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Osmotic and activity coefficients from effective potentials for hydrated ions

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Based on a method we previously suggested [Phys. Rev. E **52**, 3730 (1995)], effective interaction potentials between Na^+ and Cl^- ions have been derived from interionic radial distribution functions (RDF) in molecular dynamics (MD) simulations of aqueous NaCl solution. The effective interaction potentials between the hydrated ions, which reproduce the original ion-ion RDF curves, can be used further to construct a corresponding ionic solution in a much larger scale and to calculate any properties dependent on the structure of the electrolyte solution. In a subsequent Monte Carlo (MC) simulation, using the effective potentials, the osmotic and activity coefficients are calculated for the ions. Calculation of these properties directly from atomic MD or MC simulations is beyond the capacity of the present computers due to the very large number of molecules required in the simulations to obtain reliable results. A very good agreement with the experimental results is obtained. Effects of three-body interactions and concentration dependencies of the effective potentials are discussed. [S1063-651X(97)01405-0]

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I. INTRODUCTION

An obvious dilemma in computer modeling of condensed matter, at the atomic level, is the fact that as the system is described in more detail and more rigorously, the number of atoms that can be included in the model becomes smaller. In spite of the rapid development of the computer technology, tractable system sizes used in computer simulations range from 10^3 to 10^4 in most applications, covering time scales of a few hundreds of picoseconds. However, realistic simulations of complex biomolecules in water solution with natural contents of ions require a much larger number of atoms. Not discussing, at the moment, how meaningful atomistic computer simulations of very large molecular aggregates really are, we turn to the challenging problem of trying to simplify the more sophisticated models for large complex systems, while keeping as much important original information as possible.

In this work we present such a simplified model for ionic solutions, conceptually related to the primitive electrolyte model (PEM), based on the continuum solvent model and hydrated ions. In PEM, the potential $1/\varepsilon r$ is often used in simulations of ionic solutions. This, of course, is a rather crude approximation, especially at short interionic distances. For our purposes, a better potential could be the one taking somehow into account the solvation structure around the ions. This can be constructed, for example, by carrying out molecular dynamics (MD) simulations of ionic solutions using good quality all-atom interaction potentials, as we suggested earlier [1]. In this method, so-called effective potential functions (EPF) are derived from interionic radial distribution functions (RDF). These EPFs in hand, the initial problem can be either scaled up to much larger dimensions or the EPFs can be transferred into another problem, containing the same substance on a larger scale.

In a wider perspective, the effective potential method is related to the idea of ''global approach'' in statistical mechanical modeling, promoted by Clementi [2]. According to this picture, starting from accurate *ab initio* electronic calculations, the final results are supplied as an input to a next successive level, this being a classical mechanical treatment of atoms. The output from atomistic simulations will serve as a starting point to conformational calculations of macromolecules and low amplitude dynamics within the framework of hydrodynamics. The idea of information fed into a next level makes the whole process self-consistent.

It was shown in our previous paper [1] that site-site radial distribution function data can be used to derive a set of site-site pair interaction potentials using a rapidly convergent simulation procedure (the same problem was also recently addressed by Soper [3]). If the interactions between the particles are assumed to be pairwise additive, one can prove [4,5] that there is a unique relationship between the pair potential and RDF. More precisely, if two different pair potentials are found to reproduce the same RDF, they only differ by a constant from each other. Now, by assuming that pair potentials always approach zero at large distances, this constant can be found fixed and the solution to the reverse problem is unique as well. Having obtained the effective pair potentials, one can use them to calculate other properties of the system, including all the higher-order correlation functions. Of course, higher correlations are determined by the RDFs only through the pairwise interactions. In real liquid systems the many-body forces are often important. They may lead to differences in higher-order correlation functions in comparison to pair potentials. In empirically parametrized pair potentials, used in most atomistic computer simulations, part of the many-body interactions become included in an average way after fitting them to experimental data, measured on macroscopic samples.

In this work we calculate the effective potentials for Na^+ and Cl^- ions in aqueous solution for varying salt concentrations. These calculations are based on data obtained in our previous work, and all the computational details are found in Refs. [1,6]. The EPFs are applied to calculate the osmotic and activity coefficients, using standard Monte Carlo techniques for the purpose. These two quantities are directly measurable and are given in chemistry handbooks. A

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comparison with experimental data may serve as a test of reliability of the effective potentials derived from radial distribution functions. Indirectly they also evaluate the quality of the original atomic site-site pair potentials.

