

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/234164247>

Large ionic clusters in concentrated aqueous NaCl solution

ARTICLE *in* THE JOURNAL OF CHEMICAL PHYSICS · SEPTEMBER 1999

Impact Factor: 2.95 · DOI: 10.1063/1.479783

CITATIONS

63

READS

18

2 AUTHORS, INCLUDING:



Fernando Luís Barroso da Silva

University of São Paulo

24 PUBLICATIONS 349 CITATIONS

SEE PROFILE

Large ionic clusters in concentrated aqueous NaCl solution

Léo Degève^{a)}

Grupo de Simulação Molecular, Depto. de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, 14040-901 Ribeirão Preto, SP, Brasil

Fernando Luís B. da Silva

Grupo de Simulação Molecular, Depto. de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, 14040-901 Ribeirão Preto, SP, Brasil, and Physical Chemistry II—P.O. Box 124—Lund University, S-221 00 Lund, Sweden

(Received 29 May 1998; accepted 11 June 1999)

The stability of the local structure of aqueous 1.0 M NaCl solution at 293 K was investigated by molecular dynamics simulations. The mean and maximum life-times of the ion pairs were determined to be 0.13, 0.14 and 0.27 ps for negatively charged, neutral and positively charged ions pairs, respectively. The stability of non-neutral ion pairs was studied from the structure of the anion–cation radial distribution function and other structural functions. We found that non-neutral ions pairs are stabilized by at least one counter-ion forming in this way large ionic clusters that include the hydration molecules. About 25% of the ions are included in neutral clusters formed by a minimum of four ions. The existence of these large clusters obfuscates the commonly accepted chemical reaction scheme for the interconversion of ion pairs in aqueous solutions. © 1999 American Institute of Physics. [S0021-9606(99)50134-7]

I. INTRODUCTION

The behavior of aqueous solutions in the bulk or at the interfaces has receiving considerable attention for many years. It is clear that the understanding of these processes has a wide range of technological applications and theoretical developments in liquid purification, homogeneous and non-homogeneous catalysis, transport, biophysical processes, chemical technology, petrochemistry, theory of chemical and physical processes.^{1–9} One particular aspect of great interest is the interconversion of ion pairs in solution due to its direct relation with important chemical reactions.^{10,11} However, this mechanism remains poorly understood.¹⁰ The reaction scheme that is more accepted is $A^+ + B^-$ (free ions) $\rightleftharpoons A^+ \parallel B^-$ (solvent separated ion pair—SSIP) $\rightleftharpoons A^+ | B^-$ (contact ion pair—CIP) $\rightleftharpoons AB$ (reaction product), where the specific role and nature of these ion pairs are still uncertain.^{10,12} The so-called computer experiments, or simulation techniques, can by-pass experimental and theoretical difficulties and furnish a molecular level characterization for these intermediate states and barriers separating them.^{3,10,12} They can also provide detailed information on the local concentration in the neighborhood of molecules or macromolecules at nonhomogeneous interfaces^{13–16} or around ions in solutions using either the usual radial distribution function (rdf)^{17,18} and/or multi-variable distribution functions.^{13–16,19–22}

Recently, we presented an analysis of the structure of an electrolyte solution at finite concentration, precisely aqueous 1.0 M NaCl solution.³ One important point in that study was that the analysis focused on the ion pairs that were identified by the fact that two ions share at least two hydration mol-

ecules. The main idea was based on the fact that the number of water molecules in the first solvation shells of these ions are quite stable and close to six, i.e., 6.00 ± 0.27 for Na^+ and 5.73 ± 0.99 for Cl^- .²² The fluctuations in these hydration numbers are small because ion–water energies are lower than the bulk energy.²² Another observation is that only few exchanges between hydration molecules and the bulk are observed.²³ These stability conditions suggest that ion association must occur keeping as far as possible the solvation shells. At least two cases of ion pairing can be identified. The simplest one is the case where there is the direct contact between the ions (this is the commonly accepted definition of ion association^{24–26}). The second one is detected when the solvated water molecules are shared by two ions keeping them close or making them approach each other. This will maintain the stability of the structure.³ The consequence is the stabilization of the clusters formed by two ions altogether with all their solvation molecules. In all ion association, the ions must share some water molecules in their solvation shells: their number cannot be less than two excluding the cases of single nonassociating collisions. Therefore, the sharing of the minimum of two water molecules by two ions can be a good criterion for the identification of an ion association.³ As a result, it was observed³ that the fractions of associated ions were unexpectedly high, e.g., 0.46 for the cations and 0.32 for the anions. In particular, associations between identical ions were largely observed. For instance, roughly 13% of the anions and 16% of the cations are associated in non-neutral pairs.³ These pairs were studied before by other authors in different ways mainly on primitively modeled solutions.^{27–29} However, apparently no information on the stabilization process of charged pairs was obtained. Studies on nonprimitive models for electrolyte solutions were also able to predict the stability of some ion pairs from

^{a)} Author to whom correspondence should be addressed; electronic mail: leo@obelix.ffclrp.usp.br

the mean force potential, such as the $\text{Cl}^- - \text{Cl}^-$ pair,³⁰ while the stability of $\text{Na}^+ - \text{Na}^+$ pairs was not predicted. Consequently, the present question is to determine what is the stabilization mechanism of highly repulsive charged pairs and to determine if the stabilization process is mainly explained by the solvent or ions properties.

II. METHOD

Systems constituted by 2117 water molecules and 40 NaCl were submitted at 293 K to molecular dynamics simulation.^{18,31,37} The volume was adjusted to correspond to a density equal to 1.1402 kg/l so that the electrolyte concentration was 0.993 M. These conditions correspond to NaCl solutions under atmospheric pressure. Solvent molecules were described by the TIP4P water model³³ and their interactions with the ions by a 6–12 plus Coulomb interaction potential.³⁴ Ion–ion interactions were modeled by the GROMOS force-field.³⁸ Periodic boundary conditions and minimum image convention were adopted. The long-range electrostatic energies were included through a Poisson–Boltzmann generalized reaction field³² with a spherical cut-off at 1.5 nm. The Newton movement equations were integrated by a time step of 1.0 fs and the total simulation time was 0.2 ns. Quaternions³⁶ and the Gear predictor–corrector method³⁷ were used.

