A Molecular Dynamics Study of Aqueous Solutions. VII. Improved Simulation and Comparison with X-Ray Investigations of a NaCl Solution

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The molecular dynamics simulation has been improved by introducing the Ewald summation for ion-ion interactions. On the basis of the Pauling radii new Lennard-Jones parameters have been derived for the halide ions. The results of a simulation of a system consisting of 200 water molecules, 8 sodium and 8 chloride ions are compared with x-ray investigations of a 2 molal NaCl solution through the structure functions. The first neighbor model commonly used in the x-ray analysis of multicomponent liquids is fitted to the experimental structure function and to the structure function calculated from the radial pair correlation functions of the simulation. The parameters of the two fits and the radial pair correlation functions calculated from the fitted first neighbor model are compared. On the basis of this comparison the usefulness and the limitations of the first neighbor model are discussed.

I. Introduction

The average ion-water distances in the first hydration shells of various alkali and halide ions determined from preceding molecular dynamics simulations (MD) agreed for cations with the results of x-ray and neutron diffraction studies in the limits of experimental error. For anions these MD values were smaller than the experimental ones by about 0.5 Å (see Table 3 in paper III of this series[1]). The reason for this discrepancy was the simplification used in the determination of the Lennard-Jones parameters (LJ) in the ion-ion and ion-water pair potentials. The LJ parameters for isoelectronic cations and anions had been chosen to be the same and have been taken from the corresponding noble gases. As it is known from crystallographic data[2] that ionic radii for anions are significantly larger than the ones for isoelectronic cations the results of the MD calculations are in error as far as the anions are concerned. LJ parameters for ions are not available in the literature. Therefor in section III a procedure is described to determine improved LJ parameters.

Furthermore for ion-ion interaction the Ewald-method[3] has been introduced, leading to an improvement in the calculation of the coulombic part of the potential energy.

With these improvements a 2.2 molal sodium chloride solution has been simulated. The calculated radial pair correlation functions are compared in detail with results of x-ray investigations. The first neighbor model (FNM) usually employed in the determination of structures from diffraction experiments is checked on its usefulness.

II. Details of the Calculations

The basic periodic box with a sidelength of 18.42 Å contained again 200 water molecules, 8 sodium and 8 chloride ions resulting in a density of 1.08 g/cm³. The analytic form of the pair potentials was the same as employed in previous simulations and is given in paper III of this series[1]. While the parameters in the ST2 water model remained unchanged, new parameters in the LJ part of the pair potentials for ion-ion and ion-water interactions were used. They are given in Table 1 in the following section.

In calculating the correct coulombic energy for the ion-ion interactions, resulting from an unlimited number of image ions, the Ewald summation was used[3]. As the ions residing in the first and second neighbor image boxes were included into the direct calculation of the so called error function part, a suitable choice of the separation parameter allowed to neglect the Fourier part of the Ewald sum. The cut-off parameters for ion-water and water-water

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Table 1. Lennard-Jones parameters in the pair potentials for cation-cation, anion-anion, and anion-water interactions and the constants of the pair potential as given in eq. (1). The parameters used for the Na^+-Cl^- interaction are: $\sigma = 3.87$ Å and $\varepsilon = 28.3 \cdot 10^{-16}$ erg.

Jon	Pauling radius [Å]	b [10^{-12} erg]	B [$Å^{-1}$]	c [10^{-12} erg]	σ_{JJ} [Å]	ε_{JJ} [10^{-16} erg]	σ_{JW} [Å]	ε_{JW} [10^{-16} erg]
Li^+	0.60				2.37	24.8	2.77	37.2
Na^+	0.95	1.265	5.07	7.76	2.73	59.4	2.92	54.8
F^-	1.36				4.0	8.22	3.53	20.5
K^+	1.33	1.055	4.12	84.7	3.36	186.0	3.25	94.4
Cl^-	1.81				4.86	27.9	4.02	30.8
Rb^+	1.48	0.897	3.88	174.1	3.57	266.0	3.39	106.5
Br^-	1.95				5.04	44.9	4.16	35.7
Cs^+	1.69	0.752	3.53	405.0	3.92	354.0	3.61	110.0
J^-	2.16				5.40	67.8	4.41	37.9

interactions remained half of the sidelength of the basic box and 7.1 Å, respectively. The introduction of the Ewald summation allowed to dismiss temperature control, but a drift to higher temperatures remained resulting in an average temperature of the simulation of about 35 °C. The simulation, on which the results given here are based, extended over 6000 time steps equivalent to a total elapsed time of 0.65 psec.