Calculations of the osmotic and activity coefficients using molecular computer simulation methods require determination of the osmotic pressure and chemical potential (or free energy) for a sufficiently large sample, including hundreds of ions dissolved in solution consisting of tens of thousands of water molecules. Clearly, such simulations cannot be done, at the present, with explicit representation of the solvent molecules. Besides the very large number of molecules needed, the ion-ion interactions in solution are two orders of magnitude weaker than the ion-water interactions, requiring very long simulations for accurate enough results, not at least since the hydrated ions are diffusing very slowly.

Osmotic coefficients have been calculated previously using the primitive electrolyte model [7,8]. The PEM model has also been used to calculate the activity coefficients [9]. In using PEM, the Coulombic potential is furnished with the experimental dielectric constant ($\varepsilon = 78$ for water at 298 K) and hard-core repulsive potential defined by the ''hydrated radius,'' which is actually only an adjustable parameter, fitted to reproduce experimental data for each specific ion type. These types of calculations use only a marginal amount of computing time, compared to molecular computer simulations of electrolyte solutions with a corresponding number of ions.

A simulation of ionic systems using effective potentials consumes the same small amount of computing time as the corresponding simulation using the primitive electrolyte model, but reproduces the solute distribution functions to the same accuracy as the all-atom simulation with solvent molecules explicitly included. It should be stressed that no adjustable parameters such as the ''hydration radius'' have been used. The concept of effective potentials, as described in this work, can be applied to other types of solutions as well. Several works are currently in progress from our laboratory along these lines.

II. CALCULATION OF EFFECTIVE POTENTIALS

In this section we briefly recapitulate the computational procedure from our previous papers [1,6] for convenience and to provide a basis for the discussion of the method.

A. Molecular dynamics simulations

The reference ion-ion RDFs have been obtained from molecular dynamics simulations of Na^+ and Cl^- ions in water solution, using a standard type of force field, in which all the intermolecular interactions are expressed as a sum of the electrostatic and the Lennard-Jones potentials with parameters, fitted for each atomic type. We have chosen the flexible simple point charge (SPC) water model [10] and the Smith-Dang parameters for ion-water and ion-ion interactions [11]: σ=2.35 Å, and $\varepsilon = 0.544$ kJ/M for Na^+ and $\sigma = 4.4$ Å and $\varepsilon = 0.42$ kJ/M for Cl^-. The atom-atom potentials are expressed as

$$U(r_{ij}) = \frac{q_i q_j}{r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right], \qquad (1)$$

where off-diagonal Lennard-Jones parameters σ_{ij} and ε_{ij} are given using the combination rules:

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2, \qquad \varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}. \qquad (2)$$

TABLE I. Simulation parameters.

Run	1	2	3	4	5	6
No. of H_2O	490	1960	248	484	236	220
No. of ion pairs	5	20	4	8	10	18
Salt concentration, *M*	0.55	0.55	0.87	0.9	2.2	4.1
Average box length, Å	24.5	38.7	19.8	24.4	19.4	19.3
Simulation time, ns	3	2	3.5	2	3	3

We have used constant-temperature constant-pressure molecular dynamics algorithms in all our MD simulations, keeping the temperature at 300 K and the pressure 1 atm. Other characteristic simulation parameters are given in Table I.

The simulations are performed at four different salt concentrations. Further, in two of these (0.55*M* and 0.9*M*) the box size is varied to evaluate possible size effects. Cubic cells are used in all the simulations together with periodic boundary conditions. The Ewald method is applied for the treatment of long range electrostatic interactions. We have used the double time step algorithm by Tuckerman *et al.* [12] with a small time step of 0.2 fs for intramolecular and short range (less than 5 Å) intermolecular interactions, and a large time step of 2 fs for the nonbonded interactions beyond 5 Å. The calculations were carried out on an IBM SP2 at the center of parallel computers, the Royal Institute of Technology, Stockholm using a parallel message passing (MPI) version of the simulation program.

The resulting reference ion-ion RDF for 0.9*M* and 4*M* concentrations are shown in Fig. 1. For more detailed information on these simulations (RDFs for all considered cases, dynamical properties of ions, analysis of statistical errors, etc.) the reader is referred to our previous paper [6].

