 2. This is clearly a daunting task. However, if all the poles are neglected, which is a reasonable approximation at liquid densities, the routine solution for various values of L is relatively simple. Also as the analytic structure of the solution is now understood, it may be feasible to use a completely numerical approach to the calculation of $Q(r)$, and hence the radial distribution function $g(r)$. This approach would allow the same flexibility in density ρ and intramolecular spacing L as the programs of Lowden.

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