

On the Validity of the Debye-Hückel Laws for Dilute Electrolyte Solutions Tested by High-Precision Monte Carlo Simulations.* Towards a Rational Thermodynamics. V

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The restricted, primitive model (RPM) of electrolyte solutions (equally sized, oppositely charged hard spheres in a dielectric continuum) has been investigated by Monte Carlo simulation at five different concentrations corresponding to highly dilute electrolyte solutions. The Bjerrum parameter (the Bjerrum length divided by the contact distance a) was 1.546 in all simulations. In order to make extrapolations to an infinite, thermodynamic system, simulations have been performed using from $N = 32$ to 1000 ions (for each of the five concentrations) in a cubic box with periodic boundary conditions. The Metropolis method has been used with a minimum image approximation for the energy of the configurations. It is necessary to use between one and two million Metropolis configurations in each simulation in order to obtain the precision required in the present study. The excess energies, the excess heat capacities, the values of the radial distribution functions and the osmotic coefficients are calculated. The Helmholtz excess electrostatic free energies are also calculated in the same sampling by the Salsburg-Chesnut method. The method seems to work, although the convergence is very slow when N is large. The mean excess energy $E(ex)/NkT$ converges towards the Debye-Hückel limiting law (DHLL) more rapidly than given by the usual Debye-Hückel (DH) law. The approach to DHLL for the excess electrostatic free energy and especially for the excess heat capacity seem to be quite complex. The peculiar behaviour of the latter two thermodynamic functions is seen as shadows of the negative deviations from the DHLL known to occur for higher values of the Bjerrum parameter (corresponding to 2:2 electrolytes). The radial distribution functions have also been determined. They are well in accordance with the so-called DHX model. The DHX values for the excess energy were also found to be close to the Monte Carlo values. The calculated Monte Carlo values for the osmotic coefficients were close to those given by the Debye-Hückel expression without inclusion of the excluded volume term.

The Debye-Hückel law for electrolyte solutions¹ was derived in a somewhat strange manner, involving a mixture of macroscopic and microscopic points of view. Therefore, the law has been the subject of much debate in the literature

ever since it appeared. Some of the suspicious steps in the theory are the use of the Poisson-Boltzmann equation, in which an equation resulting from time-averaging (the Poisson equation from continuum electrostatics) is combined with a statistical formula (Boltzmann equation), and the linearisation of the Poisson-Boltzmann equation which is obviously not valid close to any selected ion and which leads to absurd results

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such as negative concentrations of co-ions in the neighbourhood of a selected ion. Furthermore, various rather roundabout charging procedures (Debye charging and Güntelberg charging) have to be applied. The latter procedures may be circumvented in a more modern formulation of the DH theory based on radial distribution functions,² but this method does not improve on the other weaknesses of the theory. For example, only the excluded volume of the central ion is taken into account, whereas the ions in the ionic cloud are treated as point particles. In the MSA theory, which is isomorphous with the Debye-Hückel theory, the excluded volume is treated in a more consistent way.³

Actually, an attempt to formulate a rigorous statistical mechanical theory was made some 10 years before Debye and Hückel by Milner,^{4,5} who made extensive calculations on the average virial of a mixture of ions in a dielectric continuum. Debye and Hückel refer to the work of Milner in their 1923 paper, but they do not discuss it. Milner treats point charges – or rather charges with a very small repulsive core in order to avoid collapse – avoiding the use of the Poisson equation. He attacked directly with astonishing courage the problem of the evaluation of the average virial (mean energy) of a central ion in a finite, spherical system of ions. Arranging the ions according to their proximity to the central ion, each sign sequence (+ + - + - - etc.) makes a contribution to the average virial which can be expressed analytically in terms of the gamma function. The contributions for all sequences then have to be summed, but this cannot be done analytically. Finally, the radius of the finite system has to go to infinity, keeping constant the average density of positive and negative ions (the thermodynamic limit).

Milner's calculations are not easily checked, however, and there seem to be some errors and many uncertainties involved. For example, it appears that spherical symmetry of ions around the central ion has been tacitly assumed for all the configurations for which the energy is calculated (Ref. 4, p. 555). This is certainly only true in time average, and the immediate delight at the avoidance of the Poisson equation is hereby somewhat disturbed. Furthermore, the extrapolation to an infinite number of particles seems very uncertain (Ref. 4, figure on p. 577). With the knowledge we now have about the difficulties associated

with long-range electrostatic forces in statistical mechanics, this is not at all surprising. Milner could only treat a very limited number of ions in the sequence – all calculations being made by hand – and he did not suppress surface effects using periodic boundary conditions. Milner's final result for the average virial is expressed in terms of a calculated function of a dimensionless quantity (h) proportional to the cube-root of the concentration. In a footnote (Ref. 4, p. 575), Milner gives an analytical formula for the average virial at very small values of h , but he does not derive it in the text. The average virial should be proportional to h to the power 3/2 in that limit, i.e. to the square-root of the concentration, as in the Debye-Hückel limiting law (DHLL).

In his second paper,⁵ Milner discusses the consequences of his theory for the osmotic pressure and the freezing point depression of electrolyte solutions. A plot of the above-mentioned function of h is given. The function is clearly singular at infinite dilution ($h = 0$), indicating the square-root dependence to be limited to an extremely restricted region. When the analytical result for small h (footnote, Ref. 4) is introduced into e.g. the Milner equation for the osmotic coefficient, results similar to those for the DH limiting law are found, although the proportionality constants unfortunately seem not to be the same.

Milner's work has largely been overlooked, but post-Debye-Hückel authors have tried to remedy the flaws of the DH theory in various ways. Models based on the solution of the non-linear Poisson-Boltzmann equation are now generally abandoned by theoreticians – although not by electrochemists and in surface and colloid science – because such solutions are inconsistent with statistical mechanics. The first attempt to derive the DH limiting law (DHLL) by rigorous statistical mechanics was due to Mayer.⁶ Mayer showed that the DHLL could be derived by summation of certain ring-graph contributions to his expression for the osmotic pressure. However, it is not at all clear why the contributions from all the other graphs may be neglected. Probably the most straightforward way to derive the DHLL is to make reasonable approximations to the so-called BBGKY hierarchy of equations,⁷ but this method also entails inherent assumptions concerning relative smallness of terms.

Equally interesting is the nature of the first deviation from the DHLL when the concentra-

tion of electrolyte is increased. Is this deviation as anticipated by Debye and Hückel? Some of the present authors have shown⁸ that the Debye-Hückel law supplemented with an excluded volume term (DHEV) has the same first powers in its expansion as the Mean Spherical Approximation (MSA) theory and also the theory of Schmitz *et al.* based on expansion of the BBGKY hierarchy in the plasma parameter (Ref. 23, pp. 389–411). Furthermore, experimental data for the mean ionic activity coefficients in the moderately dilute region (0.001 to 0.01 mol dm⁻³ for 1:1 electrolytes) conform well to such models, with quite, though not completely, consistent sums of ionic radii.⁸

Other sources of information come from Monte Carlo studies^{9–20} and from solutions of the HNC integral equation.²¹ When the relative excess energy $E(ex)/E(ex, DHLL)$ is plotted against κa (κ = inverse Debye-Hückel screening length, a = contact distance) for such data, systematic deviations from unity seem to persist down to very small values of κa (see Ref. 19, Fig. 1). The deviations are more marked the higher the Bjerrum parameter B . The Bjerrum parameter is defined as the ratio between the Bjerrum length and the contact distance. We have

$$B = z^2 e_0^2 / (4\pi\epsilon kTa) \quad (1)$$

for a symmetric ($z:z$) electrolyte in a medium with absolute permittivity ϵ . In eqn. (1), e_0 is the unit charge, k is Boltzmann's constant and T is the absolute temperature. HNC calculations and Monte Carlo (MC) calculations support each other, and they seem to deviate from the values given by the extended theory of Debye and Hückel taking into account the contact distance a . For 2:2 electrolytes ($B \approx 7$), the MC calculations of Rogde and Hafskjold¹⁸ suggest that the direction of deviation from the DHLL at very small concentrations may even be the opposite of that predicted by the extended DH law! Their studies were made with only 216 ions, but the energies were calculated by the Ewald method. However, apart from the results given in a preliminary paper,¹⁹ neither MC nor HNC calculation have been performed for 1:1 electrolytes ($B \approx 1.5$) at extreme dilutions in order to test the DHLL and the first deviation from DHLL.

