

RESEARCH ARTICLE | JULY 01 1982

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*J. Chem. Phys.* 77, 509–520 (1982)

<https://doi.org/10.1063/1.443606>



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# Application of an extended RISM equation to dipolar and quadrupolar fluids

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(Received 27 November 1981; accepted 16 December 1981)

A generalization of the RISM integral equation for site-site pair correlation functions previously proposed by us is discussed and applied to model liquids composed of strongly polar diatomic molecules. The nonuniform molecular charge distribution is represented by the introduction of charged interaction sites. The generalization consists of applying closure conditions analogous to those which are known to be reasonable for the description of atomic ionic fluids, and the corresponding renormalization of the contributions arising from long range forces. We discuss both the symmetry properties of the pair correlation functions in special cases and the dielectric properties implied by theory. Applications are presented for three two-site models which differ substantially in the degree of asymmetry of the non-Coulombic potential between the two sites, and for three three-site models for Br<sub>2</sub>. The two sites models are compared to computer simulation results, and those for Br<sub>2</sub> to experimental results. The analysis shows that the integral equation is well balanced in that in every case the qualitative features of the liquids structure which are introduced by polarity are well represented, even in cases where the site-site potentials are individually much larger than  $k_B T$ . In cases where the molecular shape and polar forces are in competition, the results are of comparable accuracy to the corresponding theory for nonpolar systems. In the extreme case where changes in orientational structure can occur without interfering with packing requirements, the results appear quantitatively less reliable.

## I. INTRODUCTION

Integral equations based on the Ornstein-Zernike formulation<sup>1</sup> have proven to be a powerful approach for obtaining approximate pair correlation functions in dense fluids.<sup>2</sup> Included in these successes are descriptions of simple<sup>2</sup> and ionic<sup>3,4</sup> atomic fluids, and nonpolar molecular fluids.<sup>5</sup>

In order to provide realistic models for molecular fluids, a fruitful approach has been the use of interaction site models (ISM).<sup>6</sup> That is, models in which the interaction between molecular species is represented by a sum of pairwise additive spherically symmetric potentials which act between specified points located in each molecule. Such model potentials have formed the basis for treatments of a wide range of polar molecular systems.<sup>7-10</sup>

The statistical mechanical formalism for interaction site representations has been developed in detail by Chandler and co-workers<sup>6,11-14</sup> as well as by others.<sup>15-19</sup> For fluids composed of molecules which interact primarily via harsh repulsive forces a successful integral equation formulation known as the RISM equation has been developed<sup>11</sup> and successfully applied to a number of examples.<sup>5,20</sup>

Recently, we proposed<sup>21</sup> an extension of this theory designed for application to polar liquids in which the nonuniform molecular charge distribution is represented via an ISM with charged interaction sites. The extension is based on the use of closure relations directly analogous to those which are known to be valuable for the description of atomic ionic fluids.<sup>3,4,22,23</sup> It is the latter which would be obtained from the ISM in the absence of intramolecular bonds. In our preliminary report, we presented an application of the theory to a liquid composed of model diatomics, and showed that the theory qualitatively reproduced the structure (site-site

radial pair correlation functions) determined from a computer simulation of the same system.

The purpose of the present paper is to present the theory in more detail and to present a series of calculations employing more general molecular models with the goal of exploring the predictive capabilities of the integral equation. In Sec. II, we present the theoretical basis for our calculations. In Sec. III, we present results for a series of diatomic, two-center models of increasing site size asymmetry. For these models we compare in each case to results obtained from molecular dynamics computer simulations. In Sec. IV, we present results obtained for three-center models of liquid bromine in which the quadrupolar charge distribution is represented via a three-point charge model, rather than by the leading multipole. Here, we compare to experimental scattering data.<sup>24,25</sup> The conclusions are presented in Sec. V.

## II. INTEGRAL EQUATION FORMULATION

In this section we describe the theoretical formulation to be applied in this paper. We assume that the reader is familiar with the formalism<sup>26</sup> associated with integral equation treatments of atomic fluids as well as the interaction site formalism and RISM theory for molecular fluids.<sup>5</sup> We use the renormalization techniques and notation of Rossky and Dale,<sup>27</sup> and the reader is referred there for a detailed discussion of this aspect.

### A. Renormalized RISM equation

For a multicomponent atomic fluid the usual Ornstein-Zernike (OZ) integral equation can be written as

$$h_{\alpha\gamma}(r) = c_{\alpha\gamma}(r) + \sum_{\lambda} \rho_{\lambda} c_{\alpha\lambda} * h_{\lambda\gamma}(r), \quad (1)$$

where  $h$  is an interatomic pair correlation function and  $c$  is the corresponding direct correlation function for particles separated by a distance  $r$ . The subscripts label atomic species and  $\rho_\lambda$  is the number density of species  $\lambda$ . Here  $*$  denotes the spatial convolution.

In order to make the most direct connection to the integral equation for molecular fluids, it is instructive to construct a matrix, denoted  $\rho$ , having the elements

$$\rho_{\alpha\gamma} = \rho_\alpha \delta_{\alpha\gamma} . \quad (2)$$

Then the usual OZ equation, Eq. (1), can be written in matrix form as

$$h = c + c * \rho h \quad (3)$$

or equivalently, using the chain sum notation of Rossky and Dale<sup>27</sup>:

$$h = c[c|\rho] \\ = [\text{sum of all simple connected chains of one or more } c \text{ bonds on black } \rho \text{ vertices between terminal white } 1 \text{ circles}] . \quad (4)$$

For molecular fluids the so-called RISM integral equation<sup>11</sup> can be written in analogous form. That is,

$$\rho_{\alpha_M} \rho_{\gamma_{M'}} h_{\alpha_M \gamma_{M'}}(r) \\ = \sum_{\lambda_M, \beta_{M'}} \omega_{\alpha_M \lambda_M} * c_{\lambda_M \beta_{M'}} * \omega_{\beta_{M'} \gamma_{M'}}(r) \\ + \sum_{M''} \sum_{\lambda_{M''}, \beta_{M''}} \rho_{M''} \omega_{\alpha_M \lambda_{M''}} * c_{\lambda_{M''} \beta_{M''}} * h_{\beta_{M''} \gamma_{M''}}(r) , \quad (5)$$

where

$$\omega_{\alpha_M \gamma_{M'}} = \rho_M \delta_{\alpha_M \gamma_{M'}} \delta(r_{\alpha_M} - r_{\gamma_{M'}}) \\ + \rho_M (1 - \delta_{\alpha_M \gamma_{M'}}) s_{\alpha_M \gamma_{M'}}(r_{\alpha_M} - r_{\gamma_{M'}}) . \quad (6)$$

$\rho_{\alpha_M}$  is the number density of sites of type  $\alpha$  in molecules of species  $M$ ,  $\rho_M$  is the number density of molecules of species  $M$ , and  $s_{\alpha_M \gamma_{M'}}$  is the intramolecular pair correlation function between sites  $\alpha_M$  and  $\gamma_{M'}$  in a molecule of species  $M$ .

Since  $\rho_{\alpha_M} = \rho_M$ , we can write the equation most compactly in terms of a (diagonal) matrix  $\rho$  whose elements are given by

$$\rho_{\alpha_M \gamma_{M'}} = \rho_M \delta_{\alpha_M \gamma_{M'}} . \quad (7)$$

Then, in matrix form, Eq. (5) is

$$\rho h \rho = \omega * c * \omega + \omega * \rho c * \rho h . \quad (8)$$

In analogy with Eq. (4), we have

$$h = c[c|\omega] \\ = \{\text{sum of all simple connected chains of one or more } c \text{ bonds on black } \omega \text{ hypervertices between terminal white } 1 \text{ circles}\} . \quad (9)$$

Defining  $t = h - c$ , we have

$$t = c[c|\omega] - c \equiv c'[c|\omega] . \quad (10)$$

For nearly rigid molecules, the Fourier transform of the intramolecular pair correlation function  $s$  can be represented by

$$\hat{s}_{\alpha_M \gamma_{M'}}(k) = \exp[-(k \delta r_{\alpha_M \gamma_{M'}})^2 / 2] \frac{\sin(k L_{\alpha_M \gamma_{M'}})}{(k L_{\alpha_M \gamma_{M'}})} , \quad (11)$$

where  $\delta r_{\alpha_M \gamma_{M'}}$  is a Gaussian width for the deviation around the average bond length  $L_{\alpha_M \gamma_{M'}}$ . In Eq. (11), and throughout the paper, we denote the Fourier transform by a carat. For  $\delta r = 0$ , we have a rigid bond, but for any  $\delta r \leq 0.05 \text{ \AA}$  the results differ negligibly. In the present work we have uniformly employed  $\delta r_{\alpha_M \gamma_{M'}} = 0.05 \text{ \AA}$ .