Ion–ion rdf $g_{\text{ion},\text{ion}'}(r)$, where *ion* could be both the anion and the cation and *r* is the interionic distance, were calculated in the usual way.¹⁸ As it will be seen, the $g_{\text{Na}^+,\text{Cl}^-}(r)$ function presents two very well defined peaks at short distances. The first peak P_1 is included in the range of $r=0.0$ to $r=r_{\text{min},1}$ and the second peak P_2 in the range of $r_{\text{min},1}$ to $r_{\text{min},2}$, where $r_{\text{min},1}$ and $r_{\text{min},2}$ correspond to the positions of the first and second $g_{\text{Na}^+,\text{Cl}^-}(r)$ minima, respectively (it will be noted that $r=r_{\text{min},1}=0.34$ nm and $r_{\text{min},2}=0.58$ nm). The ionic structures that are responsible for these peaks will be resolved from the fraction of ions present in P_1 and P_2 . This entity will denote $S_{\text{ion}}(n_1^k, n_2^k)$, where the subscript *ion* is the reference anion, or cation, at the origin. The numbers of counter-ions of type *k* in P_1 and P_2 are given by n_1^k and n_2^k , respectively. For instance, assuming that the Na^+ is on the center, $S_{\text{Na}^+}(n_1^{\text{Cl}^-}, n_2^{\text{Cl}^-})$ records the frequency that the number of counter-ions Cl^- presents on peak $P_1(n_1^{\text{Cl}^-})$ and, simultaneously, in $P_2(n_2^{\text{Cl}^-})$, appeared during the observation time. The $S_{\text{ion}}(n_1^k, n_2^k)$ functions were not calculated from the radial distribution functions. Instead, they were calculated by direct counting of the respective occurrence during the simulation process, after the proper equilibration of the system.

The counter-ions present in n_1^k and n_2^k are possibly distributed in space according to the local energy minima, so that we can define three partial radial distribution functions $g_{\text{ion}}^{11}(r)$, $g_{\text{ion}}^{12}(r)$ and $g_{\text{ion}}^{22}(r)$, where the exponents 11, 12 and 22 refer to the simultaneous presence of counter-ions in peaks P_1 and P_1 , P_1 and P_2 , and in P_2 and P_2 , respectively. The distance *r* is the separation distance between the counter-ions in the respective cases. It is convenient as well to determine the distribution functions of the angle Ψ formed by one counter-ion, the central ion and the second counter-ion: Ψ_{ion}^{11} , Ψ_{ion}^{12} and Ψ_{ion}^{22} . For example, $\Psi_{\text{Na}^+}^{11}$ refers to the

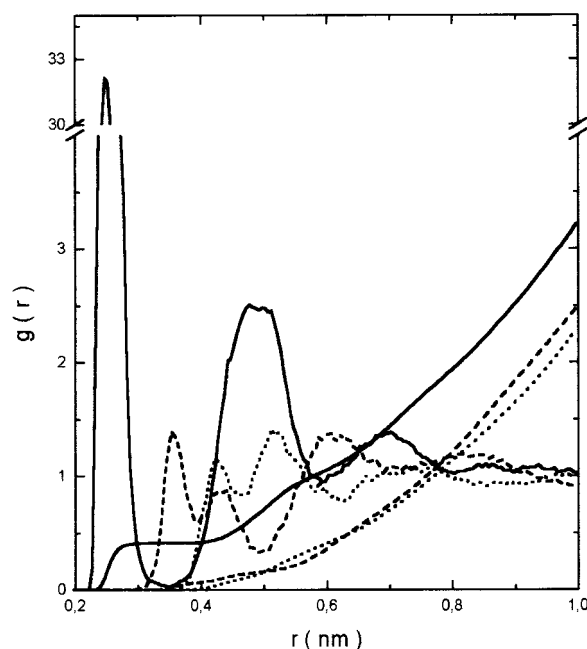


FIG. 1. The ionic radial distribution functions as a function of the separation distance *r* between the ions: $g_{\text{Cl}^+,\text{Cl}^-}(r)$ (dots), $g_{\text{Na}^+,\text{Cl}^-}(r)$ (solid line) and $g_{\text{Na}^+,\text{Na}^+}(r)$ (dashed line). The running integrals of these curves are also represented.

angle formed by one Cl^- , a central Na^+ and a second Cl^- , when both Cl^- 's are in P_1 . Analogously, if the anions are in different peaks, the corresponding function is $\Psi_{\text{Na}^+}^{12}$. The partial radial distribution functions $g_{\text{ion}}^{11}(r)$, $g_{\text{ion}}^{12}(r)$ and $g_{\text{ion}}^{22}(r)$, together with the angles Ψ allow us to determine accurately the most frequent interionic distances, and hence will allow us to associate the respective configurations with the features of the ion–ion radial distribution functions.

III. RESULTS

The mean total configurational energy was found to be -17.4 ± 0.1 kcal/mol. The configurational energy for the interactions between the water molecules was -7.047 ± 0.07 kcal/mol, which is slightly above the configurational energy of the pure TIP4P water bulk phase (-10.07 kcal/mol³⁰). Ion–water energy was equal to -4.2 kcal/mol. These results are similar to the Monte Carlo data formerly obtained.³ The diffusion coefficients for Na^+ , Cl^- and water molecules were determined as being equal to 1.23, 2.5 and $4.60 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, respectively. These numbers are in good agreement with the results obtained by the same ions models and rigid SPC water model.³⁵ Some difference between our result for the diffusion coefficient and the value $2.96 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for pure TIP4P water³⁸ is observed while the concordance with more recent data³⁹ is good.