III. Lennard-Jones Parameters

In the previous simulations the parameters of the 6;12 Lennard-Jones potential, used to describe the non-coulombic part of the pair potentials, were chosen to be the same for cationic and anionic interactions and taken from the isoelectronic noble gases. This simplification has led to disagreement between simulation and the results of x-ray investigations as far as the average anion-oxygen distances are concerned, while in the limits of error agreement was found in the case of the cations (see Table 3 in paper III of this series[1]). Comparing e.g. Pauling radii[2] it is obvious that halide ions have a larger ionic radius than the isoelectronic alkali ions, which are much more similar in size to noble gases than the halide ions. Because of this similarity and the agreement between simulation and x-ray results in respect to cation-oxygen distances the LJ parameters for alkali ions have not been changed. In order to describe all interactions consistently new LJ parameters had to be determined for the halide ions on the basis of the Pauling radii. As there exist no direct relationships between Pauling radii and the σ and ε of the LJ potential the following procedure has been chosen.

In ionic systems the non-coulombic interactions are frequently described by a potential of the form

$$\varphi(r) = b \exp[B(r - R_{ij})] - C/r^6 \qquad (1)$$

where b, B and C are constants and R_{ij} is the sum of the radii of the ions involved. For each of the four cations Na^+, K^+, Rb^+ and Cs^+ the potential given in Eq. (1) with the corresponding Pauling radii has been fitted to a 6;12 LJ potential with σ and ε taken from the isoelectronic noble gases and the constants b, B and C have been determined. To the new potential with these constants and the corresponding anionic Pauling radii a 6;12 LJ potential was refitted and the σ and ε for the halide ions determined from this fit. Knowing the parameters for anion-anion interactions the parameters for cation-anion and anion-water interactions have been determined by applying Kong's combination rules[4]. The results of this procedure are given in Table 1.

IV. X-Ray Structure Function

Static properties of aqueous solutions derived from MD simulations can be checked by diffraction measurements through the structure function $H(s)$, given by:

$$H(s) = [I(s) - \sum_{\alpha} x_\alpha f_\alpha^2(s)]/[\sum_{\alpha} x_\alpha f_\alpha(s)]^2 , \qquad (2)$$

where $I(s)$ is the corrected absolute intensity function determined in dependence on the scattering variable $s = (4\pi/\lambda) \sin \vartheta/2$, and x_α and $f_\alpha(s)$ are the mole fraction and the scattering amplitude for a particle of type α, respectively. This total structure function can be expressed as a sum of weighted partial structure functions $h_{\alpha\beta}(s)$:

$$H(s) = \sum_{\alpha \leqq \beta} c_{\alpha\beta}(s)\, h_{\alpha\beta}(s) \qquad (3)$$

which are related to the radial pair correlation functions $g_{\alpha\beta}(r)$ through:

$$h_{\alpha\beta}(s) = \varrho_0 \int (g_{\alpha\beta}(r) - 1)\, j_0(s\, r)\, \mathrm{d}\mathbf{r}\,, \qquad (4)$$

where ϱ_0 is the average number density of the particles and j_0 the zeroth order spherical Bessel function. The weighting functions $c_{\alpha\beta}(s)$ can be written in the form:

$$c_{\alpha\beta}(s) = [(2 - \delta_{\alpha\beta})\, x_\alpha\, x_\beta\, f_\alpha(s)\, f_\beta(s)]/[\sum_\alpha x_\alpha\, f_\alpha(s)]^2 \qquad (5)$$

with $\sum_{\alpha \leqq \beta} c_{\alpha\beta}(s) = 1$.

Since the $c_{\alpha\beta}(s)$ depend only weakly on s they can for comparison be approximated by their average values:

$$\langle c_{\alpha\beta} \rangle = \int c_{\alpha\beta}(s)\, \mathrm{d}s / \int \mathrm{d}s\,. \qquad (6)$$

The $\langle c_{\alpha\beta} \rangle$ for a 2 molal aqueous NaCl solution are given in Table 2 for x-ray diffraction experiments if the solution is considered to be a four component system. The corresponding values for neutron diffraction are added in italics. For electron scattering experiments, which have been done up to now only for pure water[5], the $\langle c_{\alpha\beta} \rangle$ are almost the same as for x-ray scattering.

For the comparison of MD results with x-ray diffraction experiments it is justified to treat the NaCl solution as a three component system. The resulting $\langle c_{\alpha\beta} \rangle$ are given in Table 3. The scattering amplitudes $f_\alpha(s)$ for the calculation of the $\langle c_{\alpha\beta} \rangle$ in Table 2 and Table 3 are taken from the literature[6,7]. Considering that the experimental error is of the order of a few percent the ion-ion contributions to the total structure function are negligible, as can be seen from Table 3, and $H(s)$ consists of only three partial structure functions. This fits to the present situation in MD simulation, where also ion-ion radial pair correlation functions are not available because of poor statistics.