Equation (9) is the integral equation used in this work. However, in the presence of partially charged sites one expects that  $c(r)$  will be long ranged and it is highly desirable to rewrite Eq. (9) in a renormalized form. To this end, we introduce  $\psi(r)$  defined by

$$(c(r) - \psi(r)) \xrightarrow[r \text{ large}]{} 0 \quad (12)$$

and rewrite Eq. (10) in terms of the short ranged function:

$$c(r) - \psi(r) = c_s(r) .$$

That is,

$$t = c'[c - \psi + \psi|\omega] \\ = c'[\psi|\omega] + c'[c_s|\omega + \rho c[\psi|\omega]\rho] , \quad (13)$$

where we have used the identities given in Ref. 27. Defining

$$Q = c[\psi|\omega] = c'[\psi|\omega] + \psi , \quad (14)$$

$$\tau = t - c'[\psi|\omega] = t - Q + \psi , \quad (15)$$

and

$$V = \omega + \rho c[\psi|\omega]\rho , \quad (16)$$

Eq. (13) reduces to

$$\tau = c'[c_s|V] \quad (17)$$

or

$$h = c_s + Q + \tau = c[c_s|V] + Q . \quad (18)$$

We know<sup>19</sup> that for atomic fluids ( $s=0$ ),

$$c \xrightarrow[r \text{ large}]{\text{atomic}} -\beta u_{ir} \equiv \phi , \quad (19)$$

where  $u_{ir}(r)$  is the longest ranged part of the interatomic potential, and  $\beta = 1/k_B T$  where  $k_B$  is Boltzmann's constant and  $T$  is the temperature. Thus, in this case Eq. (14) simplifies to

$$Q = c[\phi|\rho] . \quad (20)$$

When  $u_{ir}$  is Coulombic,  $Q$  is equal to a Debye-Hückel screened potential  $\phi_{DH}$ , and Eq. (17) is recognized as the renormalized form of the OZ equation frequently employed in integral equation treatments of ionic systems.<sup>3</sup>

For molecular systems, if we assume that  $c$  behaves asymptotically for the case of an ISM with charged sites as it does for the atomic case,  $Q$  can be evaluated analytically<sup>14,15</sup> and it is found to behave asymptotically as  $r^{-6}$  rather than exponentially as is the case for atomic fluids. As discussed elsewhere,<sup>14</sup> this result follows from the interference between intermolecular

and intramolecular correlations. In this context, it is interesting to explicitly separate the atomiclike and intramolecular contributions to  $Q$ . That is, using Ref. 27 Eq. (A5), we have

$$Q = c[\phi|\omega] = c[\phi|\rho] + c^{alt}[s|c[\phi|\rho]] \\ = q + c^{alt}[s|q], \quad (21)$$

where

$$q \equiv c[\phi|\rho], \quad (22)$$

and where  $c^{alt}$  is the sum of all simple connected chains on black  $\rho$  vertices (between terminal white  $l$  circles) consisting of two or more *alternating*  $s$  and  $q$  bonds.<sup>27</sup> For atomic ionic fluids  $Q = q = \phi_{DH}$ , as noted above, and decays exponentially. Thus it is clear that, as indicated, it is the insertion of intramolecular correlations that produce the qualitatively different behavior found for molecular fluids.

## B. Closure relations

For atomic fluids, it is well known that the usual OZ equation<sup>1</sup> can be closed via an approximate relation between  $h$  and  $c$ .<sup>2,26</sup> For molecular fluids with site-site interaction potentials which are predominantly hardcore, a closure relating the site-site correlation functions which is directly analogous to that in the atomic Percus-Yevick theory<sup>2,26</sup> has been shown to lead to qualitatively correct results for short-range fluid structure.<sup>5</sup> In our preliminary report,<sup>21</sup> we took the approach that a reasonable corresponding choice for polar molecular fluids is one which is directly analogous to that which provides a reasonable description of atomic ionic fluids.<sup>3,4</sup> This leads to two proposed forms, namely PYA-like<sup>22</sup> and HNC-like closures.<sup>3,22</sup>

We denote the site-site pair potential by  $u$  and define

$$\beta u^* = \beta u + \phi, \quad (23)$$

where, here,

$$\phi_{\alpha_M \gamma_{M'}}(\gamma) = \frac{-\beta Z_{\alpha_M} Z_{\gamma_{M'}}}{\gamma}, \quad (24)$$

and  $Z_{\alpha_M}$  is the charge on site  $\alpha_M$ . Then, we have<sup>21</sup> the direct analogs of the atomic case<sup>21,27</sup>:

$$c_{\alpha_M \gamma_{M'}} - \phi_{\alpha_M \gamma_{M'}} = \exp[\beta u_{\alpha_M \gamma_{M'}}^* + Q_{\alpha_M \gamma_{M'}}] (1 + \tau_{\alpha_M \gamma_{M'}}) \\ - 1 - \tau_{\alpha_M \gamma_{M'}} - Q_{\alpha_M \gamma_{M'}} \quad (\text{PYA}) \quad (25)$$

and

$$c_{\alpha_M \gamma_{M'}} - \phi_{\alpha_M \gamma_{M'}} = \exp[-\beta u_{\alpha_M \gamma_{M'}}^* + Q_{\alpha_M \gamma_{M'}} + \tau_{\alpha_M \gamma_{M'}}] \\ - 1 - \tau_{\alpha_M \gamma_{M'}} - Q_{\alpha_M \gamma_{M'}} \quad (\text{HNC}) \quad (26)$$

where

$$Q = c[\phi|\omega] \quad (27)$$

and

$$\tau = t - Q + \phi. \quad (28)$$

With either of these closures it is clear that for large  $r$ ,  $c$  is asymptotically equal to  $\phi$ . Thus Eq. (25) and Eq. (26) yield renormalized expressions for  $c_s$  [see Eq. (13)].

It has, however, been recently pointed out explicitly by Stell and co-workers<sup>19</sup> that this asymptotic form for  $c$  is not, in general, consistent with the relationship between the second moments of  $h$  and the dielectric constant  $\epsilon$  [see Eq. (31), below]. Consequently, the dielectric constant which follows from the implicit constraint that  $c$  is asymptotically equal to  $\phi$  is incorrect, and can be shown to be given by<sup>15,17</sup>

$$\epsilon = 1 + 3y, \quad (29)$$

where

$$y = \sum_M \frac{4\pi\beta}{9} \rho_M \langle \mu_M^2 \rangle \quad (30)$$

and  $\langle \mu_M^2 \rangle$  is the mean square molecular dipole moment. This result follows from the integral equation closure and the second moment expression for  $\epsilon$ .<sup>14,15</sup> That is,

$$\epsilon = \left( 1 - 3y - 4\pi\beta \sum_{\substack{M, M' \\ \alpha, \gamma}} Z_{\alpha_M} Z_{\gamma_{M'}} \rho_M \rho_{M'} \hat{h}_{\alpha_M \gamma_{M'}}^{(2)} \right)^{-1}, \quad (31)$$

where  $\hat{h}_{\alpha_M \gamma_{M'}}^{(2)}$  is defined by the small  $k$  expansion of the Fourier transform of  $h$ , namely

$$\hat{h}(k) = \hat{h}^{(0)} + k^2 \hat{h}^{(2)} + \dots \quad (32)$$

It is of interest to examine the origin of contributions to  $\epsilon$  from the standpoint of the renormalized integral equation [Eq. (18)]. From Eq. (18), we have

$$h = Q + c[c_s|V] \equiv Q + \Lambda. \quad (33)$$

Thus

$$\hat{h}^{(2)} = \hat{Q}^{(2)} + \hat{\Lambda}^{(2)}. \quad (34)$$

If  $Q$  decays at least as fast as  $r^{-6}$  then from Eq. (6) and Eq. (16) we can write

$$\hat{V}_{\alpha_M \gamma_{M'}} = \rho_M \delta_{MM'} + \hat{V}_{\alpha_M \gamma_{M'}}^{(2)} k^2 + O(k^4), \quad (35)$$

where  $\hat{V}^{(2)}$  is defined analogously to  $\hat{h}^{(2)}$  and where the remainder is not necessarily analytic but contains no terms of order  $k^2$ .