Experimentally, the validity of the limiting law

is not so clear cut as many think. It is quite difficult to measure EMF values of electrochemical cells with a *repeatability* much less than ± 0.1 mV. Furthermore, normal oxidation potentials are normally found by extrapolation procedures *assuming* the extended law of Debye and Hückel to be valid. At least, it is assumed that the first deviation from DHLL has the same power in the ionic strength as predicted by the extended DH law. Therefore, the electrochemical verifications of DHLL are somewhat circuitous. Probably the most careful experimental studies ever performed were made by N. J. Anderson, who studied HCl solutions with hydrogen and Ag/AgCl electrodes down to $3 \cdot 10^{-5}$ mol/dm³,²² where Nernst ideality may be assumed. His results are said to corroborate the DHLL for HCl solutions, but some circuitry still seems to be involved in his procedures for the determination of the standard electrode potential difference. Furthermore, the concentrations of the measuring solutions were given on the basis of dilution of a stock solution. They were not independently controlled afterwards by other means, e.g. conductometry. For this reason we are presently trying to repeat these experiments using high-precision measuring equipment in cooperation with the authorized pH-calibration department at Radiometer A/S. Measurements of heats of dilution by precision calorimetry are sometimes claimed to be the best test of DHLL, but the monograph of Falkenhagen (Ref. 23, Table 23, p. 146) reveals considerable uncertainty also for this method.

In short, DHLL as well as the first deviation from DHLL still remain to be studied carefully, both theoretically and experimentally. In the present paper we continue the Monte Carlo (MC) calculations of the excess energy, the electrostatic Helmholtz free energy and the excess heat capacity for the restricted primitive model (RPM) at a very low concentration and a Bjerrum parameter $B = 1.546$ which we have reported on in previous publications.^{19,20} The radial distribution functions are also calculated (with some inaccuracy). From the excess energy and the values of the radial distribution functions at contact, the osmotic coefficients are also calculated. The calculations show that the extensions of DHLL which are used in practical electrochemistry today are somewhat incorrect, since they do not represent rigorous statistical-mechanical values for the RPM. As a consequence, the contact distances

fitted to activity coefficient data for dilute electrolytes by comparison with Debye-Hückel Excluded Volume theory (DHEV, Ref. 8) will probably be too high.

Method

Canonical ensemble Monte Carlo calculation of the excess energy is normally performed by the Metropolis method,²⁴ where one randomly chosen particle is moved at a time in a random fashion. The move is accepted if the energy goes downhill and accepted in proportion to the factor $\exp(-\Delta U/kT)$ in the opposite case. It is rejected in proportion to $1-\exp(-\Delta U/kT)$, and the previous configuration is sampled once more. This constitutes an ergodic Markov process with equilibrium sampling properties as prescribed in statistical mechanics (detailed balance of all admissible microscopic transitions). The method is introduced in order to avoid sampling over a lot of states with high energy and extremely low statistical weight. In order to avoid surface effects, periodic boundary conditions are used. That is, we consider $N/2$ positive ions and $N/2$ negative ions in a cubic box with edge length L measured in terms of ionic diameters. The box is surrounded by 26 similar boxes with shadow particles moving like the original ones. Each particle in the middle box is assumed to interact with all particles in a cubic box with the selected particle in the center and with an edge length equal to L (*minimum image approximation*). In this way, a particle never "discovers the cheating" introduced by periodicity. Nevertheless, the periodicity affects indirectly the thermodynamic results for finite values of N . Therefore, a way has to be found to extrapolate the results to an infinite number of particles in the central box. As mentioned, this problem was also one that confronted Milner.^{4,5}

In the computer programme we have constructed, the sampling may be begun starting from two widely different initial conditions. For 64, 216, 512 and 1,000 particles (corresponding to an even number of ions – 4, 6, 8 and 10 – in a direction parallel to the edge of the box) we started with a simple lattice configuration, for which the initial energy is rapidly calculated. For all the other values of N mentioned in the present paper a lattice was constructed with 64 ions for the values $N = 32, 34, 36, 44$ and 50 ions, and the excess number of ions was removed evenly, re-

specting electroneutrality. For $N = 68, 80, 100$ and 150 ions, a lattice with 216 ions were used with random removal; for $N = 350$ the 512-lattice was used, and for $N = 700$ the 1000-lattice was used.

The computing time for each configuration is roughly proportional to N rather than to the square of N . The reason is that each configuration in the Metropolis sampling is not a "new" configuration, since only one ion is moved at a time. We then have to calculate only the new interaction of the moved ion with the rest of the ions. Due to symmetry in the integral kernel with respect to interchange of the particles, the precision is roughly the same with the same number of configurations regardless of the number of particles. This is the great strength of Monte Carlo calculations of multiple integrals.

It has been said that a rejection rate around 50% (sum of hard sphere overlaps and electrostatic Boltzmann rejections) is optimal, and the maximum change in position in any of the three directions (D) is adjusted to give a rejection rate around this value. However, with the values of the dimensionless concentrations $\rho^* = N/L^3$ studied in the present paper, the rate of rejection is only about 10% even with the maximum reasonable choice of D , namely $L/2$. Therefore, there is no reason not to choose $D = L/2$ to obtain the maximum "stirring rate". In the present study it was found necessary to take account of a total number of configurations exceeding considerably that in any calculations made before, in order to obtain reliable values of the thermodynamic quantities. In order to avoid cumulating numerical errors, the total energy was recalculated for every 5000 configurations. The random number generator was also reseeded for every 5000 configurations.

We used two different types of computers in this study (with two different random number generators). Most of the calculations were run in parallel on four to eight 8–10 MHz IBM-compatible Taiwanese AT computers (trademark COPAM) with INTEL 80286 processor and with an INTEL 80287 mathematics co-processor, but some of the calculations were made on a VAX 11/750 installed at Radiometer A/S. The programming languages were compiling Turbo-87 Pascal for the AT-computers (16 significant digits, exponents between -308 and $+308$ powers of ten) and compiling VAX 11 Pascal for the

VAX computer (7–16 digits and exponents between -38 and $+38$ powers of ten). No differences between the results from the two computer systems, apart from the unavoidable statistical differences, were ever observed.

The standard reference works on MC calculations for the RPM are the papers by Card and Valleau,¹¹ and by Rasaiah *et al.*¹² In these papers, the excess Helmholtz free energy $F(\text{ex})$ is not directly calculated. We wished to calculate this quantity, however, to test the DHLL and the first deviation from DHLL, not only for the excess energy (equal to the excess Gibbs free energy at infinite dilution), but also for the excess Helmholtz free energy (equal to $2/3$ of the excess energy at infinite dilution). The value of $F(\text{ex})/NkT$ can be obtained on the same sampling as $E(\text{ex})/NkT$ by the method of Salsburg and Chesnut.²⁵⁻²⁷ This procedure has been criticised in a review paper of Wood²⁸ on MC studies of simple liquid models. The method is said to converge extremely slowly and to be without value for hard core systems. However, it may be rigorously shown¹⁹ that for the case of a hard sphere potential with some “soft potential”, the Salsburg-Chesnut method yields the excess Helmholtz free energy over and above the free energy of the same system with hard sphere interactions only. For electrostatic systems one should obtain the *electrostatic Helmholtz free energy* ($\Delta F(\text{ex})/NkT$) in this way after infinitely many samplings. However, the meaning of “infinitely many” in practical terms has to be established experimentally. In the present study we show that acceptable values of $\Delta F(\text{ex})/NkT$ may be obtained after taking account of 1–2 million Metropolis configurations by the Salsburg-Chesnut method in the very dilute systems treated here. However, the values are less reliable than the values of $E(\text{ex})/NkT$. This is not strange, since the Metropolis method is optimized for finding $E(\text{ex})/NkT$. For finding $\Delta F(\text{ex})/NkT$ the method is not at all optimal, since heavy emphasis is laid on very seldomly occurring configurations with high configurational energy in that one samples values of $\exp(+U_N/kT)$ over the Metropolis states dominated by low U_N/kT , where U_N is the electrostatic energy of some configuration in N ions. The advantage of the Salsburg-Chesnut method is that the Helmholtz free energy is obtained in the same sampling as the excess energy. The excess heat capacity at constant volume $C_V(\text{ex})/Nk$ is also obtained during

the Metropolis sampling from the variance of the energy fluctuations.

