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Corrections to the HNC equation for associating electrolytes

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The accuracy of the HNC approximation and modifications based on a simple approximation for the sum of bridge graphs has been studied for a charged soft sphere model for dilute aqueous 2-2 electrolytes. The accuracy is judged based on extensive Monte Carlo (MC) simulation for three representative concentrations: 0.005, 0.0625, and 0.2 M. The MC simulations find monotonically increasing like-charge correlation functions in agreement with the modified HNC results but in contrast with the HNC prediction of a local maximum at low concentration. Nevertheless, HNC provides the best overall quantitative match with MC except at very low concentration; at 5 mM the modifications are a significant improvement. For unlike charge correlations, there is good agreement among all methods; at the ionic contact peak, however, HNC underestimates the peak height and the modifications provide improved accuracy.

I. INTRODUCTION

The spatial distribution of ions in electrolyte solutions is of broad importance in the interpretation of such phenomena as interionic chemical reaction rates,¹⁻³ electrical conductivity,⁴ and polyelectrolyte solution structure.⁵ In particular it is of interest to understand the extent to which ions associate into pairs and larger clusters. Studies of model systems^{2,3,9,11} indicate that although ionic association is a relatively minor feature of aqueous 1-1 simple electrolyte solutions, it can be quite important for less polar solvents and/or more highly charged ions.

One route to the study of such association is via theoretical examination of the ionic distribution functions for simplified models. The simplest ionic distribution functions which can be considered in order to characterize the equilibrium structure are the radial pair distribution functions between species. These can be obtained for model systems by various approximate integral equation methods⁶ or by computer simulations.⁷ Foremost among integral equation theories for ionic systems is the hypernetted chain (HNC) approximation,^{8,9} which has been shown to be in generally excellent agreement with simulation results.⁹⁻¹¹ However, exceptions occur in certain cases for the strongly associating systems.¹⁰⁻¹²

Significant discrepancies between HNC and Monte Carlo (MC) simulation results have been indicated^{10,11} for the relative distribution of *like* charged ions for studied continuum solvent models of 2-2 aqueous atomic electrolytes, although for counterion distributions the results seem quite good. At concentrations where packing forces are unimportant, HNC nearly always predicts a monotonically increasing like-charged ion radial pair correlation function $g_{++}(r)$ where r is the separation of the ions. The exception is a dilute regime (stoichiometric molarities c_{st} between about 10^{-1} and 10^{-4}) of 2-2 electrolytes in which a local maximum occurs, and it is this nonmonotonicity which is in doubt.^{11,13}

For the restricted primitive model (hard spheres of equal radii and charge magnitudes) this maximum occurs at $2R$ where R is the hard sphere diameter. For a corresponding soft sphere model¹¹ the maximum also occurs at about $2R$ if R is defined to be the position of the minimum in the unlike charged pair potential. This short range enhancement of $g_{++}(r)$ at low concentrations had been attributed to the existence of triple ion clusters $(+ - +)$.¹⁴ A corresponding maximum was also found in an HNC study of model colloidal particles with high surface charge density in 1-1 electrolyte solution.¹² Here, this feature was interpreted as an indication of ionic association consisting of a layer of small counterions between two much larger colloid particles. In contrast, DLVO and more recent colloid theories^{15,16} predict a colloid-colloid interaction which is always repulsive in the absence of van der Waals forces.

The limited simulation studies available are inconclusive. A recent MC study of the 2-2 restricted primitive model¹⁰ presented some evidence for the existence of a local maximum at $c_{st} = 0.0625$ M and at slightly larger distance, although no such evidence appears in other MC studies¹¹ at lower concentration.

These considerations have spurred additional theoretical studies focusing on the HNC approximation.^{13,17} These suggest that the maximum in $g_{++}(r)$ is, in fact, an artifact of the HNC approximation. Teubner¹³ has employed the HNC approximation for a simplified model problem which can be compared with an exact solution via the classical theory of Gouy and Chapman.¹⁵ For a model of colloid particles in a monovalent salt solution, he finds that for small surface potentials there is agreement. However, for colloid particles with high surface charge density HNC predicts a maximum in the colloid-colloid $g_{++}(r)$ which is absent in the exact, classical theory. The trend in this colloid study parallels that found with HNC for both colloidal¹² and simple electrolytes¹¹ in that the peak appears only in the more highly charged systems.