NaCl solutions have been investigated by x-ray[8,9] and neutron[10] diffraction studies. The numerical values used in this work are from measurements of one of us (G. P.) and his coworkers at 25 °C[11].

In Fig. 1 the function $sH(s)$ derived from the experiment (points) is compared with the one calculated from the radial pair correlation functions derived from the MD simulation (full line). It is not quite clear what causes the discrepancy at the first maximum, where the experimental curve shows a double peak. One reason could be that the average temperature of the simulation is slightly higher than the temperature during the experiment. In spite of this discrepancy the agreement between both curves can be considered good and the

Table 2. Averaged weighting functions of the four component system for x-ray and neutron (italic) scattering experiments.

	Na^+	Cl^-	O	H, *D*
Na^+	0.002 *0.000*	0.007 *0.000*	0.072 *0.004*	0.005 *0.009*
Cl^-	—	0.007 *0.000*	0.135 *0.011*	0.008 *0.025*
O	—	—	0.661 *0.088*	0.094 *0.403*
H, *D*	—	—	—	0.007 *0.459*

Table 3. Averaged weighting functions of the three component system for x-ray scattering experiments.

	Na^+	Cl^-	H_2O
Na^+	0.003	0.009	0.088
Cl^-	—	0.010	0.162
H_2O	—	—	0.728

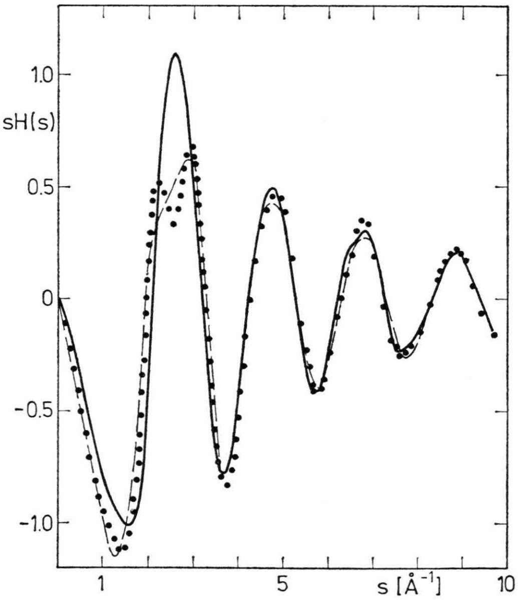

Fig. 1. X-ray structure functions for a 2 molal NaCl solution from experiment (···), molecular dynamics simulation (——) and a first neighbor model fit to the experimental one (– – –).

conclusion seems to be justified that the assumed pair potentials describe the static properties of the solution in a satisfactory way. The ST 2 water model, which proved its usefulness in the case of pure water[12] seems also appropriate to describe ionic solutions.

V. First Neighbor Model

In theoretical investigations[13] as well as in the interpretation of experimental results[14–20] the properties of electrolyte solutions are often successfully described by models which treat ionic hydration only in terms of nearest neighbor interactions. The basic assumptions of the first neighor model(FNM): are:

1) The system consists of three components, the hydrated cation, the hydrated anion and "free" water (water molecules which do not belong to the hydration shells).
2) The discrete hydration shells around the ions and around the "free" water molecules extend only to the first neighbors and have a maximum degree of symmetry (necessary for reduction of free parameters).
3) There exists no interaction between the different hydrated species, an averaged uniform distribution of the water molecules is assumed for distances greater than the nearest neighbor distances.

The FNM was first introduced into the x-ray analysis of multicomponent liquids by Narten and Levy[21]. The FNM used here is a modified version[11] of the one frequently applied to x-ray measurements of aqueous solutions by Licheri et al.[17]. The modification consists in dropping the assumption that the "free" water structure is the same as in the pure solvent, thus allowing to include possible changes in solvent structure.

The structure function for the FNM is given by

$$H_{\mathrm{FNM}}(s) = \sum_{\alpha} X_{\alpha} \mathscr{H}_{\alpha}(s) \tag{7}$$

where α denotes either the hydrated cation or the hydrated anion or a hydrated water molecule. X_{α} are the mole fractions of the three aggregates and $\mathscr{H}_{\alpha}(s)$ the partial structure function of aggregate α.