Writing out  $\hat{\Lambda}$  explicitly we have

$$\rho \hat{\Lambda} \rho = \hat{V} [1 - \hat{c}_s \hat{V}]^{-1} \hat{c}_s \hat{V}. \quad (36)$$

Thus the contribution to  $\epsilon$  from  $\rho \hat{\Lambda}^{(2)} \rho$  [see Eqs. (31) and (34)] arises from the term of order  $k^2$  in

$$\sum_{M, M'} \sum_{\alpha, \gamma} Z_{\alpha_M} \{ \hat{V} [1 - \hat{c}_s \hat{V}]^{-1} \hat{c}_s \hat{V} \}_{\alpha_M \gamma_{M'}} Z_{\gamma_{M'}}. \quad (37)$$

However, from Eq. (35), it is clear that for neutral molecules, where

$$\sum_{\alpha} Z_{\alpha_M} = 0 \quad (38)$$

the leading  $k$  dependence in Eq. (37), above, will arise from  $\hat{V}^{(2)}$  on *both* sides of the matrix in brackets in that equation. If  $c_s$ , which is explicitly a shorter ranged function than  $c$ , decays at least as fast as  $r^{-4}$ , the lowest order contribution to Eq. (37) is thus  $O(k^4)$  and  $\Lambda$  does *not* contribute to  $\epsilon$ . Correspondingly,

$$\epsilon = \left( 1 - 3y - 4\pi\beta \sum_{\substack{M, M' \\ \alpha, \gamma}} Z_{\alpha_M} Z_{\gamma_{M'}} \rho_M \rho_{M'} \hat{Q}_{\alpha_M \gamma_{M'}}^{(2)} \right)^{-1}, \quad (39)$$

where  $Q$  is given by Eq. (14).

If we put  $\psi = \phi$  the contribution to  $\epsilon$  from  $Q$  can be evaluated analytically<sup>14,15</sup> to give Eq. (29). If one permits the more general form, which is correct for neutral two site diatomics,<sup>19</sup>

$$\hat{\psi} = A\hat{\phi}, \quad (40)$$

where  $A$  is a  $k$  independent proportionality constant, then a corresponding analysis yields<sup>19</sup>

$$\epsilon = \frac{1 + 3Ay}{1 + 3(A-1)y}. \quad (41)$$

We note that although with  $A=1$  this is the low density ideal gas result for  $\epsilon$  it is *not* that which would be obtained if  $\hat{h}^{(2)}$  were zero, as in an ideal gas, as is clear from Eq. (31); in fact,  $h$  makes a nontrivial contribution to  $\epsilon$ .

Although  $\epsilon$  is not given satisfactorily by a closure which requires that  $\psi = \phi$ , the description of short wavelength phenomena is not established and we proceed in the next two sections to describe results intended to elucidate this behavior.

### III. DIPOLAR DIATOMIC FLUIDS

In this section we describe results obtained for three examples of diatomic molecules with a "finite" dipole, i.e., with two point charges of equal magnitude and opposite sign. The first of these has been described in our first report<sup>21</sup> and the results are presented only briefly here for completeness.

Each model consists of a pair of Lennard-Jones spheres, each centered at an atomic nucleus, with the two point charges also located at the nuclear sites. The models are then characterized by the Lennard-Jones parameters of each site, the magnitude of the charge, and the bond length. These are summarized in Table I. We use the usual combining rules for Lennard-Jones interaction parameters, namely,

$$\epsilon_{\alpha M \gamma M'} = (\epsilon_{\alpha M \alpha M'} \epsilon_{\gamma M' \gamma M'})^{1/2} \quad (42a)$$

and

$$\sigma_{\alpha M \gamma M'} = \frac{\sigma_{\alpha M \alpha M'} + \sigma_{\gamma M' \gamma M'}}{2}. \quad (42b)$$

The intermolecular site-site potential is then given by ( $r$  is the site-site separation):

$$u_{\alpha M \gamma M'}(r) = 4\epsilon_{\alpha M \gamma M'} \left[ \left( \frac{\sigma_{\alpha M \gamma M'}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha M \gamma M'}}{r} \right)^6 \right] + \frac{Z_{\alpha M} Z_{\gamma M'}}{r}. \quad (43)$$

The integral equation is solved in the same manner as for atomic fluids, using an iterative scheme and performing the convolutions via Fourier transforms.<sup>3,28</sup> Typically, the solution involves three steps: a solution for the corresponding atomic fluid ( $s=0$ ), usually at a somewhat lower density than that finally desired; the introduction of the intramolecular correlations; and finally the introduction of site charges. The second step is in each case the most challenging in the context of obtaining a converged iterative solution.

Computer simulation data has been evaluated for

TABLE I. Models for dipolar diatomic fluids.

Model	1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>b</sup>
$\sigma_{++}$ (Å)	3.341	2.735	0.4
$\sigma_{--}$ (Å)	3.341	3.353	3.353
$\epsilon_{++}/k_B$ (K)	44.0	20.0	20.0
$\epsilon_{--}/k_B$ (K)	44.0	259.0	259.0
$L_{+-}$ (Å)	1.1	1.257	1.3
$Z_+(e)^c$	0.2	0.2	0.2
$T$ (K) <sup>d</sup>	72.0	210.0	210.0
$\rho$ (Å <sup>-3</sup> ) <sup>d</sup>	0.01867	0.018	0.018

<sup>a</sup>N<sub>2</sub>-like model.

<sup>b</sup>HCl-like model; H corresponds to the positively charged site, and Cl to the negatively charged.

<sup>c</sup>Magnitude of site charge, if not zero, in units of the magnitude of the electronic charge.

<sup>d</sup>Thermodynamic conditions used here for fluid.

comparison, and is obtained from a sample of 216 molecules using periodic boundary conditions and a spherical cutoff for the potential at an intermolecular center of mass distance of 10 Å. We have already demonstrated<sup>21</sup> that the site-site correlation functions are insensitive to the boundary conditions at short range, so there is no reason to expect that this feature of the calculations should influence our comparisons.

#### A. Dipolar N<sub>2</sub>

The first model to be considered, Model 1 in Table I, is, in the absence of site charges, equivalent to one that has been used for molecular nitrogen,<sup>20,29</sup> and has been considered in our first report.<sup>21</sup> It should be noted that in the dipolar model the charge interaction is quite large. For the present temperature (72 K) the difference between  $u_{++}(\sigma_{++})$  and  $u_{+-}(\sigma_{+-})$  is approximately  $56 k_B T$ .

Results of a calculation carried out at  $T=72$  K and a molecular number density of  $\rho=0.01867$  Å<sup>-3</sup> are presented in Figs. 1 and 2. In Fig. 1, we show the like and unlike charge site-site intermolecular correlation functions obtained from the integral equation, the dashed line shows the result for the  $Z=0$ . Figure 2 shows a comparison with results obtained from molecular dynamics computer simulation for the same model. Results from both the HNC-like and PYA-like closures are shown, and, as usual,  $g=h+1$ .

The interpretation of the observed structure has been presented earlier.<sup>21</sup> Here, we only comment on the general features. First, we note that the simulation and integral equation results are in good agreement. The quality of the comparison made here is comparable to that between theory and simulation for the *uncharged* site model.<sup>20,21</sup>

Of special note is the apparent symmetry exhibited by the displacement of the charged site correlation functions with respect to the uncharged site result. Denoting the latter correlation function as  $g^*$ , we find that to better than 1% accuracy,

$$g_{++}(r) + g_{--}(r) = 2g^*(r). \quad (44)$$

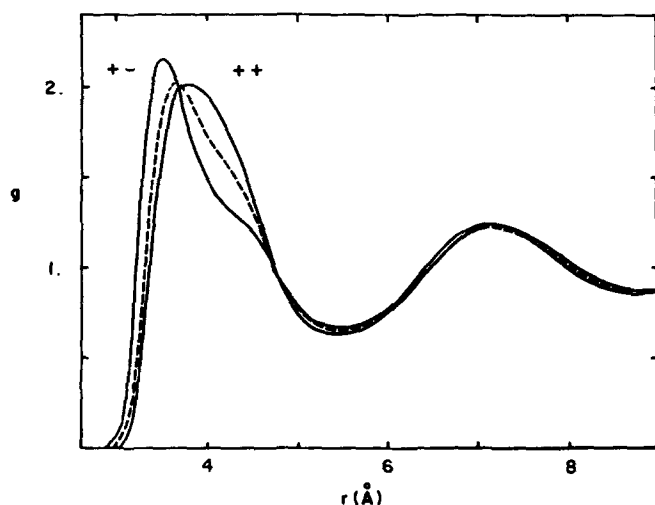


FIG. 1. Site-site pair correlation functions for  $N_2$ -like model (Table I, Model 1) using PYA-like closure [Eq. (25)]; the dashed line is the result for zero site charge.