The $g_{\text{Cl}^+,\text{Na}^+}(r)$ distribution function is displayed in Fig. 1. It presents a first very well defined peak of 32.15 at $r=0.25$ nm and a smooth second one of 2.5 at $r=0.48$ nm, a typical trait of strong long-range electrostatic attraction and a short-range soft core repulsion. This data is similar to results obtained with SPC water and the same ion–ion interaction potential reported in the literature.³⁵ In Fig. 1, the number of

TABLE I. Positions (nm) and intensities of the first two extrema of the radial distribution functions and the corresponding value of the coordination number calculated until the corresponding minimum, $n(r_{min})$.

r_{max}	$g(r_{max})$	r_{min}	$g(r_{min})$	$n(r_{min})$
$g_{Cl^-,Cl^-}(r)$				
0.43	1.15	0.47	0.83	0.10
0.51	1.41	0.63	0.78	0.47
$g_{Na^+,Cl^-}(r)$				
0.25	32.15	0.34	0.83	0.41
0.48	2.50	0.58	0.95	1.05
$g_{Na^+,Na^+}(r)$				
0.35	1.39	0.39	0.59	0.06
0.44	0.88	0.49	0.32	0.15

cations–anions neighbors is also plotted. This graphic shows that the first $g_{Cl^-,Na^+}(r)$ peak corresponds to 0.41 ions so that the fraction of ions in contact and consequently associated in neutral pairs is 0.41. The second $g_{Cl^-,Na^+}(r)$ peak and the number of neighbors profile indicate the existence of a structure in the $r=0.49$ nm region too. The other rdfs, $g_{Cl^-,Cl^-}(r)$ and $g_{Na^+,Na^+}(r)$, are also plotted in Fig. 1. These functions are badly defined such that the comparison with published data³⁵ is not fruitful. However, in all cases these functions present a first, but not so well defined peak corresponding to a mean of a 0.1 Cl^- ion near each Cl^- and 0.06 in the Na^+ case. More data are summarized in Table I.

The analysis of the stabilities or mean life-times begins with the ion–ion rdfs. The characteristics of the various ion–ion rdf are fundamentally different; see Fig. 1. If we compare either $g_{Cl^-,Na^+}(r)$ with $g_{Cl^-,Cl^-}(r)$ or with $g_{Na^+,Na^+}(r)$, only the $g_{Cl^-,Na^+}(r)$ function presents two very well defined peaks. This might indicate that a relatively long-range structure of counter-ions exists around the central cation or anion. From data of Fig. 1, the values of $r_{min,1}$ and $r_{min,2}$ are identified as equal to 0.34 and 0.58 nm, respectively. The corresponding $S_{ion}(n_1^k, n_2^k)$ data are reported in Table II. Both frequencies $S_{Cl^-}(n_1^{Na^+}, n_2^{Na^+})$ and $S_{Na^+}(n_1^{Cl^-}, n_2^{Cl^-})$ are very similar showing roughly that 30% of the ions have no neighbor in either P_1 or P_2 , 44% one in P_1 or P_2 so that about

TABLE II. The frequencies $S_{Cl^-}(n_1^{Na^+}, n_2^{Na^+})$ and $S_{Na^+}(n_1^{Cl^-}, n_2^{Cl^-})$. See the text for details.

$S_{Cl^{-}}(n_1^{Na^{+}}, n_2^{Na^{+}})$					
	$n_2^{Na^{+}}=0$	$n_2^{Na^{+}}=1$	$n_2^{Na^{+}}=2$	$n_2^{Na^{+}}=3$	
$n_1^{Na^{+}}=0$	0.302	0.255	0.079	0.006	
$n_1^{Na^{+}}=1$	0.179	0.114	0.015	0.002	
$n_1^{Na^{+}}=2$	0.046	0.004	0.000	0.000	
$S_{Na^{+}}(n_1^{Cl^{-}}, n_2^{Cl^{-}})$					
	$n_2^{Cl^{-}}=0$	$n_2^{Cl^{-}}=1$	$n_2^{Cl^{-}}=2$	$n_2^{Cl^{-}}=3$	$n_2^{Cl^{-}}=4$
$n_1^{Cl^{-}}=0$	0.296	0.257	0.069	0.009	0.001
$n_1^{Cl^{-}}=1$	0.203	0.109	0.015	0.003	0.000
$n_1^{Cl^{-}}=2$	0.004	0.004	0.000	0.000	0.000

25% of the ions are embedded in clusters of three or more ions. The frequency of these clusters is so large that we can study their structure by means of the partial radial distribution functions $g_{ion}^{11}(r)$, $g_{ion}^{12}(r)$ and $g_{ion}^{22}(r)$ [see Figs. 2(a)–(c)], and from the angles Ψ_{ion}^{11} , Ψ_{ion}^{12} and Ψ_{ion}^{22} [see Figs. 3(a)–(c)]. In Fig. 2(a), one sharp peak is present in $g_{Na^+}^{11}(r)$ and two peaks in $g_{Cl^-}^{11}(r)$ at the same distance as those found at the $g_{Cl^-,Cl^-}(r)$ and $g_{Na^+,Na^+}(r)$ peaks (see Fig. 1). Despite some fluctuations, a similar behavior is observed in Fig. 2(b). Figure 2(c) shows a double behavior taking into account the electrostatic repulsion at a large distance and the formation of ion pairs at short distances. Comparing the positions of the peaks in Fig. 1 and in Figs. 2(a)–(c), the identification of the nature of the peaks, or bumps, comes out with no efforts. The first peak of $g_{Cl^-,Cl^-}(r)$ at 0.43 nm appears at least partially as a consequence of the first peaks presented at the three partial distributions, $g_{Na^+}^{11}(r)$, $g_{Na^+}^{12}(r)$ and $g_{Na^+}^{22}(r)$, while the second peak is related to the second one found at $g_{Na^+}^{12}(r)$ and $g_{Na^+}^{22}(r)$. Similar identifications can be made between $g_{Na^+,Na^+}(r)$ and $g_{Cl^-}^{11}(r)$, $g_{Cl^-}^{12}(r)$ and $g_{Cl^-}^{22}(r)$. The correlations between the peaks and their positions are exactly one to one. This is an obvious influence of the solvent as a quite important factor on the determination of the peak positions, i.e., the structure of the medium is largely defined by the solvation structures of the ion pairs. The remark includes the cation–anion pairs that are the starting point of the present analyses. A comparison between the three partial rdf for the anion and for the cation reveals one characteristic difference. In the anion case as the reference ion, the cation–cation distribution presents two peaks that must be associated with the high stability of the cationic pairs. This explains the high stability of the first cationic hydration shell by the presence of one anion turning the cluster energetically stable.