In light of the results outlined above, and the interest in associating electrolyte solutions, in the present

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paper we examine the accuracy of the HNC approximation in more detail and evaluate the accuracy of particular approximate corrections to the HNC approach. It is well known that HNC neglects a class of terms⁸ (bridge graphs) in the cluster expansions for the pair correlation functions. A modification of HNC (termed BHNC) which includes an approximation for these terms has been suggested¹¹ and briefly considered for one soft sphere model. For all c_{st} below about 0.2 M BHNC yields a monotonically increasing $g_{++}(r)$. A rationale for this result in terms of specific ionic configurations and corresponding graphical contributions has been proposed. The origin of the local maximum in the like charge correlation functions has also been discussed more recently by other authors.¹⁷

However, the value of BHNC and related modifications has not been subjected to a detailed study, including comparison with accurate simulation results. In this paper we present such a study. Section II describes the model systems, integral equations, and simulation methods. The models correspond to dilute aqueous 2–2 electrolyte solutions at room temperature. We adopt the restricted primitive model (RPM) with the previously studied¹⁰ hard sphere diameter of 4.2 Å and a corresponding model with a soft repulsive core.

In part A of Sec. II, we introduce a modification of HNC which, like BHNC, requires the evaluation of an approximation for the bridge graph terms neglected by HNC. The evaluation of this approximation is described in part B. In part C, we present the simulation methods employed. They consist of the usual Metropolis Monte Carlo (MC) method and a biased MC procedure which achieves better sampling in the region of configuration space where like ions are near contact. The results are reported and compared in Sec. III. The conclusions of this study are presented in Sec. IV.

II. THEORETICAL METHODS

We investigate two model systems, a previously studied RPM with a hard sphere diameter of 4.2 Å and an analogous model¹¹ with a soft repulsive core. The effective pair potential for the soft sphere model has the form¹⁸

$$u_{ab}(r_{12}) = \frac{Bk_B \left(\frac{\sigma_{ab}}{r_{12}} \right)^9 + \frac{Z_a Z_b e^2}{\epsilon r_{12}}},$$

where a and b are the species labels of particles 1 and 2, respectively, and have the possible values $+$ and $-$, e is the magnitude of the electronic charge, Z_a is the signed charge in units of e for species a , ϵ is the bulk dielectric constant of the solvent, and k_B is Boltzmann's constant. For $\sigma_{ab} = 2.8428$ Å and $B = 5377.75$ Å K, the soft sphere model corresponds closely to the RPM of diameter 4.2 Å, in the sense that very similar structure and thermodynamics are obtained.¹¹ For both models we set $T = 298.16$ K and $\epsilon = 78.358$.

A. HNC and modifications

In order to facilitate our discussion we briefly review the basis of the integral equation formulation. We define $h_{ab}(r_{12})$ by

$$h_{ab}(r_{12}) = g_{ab}(r_{12}) - 1. \quad (1)$$

The exact density expansion of $h_{ab}(r_{12})$ is an infinite sum of integrals which are usually written in a graphical notation. The terms (graphs) can be precisely divided into subsets according to topological criteria and summed to give the quantities $c_{ab}(r_{12})$, $t_{ab}(r_{12})$, and $s_{ab}(r_{12})$ which are related by

$$h_{ab}(r_{12}) = c_{ab}(r_{12}) + t_{ab}(r_{12}), \quad (2)$$

$$h_{ab}(r_{12}) = \exp[-\beta u_{ab}(r_{12})] \exp[t_{ab}(r_{12}) + s_{ab}(r_{12})] - 1. \quad (3)$$

The direct correlation functions $c_{ab}(r_{12})$ and $h_{ab}(r_{12})$ are related via the Ornstein–Zernike (OZ) equation.^{6,19} Hence, using Eq. (2) to eliminate $h_{ab}(r_{12})$, we require only an approximation for $s_{ab}(r_{12})$ to obtain the functions $h_{ab}(r_{12})$.

The HNC approximation is $s_{ab}(r_{12}) = 0$. This is equivalent to neglecting the class of terms called bridge graphs in the density expansion of $c_{ab}(r_{12})$. The leading bridge graph involves functions of the coordinates of four particles and is given by^{8,20}

$$s_{ij}^*(r_{12}) = \frac{1}{2} \sum_k \sum_l \rho_k \rho_l \int f_{ik}(r_{13}) f_{kj}(r_{32}) f_{il}(r_{14}) f_{lj}(r_{42}) \times f_{kl}(r_{34}) d^3 r_3 d^3 r_4, \quad (4)$$

where i , j , k , and l are the species subscripts for particles 1, 2, 3, and 4, respectively, r_{12} is the separation of particles 1 and 2, and $f_{ik}(r_{13})$ is the Mayer f function defined by

$$f_{ik}(r_{13}) = \exp[-\beta u_{ik}(r_{13})] - 1. \quad (5)$$

Instead of considering only the one graph we can sum an infinite number of related graphs by replacing the f “bonds” by h bonds. This procedure consists of calculating $h_{ab}(r_{12})$ with the HNC approximation in a preliminary step, and using it to obtain a renormalized leading correction^{11,21}

$$s'_{ij}(r_{12}) = \frac{1}{2} \sum_k \sum_l \rho_k \rho_l \int h_{ik}(r_{13}) h_{kj}(r_{32}) h_{il}(r_{14}) h_{lj}(r_{42}) \times h_{kl}(r_{34}) d^3 r_3 d^3 r_4. \quad (6)$$

This expression has been given limited examination¹¹ for doubly charged particles and is definitely appreciable for c_{st} in the range less than about 0.1 M and r_{12} less than a few diameters. The expression is diminished by the density factors at extremely low concentration and by screening effects at higher concentration.