An alternative to the Salsburg-Chesnut method for $\Delta F(\text{ex})/NkT$ would be time-consuming multistage sampling methods such as described by Valleau and Card,¹³ or the “umbrella sampling” technique described by Valleau and Torrie.³⁰ Alternatives to the minimum image (MI) approximation for the configurational energy are spherical cut-off (SCO) or Ewald summation (ES).²⁹ SCO can be left out, since it has been shown to yield poor results (this is another reason for the failure of Milner’s early calculations!). ES is a generalisation of infinite Madelung summation. The total energy is evaluated for an infinity of mirror lattices at each stage. Some authors think that ES yields a quicker extrapolation to the thermodynamic limit ($N = \infty$). However, the method is more time-consuming than the MI method for each N , and Valleau and Whittington²⁹ have criticised the ES method for making false long-range correlations between particles.

The radial distribution functions $g_{++}(r) = g_{--}(r)$ and $g_{+-}(r)$ have been sampled simultaneously with $E(\text{ex})/NkT$, $\Delta F(\text{ex})/NkT$ and $C_V(\text{ex})/Nk$ from $r = a$ to $r = 4a$ in 60 spherical shells of thickness $0.05a$ around each of the N ions. In some cases, 60 shells of thickness $0.1a$ were used (range $r = a$ to $r = 7a$). The contact values $g_{++}(a) = g_{--}(a)$ and $g_{+-}(a)$ may hereby be found by polynomial extrapolation, with some uncertainty. Fortunately, the precise values of the contact values are not very important for the evaluation of osmotic coefficients at the high dilutions studied here. For precise extrapolation to the thermodynamic limit of $E(\text{ex})/NkT$, $\Delta F(\text{ex})/NkT$ and $C_V(\text{ex})/Nk$, a large number of values of N is used for each concentration, and the limit is obtained by polynomial extrapolation to $1/N = 0$ (degree 1 or 2 in the variable $1/N$ at the 95% significance level). The polynomials used are least-squares polynomials orthogonally generated over the set of abscissae. In such polynomials, each new coefficient of the orthogonal polynomial of the highest degree is statistically independent of the previous coefficients, so that the significance of the new coefficient can be evaluated by a Student’s *t*-test at a selected level of significance.³¹⁻³³

Table 1. Monte Carlo values obtained for $B = 1.546$ (RPM).

N^a	Millions of configs.	$-E(\text{ex})/NkT$ $\times 100$	$-\Delta F(\text{ex})/NkT$ $\times 100$	$+C_V(\text{ex})/Nk$ $\times 100$	$g_{+-}(a)$	$g_{++}(a)$ $= g_{--}(a)$	$(1-\Phi)$ $\times 100^b$	Com- puter
$q^* = 2 \cdot 10^{-5}$								
64	1.5	1.836	1.549	0.5439	$3.43 \pm .13^c$ (3rd) ^d	$0.272 \pm .028^c$ (2nd)	0.6042	AT
100	1.955	1.746	1.423	0.5965	$3.69 \pm .21$ (2nd)	$0.357 \pm .040$ (1st)	0.5735	AT
150	1.5	1.687	1.348	0.6139	$3.39 \pm .20$ (2nd)	$0.142 \pm .052$ (2nd)	0.5549	AT
216	2.36	1.625	1.249	0.6634	$4.21 \pm .28$ (3rd)	$0.278 \pm .035$ (1st)	0.5323	AT
350	1.44	1.592	1.171	0.7061	$3.92 \pm .25$ (2nd)	$0.087 \pm .050$ (2nd)	0.5222	AT
512	1.625	1.565	1.140	0.7281	$4.47 \pm .29$ (3rd)	$0.289 \pm .035$ (1st)	0.5117	AT
700	1.49	1.552	1.125	0.7491	$5.55 \pm .32$ (4th)	$0.299 \pm .036$ (1st)	0.5051	AT
1000	1.715	1.542	1.040	0.8347	$4.62 \pm .25$ (3rd)	$0.298 \pm .031$ (1st)	0.5037	AT
$q^* = 6.4 \cdot 10^{-5}$								
32	1.1	3.297	2.819	0.9208	$2.99 \pm .16$ (2nd)	$0.296 \pm .027$ (1st)	1.077	AT
44	1.5	3.174	2.642	1.014	$4.06 \pm .17$ (3rd)	$0.178 \pm .031$ (2nd)	1.030	AT
64	2.0	3.037	2.458	1.081	$4.56 \pm .16$ (4th)	$0.227 \pm .023$ (2nd)	0.9802	AT
100	1.625	2.916	2.292	1.137	$4.19 \pm .18$ (2nd)	$0.217 \pm .026$ (1st)	0.9425	AT
150	1.845	2.869	2.212	1.184	$5.10 \pm .11^c$ (8th)	$0.215 \pm .028^c$ (4th)	0.9207	AT
216	1.015	2.806	2.098	1.235	$3.18 \pm .13$ (2nd)	$0.163 \pm .045$ (2nd)	0.9129	AT
350	1.2	2.745	2.054	1.267	$3.38 \pm .10^c$ (4th)	$0.310 \pm .023^c$ (2nd)	0.8903	AT
512	1.21	2.730	1.965	1.330	$4.44 \pm .21$ (3rd)	$0.328 \pm .026$ (1st)	0.8780	AT
700	1.225	2.709	2.001	1.340	$4.15 \pm .13^c$ (4th)	$0.263 \pm .027^c$ (3rd)	0.8734	AT
$q^* = 1.25 \cdot 10^{-4}$								
32	1.8	4.391	3.680	1.366	$4.28 \pm .12$ (4th)	$0.201 \pm .018$ (2nd)	1.405	AT
44	1.4	4.236	3.468	1.442	$3.99 \pm .12$ (3rd)	$0.187 \pm .037$ (3rd)	1.357	AT
64	0.92	4.058	3.213	1.553	$3.72 \pm .18$ (3rd)	$0.313 \pm .028$ (1st)	1.300	AT
100	1.15	3.958	3.069	1.612	$3.75 \pm .12$ (4th)	$0.249 \pm .027$ (2nd)	1.267	AT
150	2.1	3.905	2.962	1.667	$4.14 \pm .08^c$ (6th)	$0.252 \pm .017^c$ (3rd)	1.244	AT
216	1.015	3.834	2.840	1.748	$5.27 \pm .17$ (6th)	$0.109 \pm .043$ (4th)	1.208	AT
512	1.5	3.744	2.745	1.771	$4.00 \pm .11$ (4th)	$0.304 \pm .026$ (2nd)	1.192	AT
700	1.535	3.743	2.779	1.859	$4.99 \pm .12^c$ (7th)	$0.251 \pm .017^c$ (3rd)	1.179	AT

(contd)

Table 1 (contd).