B. Effective potentials for ions

The basic methodology for reconstruction of pair potentials from RDFs, using an iterative Monte Carlo procedure

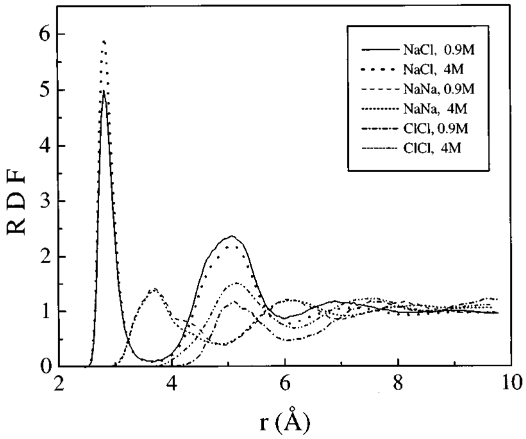

FIG. 1. Radial distribution functions of Na^+ and Cl^- ions at 0.9*M* and 4*M* salt concentration.

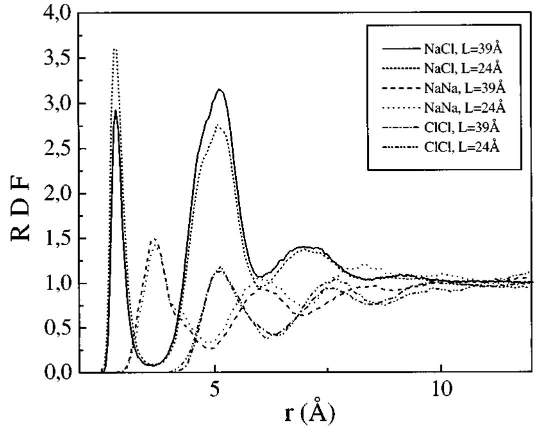

FIG. 2. Radial distribution functions of Na^+ and Cl^- ions at $0.5M$ salt concentration and different simulation box size L.

and its application to an ionic system with long range electrostatic interactions, is given in our previous work [1]. The reverse simulations, aiming at obtaining the effective potentials, are carried out in the NVT ensemble, using the same box size and the same number of ions as in the original MD simulations (but without the explicit water molecules). Possible size effects on the RDFs should therefore to a large degree cancel out in the direct MD and the reverse Monte Carlo (MC) simulations. To control this, we have carried out the calculations of the RDFs and the effective potentials at the same ion concentration but different system sizes. The RDFs and the corresponding effective potentials for runs 1 and 2 are shown in Figs. 2 and 3, respectively. It is possible to see that the differences in the effective potentials are less pronounced than the differences of RDFs. The same observation holds for runs 3 and 4, performed at $0.9M$ concentration.

In all the cases the effective potential makes 1–2 oscillations, thereby reflecting the molecular nature of the solvent, and then finally approaches the primitive model potential with dielectric constant close to 80. In our largest simulation (run 2), with the cubic box side length of 39 Å, the effective potential was calculated for distances up to 19 Å. One can see in this case (Fig. 3) that the effective potential almost perfectly coincides with the Coulombic potential with $\varepsilon = 78$ at distances greater than 10 Å. This confirms that the flexible SPC water model has a dielectric constant close to the experimental value [13].

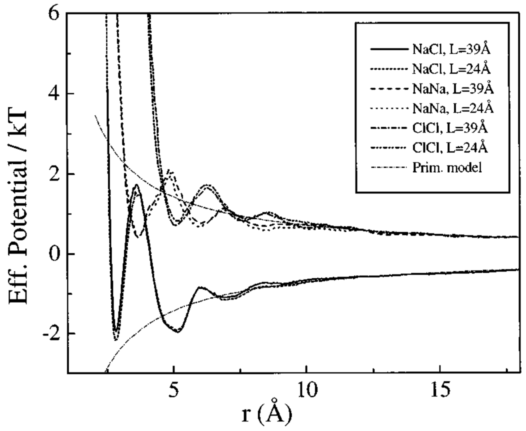

FIG. 3. Effective potentials for RDFs in Fig. 2.

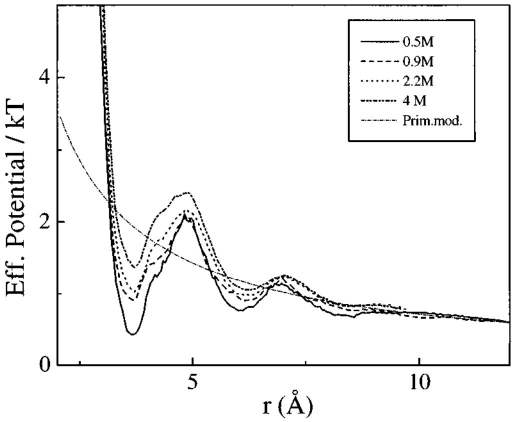

FIG. 4. NaNa effective potentials obtained at different concentrations.