A modification of HNC,¹¹ called BHNC, employed the quantity $s'(r)$ within the simplest approximation, namely

$$g_{ij}^{\text{BHNC}}(r_{12}) = \exp[s'_{ij}(r_{12})] g_{ij}^{\text{HNC}}(r_{12}) \quad (7)$$

which is just Eq. (3) with the substitutions $t = t^{\text{HNC}}$ and $s = s'$. For the c_{st} extremes of 10^{-4} and 0.2 M, the BHNC and HNC results are nearly identical, $\exp[s'(r)]$ being always very near unity and $g_{++}(r)$ increases monotonically. It is for concentrations between these, however, that HNC predicts a maximum in $g_{++}(r)$. In contrast, the BHNC results are monotonic, in apparent accordance with biased Monte Carlo data.

In the present work we incorporate $s'(r)$ directly into

the iterative scheme, putting $s = s'$ in Eq. (3) at the outset. This procedure, which we term here HNC + B, follows the general approach suggested by Lado,²² usually called the reference hypernetted chain (RHNC) method. RHNC-type prescriptions have the additional advantage that the results necessarily satisfy the Stillinger-Lovett moment conditions,²³ since $s'(r)$ is short ranged.

Although HNC + B still neglects an infinite set of graphs, it includes infinite sets which are neglected by HNC and BHNC, and is therefore more complete in this sense. However, the success of various approximations depends crucially on cancellations between included and excluded graphs, and therefore a more complete set of graphs need not imply a more accurate pair correlation function.

For ionic solutions it is convenient to transform Eqs. (3) and (4) by dividing the effective pair potential into a short range and a long range part and then carry out the Mayer resummation of the long range portion.²⁴ The transformed equations and the recursive algorithm used in the HNC and BHNC calculations are described in detail elsewhere.^{25,26} The HNC + B algorithm differs only by including $s'(r)$ in the resummed closure relation.

B. Computation of $s'(r)$

We have evaluated $s'_{ij}(r_{12})$ by two methods. The first is Monte Carlo numerical integration, which has previously been applied to this problem.¹¹ The integration is performed over a truncated volume as described there. For each r_{12} and set of species reported here, 800 000 trial particle moves were made for the present study. We have also evaluated $s'_{ij}(r_{12})$ via a Legendre polynomial expansion method closely analogous to one used in the work of Barker and Monaghan.²⁷ Using a spherical coordinate system with particle 1 at the origin and particle 2 on the polar axis, and defining θ_{213} to be the angle with vertex at particle 1 and endpoints at particles 2 and 3, we have, for example, the expansion

$$h_{ij}(r_{23}) = \sum_{b=0}^{\infty} A_b^{ij}(r_{12}, r_{13}) P_b(\cos \theta_{213}), \quad (8)$$

where A_b is the coefficient of Legendre polynomial P_b . Expanding three of the five h functions in s'_{ij} and simplifying leads to

$$\begin{aligned} s'_{ij}(r_{12}) = & \frac{1}{2} \sum_k \sum_l \rho_k \rho_l 16\pi^2 \int_0^\infty \int_0^\infty r_{13}^2 r_{14}^2 h_{ik}(r_{13}) \\ & \times h_{il}(r_{14}) A_b^{kj}(r_{12}, r_{13}) A_b^{lj}(r_{12}, r_{14}) A_b^{kl}(r_{13}, r_{14}) \\ & \times dr_{13} dr_{14}. \end{aligned} \quad (9)$$

Several numerical approximations are made in the calculation of s'_{ij} using the latter route. We perform a Simpson's Rule numerical integration using 151 points and truncating at 30 Å. Also, the Legendre polynomial expansion [Eq. (9)] is truncated after the fourth term. The effect of these approximations has been examined. We conclude that this procedure always provides at least two significant digits, which is satisfactory for our purposes, and, in general, superior to the MC integration.

C. Simulation methods

The well-known Metropolis Monte Carlo (MC) simulation method⁷ was used to obtain pair correlation functions for several models and concentrations. The calculations were carried out for either 64 or 200 particles in an appropriately sized cubic cell with periodic boundary conditions and minimum image truncation. The maximum displacement in the trial moves was chosen to give a moderate acceptance probability, which varied here between 0.3 and 0.5. The ions, initially in a cubic lattice, are equilibrated for a number of passes (trial moves per particle) and data for $g(r)$ is collected during an additional segment. The details of the four new runs and one previously reported study¹¹ are collected in Table I. It should be noted that all of the runs reported here are quite long compared to those previously considered^{10,11} for such systems.