It is, in fact, not difficult to see the origin of this result. Since we are interested in the properties of the increments to  $g^*$ , we desire to first reorganize the integral equation so that these terms are explicit. Starting with Eq. (9) we have<sup>27</sup>

$$\begin{aligned} h &= c[c|\omega] = c[c^*|\omega] + c[c - c^*|\omega + \rho c[c^*|\omega]\rho] \\ &= h^* + c[c - c^*|\omega + \rho h^*\rho], \end{aligned} \quad (45)$$

or introducing

$$\delta h = h - h^* = g - g^* = \delta g, \quad (46)$$

$$\delta g = c[\delta c|\omega + \rho h^*\rho]. \quad (47)$$

We can, further, renormalize with respect to the long range part of  $c$  (we assume  $c^*$  is short ranged). Starting with Eq. (47), we have (see Ref. 27)

$$\begin{aligned} \delta g &= c[\delta c - \psi + \psi|\omega + \rho h^*\rho] \\ &= c[\psi|\omega + \rho h^*\rho] \\ &\quad + c[\delta c - \psi|\omega + \rho h^*\rho + \rho c[\psi|\omega + \rho h^*\rho]\rho]. \end{aligned} \quad (48)$$

Denoting

$$R = c[\psi|\omega + \rho h^*\rho], \quad (49)$$

we have

$$\delta g = R + c[\delta c - \psi|\omega + \rho h^*\rho + R], \quad (50)$$

which is still completely equivalent to Eq. (9).

The symmetry behavior of  $\delta g$  depends on the closure used. Here we are concerned with diatomics which in the absence of site charges are homonuclear, i.e., the four elements of the  $2 \times 2$  matrix  $h^*$  are all equal as are those of  $c^*$ . For a neutral diatomic with two charged sites,<sup>19</sup>  $\psi_{\alpha M' M'} \propto Z_{\alpha M} Z_{\beta M'}$  so that  $\psi$  has the symmetry of the matrix  $Z$  defined by

$$\psi \propto \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \equiv Z. \quad (51)$$

It follows directly that for the present symmetric di-

atomic case

$$R \propto Z \quad (52)$$

and hence, via Eq. (50), that if  $\delta c \propto Z$  so is  $\delta g$  (and vice-versa) which is the desired result. A corresponding behavior follows for  $\delta t = \delta h - \delta c$ .

For the closures to be considered here [Eqs. (25) and (26)], we have (see Sec. II)  $\psi = \phi$  and one can obtain directly

$$\begin{aligned} (\delta c - \psi)_{\alpha M' M'} &= \{h_{\alpha M' M'}^* Q_{\alpha M' M'} + (\exp[-\beta u_{\alpha M' M'}^*] - 1) \delta \tau_{\alpha M' M'}\} \\ &\quad + g_{\alpha M' M'}^* (\exp[Q_{\alpha M' M'}] - 1 - Q_{\alpha M' M'}) \\ &\quad + \exp[-\beta u_{\alpha M' M'}^*] (\exp[Q_{\alpha M' M'}] - 1) \delta \tau_{\alpha M' M'}, \end{aligned} \quad \text{(PYA)} \quad (53)$$

where

$$\delta \tau = \tau - t^* = t - t^* - Q + \phi$$

and

$$\begin{aligned} (\delta c - \psi)_{\alpha M' M'} &= [h_{\alpha M' M'}^* (\delta \tau_{\alpha M' M'} + Q_{\alpha M' M'})] \\ &\quad + g_{\alpha M' M'}^* (\exp[\delta \tau_{\alpha M' M'} + Q_{\alpha M' M'}] - 1 \\ &\quad - \delta \tau_{\alpha M' M'} - Q_{\alpha M' M'}) . \end{aligned} \quad \text{(HNC)} \quad (54)$$

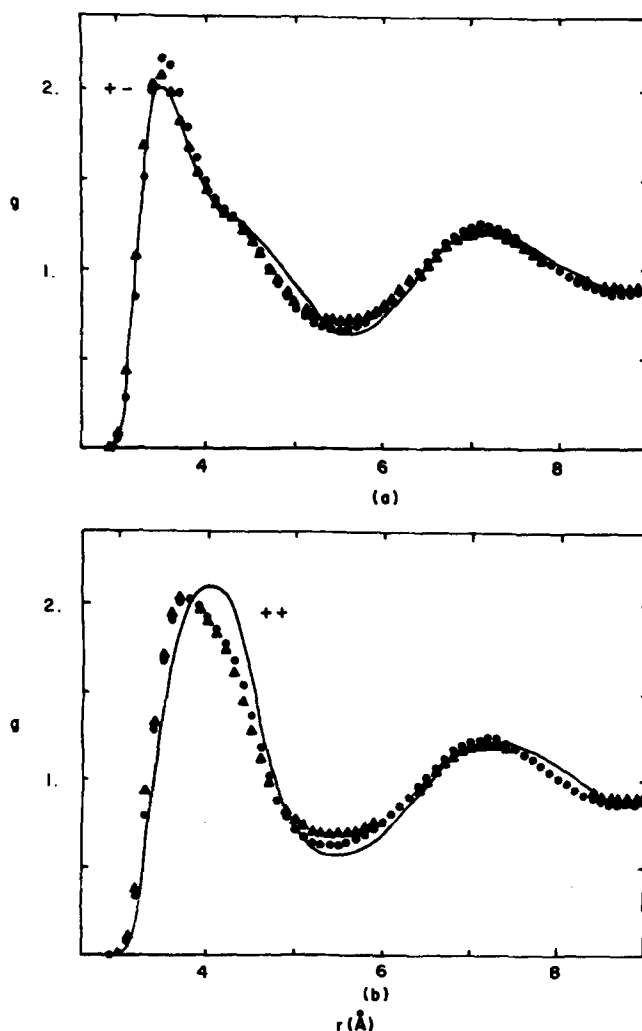


FIG. 2. Comparison of site-site pair correlation functions for dipolar  $N_2$ -like model from simulation (solid line), PYA-like closure (circles), and HNC-like closure (triangles).

In the equations above,  $h^*$  and  $g^*$  are the solutions for the uncharged site case using the corresponding closure; i.e., PYA [Eq. (25)] for  $h^*$  in Eq. (53) and HNC [Eq. (26)] for  $h^*$  in Eq. (54), where in this case  $\psi = Q = 0$ .

It is evident that, in general, one does *not* expect these closures to exhibit the symmetry observed [Eq. (44)]. For example, in both Eq. (53) and Eq. (54) the term  $g^* e^Q$  violates the symmetry requirements, as does  $g^* e^{\delta\tau}$  in the latter equation. However, at high density  $Q$  decays to a very small amplitude very rapidly, and in either case both  $\exp(-\beta u^*)$  and  $g^*$  vanish for small intersite distances. Hence at liquid densities the corresponding products ( $g^* Q$ ) are very small everywhere. If we drop such terms in the closure, the right-hand side of Eq. (53) reduces to the term in brackets which it is clear admits a solution having the symmetry property of Eq. (44). For Eq. (54), the HNC-like closure, the relationship obtained after simplification retains, in the term proportional to  $g^*$ , a contribution of the form

$$g^*(e^{\delta\tau} - 1 - \delta\tau), \quad (55)$$

which will not exhibit the symmetry property, while the other term, in brackets, if taken alone, would lead to a symmetric splitting. It is an empirical result that  $\delta\tau$  is relatively small and hence that the leading term in Eq. (55),  $g^* \delta\tau^2/2$ , leads to very small deviations from the symmetry property in the present case.

We note that it is clear from Eq. (47) that in the absence of any special symmetry in  $h^*$ , one does not anticipate any special symmetry in  $g$ .

## B. Heteronuclear HCl-like models

We next turn to two heteronuclear models, which have substantial asymmetry. The first of these (Model 2, Table I) is based on a model proposed for HCl by Powles,<sup>30</sup> and is characterized as described in the table. The second (Model 3) differs from this primarily in a substantial reduction in the Lennard-Jones  $\sigma$  associated with the H-like site, so that in the absence of site charge this site is essentially completely enveloped by the larger Cl-like site. The latter model was chosen for study since the contributions to liquid structure from short range repulsive interactions involving H-like sites should be very small and hence one expects that in this case the introduction of site charges should have a relatively large influence on site-site correlation functions. It thus provides a quite challenging test of the theoretical approach.