$N^{\#}$	Millions of configs.	$-E(\text{ex})/NkT$ $\times 100$	$-\Delta F(\text{ex})/NkT$ $\times 100$	$+C_V(\text{ex})/Nk$ $\times 100$	$g_{+-}(a)$	$g_{++}(a)$ $= g_{--}(a)$	$(1-\Phi)$ $\times 100^b$	Com- puter
$q^* = 2.5 \cdot 10^{-4}$								
32	1.92	5.891	4.832	2.008	$4.28 \pm .10$ (4th)	$0.259 \pm .015$ (2nd)	1.845	AT
44	1.03	5.731	4.577	2.142	$3.78 \pm .12$ (3rd)	$0.227 \pm .019$ (2nd)	1.805	AT
64	1.06	5.539	4.318	2.244	$3.42 \pm .09$ (2nd)	$0.254 \pm .021$ (2nd)	1.750	AT
100	1.015	5.437	4.139	2.325	$4.17 \pm .11$ (4th)	$0.221 \pm .025$ (3rd)	1.697	AT
150	1.325	5.341	3.995	2.437	$3.95 \pm .09$ (5th)	$0.241 \pm .013$ (3rd)	1.671	AT
216	1.635	5.290	3.855	2.474	$4.90 \pm .18$ (5th)	$0.270 \pm .015$ (2nd)	1.628	AT
512	1.47	5.186	3.785	2.531	$4.31 \pm .10$ (5th)	$0.226 \pm .018$ (2nd)	1.610	AT
700	1.065	5.178	(3.915) ^e	2.446	$4.02 \pm .12^c$ (6th)	$0.255 \pm .018^c$ (3rd)	1.614	AT
$q^* = 5 \cdot 10^{-4}$								
32a	1.00	7.864	6.312	2.896	$4.86 \pm .11$ (6th)	$0.297 \pm .018$ (2nd)	2.351	VAX
32b	2.04	7.838	6.288	2.861	$3.81 \pm .05$ (4th)	$0.245 \pm .012$ (2nd)	2.400	AT
34	1.03	7.840	6.275	2.900	$3.81 \pm .07$ (3rd)	$0.258 \pm .015$ (2nd)	2.400	AT
36	1.035	7.793	6.211	2.879	$3.70 \pm .07$ (4th)	$0.207 \pm .022$ (3rd)	2.393	AT
44a	1.00	7.686	6.012	3.021	$3.78 \pm .09$ (4th)	$0.250 \pm .011$ (2nd)	2.351	VAX
44b	1.00	7.694	6.025	3.033	$3.71 \pm .07$ (3rd)	$0.250 \pm .015$ (2nd)	2.357	VAX
50	1.19	7.598	5.903	3.041	$3.89 \pm .07$ (4th)	$0.270 \pm .013$ (2nd)	2.315	AT
64	1.00	7.559	5.845	3.121	$4.55 \pm .13$ (6th)	$0.287 \pm .017$ (2nd)	2.266	VAX
68	1.00	7.532	5.784	3.158	$4.25 \pm .10$ (6th)	$0.281 \pm .012$ (2nd)	2.273	AT
80	0.97	7.465	5.693	3.162	$3.83 \pm .09$ (4th)	$0.264 \pm .014$ (2nd)	2.274	AT
100	1.00	7.411	5.342	3.220	$3.69 \pm .08$ (3rd)	$0.242 \pm .014$ (2nd)	2.264	VAX
512a	0.50	7.180	(5.278) ^e	3.502	$4.13 \pm .10$ (3rd)	$0.268 \pm .024$ (2nd)	2.163	VAX
512b	1.00	7.164	5.051	3.523	$3.99 \pm .08$ (4th)	$0.245 \pm .017$ (2nd)	2.166	VAX
1000	1.00	7.149	(5.687) ^e	3.466	$3.69 \pm .08$ (3rd)	$0.221 \pm .023$ (3rd)	2.178	VAX

^aa,b after number of ions stand for independent simulations. ^bThe osmotic coefficients are calculated by eqn. (5) using the mean contact values given in the two preceding columns. ^cThe range in which radial distribution functions are sampled is from a to 7a. Normally, the range is from a to 4a. ^dThe degree of the most significant polynomial at the 95% level fitting the 60 sampled values of the radial distribution functions is given in parentheses. ^eThe value is deleted, because the number of configurations is probably not sufficient for convergence.

Results

The RPM has only two parameters: The Bjerrum parameter B given by eqn. (1) and the dimensionless total ion concentration q^* given by eqn. (2):

$$q^* = N/L^3 = \rho a^3 \quad (2)$$

(L is the edge length of the central cubic box measured in units of a , ρ is the total concentration of ions in particles per m^3). The Bjerrum parameter encompasses variation in charge type (1:1, 2:2, 3:3 electrolytes etc.), in solvent (ϵ) in temperature (T) and in contact distance (a). All calculations in the present paper and in the two preceding papers^{19,20} have been performed with $B = 1.546$. By elimination of a from eqns. (1) and (2) and by change of units, the salt concentration in mol salt per dm^3 (C_s) for $B = 1.546$ is given by

$$C_s = (1.7428 \cdot 10^{-5}) \cdot (q^*) \cdot [\epsilon_r \cdot (T/298.16)/(z^6)] \quad (3)$$

In water at 298.16 K, the relative permittivity is $\epsilon_r = 78.54$ and we have:

$$C_s = 8.4435 \cdot q^*/(z^6) \quad (4)$$

The lowest dimensionless concentration we have considered here amounts to $q^* = 2 \cdot 10^{-5}$ at $B = 1.546$. For a 1:1 electrolyte in water this corresponds to a salt concentration $C_s = 1.689 \cdot 10^{-4}$ mol dm^3 , which is normally considered as an extremely low concentration for which the DHLL should be valid. (Note that for a 2:2 electrolyte, $z = 2$, the concentration considered is 64 times lower, i.e. $2.638 \cdot 10^{-6}$ mol dm^3).

The Monte Carlo runs are summarized in Table 1. The first 5000 configurations have been omitted from the samplings. This omission has significance for only a few of the heat capacities starting with an irregular lattice with a large number of particles (e.g. $N = 700$), where initially strongly deviating samplings are often found (in a single case with $N = 1000$ and $q^* = 2 \cdot 10^{-5}$ highly deviating sampling of the heat capacity suddenly occurred after around 1.3 million configurations, most probably making the cumulated value of $C_v(ex)/Nk$ too high during several hundreds of thousands of subsequent configurations. Stochastically, such a deviation should be extremely unlikely, and it was also the only one found in the whole data material).

The excess osmotic coefficient, $\Phi - 1$, is calculated for each simulation using the pressure equa-

Table 2. Extrapolated thermodynamic quantities for $B = 1.546$ (RPM).

q^*	κa	$-E(ex)/NkT$ $\times 100$	$-\Delta F(ex)/NkT$ $\times 100$	$+C_v(ex)/Nk$ $\times 100$	$(1 - \Phi)$ $\times 100$
0	0	0	0	0	0
$2 \cdot 10^{-5}$	$1.9712 \cdot 10^{-2}$	$1.5126 \pm .0042$ (2nd) ^a	$1.021 \pm .019$ (2nd)	$0.822 \pm .025$ (2nd)	$0.4927 \pm .0020$ (2nd)
$6.4 \cdot 10^{-5}$	$3.5261 \cdot 10^{-2}$	$2.6776 \pm .0079$ (2nd)	$1.928 \pm .016$ (2nd)	$1.387 \pm .013$ (3rd, 90 and 95 %) $1.348 \pm .017$ (2nd)	$0.8656 \pm .0035$ (2nd)
$1.25 \cdot 10^{-4}$	$4.9279 \cdot 10^{-2}$	$3.728 \pm .012$ (1st)	$2.722 \pm .017$ (1st)	$1.852 \pm .023$ (2nd)	$1.1695 \pm .0057$ (2nd)
$2.5 \cdot 10^{-4}$	$6.9691 \cdot 10^{-2}$	$5.140 \pm .013$ (2nd)	$3.734 \pm .023$ (1st, 95 %) $3.684 \pm .025$ (2nd, 90 %)	$2.524 \pm .019$ (1st)	$1.5877 \pm .0065$ (2nd)
$5 \cdot 10^{-4}$	$9.8559 \cdot 10^{-2}$	$7.118 \pm .012$ (2nd)	$5.114 \pm .053$ (1st)	$3.527 \pm .063$ (1st)	$2.165 \pm .011$ (1st)

^aDegree of most significant extrapolating polynomial in $1/N$ at the 95 % significance level given in parentheses.