At very low concentrations the usual MC procedure produces few like-ion pairs with separations between R and $3R$ which is the region of most interest here. In order to improve the statistics in this part of configuration space a biased MC method was used. The biasing consists of choosing a particular pair of positive ions, say 1 and 2, and replacing their pair potential $u_{++}(r_{12})$ with a modified pair potential $u'_{++}(r_{12})$. For r_{12} greater than some chosen value, in our case 20 Å, $u'_{++}(r_{12})$ is set to infinity in order to assure rejection of the configuration. Thus every accepted configuration of the

TABLE I. Simulation parameters.

Concentration (c_{st} , M)	Model	Number of particles	Maximum displacement per move ^a	Acceptance probability	Equilibration (passes)	Equilibrium run length (passes)
0.005 ^c	soft	64	$L/4$	0.47	5320	41 760
0.0625	soft	64	$L/4$	0.31	5620	10 440
0.2 ^d	soft	216	$L/4$	~ 0.5	~ 300	500
0.0625	hard	64	$L/4$	0.30	400	15 660
0.0625	hard	200	$L/8^b$	0.35 ^b	500	5 000

^a L is the edge length of the cubic cell.

^bDuring equilibration the maximum displacement was $L/4$ and the acceptance probability was 0.26.

^cBiased MC for like-ion correlation function only.

^dFrom Ref. 11.

TABLE II. Bridge graph approximation^a $s'(r)$.

$r(\text{\AA})$	$s'_{++}(r)$					$s'_{+-}(r)$				
	0.005 M		0.0625 M		0.2M	0.005 M		0.0625 M		0.2M
	MCI ^b	LP ^c	MCI ^b	LP ^c	LP ^c	MCI ^b	LP ^c	MCI ^b	LP ^c	LP ^c
4.2	-3.169	-3.243	-0.624	-0.547	-0.024	0.194	0.175	0.218	0.171	0.075
6.3	-2.070	-2.079	-0.404	-0.365	-0.036	0.142	0.142	0.139	0.113	0.041
8.4	-1.266	-1.374	-0.273	-0.286	-0.069	0.091	0.110	0.072	0.071	0.024
10.5	-0.400	-0.478	-0.072	-0.083	-0.018	0.054	0.080	0.030	0.036	0.009
12.6	-0.132	-0.158	-0.015	-0.017	-0.002	0.035	0.056	0.011	0.014	0.002
14.7	-0.052	-0.069	-0.003	-0.004	-0.0004	0.025	0.043	0.005	0.007	0.0004
16.8	-0.023	-0.031	-0.0004	-0.0006	...	0.017	0.031	0.002	0.003	...
18.9	-0.011	-0.016	...	0.00002	...	0.012	0.023	...	0.0014	...
21.0	-0.005	-0.008	...	0.00010	...	0.008	0.016	...	0.0006	...

^aSoft spheres.^cLegendre polynomial expansion.^bMonte Carlo integration.^dBased on five million trial moves, all others are 800 000.

system contains at least one like-ion pair of interest.

A previous biased study of this system¹¹ used $u_{++}(r_{12})$ without modification for r_{12} inside the chosen cutoff. Since $u_{++}(r_{12})$ rises sharply for small r , the upper portion of this range is sampled more often. More uniform sampling and a consequent improvement in the small r statistics can be achieved by "flattening" the pair potential. Therefore, for $r_{12} \leq 20 \text{ \AA}$, we define a modified pair potential

$$u'_{++}(r_{12}) = u_{++}(r_{12}) - w'(r_{12}) \quad (10)$$

where

$$w'(r_{12}) = 29.5 \exp[-0.13364(r_{12})^2] + 0.47 \quad (11)$$

The function $w'(r_{12})$ is a reasonable fit in the region of interest to the approximate potential of mean force $w(r_{12})$ defined by $\beta w(r_{12}) = -[\ln g_{++}^{\text{HNC}}(r_{12})]$, where we have used the HNC result for g_{++} . [The additive constant in Eq. (11) has no influence on the sampling here.] The constrained pair potential produces a g'_{++} which, after removing the bias induced by the potential $w'(r_{12})$ [Eq. (11)], is proportional to the unconstrained g_{++} . The proportionality constant is obtained by comparing g'_{++} (17.75 Å) to the g_{++}^{HNC} (17.75 Å). HNC is expected to be reliable at this distance since $s'(r)$ is shorter ranged.¹¹

III. RESULTS

As discussed in Sec. I, outside the range of concentrations between about 10^{-1} and 10^{-4} M the HNC approximation appears to be quite accurate for the present system. We have made a detailed study of the representative concentrations 0.005, 0.0625, and 0.2 M. From previous studies¹⁴ 0.005 M appears to give the most pronounced peak in $g_{++}(r)$, and the greatest disagreement between HNC and MC.¹¹ 0.0625 M is an intermediate concentration for which a hard sphere model simulation has been reported,¹⁰ while previous evidence¹¹ suggests that 0.2 M is in the regime of reasonable agreement between HNC and MC.

