

Symmetric Associating Electrolytes: GCMC Simulations and Integral Equation Theory

V. Vlachy,[†] T. Ichiye,[‡] and A. D. J. Haymet*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received May 7, 1990

Abstract: Electrolytes symmetric in charge and size are studied at different concentrations by using both grand canonical Monte Carlo simulations and two integral equations. First, we compare the simulation results for the long-wavelength limit of the partial structure factor for particle number fluctuations, $S_{NN}(0)$, with the predictions of the hypernetted chain (HNC) integral equation. Mean activity coefficients are also evaluated. The data simulate a 2:2 electrolyte in aqueous solution at 298 K, and also a more strongly interacting 2:2 electrolyte in a solvent of lower dielectric constant, such as 30% dioxane in water. The results show that the HNC integral equation underestimates considerably the fluctuations in the number of particles in the concentration range around 0.07 mol/dm³. The dependence of $S_{NN}(0)$ on the dielectric constant is also examined. The correlation functions obtained from the HNC equation are in poor agreement with the simulations, especially at the lower dielectric constant. A possible solution to this problem is presented with use of the new IPY closure proposed recently by Ichiye and Haymet. This closure leads to good agreement with simulation data.

1. Introduction

The development of quantitative theories for electrolyte solutions is an important and challenging goal of liquid-state statistical thermodynamics. Since the pioneering work of Debye and Hückel in 1923,¹ which is really restricted to 1:1 electrolytes when applied to aqueous solutions, considerable progress has been achieved. The application of new techniques from statistical mechanics, such as computer simulations, has provided tests of traditional theories and models. Integral equations and perturbation theories have been proposed, and the definitive comparisons of Valleau and others²⁻⁸ show that the hypernetted chain (HNC) equation provides physically meaningful agreement with simulation results. Yet there are still unresolved problems with 2:2 electrolytes, and especially with still more highly charged electrolytes, and these are the focus of this paper. A vast amount of the data has been accumulated recently, and it has been summarized carefully in a number of review articles.⁹⁻¹⁴ It is impossible to mention all important contributions here, so we will reference articles only of direct relevance to this study.

In a previous article¹⁵ we studied the structure and thermodynamics of highly asymmetric electrolytes as models for micellar solutions. It has been found that these systems share many of the properties of more simple symmetric, but multivalent, systems such as 2:2 electrolytes. For example, in both cases the ions are strongly associated, and this makes direct application of the HNC approximation difficult. The research presented here is motivated by the facts that (i) knowledge of the structure of isotropic solutions is a prerequisite to understanding their behavior in heterogeneous systems,^{16,17} (ii) due to the symmetry in charge and in size it is easier to test improvements^{18,19} in integral equation theories beyond HNC, the development of which may also be relevant for colloidal solutions, and finally (iii) these systems are interesting per se, since some more approximate theories²⁰⁻²² suggest that the model solutions undergo spinodal decomposition in the dilute electrolyte regime, under conditions which are frequently attainable in the laboratory.

The two major methods used here to study the structure and thermodynamics of strongly interacting symmetric electrolytes are the grand canonical Monte Carlo (GCMC) simulation technique and the hypernetted chain (HNC) integral equation. Crucial bridge function improvements to the HNC equation¹⁹ are also included. Grand canonical Monte Carlo simulations have been used to study electrolyte solutions previously,^{3-5,16,17} and Valleau, Cohen, and Card⁴ have used these data for a critical

evaluation of existing electrolyte theories. One of the advantages of this method is that it yields directly the mean activity coefficient of the solution. Another advantage, somewhat neglected to date, is that in principle the so-called "fluctuation properties"²³ can be calculated directly. Here the most important is the long-wavelength limit of the partial structure factor for particle number fluctuations, $S_{NN}(0)$, defined by

$$S_{NN}(0) = [\langle N^2 \rangle - \langle N \rangle^2] / \langle N \rangle \quad (1)$$

where N is the number of particles in a certain GCMC configuration, and $\langle N \rangle$ is its grand canonical average. The quantity $S_{NN}(0)$ is related to derivatives of the activity coefficients,^{12,24,25}

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[†] Permanent address: Department of Chemistry, University of Ljubljana, 61000 Ljubljana, Slovenia, Yugoslavia.

[‡] Permanent address: Biochemistry/Biophysics Program, Washington State University, Pullman, Washington 99164.

and in simple (uncharged) liquids $S_{NN}(0)$ is proportional to the isothermal compressibility. An instability in the system, for example spinodal decomposition, is signalled by the inverse compressibility approaching zero. In modern density functional theories of freezing,²⁶ to first order in perturbation theory $S_{NN}(0)$ determines the magnitude of the fractional density change on freezing.

In this work we present (1) the results of GCMC simulations for $S_{NN}(0)$ and structural properties of 2:2 electrolytes and (2) a comparison of this data with the predictions of integral equations theories. In Section 2 we summarize the electrolyte model and theoretical methods. The results are collected in the figures and tables of Section 3. The simulation data are used to analyze critically the hypernetted chain equation results for $S_{NN}(0)$ and for certain correlation functions. In addition, a new "bridge" function correction to the hypernetted chain equation¹⁹ is tested. Our conclusions are stated in Section 4.