The same structural properties are obtained for the Ψ functions as well; see Figs. 3(a)–(c). These figures also show the same tendency to increase the interionic distance between co-ions implying definite angles that correspond to the peaks observed in Figs. 2(a)–(c). A detailed analysis of the correlations between the angles Ψ and the partial and total radial distribution functions can now be made. The position of the first $g_{Cl^-,Na^+}(r)$ maxima in Fig. 1 are $r_{max,1}=0.25$ nm and $r_{max,2}=0.48$ nm, while the peaks in $g_{Cl^-,Cl^-}(r)$ are observed at 0.43 and 0.51 nm; see Fig. 1. Yet in $g_{Na^+,Na^+}(r)$, the peaks are found at 0.35, 0.44 and 0.61 nm. From these sets of probe distances and together with the coordinates of the observed peaks in Fig. 2(a)–(c), the values of the maxima of Ψ_{ion}^{11} , Ψ_{ion}^{12} and Ψ_{ion}^{22} observed in the Figs. 3(a)–(c) are recovered.

A consistency check together with a yet more complete comparison between the partial and the full ion–ion rdfs can now be made comparing the sums of the partial rdf with the full rdf. In Fig. 4(a), $g_{Na^+,Na^+}(r)$ is compared with $g_{Cl^-}^{11}(r) + g_{Cl^-}^{12}(r) + g_{Cl^-}^{22}(r)$ and in Fig. 4(b) $g_{Cl^-,Cl^-}(r)$ with $g_{Na^+}^{11}(r) + g_{Na^+}^{12}(r) + g_{Na^+}^{22}(r)$. The $g_{Na^+,Na^+}(r)$ is extremely well reproduced mainly at short distances so that all the Na^+-Na^+ pairs are associated with counter-ions. At short distances, i.e., when both counter-ions pertain to P_1 and/or

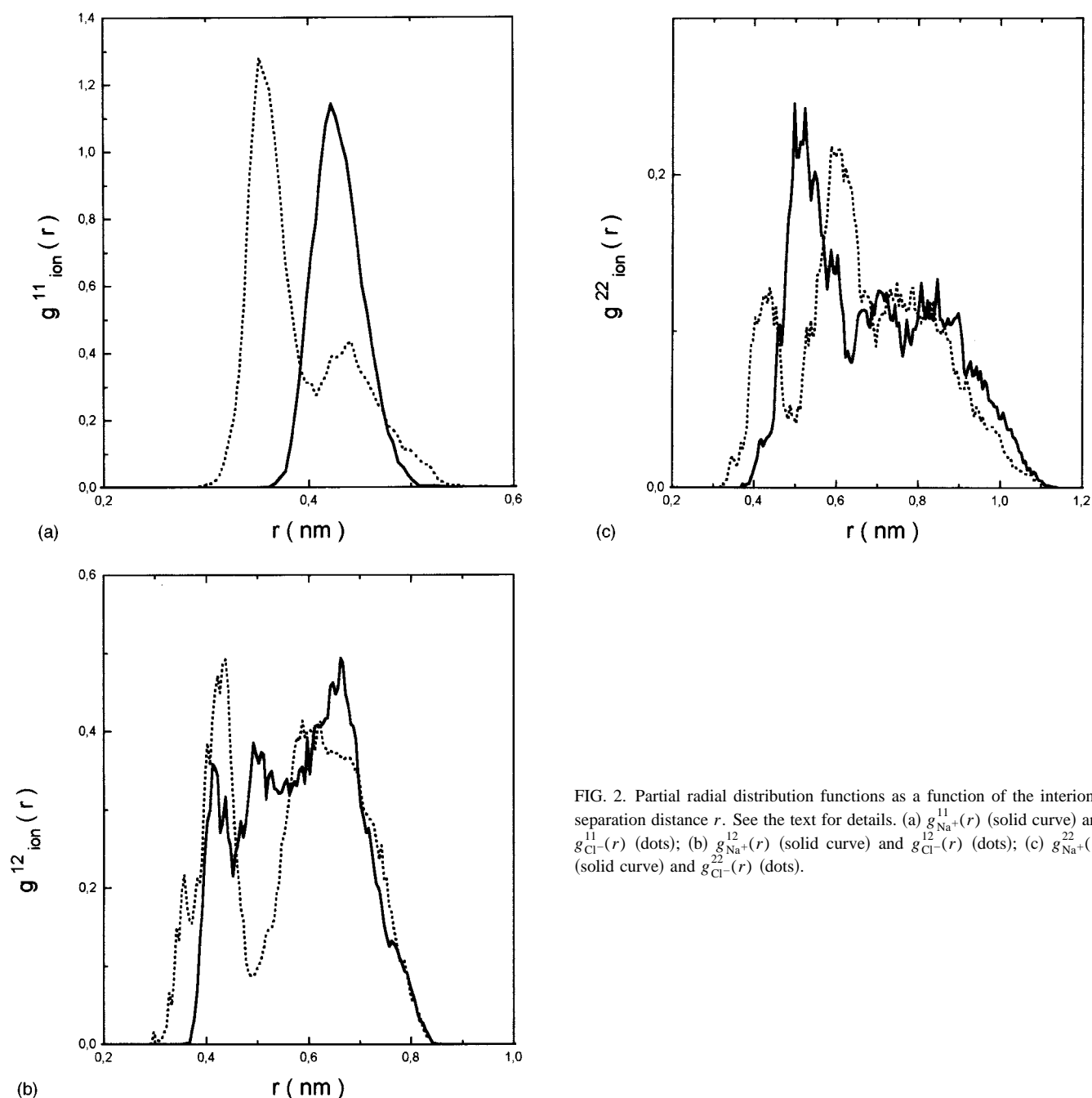
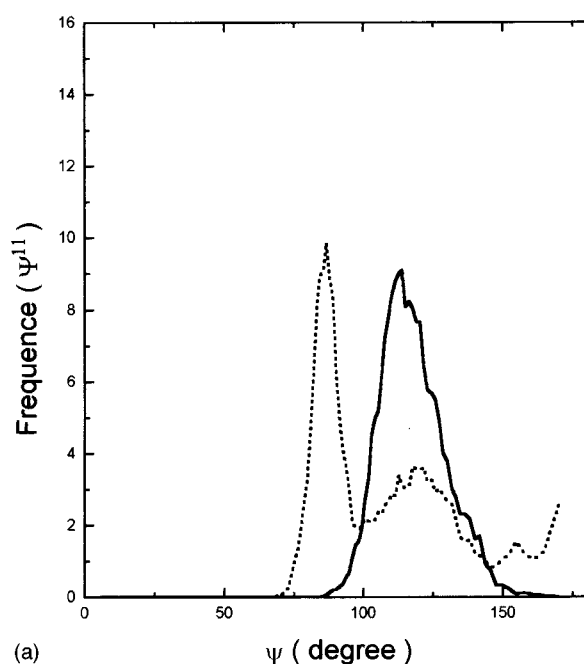