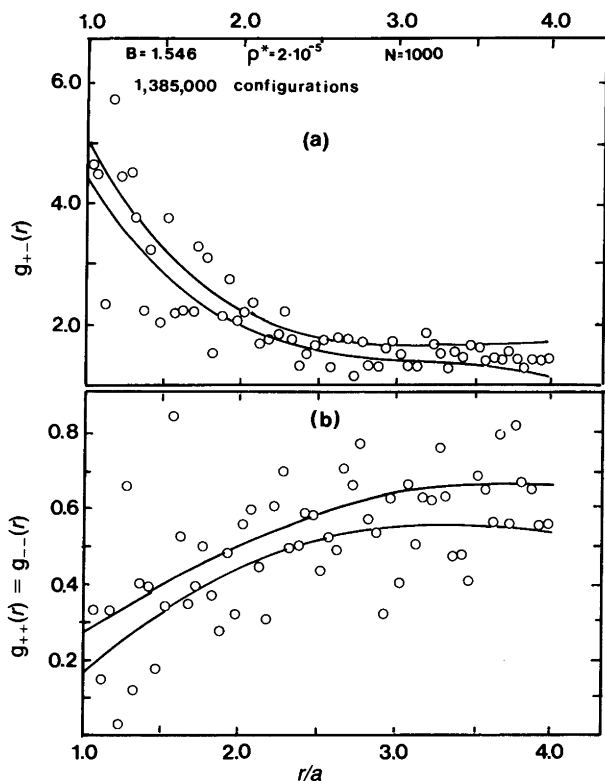


Fig. 1. Radial distribution functions after 1,385,000 configurations with $N = 1000$ ions, $B = 1.546$ and $\rho^* = 2 \cdot 10^{-5}$. Samplings are taken over each of 1000 ions in 60 spherical shells of thickness 0.05 times the contact distance. The scatter is considerable, but the data are improved by polynomial fitting. The abscissa is $(r/a) - 1$. (a) $g_{+-}(r)$, the standard error belt of the smoothed polynomial values is shown. A 3rd degree polynomial is most significant at the 95% level of significance. The contact value is extrapolated to $g_{+-}(a) = 4.73 \pm 0.27$ with the polynomial shown. After 1,715,000 configurations (Table 1), the contact value is 4.62 ± 0.25 . (b) $g_{++}(r) = g_{--}(r)$, 2nd order polynomial most significant at 95%, $g_{++}(a) = g_{--}(a) = 0.217 \pm 0.056$. With a 1st order polynomial, a smaller uncertainty is obtained (0.312 ± 0.038). Comparison with Table 1 shows that a 1st degree polynomial is significant at the 95% level after 1,715,000 configurations. The contact value is then 0.298 ± 0.031 .

tion. For the restricted primitive model (RPM) we have:

$$\Phi - 1 = [E(\text{ex})/3NkT] + (\pi \rho^*/3) \cdot [g_A(a) + g_{+-}(a)] \quad (5)$$

In eqn. (5), $g_A(a) = g_{++}(a) = g_{--}(a)$. As is apparent from Table 1, there is considerable spread in the extrapolated contact values $g_A(a)$ and $g_{+-}(a)$. This is due to the rarely occurring close encounters at high dilution. There is no systematic variation with N . Luckily, the second term in eqn. (5) is small compared to the first at small concentrations. The values of $E(\text{ex})/NkT$, $\Delta F(\text{ex})/NkT$, $C_V(\text{ex})/Nk$ and $\Phi - 1$ have been plotted against $1/N$ and fitted to the most significant least-squares polynomials at the 95% level of significance. The results of the extrapolations to $1/N = 0$ and the standard deviations of the polynomial extrapolations are given in Table 2. The relative error in the excess osmotic coefficient is somewhat greater than the relative error in the excess energy, due to the uncertainty in the

contact values. The electrostatic, negative Helmholtz free energy $-\Delta F(\text{ex})/NkT$ converges more and more slowly when either the concentration or the number of ions increases. The cumulated value of $-\Delta F(\text{ex})/NkT$ tends in such situations to move towards lower values in large jumps occurring very rarely. After a jump, the value increases asymptotically (as a decaying exponential: towards a new, slightly higher value. After many configurations (one million or more), the jumps disappear and the cumulated value stabilizes. When too few configurations are taken, $-\Delta F(\text{ex})/NkT$ will typically be too high. In few cases, the value may be somewhat too low when a large downwards jump has just occurred. A few values of $-\Delta F(\text{ex})/NkT$ have been left out in the extrapolations to $1/N = 0$ since the number of configurations most probably is insufficient.

Fig. 1 shows the sampled radial distribution functions in the range $r = a$ to $r = 4a$ for $N = 1000$ and $\rho^* = 2 \cdot 10^{-5}$ after 1,385,000 configurations. The scatter is considerable because of the high dilution. The data may be somewhat im-

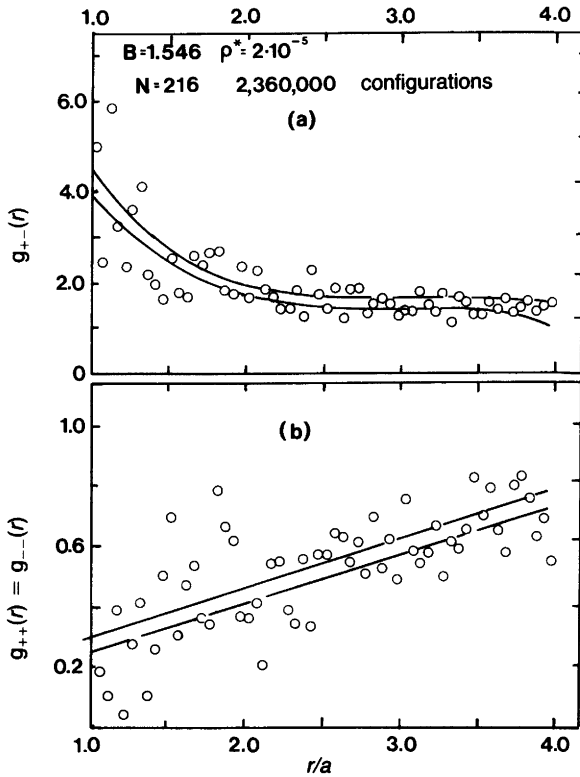


Fig. 2. Radial distribution functions, after 2,360,000 configurations with $N = 216$ ions, $B = 1.546$ and $\rho^* = 2 \cdot 10^{-5}$. In spite of the larger number of configurations, the scatter is about the same as in Fig. 1, since the averaging is not performed with so many particles. The most significant polynomials at 95 % are of 3rd order for $g_{+-}(r)$ and of 1st order for $g_{++}(r) = g_{--}(r)$. Contact values $g_{+-}(a) = 4.21 \pm 0.28$ and $g_{++}(a) = g_{--}(a) = 0.278 \pm 0.035$.

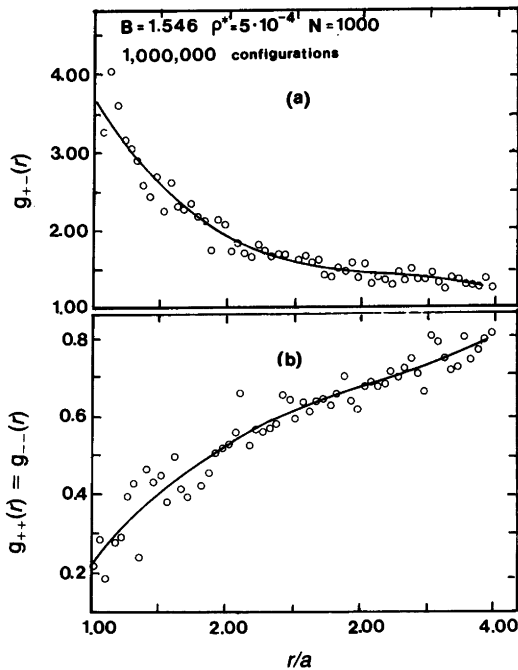


Fig. 3. Radial distribution functions after 1 million configurations for $N = 1000$ ions, $B = 1.546$ and $\rho^* = 5 \cdot 10^{-4}$. They are much better determined than for $\rho^* = 2 \cdot 10^{-5}$ due to the more frequent close encounters at higher concentrations. A 3rd order polynomial is shown for $g_{+-}(r)$ and a 2nd order polynomial for $g_{++}(r) = g_{--}(r)$. Contact values: $g_{+-}(a) = 3.69 \pm 0.08$ and $g_{++}(a) = g_{--}(a) = 0.253 \pm 0.017$.

proved by fitting the 60 points to the most significant least-squares polynomial. The standard error belts of the smoothening polynomial values are also shown in Fig. 1. For the same concentration, but with $N = 216$, the radial distribution functions are shown in Fig. 2 after 2,360,000 configurations. The scatter is still considerable. The scatter is drastically reduced when the concentration increases. Fig. 3 shows the radial distribution functions and the fitting polynomials for $N = 1000$ and $\rho^* = 5 \cdot 10^{-4}$ after 1 million configurations.