The $\mathscr{H}_{\alpha}(s)$ can be separated into a contribution from the discrete structure and from the continuum:

$$\mathscr{H}_{\alpha}(s) = \mathscr{H}_{\alpha}^{(\mathrm{D})}(s) + \mathscr{H}_{\alpha}^{(\mathrm{C})}(s) \tag{8}$$

with

$$\mathscr{H}_{\alpha}^{(\mathrm{D})}(s) = \sum_{\substack{i,j \\ i \neq j}}^{\mathrm{C}N_{\alpha}+1} \frac{f_i(s) \cdot f_j(s)}{[\sum_{\alpha} x_{\alpha} f_{\alpha}(s)]^2} \Delta_0(s\, r_{ij}^{(\alpha)}, l_{ij}^{(\alpha)}) \tag{9}$$

and

$$\mathscr{H}_{\alpha}^{(\mathrm{C})}(s) = -\frac{4\pi \varrho_0}{s} r_{\alpha \mathrm{c}}^2 c_{\alpha \mathrm{w}}(s) \Delta_1(s\, r_{\alpha \mathrm{c}}, l_{\alpha \mathrm{c}}) \tag{10}$$

where

$$\Delta_l(s\, r_{ij}, l_{ij}) = j_l(s\, r_{ij}) \exp\{-\tfrac{1}{2} l_{ij}{}^2 s^2\} \tag{11}$$

with the l-th order spherical Bessel function j_l. $f_i(s)$ is the scattering amplitude for the i-th particle in the discrete structure and the $c_{\alpha \mathrm{w}}$ are defined by Equation (5).

Free parameters of the model are the even coordination numbers CN_{α}, the mean first neighbor ion-water $\langle r_{\pm \mathrm{w}} \rangle$ and water-water $\langle r_{\mathrm{ww}} \rangle$ distances, the root mean square deviations (rmsd)

$$l_{\alpha \mathrm{w}} = \langle (\langle r_{\alpha \mathrm{w}} \rangle - r_{\alpha \mathrm{w}})^2 \rangle^{1/2}$$

and the $r_{\alpha \mathrm{c}}$ and $l_{\alpha \mathrm{c}}$ which characterize the boundary of the uniform distribution.

The availability of radial pair correlation functions (rpcf) from MD simulations offers the possibility to check the usefulness of FNM in deriving static properties of aqueous solutions from x-ray scatter-

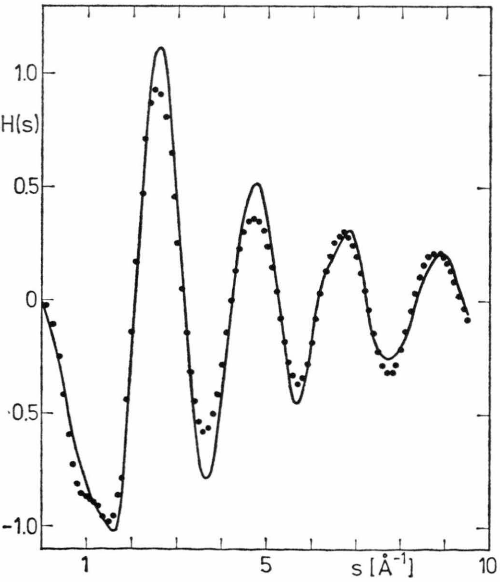

Fig. 2. A first neighbor model fit (···) to the structure function calculated from the radial pair correlation functions of the molecular dynamics simulation (—).