2. Electrolyte Model and Theoretical Methods

A. Hard and Soft Models of Electrolytes. The simplest model which captures many essential features of real electrolyte solutions is known in the literature as the primitive model.²⁻⁸ The ions are represented as charged hard spheres distributed in a structureless dielectric continuum representing the solvent, which is characterized solely by its relative permittivity. Moreover, the positive and negative ions have the same size and have the same permittivity as the "solvent" in which they are embedded. A more realistic model has been proposed by Ramanathan and Friedman,²⁷ in which the ions are "soft" spheres with a short-range potential, which has the same functional form but different parameters than the primitive model. Both "hard" and "soft" sphere models are studied in the present work. The pairwise interaction potential energy between the ions is represented by the following function:²⁸

$$\beta u_{ij}(r) = z_i z_j e_0^2 \beta / (4\pi\epsilon_0\epsilon_r r) + A_{ij}[(r^*_{i} + r^*_{j})/r]^9 \quad (2)$$

where $z_i e_0$ is the charge on the ionic species i , $\epsilon_0\epsilon_r$ is the permittivity of the system, and the parameter which measures the size of the ions is chosen here to be $A_{ij} = (1.804 \text{ nm})|z_i z_j|/(r^*_{i} + r^*_{j})$ at 298 K. As usual, $\beta = 1/k_B T$, where T is the absolute temperature and k_B is Boltzmann's constant. For the hard-sphere potential, A_{ij} is infinite if $r < (r^*_{i} + r^*_{j})$, and zero elsewhere, where r^*_{j} denotes the hard-sphere radius of ion j .

The model described by eq 2 has been investigated previously,^{28,29} and one helpful conclusion is that the soft-sphere model gives structural and thermodynamic results which can be compared with the hard-sphere model provided that the minima of the pair potential functions $u_{+-}(r)$ coincide. This minimum, denoted by the symbol "a", is a convenient measure of the size of the ions, and here it takes the value 0.462 nm. While the models studied here are clearly simplifications of nature, especially in ignoring the molecule nature of the solvent, they have proven to be a useful starting point for accurate prediction of thermodynamic properties of real electrolytes.¹⁴ Furthermore, simple models provide an important testing ground for new approximations such as those discussed below.

B. Grand Canonical Monte Carlo Simulations. The grand canonical Monte Carlo procedure used in this work has been described in detail elsewhere.^{3,5} In 1986, the GCMC method was used by two different groups to study polyelectrolyte solutions, both via charged cylinder models¹⁷ and from detailed studies of NaDNA.³⁰ In this kind of simulation, the chemical potential μ is held fixed along with the volume V and temperature T . The number of particles of type k , N_k , is allowed to fluctuate around

an average value (determined by the chemical potential). The procedure is realized in two steps. First, a randomly chosen ion (state "i") is moved into a new random position (state "j") somewhere in the simulation cube. This attempted move is accepted with probability f_{ij}

$$f_{ij} = \min\{1, Y \exp[-\beta(U_j - U_i)]\} \quad (3)$$

where U_i is the configurational energy of state i , and Y is equal to unity in this (canonical) step. Secondly, the number of ions in the system may change. A random decision is made to attempt to either insert or delete a neutral pair of ions. If the number of cations in the configuration j is $N_j^+ = N_i^+ + 1$ ($N_j^- = N_i^- + 1$), then the coefficient Y in eq 3 is given by

$$Y = \gamma^2_{+-} \langle N_+ \rangle \langle N_- \rangle / (N_j^+ N_j^-) \quad (4)$$

In eq 4, both the mean activity coefficient γ_{+-} and the average number of ions are unknown at the beginning of the simulation. During the simulation one determines the average concentration in the system, the configurational energy, the pressure, and the chemical potential. One of the goals of this simulation is to determine accurately the averages $\langle N \rangle$ and $\langle N^2 \rangle$ needed for the direct evaluation of $S_{NN}(0)$.^{31,32} In using eq 1, one subtracts two quantities of order 100 to obtain the resultant quantity of order unity. This requires long simulations; in a few cases more than 150000 "passes" (number of generated configurations per particle) are required to collect good statistics. Even so, the tables and figures show measurable numerical uncertainty in this quantity.

The probability distribution for the number of ions N at any step of the simulation is similar to that observed by us for one-component systems.³² All simulations presented here were performed in a cubical box with periodic boundary conditions and the minimum image convention. Several studies^{6,33} indicate that this is an acceptable approximation in the region of parameters and concentrations of interest here. Most of the results presented in the next section are obtained for a system of approximately 130 ions in the central box. To obtain a check of finite size effects, several simulations have been performed for 240 and 450 ions. The results for $S_{NN}(0)$ will be discussed in Section 3.