Discussion

An extrapolation to an "infinite system" will only be successful if half of the box length for the largest systems is somewhat longer than the effective range of the forces involved. In the present case, the Debye screening length $1/\kappa$ is a measure of the range of the forces involved. The value of κa is given in terms of B and ρ^* by the relationship:

$$\kappa a = \sqrt{4\pi B \rho^*} \quad (6)$$

Since we measure the box length (L) in units of the contact distance (a), we have the requirement:

$$(\kappa a L/2)_{\text{largest system}} = \sqrt{\pi B} \cdot (\rho^*) \cdot \sqrt{N_{\text{max}}} \geq \text{MIN}(7)$$

For $B = 1.546$, $\rho^* = 2 \cdot 10^{-5}$ (worst case) and $\text{MIN} = 3$ or 4 , we obtain $N_{\text{max}} \geq 564$ or 1337 . Therefore, it should be sufficient to choose up to 1000 ions, even in the worst case, in view of the rapid (approximately exponential) decrease of the mean electric potential around an ion.

The extrapolated data of Table 2 may be subjected to further statistical treatment, since smoothening polynomials of the thermodynamic properties as a function of κa may be found. It is important to include the value zero for all the excess quantities at $\kappa a = 0$, so that a total of six concentrations are considered. In the first fits, the Debye-Hückel limiting laws (DHLL) were not assumed to be necessarily valid. The resulting most significant polynomials at the 95 % level are given below:

$$-E(\text{ex})/NkT = 0.7832 \kappa a - 0.6205(\kappa a)^2 \quad (8)$$

$$-\Delta F(\text{ex})/NkT = 0.5734 \kappa a - 0.5208(\kappa a)^2 \quad (9)$$

$$+ C_v(\text{ex})/Nk = 0.4433 \kappa a - 1.9151(\kappa a)^2 + 10.615(\kappa a)^3 \quad (10)$$

$$(1 - \Phi) = 0.2540 \kappa a - 0.3584(\kappa a)^2 \quad (11)$$

The initial slopes predicted from the DHLL in the four cases are $B/2 = 0.7730$, $B/3 = 0.5153$, $B/4 = 0.3865$ and $B/6 = 0.2577$, respectively. The polynomials (8) and (11) correspond quite well with the DHLL, whereas some deviation is observed in the case of the electrostatic Helmholtz free energy and in the case of the excess heat capacity. The deviation of the heat capacity may easily be explained in terms of the considerable covariance between the coefficients of a least-squares polynomial of the third degree. It is of interest that if we force the degree of the least-squares polynomial for $(-\Delta F/NkT)$ vs. κa to be unity, we have a slope very close to the DHLL slope:

$$-\Delta F(\text{ex})/NkT = 0.5229 \kappa a \quad (12)$$

In the next step, we force the least-squares polynomials not only to go through the origin but also to have the correct limiting slope. We obtain the results:

$$-E(\text{ex})/NkT = 0.7730 \kappa a - 0.5038(\kappa a)^2 \quad (13)$$

$$-\Delta F(\text{ex})/NkT = 0.5153 \kappa a + 1.0508(\kappa a)^2 - 10.518(\kappa a)^3 \quad (14)$$

$$+ C_v(\text{ex})/Nk = 0.3865 \kappa a + 1.8467(\kappa a)^2 - 58.91(\kappa a)^3 + 378.94(\kappa a)^4 \quad (15)$$

$$(1 - \Phi) = 0.2577 \kappa a - 0.3944(\kappa a)^2 \quad (16)$$

It is possible to increase the polynomial degree by one without losing the significance, since the initial slope is fixed as well as the initial value. This has been done for $-\Delta F(\text{ex})/NkT$ and for $C_v(\text{ex})/Nk$. A more sensitive plot of $\Delta F(\text{ex})/\Delta F(\text{ex, DHLL})$ vs. κa reveals a systematic (parabolic) deviation from unity. The scatter is considerable, but the plot is certainly not linear in κa . Therefore, a third degree polynomial has been chosen in eqn. (14). A plot of $C_v(\text{ex})/C_v(\text{ex, DHLL})$ vs. κa shows that the fit of a third degree

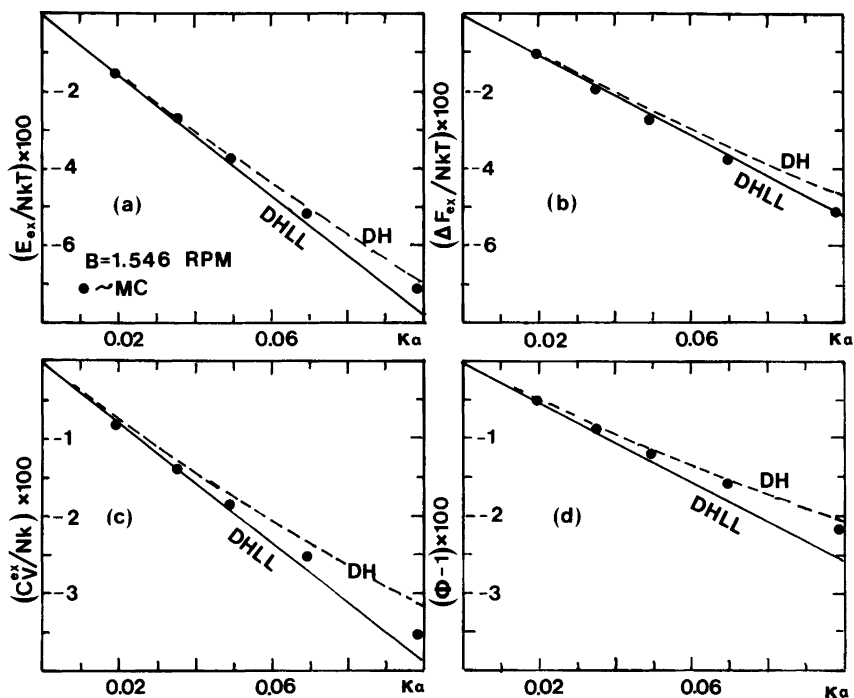


Fig. 4. (a) $E(\text{ex, MC})/NkT$, (b) $\Delta F(\text{ex, MC})/NkT$, (c) $C_v(\text{ex, MC})/Nk$ and (d) $\Phi(\text{MC}) - 1$ vs. κa , showing the approach towards the limiting laws. The Debye-Hückel values (DH) are also shown. On this coarse scale the uncertainty of the MC calculations cannot be seen.

polynomial of this quantity vs. κa is considerably better than the fit of a polynomial of second degree. Thus, a fourth degree polynomial has been selected in eqn. (15). Similar plots were made of $E(\text{ex})/E(\text{ex, DHLL})$ and $(1 - \Phi)/[1 - \Phi(\text{DHLL})]$, but no improvement could be seen on increasing the degree of the polynomial.