FIG. 2. Partial radial distribution functions as a function of the interionic separation distance r . See the text for details. (a) $g^{11}_{Na^+}(r)$ (solid curve) and $g^{11}_{Cl^-}(r)$ (dots); (b) $g^{12}_{Na^+}(r)$ (solid curve) and $g^{12}_{Cl^-}(r)$ (dots); (c) $g^{22}_{Na^+}(r)$ (solid curve) and $g^{22}_{Cl^-}(r)$ (dots).

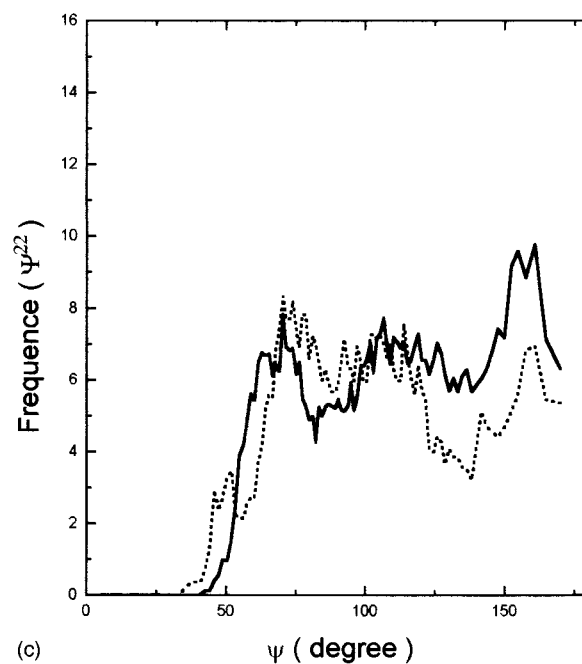
P_2 , the full rdf are always smaller than the sum of the partial rdf. This is evidence that the same two ions give more than one contribution to the partial rdf. This is possible only if the same two counter-ions are found in P_1 and/or P_2 of two different central ions. Consequently not only the Na^+-Na^+ pairs are associated with counter-ions but the Cl^--Cl^- pairs are too. The fact that the full rdf is always smaller than the sum of the partial rdf at short distance is the consequence of the existence of clusters formed by four ions, two pairs of counter-ions. The quantity of these large clusters can be deduced from the running integrals of the full rdf and from the sums of the partial rdf shown in Fig. 5. Running integrals calculated until the same minima positions as the minima of $g_{Na^+,Na^+}(r)$ and $g_{Cl^-,Cl^-}(r)$ are found to be 0.09 and 0.15, respectively. These values are exactly 50% larger than the

values in Table I, i.e., half of the ion pairs are associated to two counter-ions. The ratios of the running integrals on the sums of the partial and on the full rdf show peaks that are consequence of structural fluctuations at short distances; see Fig. 6. More important is the stabilization of these ratios near 2.0 for the Na^+-Na^+ and 3.5 for Cl^--Cl^- pairs in both cases for interionic distances at about 0.03 nm, before the first peaks of their respective distributions. These numbers indicate the existence of larger clusters.