C. HNC Integral Equation. Modern theories of liquids are based on the diagrammatic expansion of the total correlation function $h(r)$, $h(r) = g(r) - 1$, as explained for example in ref 34. The theory and numerical procedures used in this work have been published elsewhere¹⁸ and will not be repeated here. For multicomponent systems, the total correlation function may be written³⁴

$$h_{ij}(r_{12}) = \exp[-\beta u_{ij}(r_{12}) + B_{ij}(r_{12}) + h_{ij}(r_{12}) - c_{ij}(r_{12})] - 1 \quad (5)$$

where $B_{ij}(r)$ is the so-called bridge function (the infinite sum of "bridge" graphs) and $c_{ij}(r)$ is the direct correlation function, defined by the Ornstein Zernike equation

$$h_{ij}(r_{12}) = c_{ij}(r_{12}) + \sum_k \rho_k \int d\mathbf{r}_3 c_{ik}(r_{13}) h_{kj}(r_{32}) \quad (6)$$

where ρ_k denotes the number density of species k . For a two-component system there are of course three distinct direct correlation functions $c_{ij}(r)$, and three total correlation functions $h_{ij}(r)$. It is convenient to define a matrix with the elements

$$\rho_{ij} = \rho_i \delta_{ij} \quad (7)$$

and the function $\mathbf{t} = \mathbf{h} - \mathbf{c}$, in order to rewrite eq 6 in the more compact form

$$\rho \hat{\mathbf{t}} \rho = \rho \hat{\mathbf{c}} \rho \hat{\mathbf{h}} \rho \quad (8)$$

In eq 8, the carets denote Fourier transforms. In Coulombic

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Table I. Grand Canonical Monte Carlo Results for the Soft Sphere Model with $r^*_{+} = r^*_{-} = 0.14214$ nm ($a = 0.42$ nm)^a

run	$\langle N \rangle$	L/a	$10^3 c$ (mol dm ⁻³)	$S_{NN}(0)$	configs (millions)
1	119.1	64.0	5.1	1.37 ± 0.04	8.0
2	244.3	80.0	5.35	1.38 ± 0.03	16.0
3	447.7	100.0	5.02	1.32 ± 0.04	8.0

^aThe Bjerrum length λ_B is 2.857 nm. L is the length of the Monte Carlo cell.

systems, the long-range part of the potential requires special treatment. The total potential u_{ij} may be separated into a short-range and a long-range contribution ψ_{ij}

$$\psi_{ij} = -\beta u_{ij}^s + \beta u_{ij}^l \quad (9)$$

where the superscript s denotes the short-range part. Subtracting the long-range contributions

$$\hat{V}^{-1} = \rho^{-1} - \hat{\psi} \quad (10)$$

$$c^s = c - \psi \quad (11)$$

and with the definitions

$$\tau = t - q + \psi \quad (12)$$

$$\rho \hat{q} \rho = \hat{V} - \rho \quad (13)$$

we obtain the renormalized version of the Ornstein-Zernike equation, suitable for systems with Coulombic interactions

$$\rho \hat{\tau} \rho = \hat{V} \hat{c}^s [I - \hat{V} \hat{c}^s]^{-1} \hat{V} - \rho \hat{c}^s \rho \quad (14)$$

This equation can be solved numerically together with the closure defined by eq 5. Here, as in our previous work,^{15,18,19} we have used an efficient algorithm based on ideas proposed by Gillan³⁵ and Labik and co-workers³⁶ and summarized in ref 18.

D. IPY Closure for the Integral Equation. Since the early 1960's, in the absence of better approximation, the bridge function B_{ij} in eq 5 has often been set to zero, which is called the hypernetted chain (HNC) approximation. While this theory is very successful in describing 1:1 electrolytes (and other Coulombic systems), significant deviations have been observed for highly charged ions such as 2:2 aqueous electrolytes and colloids.^{4,15} This conclusion is amplified here. The integral equation theory can of course be improved if a reasonable estimate for the bridge function can be obtained.^{28,29,37} Rather than try to calculate low-order terms in the graphical expansion of the bridge function, we have investigated a "new" IPY closure proposed recently by us,¹⁹ which is only slightly more difficult to implement than the old HNC theory.

In the new theory, the bridge function is defined in terms of a new function, τ' , given by $\tau' = t - q' + \psi$, which is *similar* to eq 12, except that a new choice of the long-range part of the potential ψ' has been made. It is now the long-range part of a modified soft-sphere MSA direct correlation function, a choice influenced by the work of Madden.³⁸ Hence, the function q' is now an MSA chain sum. The bridge function is given explicitly¹⁹ by

$$B_{ij} = \ln(1 + \tau'_{ij}) - \tau'_{ij} \quad (15)$$

for like charges and for unlike charges when $\tau'_{ij} > 0$ (a rare event), and by

$$B_{ij} = \ln[2 - \exp(-\tau'_{ij})(\tau'_{ij} + 1)] \quad (16)$$

for unlike charges when $\tau'_{ij} < 0$ (the usual case). Full details are

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Table II. Grand Canonical Monte Carlo Simulation Results for the Hard Sphere Model^a

run	c (mol dm ⁻³)	$-\beta U/N$	γ_{\pm}	$-\ln \gamma_{\pm}$	$S_{NN}(0)$	configs (million)
1	0.00433	0.794	0.543	0.611	1.31 ± 0.04	5.0
2	0.03375	1.49	0.291	1.235	1.56 ± 0.04	5.0
3	0.0624	1.71	0.2325	1.459	1.65 ± 0.03	5.0
4	0.0988	1.89	0.195	1.635	1.60 ± 0.04	5.0
5	0.5188	2.58	0.108	2.23	1.31 ± 0.03	6.0

^a $a = 0.462$ nm, Bjerrum length is 2.857 nm. The uncertainties in the concentration and $\ln \gamma_{\pm}$ are estimated to be 1%.