We emphasize that we do not intend these as models for HCl, although it appears that the site-site correlation functions for the latter model (see below) are quite similar to those obtained experimentally for HCl quite recently.<sup>31</sup> It is, however, very convenient to refer to the sites by the labels H (for +) and Cl (for -) to easily distinguish between them, and we do that here.

In each case the results have been obtained for zero charge ( $Z=0$ ) and with a site charge of magnitude  $0.2e$ , where  $e$  is the magnitude of the electronic charge. With this site charge, the molecular dipole moment for each model is about 10% larger than that of HCl. All

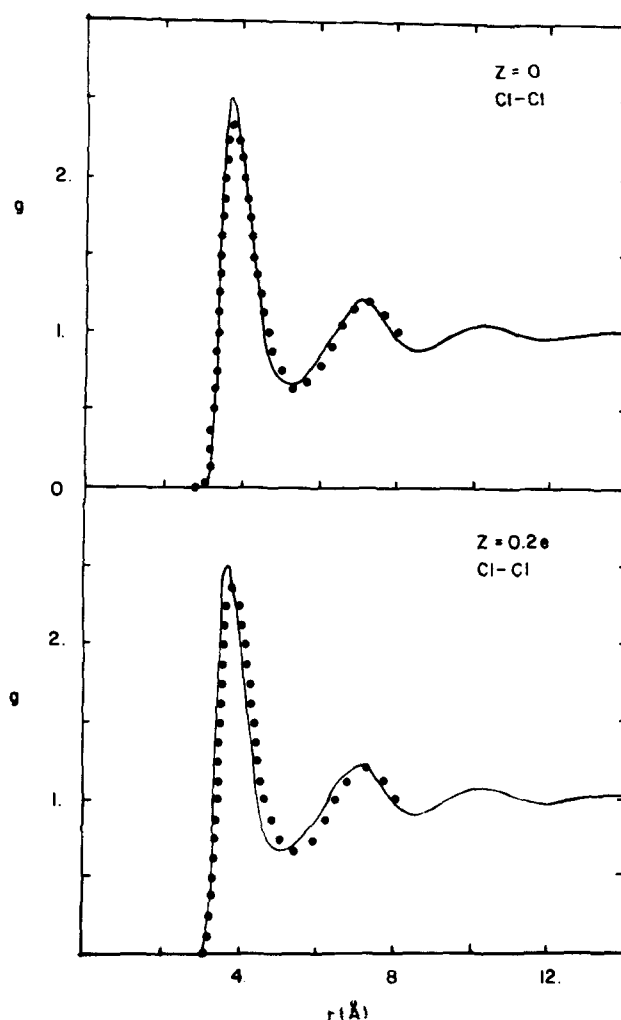


FIG. 3. Cl-Cl pair correlation functions for Model 2 (Table I). Solid lines show results from PYA-like closure [Eq. (25)]; circles from computer simulation.

studies correspond to a temperature of 210 K and a molecular number density of  $0.018 \text{ \AA}^{-3}$ .

The results for the two models are presented in Figs. 3-8. In each, the result for  $Z=0$  is given in the upper half and that for  $Z=\pm 0.2e$  in the lower half. The sites involved in the correlation function are indicated in the upper right of each figure.

Considering first Model 2, Figs. 3-5 present the three distinct site-site pair correlation functions. The solid line is obtained using the PYA-like closure [Eq. (25)] and the circles are data obtained from molecular dynamics simulation of the same model. In Fig. 5, we show also the result obtained with the HNC closure [Eq. (26)], for comparison. The difference between the PYA and HNC closure for the other pairs for Model 2 is in each case no larger than the differences seen here. Of some interest, is the small, but unphysical, negative region in  $g(r)$  for H-H pairs, a result which cannot be obtained using the HNC closure, due to the exponential form [see Eq. (26)].

The interpretation of the observed structure has been presented elsewhere<sup>30,31</sup> and we do not repeat that here.

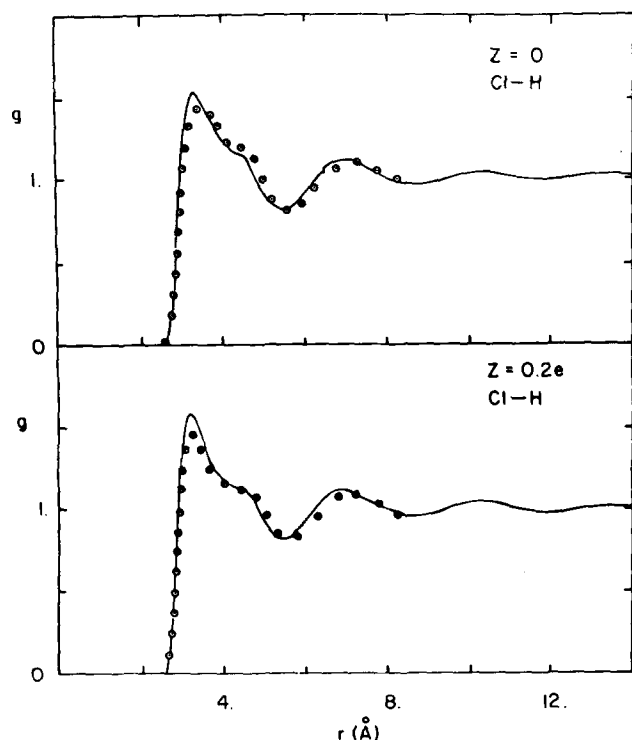


FIG. 4. Cl-H pair correlation functions for Model 2 (Table I); notation as in Fig. 3.

As is clear from the figures, the influence of site charges is not very large; the molecular packing in this asymmetric diatomic is apparently dominant. In contrast, for the homonuclear case, shown in Figs. 1 and

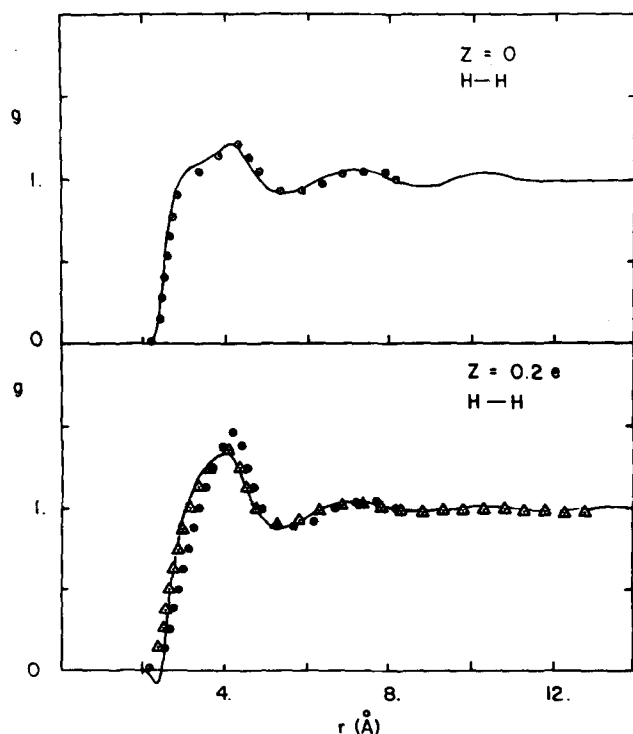


FIG. 5. H-H pair correlation functions for Model 2 (Table I); notation as in Fig. 3, with HNC-like closure [Eq. (26)] results shown as triangles.