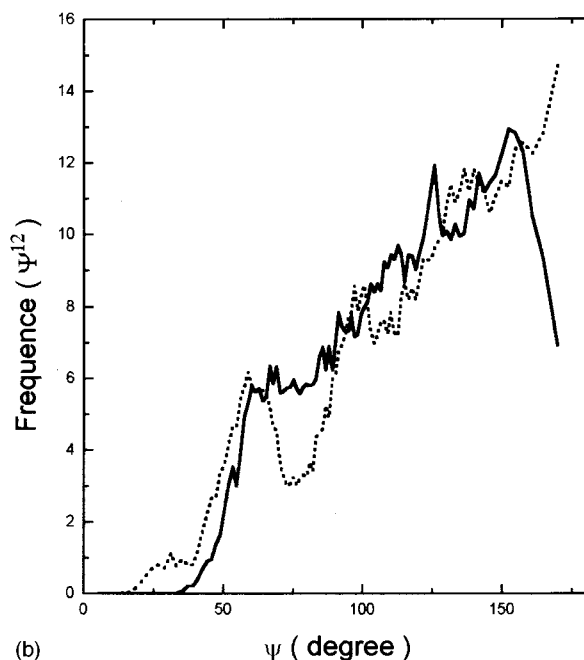
The mean life-times of the ion pairs were determined directly from the generated trajectory, see Table III, where they are listed together with the longest observed life-time. They were determined as $t_f - t_i$. The initial time t_i is defined by the moment of the first identification of the pair formation, when the first solvation shells of two ions begin to share



(a)



(c)



(b)

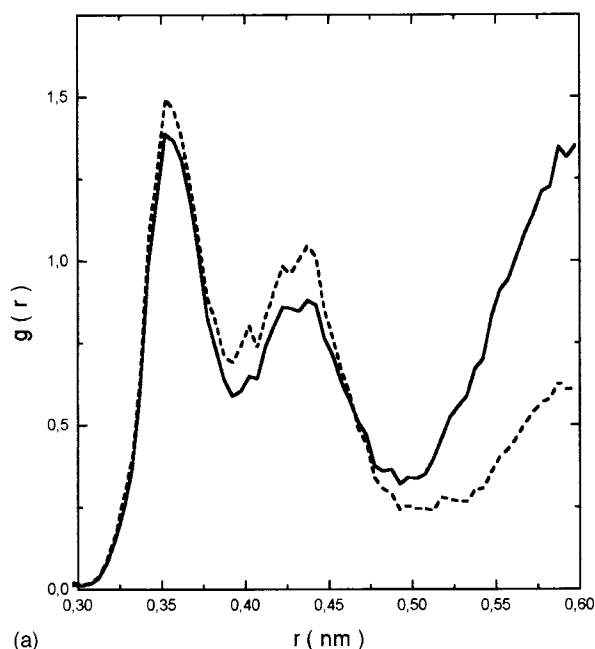
FIG. 3. Distribution functions of the angle formed by one counter-ion, a central ion and a second counter-ion, Ψ , in arbitrary units. Ψ is given in degrees. See the text for details. (a) $\Psi_{\text{Na}^+}^{11}$ (solid curve) and $\Psi_{\text{Cl}^-}^{11}$ (dots); (b) $\Psi_{\text{Na}^+}^{12}$ (solid curve) and $\Psi_{\text{Cl}^-}^{12}$ (dots); (c) $\Psi_{\text{Na}^+}^{22}$ (solid curve) and $\Psi_{\text{Cl}^-}^{22}$ (dots).

two water molecules. The final time t_f is the last time immediately before the same two ions discontinue the sharing of any two water molecules in their first solvation shells. No sort of time correlation function or “survival function”,⁴⁰ was adopted. Consequently, fluctuations in the sharing of solvent molecules, resulting in the discontinuity of the existence of the ion pair, imply the limit of its life-time. It should be noticed from the data in Table III that there is a raise on the mean life and longest life-times from the $\text{Cl}^- - \text{Cl}^-$ pairs to the $\text{Na}^+ - \text{Cl}^-$ and $\text{Na}^+ - \text{Na}^+$ pairs. The positive pairs are uncommonly stable comparing with the neutral pairs. Although they have both a mean life-time and a maximum life-time of almost twice the neutral pairs, their relative frequency (number of detected pairs) is *ca.* 10% of what is found for the neutral pairs. The last ones are surely

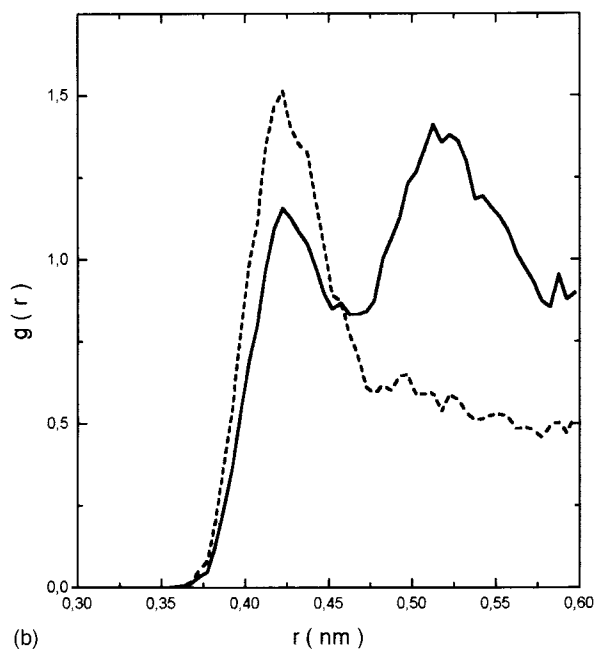
predominant.³ The numbers of detected pairs are of the same order as the numbers of ions in the first rdf peaks.