Table III. Grand Canonical Monte Carlo Results for the Soft Sphere Model (Equation 2) with $r^*_{+} = r^*_{-} = 0.15635$ nm^a

run	c (mol dm ⁻³)	$-\beta U/N$	γ_{\pm}	$-\ln \gamma_{\pm}$	$S_{NN}(0)$	configs (million)
(A) Bjerrum Length 2.857 nm						
1	0.00434	0.779	0.542	0.612	1.33 ± 0.03	6.0
2	0.0624	1.665	0.232	1.46	1.64 ± 0.03	6.0
3	0.297	2.23	0.130	2.04	1.51 ± 0.03	7.0
4	0.567	2.48	0.109	2.22	1.23 ± 0.03	6.0
(B) Bjerrum Length 4.001 nm						
5	0.00392	1.865	0.319	1.143	1.61 ± 0.1	20.0
6	0.0609	2.95	0.093	2.38	2.07 ± 0.1	20.0
7	0.0628	2.96	0.092	2.39	2.05 ± 0.1	20.0
8	0.347	3.63	0.0372	3.29	2.0 ± 0.1	10.0
(C) Bjerrum Length 4.1284 nm (225 Ion Pairs in the Central Box)						
9	0.0608	3.11	0.083	2.49	2.07 ± 0.1	24.0

^aThe uncertainties in the concentration and $\ln \gamma_{\pm}$ are approximately 1% for runs 1-4 and 2% for runs 5-9.

presented in ref 19. Both the new integral equation, called the ionic Percus-Yevick (IPY) equation, and the HNC approximation are compared below with the ("exact") GCMC data for the model electrolyte.

3. Results and Discussion

A. $S_{NN}(0)$ and Finite Size Effects. The grand canonical Monte Carlo results obtained in this study are collected in the tables. First, it is important to investigate to what degree the fluctuation property $S_{NN}(0)$ depends on the size of the system, that is on the average number of particles $\langle N \rangle$ in the basic cell. For the analysis we choose a dilute solution of 2:2 electrolyte, where these effects are expected to be large.³ We adopt the parameters $r^*_{+} = r^*_{-} = 0.14214$ nm and the Bjerrum length $\lambda_B = |z_+ z_-| \beta e_0^2 / (4\pi \epsilon_0 \epsilon_r) = 2.857$ nm to facilitate comparison with earlier work.^{28,29}

The results for $S_{NN}(0)$ and the average concentration are presented in Table I, as a function of $\langle N \rangle$. In the GCMC calculation the number of particles fluctuates, so the results for $S_{NN}(0)$ do not apply to exactly the same concentration. However, there is little concentration dependence in $S_{NN}(0)$ and the results presented in Table I represent a reasonable estimate of the size effects.

Bearing in mind the statistical uncertainties in the calculations, the conclusion is that $S_{NN}(0)$ values show little size dependence for these values of the parameters. There is a different size dependence, however, with the two particle correlation functions, $g_{ij}(r)$. With a small number of particles ($\langle N \rangle \sim 120$) we found that like and unlike correlation functions do not normalize to unity at large distances, but rather they cross and are finally about 1% apart. The effect was found much smaller for $\langle N \rangle \sim 240$, and it finally disappeared for Run 3, where a large number of particles, $\langle N \rangle \sim 440$, was studied. We also found that these inaccuracies have no significant effect on the shape of the distribution functions up to the distances $r \sim 6a$. The number of particles used in the calculations presented below is approximately 120.

The results for the hard-sphere model are presented in Table II. The ions are chosen to have diameter $a = 0.462$ nm, and the Bjerrum length $\lambda_B = 2.857$ nm, corresponding to an aqueous solution of 2:2 electrolytes at 298 K. The value of the hard-sphere radius is chosen to facilitate comparison with a recent, very precise, canonical Monte Carlo study of dilute 1:1 electrolytes.³⁹ Two

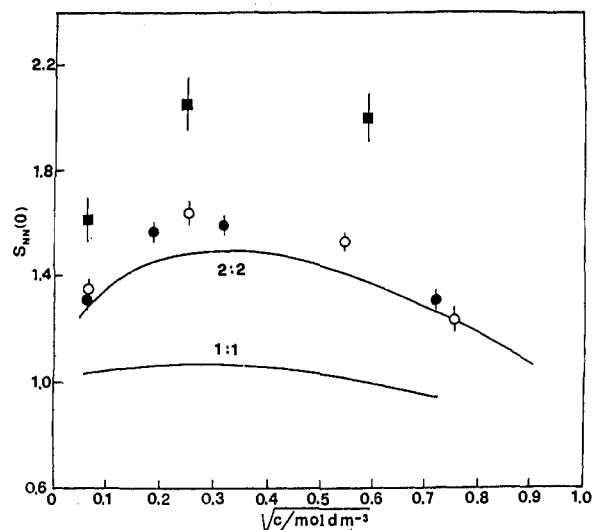


Figure 1. The quantity $S_{NN}(0)$ obtained from grand canonical Monte Carlo simulations (symbols) and the hypernetted chain (HNC) approximation (solid lines). The filled circles denote hard-sphere results (Table II), and open circles denote the soft-sphere model (Runs 1–4 of Table III), all for 2:2 electrolytes with the Bjerrum length 2.857 nm. The filled squares denote the soft-sphere model (Runs 5–8 of Table III), but with the Bjerrum length 4.001 nm. For comparison, the hypernetted chain results for 1:1 aqueous electrolyte are also displayed (lower line).

thermodynamic properties, the excess energy per particle and the mean activity coefficient, are shown at five concentrations, together with the number of configurations during which these statistics were collected. The fluctuation quantity $S_{NN}(0)$ is also tabulated and will be discussed below.