A. Results for $s'(r)$

The HNC + B and BHNC methods require $s'(r)$, the present approximation for the sum of bridge graphs.

Our results for $s'(r)$ calculated as outlined above, are collected in Table II. At small r the two methods give slightly different results but the agreement is otherwise good. For the lower concentrations $s'(r)$ appears to be a smooth curve without maxima and minima but with an inflection point at about $2R$.

The 0.2 M concentration was examined in greater detail than is shown in the table in order to define the structure in the $s'_{++}(r)$ curve. As is clear from the table in this case $s'_{++}(r)$ is not large but it is also not monotonic. It exhibits a maximum magnitude at about $r = 8 \text{ \AA}$, with a value of -0.074 . For all three concentrations, a cubic spline interpolation from the calculated points was used as input to the integral equation programs.

B. Soft sphere results

Integral equation and simulation results for the soft sphere model are shown in Figs. 1–6. Our Monte Carlo $g_{++}(r)$ data was initially collected on a 0.5 Å grid; the

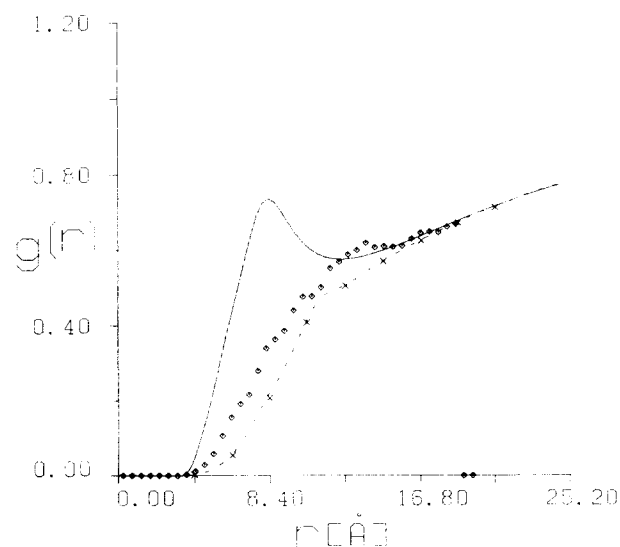


FIG. 1. Like-charge pair correlation function $g_{++}(r)$ for 0.005 M aqueous 2–2 soft spheres calculated by HNC (—), HNC + B (---), BHNC (×), and MC (○).

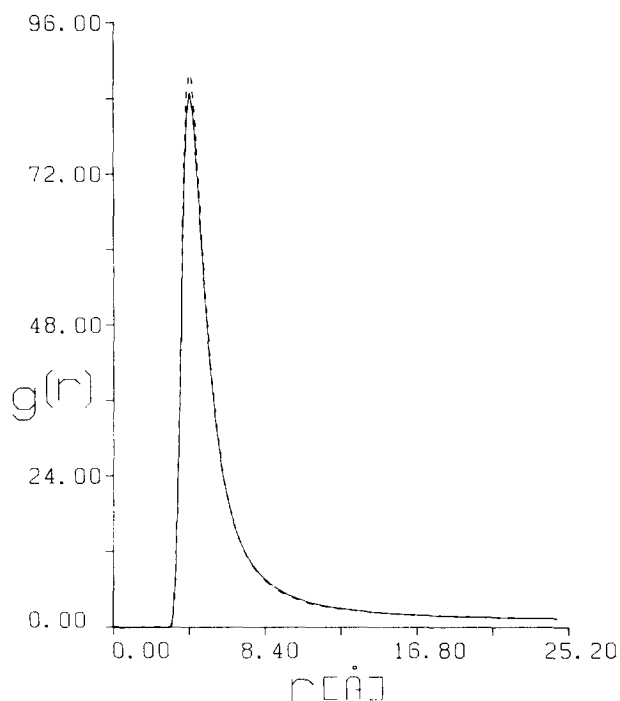


FIG. 2. Unlike-charge pair correlation function $g_{+-}(r)$ for 0.005 M aqueous 2-2 soft spheres calculated by HNC (—) and HNC+B (---).

MC points displayed have been smoothed with a 5-point moving polynomial analogous to that used in spectral treatment.²⁸ The MC $g_{+-}(r)$ points are raw data collected on a 0.1 Å grid, except that many points in the slowly varying portion of the curve have been omitted. The 0.2 M MC data for g_{++} and g_{+-} was used in its previously reported form.¹¹