IV. DISCUSSION

In a former study,³ the existence of ion pairs was confirmed. The pairs can be charged or not. The structure of these pairs is determined by the solvent because the hydration energies are so attractive that the pairs were able to be formed and to maintain some degree of stability. An important point was that the ions in these pairs must share some hydration molecules. In the case of the non-neutral pairs, the highly repulsive electrostatic interactions must prohibit the approach of the ions, at first sight. This is not the case, since the ions can approach one another; see Fig. 1. Together with



(a)



(b)

FIG. 4. A comparison of the full and partial sums of rdf: (a) $g_{\text{Na}^+, \text{Na}^+}(r)$ (solid line), $g_{\text{Cl}^-}(r) + g_{\text{Cl}^-}^{12}(r) + g_{\text{Cl}^-}^{22}(r)$ (dashed line); (b) $g_{\text{Cl}^-, \text{Cl}^-}(r)$ (solid line), $g_{\text{Na}^+}(r) + g_{\text{Na}^+}^{12}(r) + g_{\text{Na}^+}^{22}(r)$ (dashed line).

this fact, it is relevant to point out that these pairs were detected too by direct and independent inspection into the trajectories. The present results furnish the simple explanation that ion pairs can exist and that they exist in the presence of at least one counter-ion and probably two counter-ions. The resulting electrostatic energy is clearly attractive. Many consequences are immediately identified, e.g., ions in aqueous solution are not only associated in pairs, but in charged triplets and larger clusters. The running integrals of the full and sums of the partial rdf suggest strongly that many neutral clusters are formed by two anions and two cations. A rough estimation of the fraction of ions associated

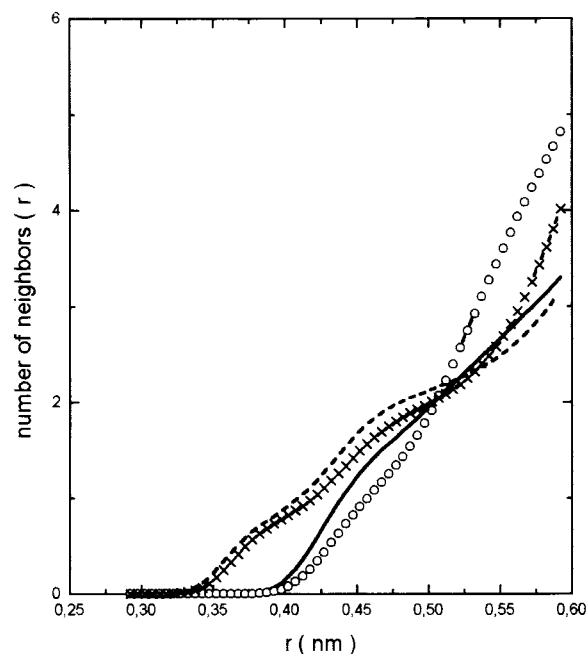


FIG. 5. Running integrals of $g_{\text{Cl}^-, \text{Cl}^-}(r)$ (circle), $g_{\text{Cl}^-}^{11}(r) + g_{\text{Cl}^-}^{12}(r) + g_{\text{Cl}^-}^{22}(r)$ (dashed line), $g_{\text{Na}^+, \text{Na}^+}(r)$ (cross), $g_{\text{Na}^+}^{11}(r) + g_{\text{Na}^+}^{12}(r) + g_{\text{Na}^+}^{22}(r)$ (solid line).

in these clusters, calculated from the fraction of non-neutral pairs, results in more than 0.25. The second consequence is that an important component of the electrolyte diffusion and self-diffusion is determined by the diffusion of large clusters containing at least three ions and a high number of solvent molecules (speculatively about 12 to 14). In order to determine this physical property, it is probably advisable to study such aggregates center of mass displacement. A third conse-

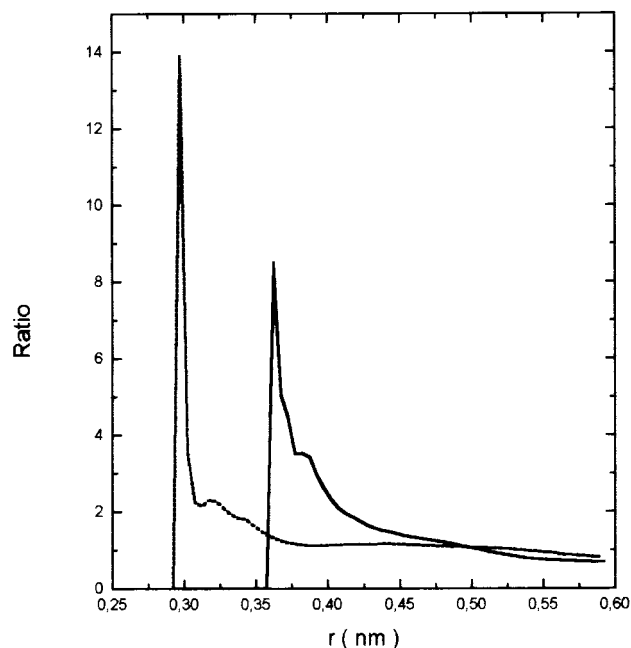


FIG. 6. Ratio of the running integral on $g_{\text{Cl}^-, \text{Cl}^-}(r)$ divided by the running integral on $g_{\text{Na}^+}(r) + g_{\text{Na}^+}^{12}(r) + g_{\text{Na}^+}^{22}(r)$ (solid curve). The same plot for the Na^+, Na^+ pairs is shown as dashed lines.

TABLE III. Life-times of the ion pairs (ps).

	Mean life-time	Relative frequency	Maximum life-time
Cl^-/Cl^-	0.13	0.193	1.41
Na^+/Cl^-	0.14	0.728	3.83
Na^+/Na^+	0.27	0.079	6.63

quence is that no structure involving only ions can be expected. This is because their relative positions in the three dimensional space are governed by the scheme of ionic hydration. The slow diffusion of the ions always observed in experiments⁴¹ and in simulations of aqueous electrolyte systems is easily explained by the existence of these large clusters.

Some question remains yet unanswered such as the extension, the kinetics of formation/destruction of the clusters; what is the fraction of the ions associated in these large clusters? What are the consequences of the existence of the clusters on the kinetics and mechanisms of the ionic reactions? How is the behavior of the clusters in external fields? This is currently under investigation and our results will be presented in a forthcoming paper.