Analogous results are presented in Table III for the soft-sphere model, described by eq 2. In these calculations $r^*_{+} = r^*_{-} = 0.15635$ nm, so that the minimum of the $+$ – potential corresponds with the minimum of the hard-core model investigated above (Table II). In case A the Bjerrum length has the value 2.857 nm, corresponding to the hard-sphere 2:2 electrolyte model presented in Table II. A second value of the dielectric constant has been investigated (case B), corresponding to a more strongly interacting system such as a 2:2 electrolyte in a 30% dioxane aqueous solution. The Bjerrum length for this case (B) is 4.001 nm (relative permittivity $\epsilon_r = 56$, at 298 K). As one can see from Table III, much longer simulation runs were needed for this strongly interacting system.

B. Concentration Fluctuations. In this work we study the dependence of the concentration fluctuations in the solution upon (i) the overall electrolyte concentration and (ii) the dielectric constant of the solution. A quantity of central interest, which has not been studied widely in previous simulations, is $S_{NN}(0)$, defined by

$$S_{NN}(0) = 1 + (1/\rho) \sum_{ij} \rho_i \rho_j \hat{h}_{ij}(0) \quad (17)$$

where $\rho = \sum \rho_i$, and the caret again denotes Fourier transform. Equation 17 is, however, just another form of eq 1, but one which is more convenient for study via integral equations.

The connection of this quantity to thermodynamics is given most simply by using temperature, chemical potential of the solvent, and electrolyte concentration c as the independent variables.¹² At constant temperature

$$S_{NN}(0)^{-1} = 1 + d \ln \gamma_{\pm} / d \ln c \quad (18)$$

which is a form of the “compressibility” equation.^{12,25,34} Therefore, eq 18 is another potential route for calculating the mean activity coefficient of electrolyte solutions.

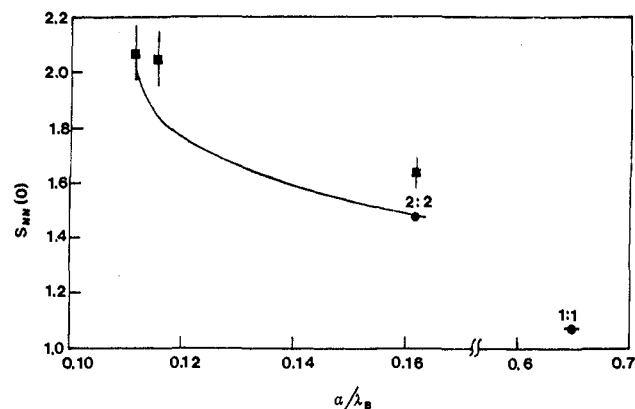


Figure 2. The quantity $S_{NN}(0)$ as a function of inverse reduced Bjerrum length a/λ_B ($a = 0.462$ nm). The solid lines are obtained from the HNC approximation, and the results corresponding to 1:1 and 2:2 electrolytes are indicated as filled circles. The grand canonical results are given as filled squares, with the error bars indicating numerical uncertainty.

One interesting fact is that a combination of eq 17 and 18 does not yield the Debye–Hückel limit for $\ln \gamma_{\pm}$ if one uses the familiar linearized form of the pair correlation function, $g_{ij} \approx 1 - z_i z_j \beta \phi_j$, where ϕ_j is the average electrostatic potential of ion j . Due to the derivative, the correct limit is obtained by including the next term in the series expansion.

It should be mentioned that eq 18 is a direct route for comparison with experimental data. The right-hand side is proportional to the diffusion coefficient, which can be measured.⁴⁰ Hence, there is no need to integrate the experimental data to obtain $\ln \gamma_{\pm}$ prior to comparison with the theory.

For the hard and soft models, the numerical values of $S_{NN}(0)$ are given in Tables I–III, together with error estimates. In addition, this quantity is plotted in Figure 1 as a function of the square root of the electrolyte concentration. Together with the grand canonical Monte Carlo data (symbols), we have included the predictions of the HNC integral equation (solid line) for the soft-sphere model. In Figure 1 the GCMC data for the charged hard-sphere fluid at $\lambda_B = 2.857$ nm are denoted by filled circles, and the results for the equivalent soft-sphere model are denoted by open circles. The error bars are also indicated in Figure 1.