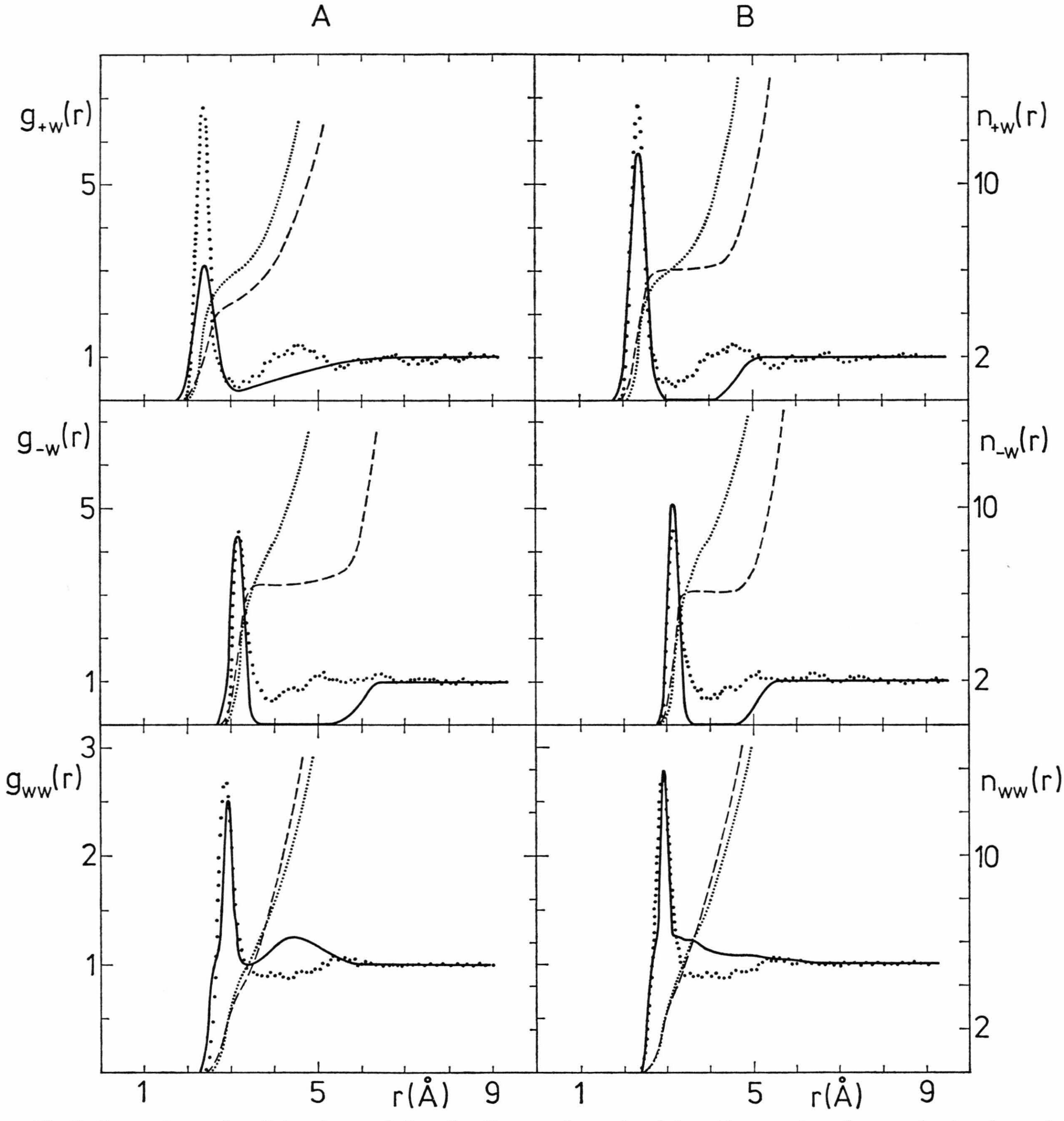

Fig. 3. Comparison of radial pair correlation functions and running integration numbers from molecular dynamics simulations (points) and from first neighbor model fits to the experimental (A) and the molecular dynamics (B) structure function.

ing experiments. In a first step the parameters of the FNM are determined by a least square fit to the structure function derived from the rpcf of the MD simulation (Fig. 2). Then the partial structure functions $h_{\pm w}(s)$ and $h_{ww}(s)$ are determined from this fit through the following relations which have been derived through a suitable rearrangement of terms in Eqs. (5)—(9):

$$h_{\pm w}(s) = \frac{CN_{\pm}}{x_w} \Delta_0(s\, r_{\pm w}, l_{\pm w}) + \mathscr{H}^{(C)}_{\pm}(s\, r_{\pm c}, l_{\pm c})/c_{\pm w}(s) \quad (12)$$

and

$$h_{\mathrm{ww}}(s) = \frac{2X_{\mathrm{w}}}{x_{\mathrm{w}}^2}\cdot CN_{\mathrm{w}}\cdot\frac{P_0}{\varrho_0}\Delta_0(s\,r_{\mathrm{ww}}, l_{\mathrm{ww}}) + 2\sum_{\alpha=+,-}\frac{m_\alpha}{c_{\mathrm{w}}x_{\mathrm{w}}}\sum_{i=1}^{\sigma_\alpha}\nu_i^{(\alpha)}\Delta_0(s\,r_{\mathrm{w}i}^{(\alpha)}, l_{\mathrm{w}i}^{(\alpha)}) + \mathscr{H}_{\mathrm{w}}^{(\mathrm{C})}(s)/c_{\mathrm{ww}}(s) \tag{13}$$

where P_0 and ϱ_0 are the number densities of aggregates and particles, respectively, the m_α are the molalities of the ions, σ_α are symmetry dependent numbers (e.g. 2 for tetrahedra, 3 for octahedra, 4 for hexahedra), the $r_{\mathrm{w}i}^{(\alpha)}$ are water-water distances of kind i in the aggregate α, $\nu_i^{(\alpha)}$ and $l_{\mathrm{w}i}^{(\alpha)}$ the corresponding numbers of such distances and the rmsd, respectively, c_{w} is the number of moles/kg water (55.51).

From these partial structure functions rpc functions are determined with the help of Eq. (4) which are compared with the rpcf derived from MD in column B of Fig. 3.