V. CONCLUSION

The structure and properties of the aqueous NaCl is governed by the solvent properties. The fact that the tetrahedral structure of water is maintained (due to the high energetic cost to be broken) together with the fact that the interionic interactions are not able to by-pass this cost, result in the extremely good solvent properties of water regarding ionic solutes. These observations are direct and indirect consequences of the high water polarity. The 1 M NaCl solution is very similar to a colloidal dispersion of entities formed by clusters of solvated and associated ions. The neutral and charged ionic clusters are energetically stable and contain at least three ions. Clusters formed by two anions and two cations are frequent and include a quarter of the all the ions. This explains the ambiguity between the number of identified paired ions and free ions. The existence of large solvated ion clusters obfuscates the apparently simplicity of the mentioned chemical reaction by the increasing of a new ion (the counter-ion) in the picture of SSIP and CIP pair schemes.

ACKNOWLEDGMENTS

This work was supported in part by the Conselho Nacional de Desenvolvimento Científico e Tecnológico and by the Fundação de Amparo à Pesquisa do Estado de São Paulo.

- ¹J. Yu, L. Degreève, and M. Lozada-Cassou, Phys. Rev. Lett. **79**, 3656 (1997).
- ²L. Degreève and M. Lozada-Cassou, Phys. Rev. E **57**, 2978 (1998).
- ³L. Degreève and F. L. B. da Silva, J. Chem. Phys. **110**, 3070 (1999).
- ⁴J. O. M. Bockris and A. K. N. Reddy, *Modern Electrochemistry* (Plenum, New York, 1970), Vol. 1.
- ⁵Faraday Discuss. Chem. Soc. **85** (1988).
- ⁶A. Ben-Naim, *Ionic Solutions* (Plenum, New York, 1980).
- ⁷J. O. M. Bockris and B. E. Conway, in *Comprehensive Treatise on Electro-chemistry* (Plenum, New York, 1980), Vol. 5.
- ⁸Y. Marcus, *Ion Solvation* (Wiley, New York, 1985).
- ⁹P. Bopp, *The Physics and Chemistry of Aqueous Ionic Solutions*, edited by M-C. Bellissent and G. W. Neilson (Reidel, Dordrecht, 1987), pp. 217–243.
- ¹⁰G. Ciccotti, M. Ferrario, J. T. Hynes, and R. Kapral, Chem. Phys. **129**, 241 (1989).
- ¹¹O. A. Karim and J. A. McCammon, Chem. Phys. Lett. **132**, 219 (1986).
- ¹²D. E. Smith and L. X. Dang, J. Chem. Phys. **100**, 3757 (1994).
- ¹³C. Quintale, Jr. and L. Degreève, J. Mol. Struct.: THEOCHEM **282**, 159 (1993).
- ¹⁴L. Degreève and C. Quintale, Jr., Chem. Phys. Lett. **208**, 530 (1993).
- ¹⁵L. Degreève and C. Quintale, Jr., Electrochim. Acta **38**, 1405 (1993).
- ¹⁶L. Degreève and C. Quintale, Jr., J. Chem. Phys. **101**, 2319 (1994).
- ¹⁷J. E. Enderby, Annu. Rev. Phys. Chem. **34**, 155 (1983).
- ¹⁸M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, New York, 1987).
- ¹⁹C. Quintale, Jr. and L. Degreève, J. Mol. Struct.: THEOCHEM **335**, 197 (1995).
- ²⁰S. M. Vecchi, C. Quintale, Jr., and L. Degreève, Biochim. Biophys. Acta **1294**, 149 (1996).
- ²¹L. Degreève and C. Quintale, Jr., J. Electroanal. Chem. **409**, 25 (1996).
- ²²L. Degreève, V. M. de Pauli, and M. A. Duarte, J. Chem. Phys. **106**, 655 (1997).
- ²³K. Hermansson and M. Wojcik, J. Phys. Chem. **102**, 6089 (1998).
- ²⁴N. Bjerrum, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **7**, 9 (1926).
- ²⁵R. M. Fuoss, J. Am. Chem. Soc. **80**, 5059 (1958).
- ²⁶G. Hummer, D. M. Soumpasis, and M. Neumann, Mol. Phys. **81**, 1155 (1993).
- ²⁷G. N. Patey and J. P. Valleau, J. Chem. Phys. **63**, 2334 (1975).
- ²⁸G. N. Patey and S. L. Carnie, J. Chem. Phys. **78**, 5183 (1983).
- ²⁹P. G. Kusalik and G. N. Patey, J. Chem. Phys. **79**, 4468 (1983).
- ³⁰B. M. Pettitt and P. J. Rossky, J. Chem. Phys. **84**, 5836 (1986).
- ³¹B. J. Alder and T. E. Wainwright, J. Chem. Phys. **31**, 459 (1959).
- ³²G. Ciccotti, D. Frenkel, and I. R. McDonald, *Simulations of Liquids and Solids* (North-Holland, Amsterdam, 1987).
- ³³W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, W. R. Impey, and M. L. Klein, J. Chem. Phys. **79**, 926 (1983).
- ³⁴L. Perera and M. L. Berkowitz, J. Chem. Phys. **95**, 1954 (1991).
- ³⁵I. G. Tironi, R. Sperb, P. E. Smith, and W. F. van Gunsteren, J. Chem. Phys. **102**, 5451 (1995).
- ³⁶D. J. Evans and S. Murad, Mol. Phys. **34**, 327 (1977).
- ³⁷C. W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations* (Prentice-Hall, Englewood Cliffs, N. J., 1971).
- ³⁸M. R. Reddy and M. Berkowitz, J. Chem. Phys. **87**, 6682 (1987).
- ³⁹D. van der Spoel, P. J. van Maaren, and H. J. C. Berendsen, J. Chem. Phys. **108**, 10220 (1998).
- ⁴⁰A. E. Garcia and L. Stiller, J. Comput. Chem. **14**, 1396 (1993).
- ⁴¹R. Mills and V. M. M. Lobo, *Self-Diffusion in Electrolyte Solutions* (Elsevier, Amsterdam, 1989).