As one may expect from previous studies,²⁸ for both hard and soft models the calculations yield similar results for $S_{NN}(0)$. However, the predictions of the HNC approximation are in only semiquantitative agreement with the GCMC data for $S_{NN}(0)$. In the range of concentrations around 0.07 M (1 M = 1 mol dm⁻³), the discrepancies for 2:2 electrolytes are considerably larger than the numerical errors of the methods. It is interesting to note that the HNC approximation underestimates the fluctuations, and therefore also $S_{NN}(0)$ for this region of parameters and concentrations. Like any approximate theory, the HNC approximation is “internally inconsistent” in that the “virial” and the “compressibility” pressures disagree markedly for 2:2 electrolytes. An additional measure of this effect is demonstrated by the fact that an approximate value of $S_{NN}(0)$ at the electrolyte concentration 0.0625 M, obtained via the “virial” route, is 1.62, in fortuitously good agreement with the simulation data.

The long-wavelength limit of the partial structure factor for particle number fluctuations $S_{NN}(0)$ is an important quantity in the theory of simple liquids, where it is related simply to the isothermal compressibility. In particular, an absolute condition for thermodynamic stability is $S_{NN}(0) > 0$. By studying this quantity, a first indication of the existence of an unusual, very low density “critical point” for dilute solutions of the charged hard spheres was discovered by Stell, Wu, and Larsen.²⁰ For molten salts, an HNC study of this quantity has been presented by Abernethy and Gillan.³⁵ They studied $S_{NN}(0)$ as a function of T^* at two different reduced densities. Below a certain reduced

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(40) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*; Reinhold Publishing: New York, 1958.

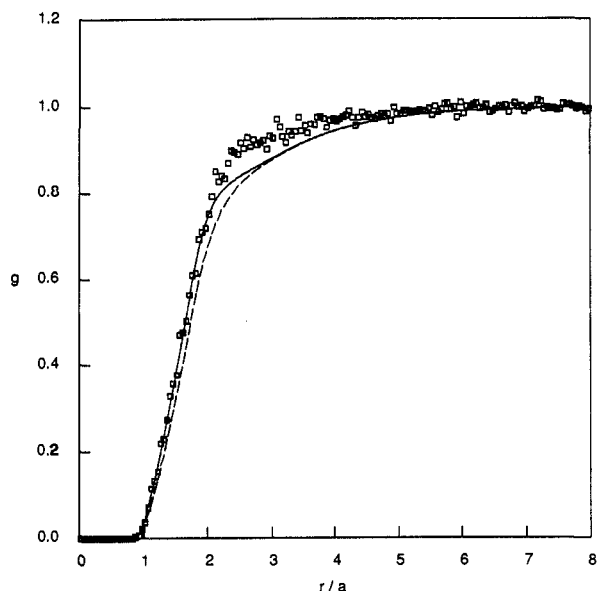


Figure 3. The correlation functions for like ions ($g_{--} = g_{++}$) for the 2:2 model electrolyte (Run 2 of Table III), namely at the concentration 0.0624 M. The symbols here represent the Monte Carlo data, the solid line is the HNC approximation, and the broken line is the IPY approximation.¹⁹

temperature, they were unable to obtain convergent solutions of the HNC approximation, even though a powerful basis set algorithm had been used. The authors interpreted this as a possible spinodal decomposition of the molten salt into two fluid phases. Recently, the examination of the HNC approximation has been extended to highly asymmetric electrolytes, and a similar conclusion concerning spinodal decomposition has been reached.⁴¹

Our results for $S_{NN}(0)$ as a function of the inverse reduced Bjerrum length a/λ_B are shown in Figure 2, for the electrolyte concentration of approximately 0.0625 mol/dm³. The predictions of the HNC approximation are included as the solid line, and the filled squares are the grand canonical Monte Carlo data for Runs 2, 7, and 9 of Table III. One observes that the fluctuations in ion number get very large around $a/\lambda_B = 0.112$, and in fact we have found it impossible to obtain fully convergent HNC solutions below this value. Although a sharp increase in $S_{NN}(0)$ is observed around this value, the HNC approximation actually *underestimates* the true value of $S_{NN}(0)$ in this region of parameters, whereas earlier work on asymmetric electrolytes strongly suggests that it overestimates fluctuations.⁴¹ In our view, the HNC theory leads to spurious predictions of spinodal decomposition.

For a simple one-component fluid, an extensive numerical study of the critical behavior of the HNC approximation has been published recently by Poll and Ashcroft.⁴² Although this study focused on a "Lennard-Jones-like" double Yukawa potential, with very short range interactions, our Figure 2 above closely resembles Figure 2 of that study.⁴² These authors concluded that there is in fact no true critical point in the HNC approximation, since $S(0)$ does not actually diverge on the critical isochore; however, there is a locus of temperatures on which $S(0)$ is finite, but below which no physical solution to the HNC approximation exists. A similarly complete numerical examination of the two component Coulombic system would be even more demanding, due to the long-range forces involved, and to our knowledge it has not been published. It would yield important information about the ability of the HNC approximation to describe critical phenomena.