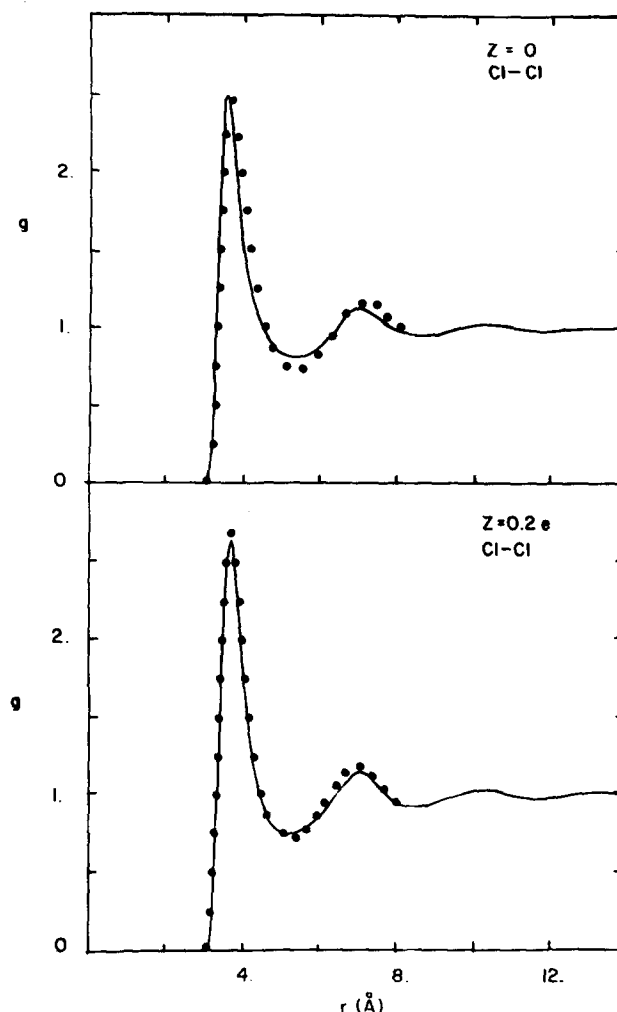


FIG. 6. Cl-Cl pair correlation functions for Model 3 (Table I). Solid lines show results from HNC-like closure [Eq. (26)]; circles from computer simulation.

2, no difference in packing structure is associated with a permutation of sites and thus the influence of charging on the nearest-neighbor peaks is substantially larger in this case.

As manifest in the individual correlation functions, the Cl-Cl correlations are essentially unaffected by the charges, while both those which involve the H site are somewhat shifted. For the H-Cl pair the small shift is such as to sharpen the smallest  $r$  peak and reduce the shoulder on the right side. For H-H, the shift is in the opposite sense, leading to reduction on the small  $r$  side and sharpening to the right.

We note that the overall comparison of simulation with the integral equation is very good. All of the features observed in the simulation are correctly represented both with respect to the direction of shifts upon charging and their magnitude.

We consider next Model 3, in which the H Lennard-Jones sphere is essentially completely embedded inside that of Cl. The results are presented in Figs. 6-8. In each case the integral equation results were obtained using the HNC closure [Eq. (26)]. In the presence of



site charges, the PYA closure leads to unacceptably negative values for the H-H correlation function at small  $r$ ; values as negative as -20 are found. Therefore, this closure was rejected.

As anticipated in the choice of this model, the correlation functions involving H sites are substantially changed by the introduction of site charges, as the orientational structure of the fluid can be perturbed with negligible effect on packing requirements. It is also clear that the integral equation is quantitatively less successful here than in the model just considered.

Considering the individual figures, the Cl-Cl correlation function (Fig. 6) is not very sensitive to the introduction of site charge. There is a slight enhancement of the oscillations in the correlation function due to the attractive molecular interactions, but, in accord with the simulation data, this is a small effect.

The H-Cl pairs show an enhanced probability, upon charging, for H-Cl contact, indicated by the shoulder between 2 and 3 Å in the simulation data and the resolved peak at too small a distance in the integral equation result. The second anticipated peak from nearest neighbors occurs at about 4.6 Å, and corresponds to the longer H-Cl distance in a linear HCl-HCl dimer. The increased amplitude of this peak in the charged case is reproduced by the integral equation, as is its position.

For the H-H pairs the trend is toward atomic pairs which are separated by a single Cl atom. As shown by the comparison with simulation data, this trend is, however, only reproduced in a qualitative way by the integral equation. It is difficult to assess to what degree

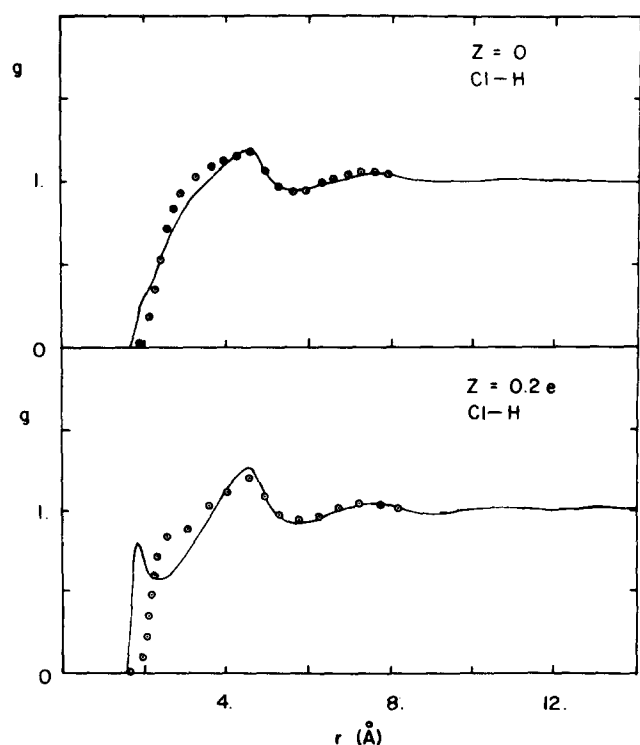


FIG. 7. Cl-H pair correlation functions for Model 3 (Table I); notation as in Fig. 6.

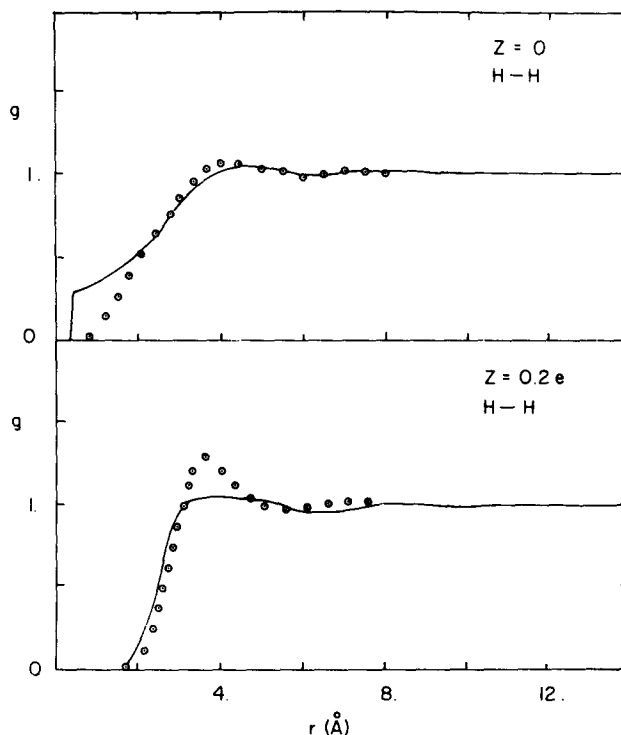


FIG. 8. H-H pair correlation functions for Model 3 (Table I); notation as in Fig. 6.

the error in the case with site charge is a reflection of the substantial error in the *zero* charge prediction (see Fig. 8). This point will be discussed further in Sec. V.

#### IV. QUADRUPOLEAR DIATOMICS-LIQUID BROMINE

The structure of liquid bromine has been the subject of a number of studies, both experimental<sup>24,25</sup> and theoretical.<sup>32-36</sup> The theoretical studies have included computer simulation of two-site models using purely Lennard-Jones site-site potentials<sup>35</sup> and of a corresponding model with the addition of a point quadrupole located at the molecular center of mass,<sup>36</sup> as well as nonsimulation studies.<sup>32-34</sup>

The uniform conclusion of these investigations is that the intermolecular correlation functions observed experimentally for Br<sub>2</sub> *cannot* be represented by a simple two-site model; the liquid structure of Br<sub>2</sub> is significantly influenced by the quadrupolar charge distribution in the molecule, in contrast to the result for the smaller diatomics N<sub>2</sub> and O<sub>2</sub>.<sup>33-35</sup> The structural feature which is most indicative of this difference is the presence of a shoulder on the smallest wave vector peak in the experimental scattering structure factor  $S(k)$ , and the corresponding development of a distinct second maximum in the Br-Br pair correlation function, at a distance of roughly the sum of the intermolecular bond length and atomic diameter.<sup>25</sup> The latter can be interpreted as resulting from an enhanced preference for T-shaped molecular pair orientations in the presence of quadrupole interactions.<sup>36</sup> Correspondingly, molecular configurations involving close approach of molecular centers are strongly repulsive.