VI. Discussion

The least square fit of the FNM to the experimental structure function (FNM-EXP), dashed line in Fig. 1, has led to the coordination numbers four for Na$^+$, six for Cl$^-$ and four for water (4–6–4). The best fit of the FNM to the structure function derived from MD resulted in a coordination number combination (6–6–4). It should be noted, however, that a fit of almost the same quality (σ) was achieved with a (6–8–4) FNM. In Table 4 the parameters of these three fits are compared with corresponding values derived from MD and defined by:

$$\langle r_{\alpha\mathrm{w}}\rangle_{\mathrm{R}} = \int_0^R r^3 g_{\alpha\mathrm{w}}(r)\,\mathrm{d}r \Big/ \int_0^R r^2 g_{\alpha\mathrm{w}}(r)\,\mathrm{d}r\,, \tag{14}$$

$$l_{\alpha\mathrm{w}}^{(\mathrm{R})} = \langle(\langle r_{\alpha\mathrm{w}}\rangle - r_{\alpha\mathrm{w}})^2\rangle^{1/2}, \quad r_{\alpha\mathrm{w}} \leqq R, \tag{15}$$

$$CN_\alpha^{(\mathrm{R})} = n_{\alpha\mathrm{w}}(R) = 4\pi\varrho_{0\mathrm{w}}\int_0^R r^2 g_{\alpha\mathrm{w}}(r)\,\mathrm{d}r\,. \tag{16}$$

The MD values are given in Table 4 for the distances R_2 and r_{m1}, marking the positions where $g_{\alpha\mathrm{w}}(r)$ is equal to one for the second time and has its first minimum, respectively. r_{m1} has been chosen as a well defined end of the first hydration shell ($CN_\alpha^{(r_{\mathrm{m1}})}$ has been defined as a hydration number in preceding papers of this series [22]), while R_2 offers itself for comparison with the FNM parameters because it can be considered as the end of the nearest neighbor interactions. The number in parentheses gives the position of the maximum in $g_{\alpha\mathrm{w}}(r)$. Values for the $l_{\mathrm{w}i}^{(\alpha)}$ which are rmsd of $\langle r_{\mathrm{w}i}^{(\alpha)}\rangle$, the average i-th nearest neighbor distance of the water molecules in the hydration shell of particle α are not available from MD. They are defined only for rigid, symmetric hydration shells and are a measure of the rigidity. The $\langle r_{\mathrm{w}i}^{(\alpha)}\rangle$ which are determined by the configuration and $\langle r_{\alpha\mathrm{w}}\rangle$ are not given explicitly in Table 4. For tetrahedral symmetry there exists only $\langle r_{\mathrm{w}1}^{(\alpha)}\rangle$. The continuum parameters $r_{\alpha\mathrm{c}}$ and $l_{\alpha\mathrm{c}}$ are a special feature of FNM and no comparable numbers can be defined in MD.

The $g_{\alpha\mathrm{w}}(r)$ and $n_{\alpha\mathrm{w}}(r)$ calculated from the partial structure functions $h_{\alpha\mathrm{w}}$ of the FNM-EXP and the (6–6–4) FNM-MD fit are compared with the functions derived from MD in column A and B of Fig. 3, respectively.

The $\langle r_{\alpha\mathrm{w}}\rangle$ for the three fits agree in the limits of expected accuracy, estimated to be ± 0.05 Å, for all three α. The slightly higher value for Na$^+$ in FNM-EXP is a consequence of the small hydration number and will be discussed in more detail below. It is obvious from Table 4 that $\langle r_{\alpha\mathrm{w}}\rangle$from the fits do not lead to the average distances for the complete hydration shell up to r_{m1}. This is a consequence of the rather symmetric peak in $g_{\alpha\mathrm{w}}(r)$ resulting from the discrete contribution of the FNM, where

$$g_{\alpha\mathrm{w}}^{(\mathrm{D})}(r) = \frac{c}{\sqrt{32\pi^3}\,\varrho_{0\mathrm{w}}\,r_{\alpha\mathrm{w}}\cdot l_{\alpha\mathrm{w}}}\cdot\frac{1}{r} \times \{\exp[-(r-r_{\alpha\mathrm{w}})^2/2\,l_{\alpha\mathrm{w}}] - \exp[-(r+r_{\alpha\mathrm{w}})^2/2\,l_{\alpha\mathrm{w}}]\}\,. \tag{17}$$

If agreement is to be expected the $\langle r_{\alpha\mathrm{w}}\rangle$ resulting from scattering experiments analysed by FNM should be compared with $\langle r_{\alpha\mathrm{w}}\rangle$ calculated from $g_{\alpha\mathrm{w}}(r)$ derived from MD or otherwise where the averaging is extended only up to R_2. The numbers in parantheses show that for larger ions like Cl$^-$ where the first peaks in $g_{\alpha\mathrm{w}}(r)$ become rather asymmetric, the position of the first maximum (r_{M1}) is in agreement with what is called average ion-water or water-water distance in FNM.