C. Pair Correlation Functions. Finally it is worthwhile examining the microscopic correlations between ions, since these correlations are responsible for the macroscopic behavior of the system. By comparison with the simulations, the accuracy of the HNC approximation is inconsistent, and it varies with the size

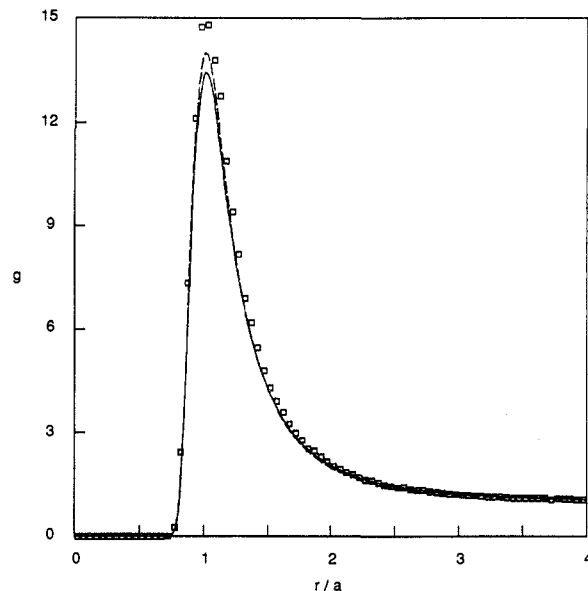


Figure 4. The correlation function for unlike ions $g_{+-}(r)$ for the same electrolyte as in Figure 3 (lines and symbols have the same meaning).

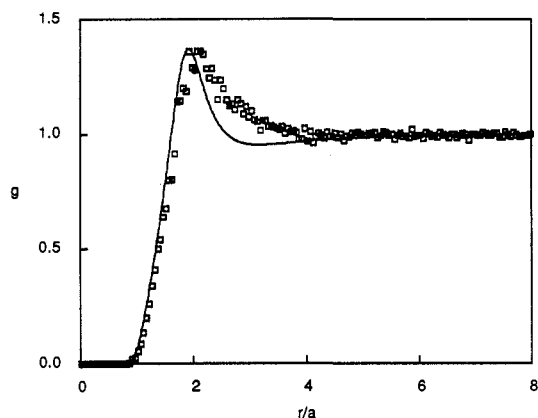


Figure 5. The correlation functions for like ions for the strongly interacting electrolyte Run 7 of Table III, namely the low dielectric solution at 0.0628 M. Lines and symbols have the same meaning as in Figure 3.

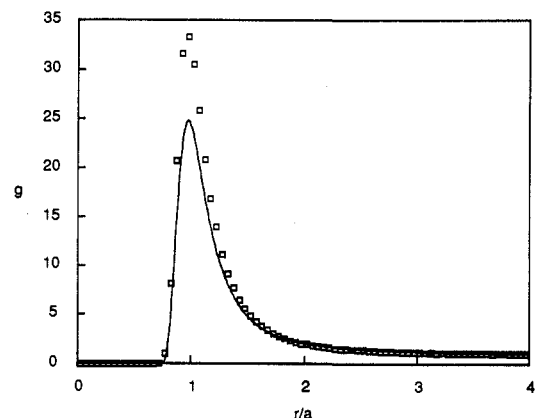


Figure 6. The correlation function for unlike ions $g_{+-}(r)$ for Run 7 of Table III (lines and symbols have the same meaning as in Figure 3). Note the strong ordering in this electrolyte.

of the ions, dielectric constant, and concentration of electrolyte. We will illustrate this in three examples shown in the figures below. The main point is that an approximation whose accuracy varies so widely is not useful.

In Figure 3 we plot the correlation function g_{++} or g_{--} for like ions as a function of a distance r , obtained by both the GCMC simulations (symbols) and the HNC theory (solid line). These

(41) Belloni, L. *Phys. Rev. Lett.* **1986**, *57*, 2026.

(42) Poll, P. D.; Ashcroft, N. W. *Phys. Rev. A* **1987**, *35*, 5167.

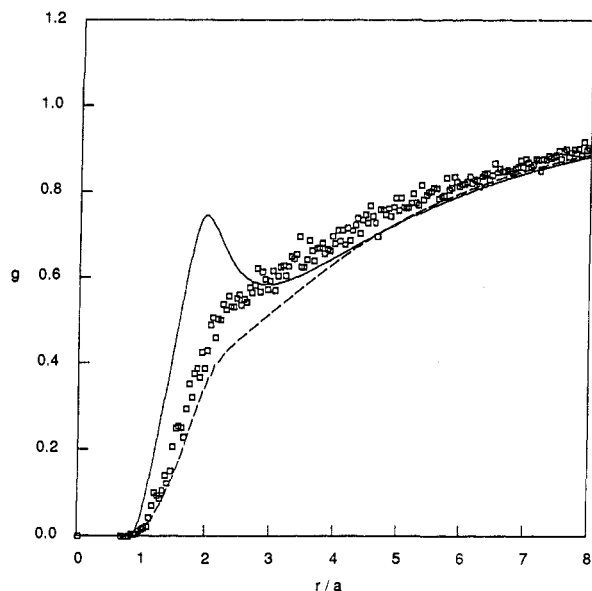


Figure 7. The correlation function for like ions, $g_{++}(r)$ or $g_{--}(r)$, for Run 2 of Table I, namely at a concentration of 0.00535 M. The symbols represent the Monte Carlo data and the solid line is the HNC approximation. The broken line is the new IPY closure.

results are for the 2-2 aqueous electrolytes at 298 K, listed as Run 2 in Table III. The corresponding correlation function for unlike ions g_{+-} is shown in Figure 4. It is clear that the HNC approximation underestimates markedly the accumulation of the positive ions next to the negative ions, as observed previously.^{28,29}