TABLE II. Models for liquid bromine.<sup>a</sup>

Model	1	2	3	4
Core type <sup>b</sup>	LJ	LJ	$r^{-9}$	LJ
$\sigma_{\text{Br-Br}}$ (Å)	3.63	3.63	5.60	3.63
$\epsilon_{\text{Br-Br}}/k_B$ (K)	245.7	130	14.5	130
$\sigma_{\text{X-X}}$ (Å)	1.0	1.0	1.0	1.0
$\epsilon_{\text{X-X}}/k_B$ (K)	0.0724	0.0724	0.2896	0.0724
$Z_{\text{Br}}(e)$	-0.48	-0.3	-0.4	0.0
$Z_{\text{X}}(e)$	0.96	0.6	0.8	0.0

<sup>a</sup>X signifies the third site located at the molecular center of mass.

<sup>b</sup>Non-Coulombic part of the site-site potential: LJ=Lennard-Jones [see Eq. (43)],  $r^{-9}$ =inverse ninth power repulsion [see Eq. (56)]. All interaction parameters determined by combining rules in Eq. (42).

Hsu *et al.*<sup>33</sup> have shown that a similar shoulder in  $S(k)$  is mimicked if one introduces center-center repulsion via the addition to a nonpolar two-site model of a large repulsive core centered at the molecular center of mass, but the corresponding Br-Br correlation function<sup>33</sup> does not look very similar to that obtained from the experiment<sup>25</sup> or simulation.<sup>36</sup>

Here we consider several models for Br<sub>2</sub> in which the nonuniform charge distribution is represented by site point charges, rather than by a point quadrupole moment at the molecular center. For the most populated configurations in liquid Br<sub>2</sub>, one does not expect substantial differences between the two models,<sup>36</sup> but the present model is representative of a much more flexible class of models, and we consider Br<sub>2</sub> in part as an example of the capabilities of the theory.

The intermolecular potential appropriate for the description of liquid Br<sub>2</sub> is not established.<sup>36</sup> Further, the unresolved discrepancies among experimental scattering measurements<sup>25</sup> make the refinement of the potential via comparison presently infeasible. Therefore our present goal is primarily to demonstrate that with reasonable choices for the potential parameters, the integral equation reproduces the qualitative features of the liquid structure rather well.

The models considered here are summarized in Table II. In each case, the model involves three interaction sites. Two are located at the Br nuclei and are equivalent; the third (denoted X) is located at the center of the internuclear axis. Each site is associated with a "core" potential of either a Lennard-Jones (LJ) type or inverse ninth power, and a site charge. A charge of  $-Z$  is located at each Br site and a charge of  $2Z$  is located at the X site. The core potential associated with the X site is included to avoid a Coulomb divergence associated with Br-X interactions. The X parameters are chosen so that the core of this site is essentially enveloped by either Br site. The Lennard-Jones interaction parameters are evaluated by the usual combining rules, as described earlier [Eq. (42)]. For the  $r^{-9}$  core potential (Model 3) it is convenient to represent the potential in terms of similar strength and size parameters; we have used the same combining rule and a po-

tential of the form

$$u_{\alpha_M \gamma_{M'}}^* = \epsilon_{\alpha_M \gamma_{M'}} (\sigma_{\alpha_M \gamma_{M'}} / r)^9. \quad (56)$$

The bond length used, 2.284 Å, is consistent with available experimental data.<sup>25,36</sup> The choices of values for  $\epsilon$  and  $\sigma$  is much more complex. Values are available from analyses in which a two site *purely* Lennard-Jones potential was assumed in fitting to thermodynamic<sup>35</sup> and solid state data,<sup>37</sup> but the usefulness of such parameters as elements in a more complex and realistic potential is questionable.

The first model in Table II includes Lennard-Jones parameter corresponding to those considered in earlier studies,<sup>35,36</sup> and chosen to fit a two-site Lennard-Jones model to experimental thermodynamics.<sup>35</sup> The site charges in Model 1 produce a quadrupole moment of  $6.0 \times 10^{-26}$  esu cm<sup>2</sup>, which corresponds to reasonable estimates of the value for Br<sub>2</sub>.<sup>34</sup>

The quadrupole moment leads to a net attractive contribution to thermodynamic parameters,<sup>36</sup> as compared to the same model in the absence of electrostatic interactions, and hence we consider in Model 2 a reduced value for the Lennard-Jones strength parameter. Examination of several values of site charge has shown, however, that a smaller site charge is needed in order to obtain qualitative agreement with experimental structure, as the smaller amplitude of the repulsive core permits closer approach of the interaction sites. Model 2 incorporates such a reduced charge.

The third model employs a functionally less repulsive inverse ninth power core potential, and site charges of intermediate size. The purpose here is to consider the influence of softening of the core, in light of experimental data.

The model labeled 4 corresponds to Model 2, except for the absence of charges, and is considered at the end of this section in the context of evaluating the self-consistency of the integral equation solutions.

We emphasize that in choosing the models in Table II, we did not attempt to quantitatively reproduce experimental scattering data, as the uncertainties in these results as well as in the present theoretical prescription

are too large to permit any significance to be attached to such a procedure.

The results obtained from the integral equation for the models are presented in Figs. 9–11. In each case the result is obtained using the HNC-like closure [Eq. (26)], at a temperature of 293.16 K and density of 3.12 g/cc, corresponding to the conditions of neutron scattering measurements.<sup>25</sup> The total structure factor is given in the upper half of each figure and the intermolecular Br–Br site–site correlation function is given in the lower half. The results in the figures for  $S(k)$  obtained from x-ray scattering were read from the graph in that reference, and hence were not considered reliable enough to transform; the lower half of the figures includes only the neutron data.

It is evident from the comparisons in the figures that in each case the qualitative features of both  $S(k)$  and  $g(r)$  are correctly produced by the integral equation. In particular, the positions of the features in  $S(k)$ , including the shoulder mentioned above, are correctly reproduced and the distinct peak at  $r \sim 6$  Å (corresponding to T-shape orientation) is present.

It is correspondingly clear that a wide range of potential parameters can produce these basic features. However, the agreement between the theory and the

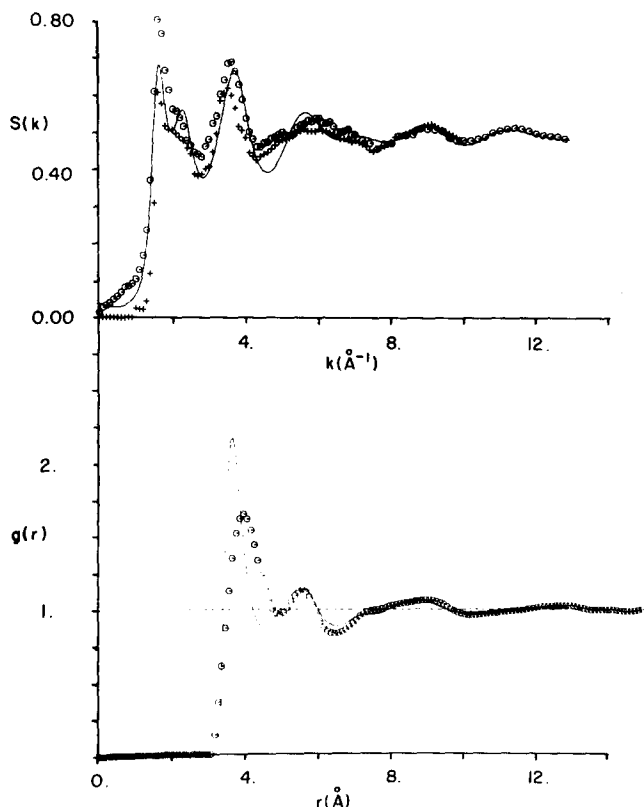


FIG. 9. Total scattering structure factor  $S(k)$  and intermolecular atom–atom pair correlation function  $g(r)$  for liquid  $\text{Br}_2$ . Theory for Model 1 (Table II). Neutron data (Ref. 25) indicated by circles, x-ray data (Ref. 24) by crosses, and integral equation [HNC-like closure, Eq. (26)] by solid line. Where the line is not visible it lies within the area covered by the experimental points.