The ion-water radial pair correlation functions from the FNM fit consist of two parts resulting from the discrete and continuous contributions to the partial structure functions. (The problems connected with $g_{\mathrm{ww}}(r)$ have to be discussed separately, because a third type of contribution exists,

Table 4. Parameters of the first neighbor model fit to the experimental structure function (FNM-EXP), to the structure function derived from the molecular dynamics simulation (FNM-MD) for two coordination number combinations and corresponding values calculated from the radial pair correlation functions of the MD simulation (MD). r_{m1} and R_2 are the distances where $g(r)$ has its first minimum and is one for the second time, respectively. The numbers in parantheses give the position of the first peak in $g(r)$.

α	Na^+					Cl^-					H_2O				
	MD		FNM-MD		FNM-EXP	MD		FNM-MD		FNM-EXP	MD		FNM-MD		FNM EXP
	r_{m1}	R_2	6-6-4	6-8-4	4-6-4	r_{m1}	R_2	6-6-4	6-8-4	4-6-4	r_{m1}	R_2	6-6-4	6-8-4	4-6-4
CN_α	6.1	5.4	6	6	4	7.9	6.8	6	8	6	6.0	5.0	4	4	4
$\langle r_{\alpha w} \rangle$	2.45	2.39 (2.34)	2.36	2.38	2.42	3.29	2.23 (3.16)	3.14	3.15	3.14	3.05	2.96 (2.91)	2.93	2.94	2.95
$l_{\alpha w}$	0.23	0.15	0.19	0.18	0.22	0.28	0.15	0.11	0.18	0.14	0.32	0.20	0.06	0.06	0.07
$l_{w1}^{(\alpha)}$	—	—	0.41	0.47	0.30	—	—	1.62	1.29	0.33	—	—	1.27	4.63	0.42
$l_{w2}^{(\alpha)}$	—	—	0.27	0.17	—	—	—	0.08	0.17	0.32	—	—	—	—	—
$l_{w3}^{(\alpha)}$	—	—	—	—	—	—	—	—	0.24	—	—	—	—	—	—
$r_{\alpha c}$	—	—	4.63	5.18	4.52	—	—	5.10	5.29	5.96	—	—	2.53	2.52	2.47
$l_{\alpha c}$	—	—	0.26	0.49	1.31	—	—	0.24	0.08	0.22	—	—	0.001	0.003	0.07
σ			$9.49 \cdot 10^{-2}$	$9.83 \cdot 10^{-2}$	$6.32 \cdot 10^{-2}$										

which results from water-water interactions in the hydration shells of the three aggregates.) The discrete contributions to the FNM-MD fit describe the first peaks of $g_{\pm w}(r)$ fairly well as can be seen from column B in Figure 3. The very symmetric peak in $g_{NaW}(r)$ from MD and the well defined, low minimum leads to agreement of the hydration number for the sodium ion between FNM-MD fit and MD. The rather asymmetric MD peak in $g_{Clw}(r)$ and the flat minimum for this larger ion results in a too small value for the coordination number derived from the best fit (6–6–4) FNM-MD even if the value $CN_{Cl}^{R_2}$ is used for comparison. But it is interesting to note that a FNM-MD fit of only slightly poorer quality (see σ in Table 4) leads to the correct hydration number. The FNM achieves this higher hydration number mainly by increasing the width of the first peak in $g_{Clw}(r)$ indicated by an increase of l_{Clw} from 0.11 to 0.18 Å.

Although the FNM fit to the experimental structure function is significantly better than the FNM-MD fit, as can be seen from σ in Table 4 and from Figs. 1 and 2, the description of the first peaks in $g_{\pm w}(r)$ is remarkably poorer, and the coordination numbers are too small even if they are compared with $CN_\alpha^{(R_2)}$ (see column A in Fig. 3). The agreement is worse in the case of the sodium ion although a better agreement is to be expected for the smaller ions as discussed above. As $H_{MD}(s)$ does not show the double peak of $H_{EXP}(s)$ (see Fig. 1), it could be concluded that the poor agreement of $g_{\pm w}(r)$ between the FNM-EXP fit and MD is a failure of the simulation. But this conclusion does not seem to be justified because this double peak appears even more pronounced in pure water too and can, therefore, hardly be responsible for incorrect $g_{\pm w}(r)$. Since $CN_{Na}^{(R_2)} = 5.4$ and the next smallest even number is too small, the continuous part of FNM has to contribute to the first peak in $g_{NaW}(r)$ resulting in an extremely large l_{NaC} of 1.31 Å. This shows in agreement with the conclusion reached in paper VI of this series[22] that coordination numbers derived from scattering experiments are generally smaller than hydration numbers derived from MD.