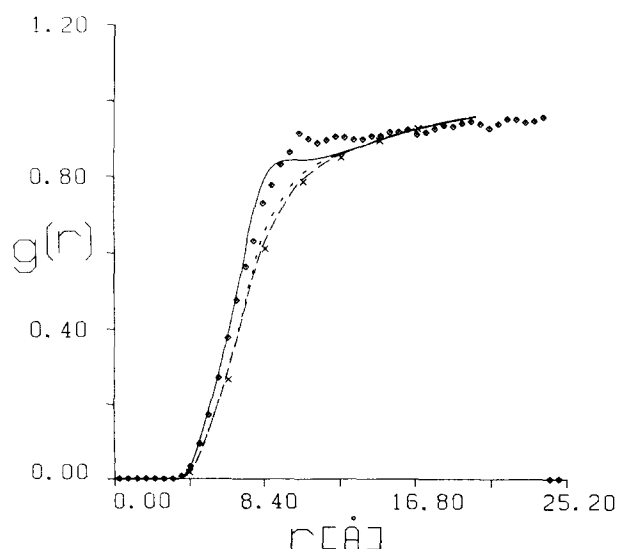


FIG. 3. Like-charge pair correlation function $g_{++}(r)$ for 0.0625 M aqueous 2-2 soft spheres calculated by HNC (—), HNC+B based on $s'(r)$ from MC integration (---), HNC+B based on $s'(r)$ from Legendre polynomial expansion (- - -), BHNC (x), and MC (◊).

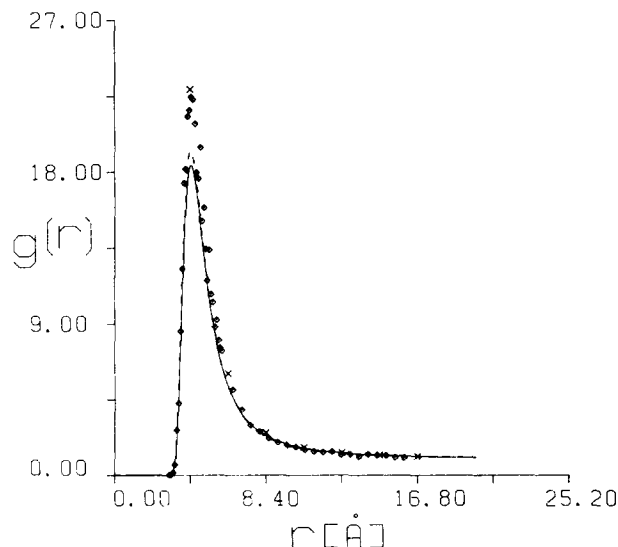


FIG. 4. Unlike-charge pair correlation function $g_{+-}(r)$ for 0.0625 M aqueous 2-2 soft spheres calculated by HNC (—), HNC+B (---), BHNC (x), and MC (◊).

The 0.005 M g_{+-} results are shown in Fig. 1. The predictions of each of the three integral equation approaches as well as the simulation data are shown. We recall that the proportionality constant for the biased MC curve has been estimated by requiring that $g_{++}^{MC}(17.75 \text{ Å})$ equal $g_{++}^{HNC}(17.75 \text{ Å})$. We find that HNC + B is close to, but greater than, BHNC. Both are monotonically increasing and considerably lower than HNC in the region where HNC predicts a pronounced maximum. With increasing r , the integral equation curves converge, although HNC + B rises very slightly above HNC near 25 Å.

The MC data indicate that, at 0.005 M, HNC + B and BHNC have the correct qualitative behavior, but that

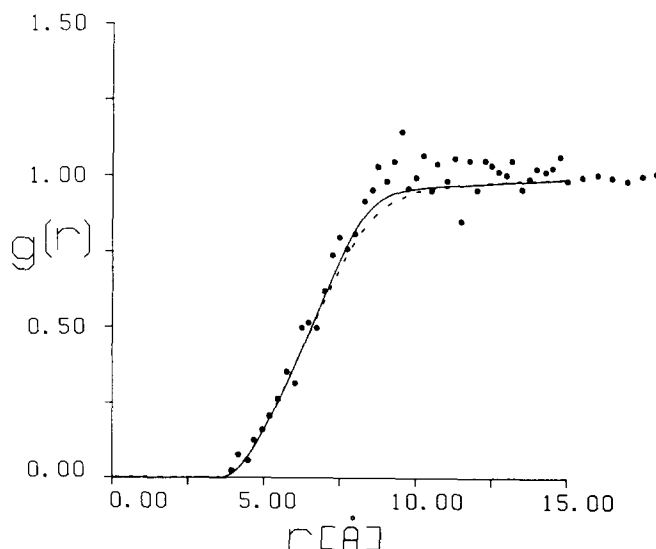


FIG. 5. Like-charge pair correlation function $g_{++}(r)$ for 0.2 M aqueous 2-2 soft spheres calculated by HNC (—), HNC+B (---), and MC (◊).