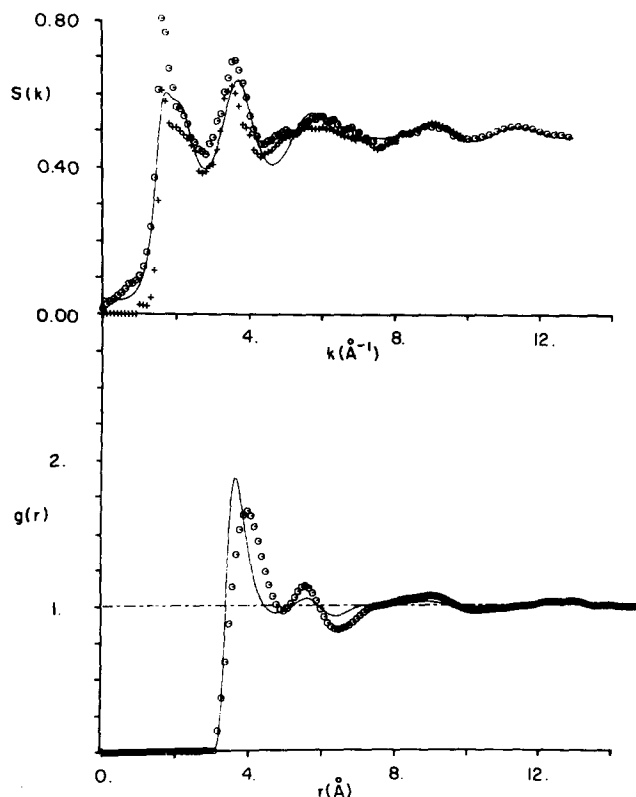


FIG. 10. Structure factor and pair correlation function for liquid  $\text{Br}_2$ ; Model 2 (Table II). Notation as in Fig. 9.

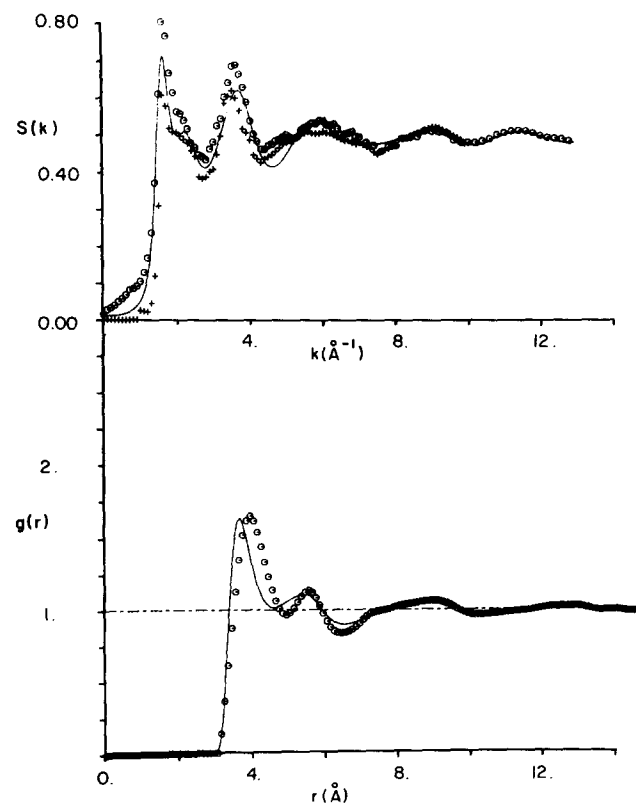


FIG. 11. Structure factor and pair correlation function for liquid  $\text{Br}_2$ ; Model 3 (Table II). Notation as in Fig. 9.

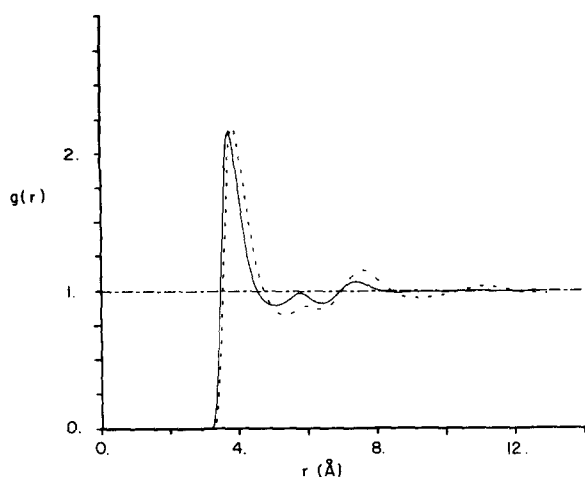


FIG. 12. Self-consistency test for integral equation treatment of  $\text{Br}_2$  models. Solid line shows the result for Model 4 (Table II) and dashed line shows the result for a two center model which is equivalent except for omission of the X site in the three-center model.

neutron data is substantially better for Model 3 (Fig. 11) than for the others considered, and is also significantly better than that we have been able to obtain with any of a variety of potentials based on a Lennard-Jones core. This case is that in which we have employed an empirical inverse ninth power core repulsion. This result strongly suggests that the experimental data are only consistent with a potential which is functionally much softer than those which have been considered in previous studies.

Finally, it is well known<sup>18,33</sup> that there exist internal inconsistencies within the RISM theory in that the inclusion of so-called auxiliary sites can influence the predicted site-site correlation functions between physical sites. Here, an auxiliary site is one which, in an exact treatment, can have no observable effect on the liquid structure because, e.g., the range of the potential associated with the auxiliary site falls wholly within the hard core of a physical site, and hence is never accessible. In the present case the X site at the center of mass is never, strictly speaking, an auxiliary site, since we use continuous potentials, but with the parameters used for  $\sigma_{\text{XX}}$  and  $\epsilon_{\text{XX}}$  one must expect that in the absence of site charges the Br-Br correlation functions will be influenced negligibly by its presence. Model 4 in Table II can be used to test the degree to which this is valid for the present calculation.

In Fig. 12 we show the Br-Br correlation functions obtained from Model 4 and from the same model with the X site omitted completely, using the HNC-like closure. The difference between these curves is one estimate of the error inherent in the present theory, and it is clear that it is comparable to the difference between the theory and experiment present, for example, in Fig. 11. It would be highly desirable to have a theoretical formulation which is self-consistent in this sense, but no such formulation for a general ISM is presently available.

## V. CONCLUSION

We have presented a discussion of an extension of the RISM integral equation to a form appropriate to polar liquids, and considered a series of applications to fluids composed of strongly polar diatomic molecules. The equation, which is based on closure relations appropriate to ionic atomic fluids and an analogous renormalization of long range interactions, has been shown to provide a qualitatively correct description of the liquid structure in the models considered.

In cases where the liquid structure is dominated by the short ranged potentials present in the absence of site charges, the integral equation leads to structural predictions which are comparable in accuracy to those obtained for the nonpolar case. However, in all cases considered the qualitative features of the polar liquid structure are correctly described by the theory. In particular, the variation with molecular shape of the ability of polar forces to compete with packing requirements is well represented by the integral equation.

The quality of the results obtained from the theory are particularly satisfying in light of the very large values taken on by individual site-site pair potentials, and the corresponding requisite cancellation which must occur in the overall result. For example, for Model 1 (Table II) for  $\text{Br}_2$  one finds that

$$u_{\text{Br-Br}}(\sigma_{\text{BrBr}}) \sim 36 k_B T,$$

and that  $u_{\text{Br-X}}(\sigma_{\text{BrX}}) \sim -114 k_B T$ , at 293 K, while for the HCl-like case Model 3 (Table I) we find

$$u_{\text{Cl-H}}(\sigma_{\text{Cl-H}}) \sim -17 k_B T,$$

$$u_{\text{HH}}(\sigma_{\text{HH}}) \sim 80 k_B T,$$

and,

$$u_{\text{ClCl}}(\sigma_{\text{ClCl}}) \sim 9 k_B T,$$

at 210 K. The theory thus appears well balanced in its incorporation of both intermolecular and intramolecular forces.

While the results presented are not completely conclusive, it appears that the present theory is significantly less accurate in the most extreme case in which orientational preferences result entirely from site charge interactions. Even in this case, the theory is qualitatively correct, but the quantitative agreement is not as good. The interpretation is clouded by the fact that for the same model in the absence of site charges the integral equation used is less than satisfactory. This observation suggests that a valuable theoretical improvement may be obtained if one reorganizes the theory so as to incorporate explicitly a zero site charge reference state of higher reliability. This approach is currently under development in our laboratory.

## ACKNOWLEDGMENTS

Support of this work by grants from the Robert A. Welch Foundation and the Research Corporation is gratefully acknowledged. One of us (P.J.R.) is grateful to the University Research Institute of the University of

Texas at Austin for partial support during the period in which this work was carried out.

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