Figs 4 (a-d) and Figs 5(a-d) show that the gross features of the present calculations are entirely consistent with DHLL, but the first deviations are apparently *not* in accordance with the laws of Debye and Hückel (DH) in common use in electrochemistry. In our formalism, these laws may be expressed as follows¹⁹:

$$E(\text{ex, DH})/E(\text{ex, DHLL}) = 1/[1 + \kappa a] \quad (17)$$

$$\begin{aligned} \Delta F(\text{ex, DH}) &= B \cdot F(\kappa a) \\ &\approx (B/3)(\kappa a)[1 - (3/4)(\kappa a)] \end{aligned} \quad (18)$$

$$F(\kappa a) \equiv [\ln(1 + \kappa a) - \kappa a + (\kappa a^2/2)]/(\kappa a)^2 \quad (19)$$

$$C_v(\text{ex, DH})/C_v(\text{ex, DHLL}) = 1/[1 + \kappa a]^2 \quad (20)$$

$$\Phi(\text{DH}) - 1 = B \cdot G(\kappa a + \Phi(\text{hard spheres}) - 1) \quad (21)$$

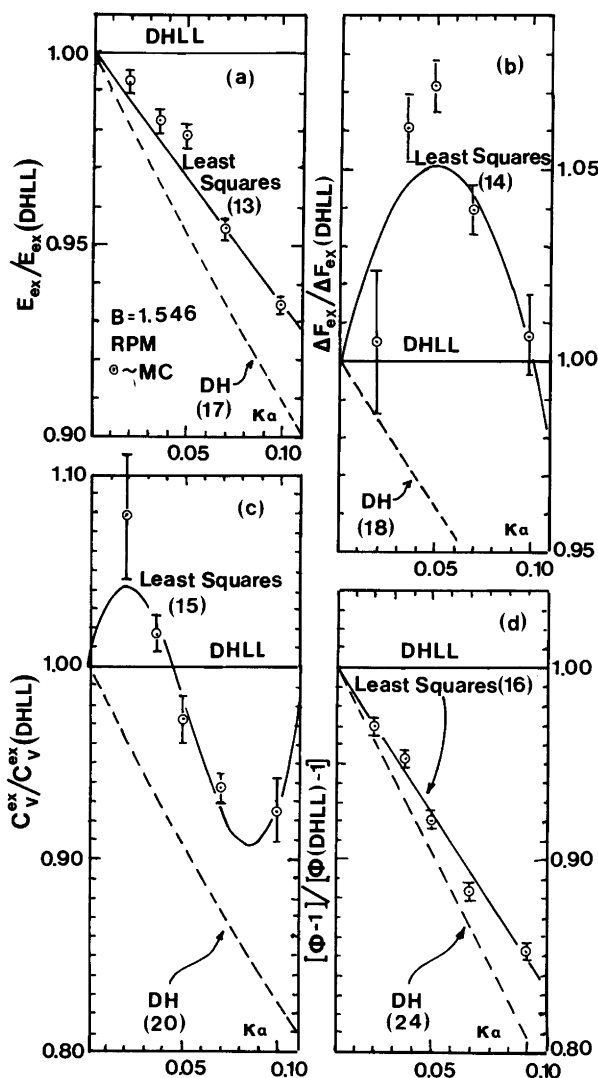
$$\begin{aligned} G(\kappa a) &\approx [\ln(1 + \kappa a) - (\kappa a/2) \\ &- (\kappa a)/\{2(1 + \kappa a)\}]/(\kappa a)^2 \end{aligned} \quad (22)$$

$$\Phi(\text{hard spheres}) - 1 \approx 2\pi\rho^*/3 = (\kappa a)^2/(6B) \quad (23)$$

$$\begin{aligned} \Phi(\text{DH}) - 1 &\approx -(B/6)\kappa a + [(B/4) \\ &+ 1/(6B)](\kappa a)^2 \end{aligned} \quad (24)$$

Comparing eqns. (16) and (24), it is interesting to note that the value 0.3944 is very close to $B/4 = 0.3865$, whereas $(B/4) + 1/(6B) = 0.4943$. Thus for the present value of B , the Monte Carlo calculations (which involve the electrostatic as well as the hard core contributions) seem to give the same results for the osmotic coefficients as the Debye-Hückel equation without accounting for the excluded volume term. Whether this is fundamental or simply coincidence cannot be discussed before calculation with other values of B have been performed. However, it seems safe to con-

Fig. 5. (a) $E(\text{ex, MC})/E(\text{ex, DHLL})$, (b) $\Delta F(\text{ex, MC})/\Delta F(\text{ex, DHLL})$, (c) $C_V(\text{ex})/C_V(\text{ex, DHLL})$ and (d) $[\Phi(\text{MC})-1]/[\Phi(\text{DHLL})-1]$ vs. κa . Magnified plots showing the approach towards the limiting laws in greater detail than Fig. 4. The uncertainty bars shown for the MC results are the ones obtained from the polynomial extrapolations to infinite systems. The least-squares polynomials are also shown. The numbers in parentheses indicate the number of the equation. The MC results are seen to approach the limiting law in a way qualitatively different from the DH laws. $\Delta F(\text{ex})$ and $C_V(\text{ex})$ both exhibit "negative deviations" from the DHLL at extreme dilution. $E(\text{ex})$ may have a slight negative deviation. The regression line for the excess osmotic coefficient given by eqn. (16) is very close to the DH expression (24) without the hard sphere term $(1/6B)(\kappa a)^2$.



clude that when data for osmotic coefficients (or for logarithms of mean ionic activity coefficients) at high dilutions are used in connection with the DH theory (or MSA theory) to calculate distances of closest contact (a) (see, for example, Ref. 8) then the distances found will most probably not be correct when B is around 1.5. This is the case for many 1:1 electrolytes in water at 25 °C. The effective values of B found will be given by $(B_{\text{eff}}/4) + 1/(6B_{\text{eff}}) \approx B_{\text{real}}/4$. Thus, the effective B will be too low and the contact distances too high.

It is well known for 2:2 electrolytes, that the RPM exhibits *negative deviations* from the Debye-Hückel limiting law for $E(\text{ex})$, i.e. deviations opposite to those predicted by the DH-theory (see for example the MC simulations of Rogde and Hafskjold at $B = 6.8116^{18}$). In our case there are apparently no negative deviations from DHLL for $E(\text{ex})$, but the values of $E(\text{ex})$ are in between $E(\text{ex, DHLL})$ and $E(\text{ex, DH})$, so it might be the first sign of a negative deviation at very small concentrations for somewhat higher values of B . A clear sign that something is going

to happen at higher B values is the peculiar concentration dependence of the excess heat capacity found in the present study, seemingly very different from the dependence predicted by the DH law. It is well known that in statistical mechanical calculations, the heat capacity is a much more sensitive quantity than the internal energy. Therefore, it is natural that the most drastic deviations from the DH law are found for $C_v(\text{ex})$.

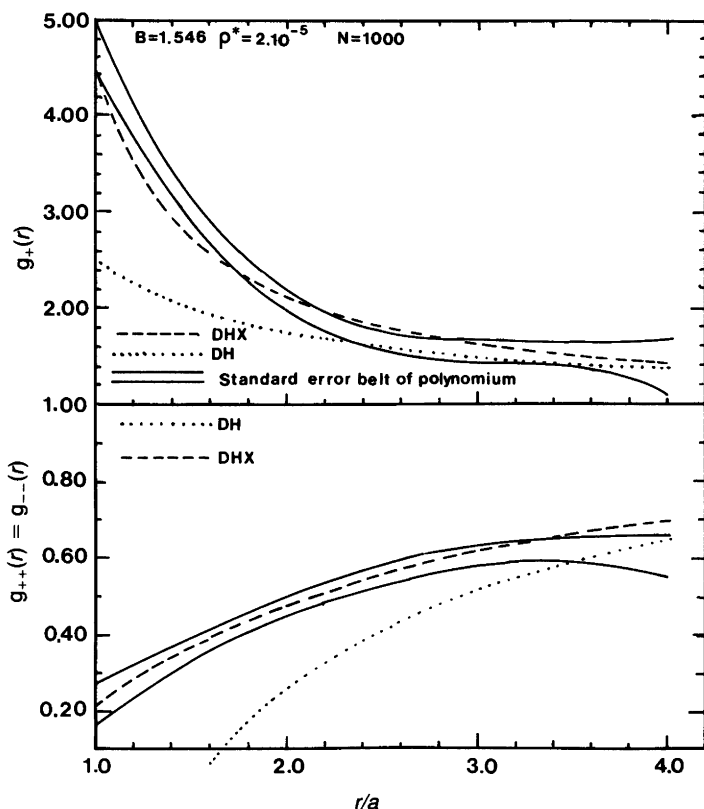
It should be mentioned that the values of the thermodynamic parameters calculated with the Mean Spherical Approximation (MSA) are exactly the same as the values calculated from the DH theory in the very dilute region considered here. This is a result of the isomorphism between the DH and the MSA theories and the fact that the shielding lengths of both theories become identical at extreme dilutions. Thus, even if the excluded volume is treated in a more consistent way in the MSA theory than in the DH theory, they seem to be equally wrong at very low concentrations.