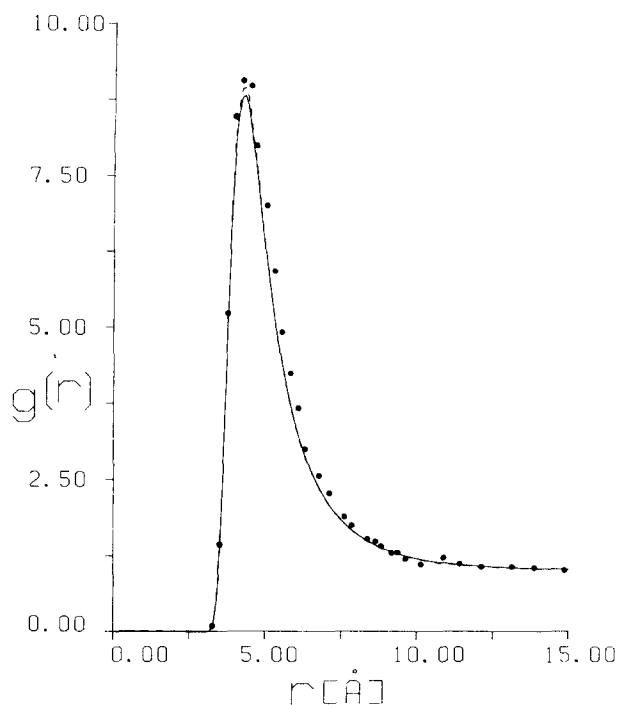


FIG. 6. Unlike-charge pair correlation function $g_{+-}(r)$ for 0.2 M aqueous 2-2 soft spheres calculated by HNC (—), HNC + B (---), and MC (●).

they are underestimates. Nevertheless, both BHNC and HNC + B show substantial improvement over the HNC when compared with the simulation. In particular, in the region around $2R$ (8.4 Å), MC is much lower than HNC and exhibits no maximum. We note that the HNC + B curve manifests an inflection point at about 12.5 Å; within the accuracy of the data the MC results cannot be assigned any such structural features.

The $+$ - $-$ correlation functions obtained from HNC and HNC + B for the 0.005 M case are given in Fig. 2. Very close agreement of all methods is found except at the top of the 4.2 Å peak. In that area, HNC + B (87.0) is higher than HNC (84.5) and BHNC is higher still (102.6 via MC integration, 100.7 via polynomial expansion; see Table II). No new simulations of this model and concentration have been done for the $+$ - $-$ case, but a previous unbiased MC study¹¹ suggests a value of about 94 for $g_{+-}^{MC}(4.2 \text{ Å})$ which is roughly midway between the BHNC and HNC + B results.

The intermediate concentration of 0.0625 M is considered in Figs. 3 and 4. The like-charged ion case is presented in Fig. 3. Two HNC + B curves were produced in order to examine the sensitivity of the calculation to the function $s'(r)$. One of the HNC + B results is based on the Legendre polynomial expansion values of $s'(r)$ and the other is based on the MC integration values. The curves shown demonstrate that the results are not sensitive to differences in $s'(r)$ of the magnitude given in Table II.

At this concentration as in the 0.005 M case, HNC + B and BHNC are corrections to HNC of the same direction and similar magnitude. In fact, all of the correlation

functions shown in Fig. 3 are in general accord. However, it is clear that on a quantitative level, the HNC is in *better* agreement with MC than are the "corrected" theories. Of most importance, we see that although the MC data appears to be monotonically increasing, it is not the local maximum, but rather the larger r depression at about 10 Å which must be assigned to the discrepancy. This is shown clearly also in the hard sphere models as will be seen below.

The 0.0625 M g_{+-} results, in Fig. 4, show the same trends already discussed for the 0.005 M case. That is, the various methods agree well except at the contact peak where the values increase in the order HNC < HNC + B < BHNC. At this higher density more reliable unbiased MC results are possible; our simulation suggests that $g_{+-}(4.2 \text{ Å}) \approx 22.4$, a figure given very closely by BHNC, while HNC + B yields a value of 19.2, and HNC a value of 18.4.

The 0.2 M results are shown in Figs. 5 and 6. As is clear from the figures, HNC + B and HNC are quite close except for a small region of each plot. In those areas, HNC is somewhat more accurate in the $++$ case, and HNC + B in the $+-$ case, as judged by comparison to the MC results. However, both integral equation results appear to lie somewhat below the MC data, which is consistent with the results described above at 0.0625 M. At the higher concentration, however, the differences are smaller. BHNC yields a value for $g_{+-}(4.2 \text{ Å})$ of 9.5, so that, again, HNC + B and BHNC bracket the MC result.