The discussion of $g_{WW}(r)$ in respect to the number of nearest neighbors has to follow similar lines as in the case of the hydration number of Na^+, but is even more complicated by a third contribution mainly in the range 4—5 Å resulting from water-

water interactions in the hydration shells (see last row in Figure 3). As the coordination number of four is too small especially in a 2.2 molal aqueous solution, where the water structure has to be disturbed, the contribution from the continuous part of the structure function has to begin at a distance smaller than the maximum of $g_{\mathrm{ww}}(r)$ for compensation. Table 4 shows that for the three fits $r_{\mathrm{wc}} \approx 2.50$ Å and that additionally the continuous part rises sharply recognizable from l_{wc}. It is an invalid feature that the third contribution prevents that $g_{\mathrm{ww}}(r)$ becomes smaller than one in the range of the minimum. But it is interesting to note that all contributions together lead to a function $n_{\mathrm{ww}}(r)$ very similar to the one derived from MD at least up to $r = 4$ Å, although a coordination number four is assumed in the fits. The overlap of discrete and continuous contributions of the structure function to $g_{\mathrm{ww}}(r)$ is not consistent with the original assumption of FNM, but the reconstructed first peaks in $g_{\mathrm{ww}}(r)$ show a relatively good agreement with the one from MD.

Finally, the overall reliability of $g_{\alpha\mathrm{w}}(r)$ can be checked in a simple way through the relation:

$$\Delta_{\alpha\mathrm{w}} = 4\pi\,\varrho_{0\mathrm{w}}\left(\int_0^R g_{\alpha\mathrm{w}}(r)\,r^2\,\mathrm{d}r - \int_0^R r^2\,\mathrm{d}r\right). \quad (18)$$

If the integral is extended to a distance R from where on $g_{\mathrm{ww}}(r) = 1$, $\Delta_{\alpha\mathrm{w}}$ has to be 0 for ions and -1 for a water molecule. Table 5 shows for $R = 9$ Å what is expected on the basis of Fig. 3 namely that $\Delta_{\alpha\mathrm{w}}$ is too small for the ions and too large for water in the case of the fits. The $g_{\alpha\mathrm{w}}(r)$ from MD lead to nearly the correct values.

Table 5. Deviations of the total number of water molecules in a sphere of radius 9 Å as calculated from the various radial pair correlation functions from the number calculated through volume times average number density of the water molecules.

	FNM-MD	FNM-EXP	MD	correct value
+w	−3.6	−4.8	−0.8	0
−w	−7.5	−16.6	0.2	0
ww	4.4	4.4	−0.9	−1

VII. Summary and Conclusions

The molecular dynamics simulation of a 2.2 molal NaCl solution has been improved by introducing the Ewald summation for ion-ion interactions and by revised Lennard-Jones parameters in the ion-ion and ion-water pair potentials. The discrepancy in the average anion-water distance between earlier simulations and scattering experiments has been resolved.

The structure function derived from the radial pair correlation functions of the simulation is in good agreement with the measured x-ray structure function of a 2 molal NaCl solution except for a discrepancy in the range of the first peak which is attributed to the generally higher temperature during the simulation.

The first neighbor model is fitted to the experimental and the simulated structure function and from both fits radial pair correlation functions are derived. The comparison of the parameters and the $g_{\alpha\mathrm{w}}(r)$ from the fits with the molecular dynamics results allow the following conclusions on the usefulness and limitations of the first neighbor model.

The average ion-water and water-water distances of the nearest neighbors derived from the fits coincide in the limits of error with the first maximum of the radial pair correlation functions calculated from the molecular dynamics simulation. They are not identical with the average distances of the complete hydration shells up to the first minimum of $g_{\alpha\mathrm{w}}(r)$.

The coordination numbers of the ions from the FNM fit are generally smaller than the hydration numbers calculated from MD by integration of $g_{\pm\mathrm{w}}(r)$ up to the first minimum.

The first neighbor model is able to describe the first peaks of the radial pair correlation functions quite well and marks rather correctly the beginning of the homogeneous distribution of the water molecules. Inherent limitations of the model prevent a correct description of the $g_{\alpha\mathrm{w}}(r)$ in the range between. Additional complications in $g_{\mathrm{ww}}(r)$ arise from the water-water interactions in the hydration shells of the ions.

The coordination number and the average first neighbor water-water distance show that the solvent structure in a 2 molal NaCl solution is rather different from the structure of the pure solvent. Thus it is questionable to use pure water structure functions in describing solvent contributions in aqueous solutions.

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