The deviation of $E(\text{ex}, \text{MC})$ from $E(\text{ex}, \text{DH})$

may be the reason for some of the poor results for the limiting slopes from the measurements of *heat of dilution* for some salts (see the introduction). The heat of dilution may easily be calculated from $E(\text{ex})$ when these values are corrected for the temperature dependence of the dielectric permittivity of the solvent. In order to measure something significant it is necessary to begin with an electrolyte solution of a concentration at which the DHLL is not valid and then dilute further. However, when a false relationship is used, the value obtained for the DHLL constant will also deviate from the theoretical value.

After the above discussion of the thermodynamic parameters, we turn to the form of the radial distribution functions $g_{+-}(r)$ and $g_A(r) = g_{++}(r) = g_{--}(r)$. We found that the so-called DHX model seems to approximate the radial distribution functions quite well at $B = 1.546$ and at the small concentrations studied here. In this model, the effective potential w_{ij} in $g_{ij}(r) = \exp(-w_{ij}/kT)$ is approximated by the mean electrostatic potential as given by the Debye-Hückel

Fig. 6. Radial distribution functions close to contact calculated by Monte Carlo (uncertainty belt of smoothed values of the most significant polynomials at the 95% significance level), by the DH assumption (dotted) and by the DHX assumption (dashed). The DHX values are statistically identical to the MC values in the "window" shown (from contact to 4 contact distances) MC values correspond to $N = 1000$, $\rho^* = 2 \cdot 10^{-5}$ and $B = 1.546$. The number of configurations is 1,385,000. See Fig. 1.



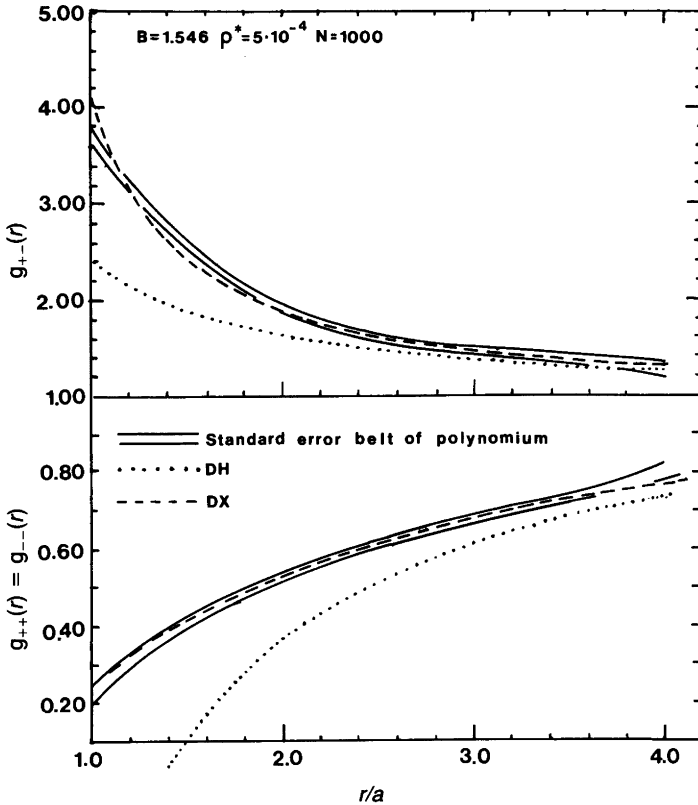


Fig. 7. Monte Carlo values (uncertainty belts) of the radial distribution functions close to contact for $N = 1000$, $\rho^* = 5 \cdot 10^{-4}$ and $B = 1.546$ (1 million configurations, see Fig. 3) compared to the DH assumption (dotted) and the DHX assumption (dashed). DHX and MC values are statistically identical.

expression. Thus, we have a double exponentiation:

$$\left. \begin{array}{l} g_{+-}(r) \\ g_{\Lambda}(r) \end{array} \right\} = \exp[\pm B \exp\{-\kappa a \{t-1\} / t(1+\kappa a)\}] \quad (25)$$

$t \equiv r/a \geq 1$

Figs. 6 and 7 show the standard error belts (for $N = 1000$ ions) for $g_{+-}(r)$ and $g_{\Lambda}(r)$ at the lowest and at the highest of the concentrations considered, as compared to the DHX model and to the DH model the latter of which is the linearisation of the first exponential in eqn. (25). The DH model is very poor close to contact, but it is asymptotically valid for large radii. The DHX model coincides with the DH model at large radii, but is much better close to contact. In fact, the correspondence between the smoothed MC data and the DHX values for the radial distribution functions is strikingly good at the concentrations considered here. The difference be-

tween the MC and the DHX values seems insignificant in the whole window shown here for both concentrations. However, the contribution to the thermodynamic properties lies mostly in the long "tails" of the radial distribution functions at great dilution which are shown on Figs. 6 and 7. The MC method is not precise enough for studying the very small differences between $g(r)$ and unity at large separations.

When the DHX assumption [eqn. (25)] is inserted into the energy integral, the DHX of $E(\text{ex})/NkT$ can be evaluated by numerical integration. The results are shown in Fig. 8. Clearly, the DHX values are very close to the regression line for the MC values, especially for the lowest concentrations. Therefore, the differences between the radial distribution functions given by the DHX model and the real radial distribution functions must be very small even far out in the tails. The DHX model seems to represent a great improvement as compared to the DH

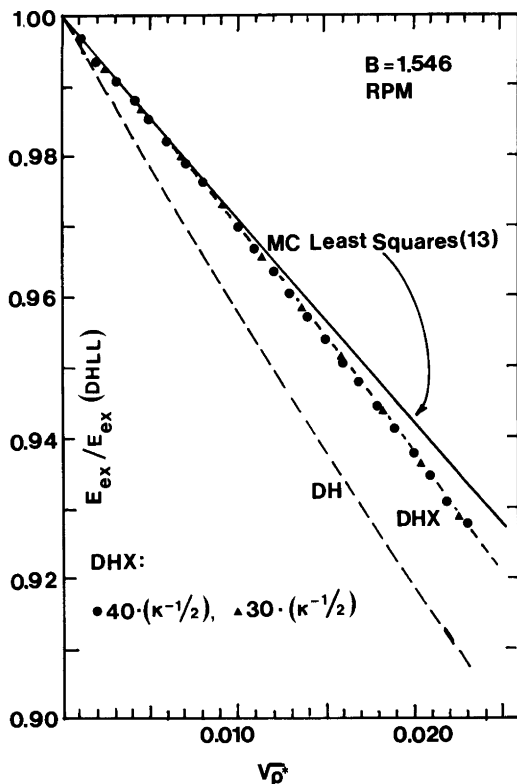


Fig. 8. $E(\text{ex})/E(\text{ex, DHLL})$ vs. the square-root of the dimensionless concentration with the DH assumption (long dashes) or the DHX assumption (short dashes) for the radial distribution function compared to the Monte Carlo values. The DHX values (obtained from the energy integral) are very close to the smoothed MC values—especially at small concentrations—and both are certainly different from the DH values. The DHX values are integrated over 40 times (●) or 30 times one half Debye length (▲). No difference is observed, but below 15 times one half Debye length the calculated excess energies deviate significantly. This is a demonstration of the importance of the long “tail” in dilute systems. Since the tail is more important the more dilute the system is, the DHX model seems to be a good approximation also for the tail at extreme dilution.

model at high dilution, at least for 1:1 electrolytes. The DHX model yields good thermodynamic results for moderately dilute solutions, it tends towards the DHLL at extreme dilution and it makes possible a discussion of the *double layer structure* close to the ions with great precision,

even at extreme dilutions where the DH model leads to absurdities such as negative local concentrations. The DHX model might with advantage replace the DH model in elementary electrochemistry textbooks (in a paper in preparation we show that a straightforward generalisation of DHX seems to work even in the case of unequal ionic radii!).

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