C. Hard sphere simulations

Our 0.0625 M simulation was done with 64 soft ions. The $g_{++}(r)$ is monotonic increasing and always less than 1. In contrast, the published simulation of 200 hard sphere ions¹⁰ manifests a peak in $g_{++}(r)$ at $\sim 11 \text{ Å}$ and a value there exceeding one. The possibility that this discrepancy was due to the different models or the dif-

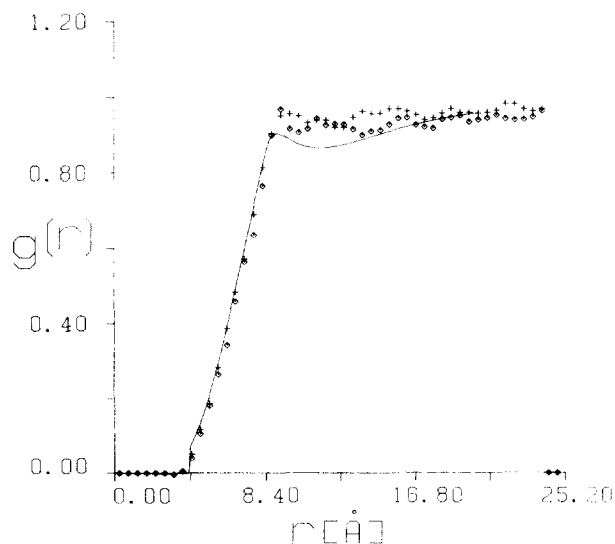


FIG. 7. Like-charge pair correlation function $g_{++}(r)$ for 0.0625 M aqueous 2-2 hard spheres calculated by HNC (—), MC with 64 ions (◇), and MC with 200 ions (+).

ferent number of ions has been examined very carefully. We have performed two additional lengthy simulations, one with 64 hard ions and one with 200 hard ions. Pertinent information is given in Table I. The data appears in Fig. 7 along with the HNC result.

For $g_{++}(r)$ the simulations agree well, the 200 ion result being perhaps slightly higher. Neither MC result crosses one or suggests a local peak. A comparison of HNC and MC leads to the same observation made for the soft sphere system. The HNC maximum at $2R$ matches the MC value there. However, the values predicted by HNC are, incorrectly, depressed in the region between about $8.4 (2R)$ and 15 \AA , as for the soft sphere model.

IV. CONCLUSIONS

Our integral equation and simulation studies have produced no evidence for nonmonotonic behavior in like charged ion correlation functions $g_{++}(r)$ in the low concentration range where packing is not important (less than about 0.1 M). These results corroborate previous indications^{11,13} that local maxima in $g_{++}(r)$ in this regime are an artifact of the HNC approximation. However, the present results show that it need not be correct to assign the error to this maxima *per se*. Although at very low (millimolar) concentration, the correct result lies well below HNC near $2R$, at 0.0625 M we find that the value at this distance is quite accurate and that the discrepancy is an unrealistic depression at larger distances. The implication is that there is a gradual transition between these extremes. At concentrations above about 0.2 M , the HNC has already been established as quite accurate.^{10,11} The HNC behavior is consistent with an overestimate of the contribution of small clusters at the lowest ionic densities and an underestimate of the contribution of *larger* clusters at somewhat higher concentrations. For the relative distribution of unlike charged ions, $g_{+-}(r)$, the HNC is at all concentrations a good approximation, although the accuracy improves with increasing ionic density.

"Corrections" to HNC which include an estimate of bridge graph contributions have been considered by employing a renormalized four point graph for this term. The results show that such a correction is quite valuable in the very dilute regime where the changes in $g_{++}(r)$ are large. In the intermediate (few hundredth molar) regime, the corrections to $g_{++}^{\text{HNC}}(r)$ introduce much smaller changes, but these are in the *incorrect* direction. For higher concentrations the sense of the correction remains incorrect, but the influence is quite small and the result differs little from the already reasonably accurate HNC solution. For unlike charged ions, these corrections are generally productive at all concentrations, reducing the relatively small discrepancies which exist at the ionic contact peak.

The alternatives considered for the introduction of the bridge function do not lead to very different results in the present studies, although the full HNC + B inclusion appears somewhat more accurate for $g_{++}(r)$. For $g_{+-}(r)$ the two approaches considered typically bracket

the MC result in the region of largest discrepancy.

In light of these results, it is important to note that the correct form of the bridge function which is implied by this work is rather complex. For $+-$ pairs, it would appear to have the character of a short range *attraction* at all electrolyte solution concentrations, although it is of decreasing importance with increasing ion density. However, for $++$ pairs, it has the form of a short range *repulsion* at the lowest concentration, evolving into an intermediate range *attraction* at higher concentrations. The latter behavior is implied by the differences shown between HNC and MC and is reflected in the calculated values of $s'_{++}(r)$ at 0.2 M , although very weakly. This complex behavior is in marked contrast to the "universality" of the bridge function encountered in the limited studies of Rosenfeld and co-workers.²⁹

In summary, the HNC approximation has been shown to be in rather good accord with simulation for unlike charge correlations over a wide range of concentrations. For like charges, the HNC + B modification is a substantial improvement in the very dilute regime, where the largest discrepancies appear. Hence, the HNC + B calculations are a better *a priori* estimate, as the corrections produce rather small changes in the regime where the bridge graph contributions are incorrectly predicted. Finally, we emphasize that the relative errors in such quantities as total local ionic densities and local charge densities which are implied by the remaining discrepancies discussed above are quite small, as the contribution of like charged ions to these results at short range is rather small.

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