The disagreement between the Monte Carlo data and the HNC approximation is larger for more strongly interacting systems (Run 7 of Table III) as shown in Figures 5 and 6. Especially interesting are the results presented in Figure 5. Both calculations reveal a pronounced peak in the like distribution function, whereas the Poisson-Boltzmann (PB) theory is forced to yield monotonic correlation functions.⁴ A smaller magnitude "bump" in $g_{++}(r)$ has already been observed in the computer simulations of the charged hard-sphere model for 2-2 electrolytes.^{3,4} This feature becomes enhanced at lower screening ($\lambda_B = 4.001$ nm), indicating strong clustering of the ions. However, the HNC approximation does not agree well with the simulation data. There is a shoulder for $r \approx 3a$ in the GCMC correlation function, which is not reproduced by the HNC results. The shoulder may indicate the existence of linear arrays of four ions, probably $+-+-$ structures. In addition, the HNC approximation underestimates grossly the accumulation of positive ions next to negative ions, even more than the aqueous solution (Figure 4) at the same concentration. Hence, while the HNC theory is extremely accurate for 1:1 aqueous electrolytes and is certainly superior to the qualitatively incorrect PB approximation, it cannot be proposed as a viable theory of 2:2 electrolytes or more strongly interacting systems. Conclusions concerning fluctuation quantities, and possible phase transitions, must therefore be treated with great caution.

Related, earlier theoretical studies of aqueous 2-2 electrolytes^{28,29} have shown that HNC approximation (i) underestimates $+-$ ion pairs at the concentrations 0.005, 0.0625, and 0.2 M, (ii) overestimates triple ion clusters ($+++$ or $---$) at 0.005 M, and somewhat overestimates them at 0.0625 and 0.2 M. They also show (iii) that a reasonable estimate for the "bridge" graphs, obtained from computationally intensive diagram evaluations, brings the theory into better agreement with the simulation data. The failure of the (unmodified) HNC approximation to describe accurately the correlation functions in strongly interacting systems is demonstrated again in Figures 5 and 6.

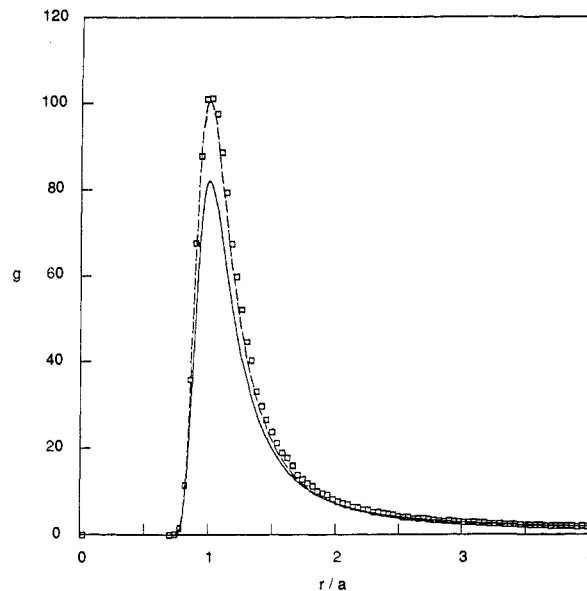


Figure 8. The correlation function for unlike ions, $g_{+-}(r)$, for the same electrolyte as in Figure 7. Lines and symbols have the same meaning as in Figure 7.

Finally, we examine the predictions of a new bridge function closure, to replace the HNC approximation $B_{ij}(r) = 0$, proposed recently by us.¹⁹ In Figures 7 and 8 we present our GCMC and integral equation results for aqueous 2-2 electrolyte (Run 2 of Table I) at a concentration of 0.00535 M. This calculation applied to a set of parameters studied previously.^{28,29} In particular, the HNC correlation function for like ions (cf. Figures 3 and 7 of our work) has been discussed thoroughly. The predictions of the new IPY closure¹⁹ are in general a measurable improvement over the HNC results. For like pairs, the new closure does not have the erroneous peak at $r = 2a$ seen in the HNC but not in the GCMC results. However, it is somewhat of an overcorrection in that now the triple ion clusters are underestimated. For unlike ions, the $+-$ ion pairs are underestimated, but are closer to the simulation data than the HNC results. At higher concentrations $c = 0.0624$ M (Figures 3 and 4), the new closure is approximately the same as the HNC for the like ion pairs, and identical with the HNC approximation for the unlike ion pairs. Thus, the new closure gives results very close to the earlier work with numerically evaluated bridge graphs^{28,29} but is computationally much more practical. Moreover, the new (and the earlier work) studies give the largest corrections at concentrations where the disagreement between HNC and simulation is worst.

4. Conclusions

In summary, GCMC simulations have been used to obtain directly the fluctuation quantities $S_{NN}(0)$, which have been used in approximate integral theories by other authors as a signature of instability. We find no evidence for instability in the range of concentrations studied. The integral equation results confirm that the HNC approximation is not a viable theory for 2:2 electrolytes, due to its highly variable accuracy. However, a new IPY integral equation¹⁹ does not suffer from the pathological features found in the HNC approximation at lower concentrations.

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