The negligible size dependence and the behavior of the effective potentials approaching the Coulombic potential at larger distances make it possible to calculate effective potentials from MD simulations of standard system sizes (with cubic box side length of about 20 Å, corresponding, for example, to 256 water molecules at 300 K), and subsequently apply them to simulations of much larger systems, supplementing the effective potential by the Coulombic potential with the experimental bulk dielectric constant at large distances.

The results on effective potentials at different concentrations are presented in Figs. 4–6. At high salt concentrations the absolute values of the effective potentials are slightly higher than at moderate concentrations. This may be interpreted as a lowering of the dielectric constant at high concentration (in case it is possible to speak about a dielectric constant of a concentrated ionic solution). Still, the dependence of the effective potential on salt concentration is rather insignificant. This makes it possible to apply the effective potentials, obtained at one salt concentration, to study ionic solutions at other concentrations.

III. OSMOTIC AND ACTIVITY COEFFICIENTS

The primary reason for calculating effective potentials is to apply them to simulate significantly larger systems with-

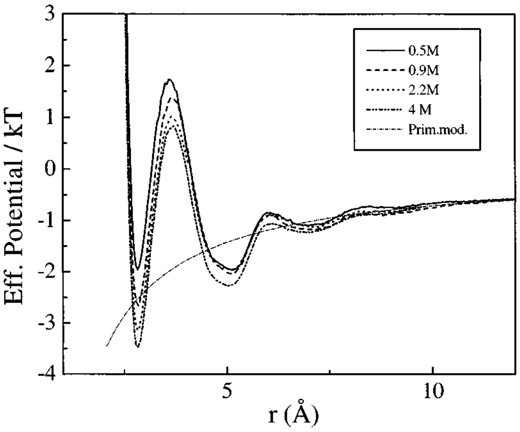

FIG. 5. NaCl effective potentials obtained at different concentrations.

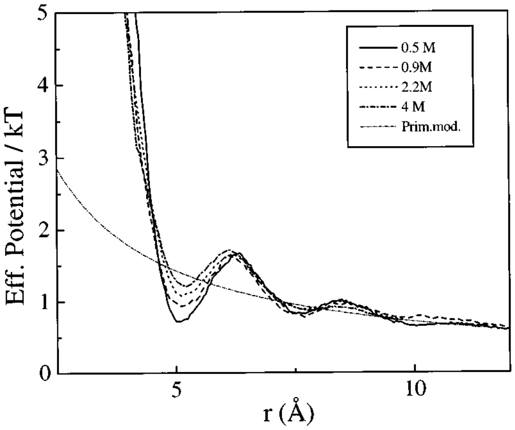

FIG. 6. ClCl effective potentials obtained at different concentrations.

out explicit account of water molecules or other solvent molecules. It is assumed here that if effective potentials reproduce the original RDFs, they will also give realistic description of other structural and even thermodynamical properties. The obvious way to check the validity of the assumption is to compare with experiment. Activity and osmotic coefficients are therefore good choices for the purpose, since their experimental values are accurately known.

The osmotic coefficient is defined as

$$\phi = \frac{1}{kT}\frac{\partial(F/c)}{\partial c}\bigg|_T = \frac{P_{\mathrm{osm}}V}{NkT} \tag{3}$$

and the activity coefficient is

$$\lambda = \exp\left(\frac{\mu_{\mathrm{ex}}}{kT}\right), \tag{4}$$

where μ_{ex} is the excess chemical potential.

If the Hamiltonian (e.g., effective potential) does not depend on the concentration, the osmotic pressure can be calculated using the standard virial expression:

$$P_{\mathrm{osm}} = \frac{NkT}{V} - \frac{1}{3V}\left\langle \sum_{i,j} \frac{\partial U}{\partial r_{ij}} r_{ij} \right\rangle. \tag{5}$$

If the interaction potential is concentration dependent, an additional term appears in the derivative expression of the free energy:

$$\phi = \frac{1}{kT}\frac{\partial(F/c)}{\partial c}\bigg|_{T,N} = -\frac{\partial}{\partial c}\ln\int_V \Pi dx_i \exp[-H(c)/kT] = \phi_0 + \Delta\phi. \tag{6}$$

The term ϕ_0 comes from the concentration dependence of the integration volume $\int_V \Pi dx_i$. This term is the osmotic coefficient for the concentration-independent Hamiltonian and is expressed by Eqs. (3) and (5). The correction $\Delta\phi$ comes from taking the derivative of $H(c)$ in Eq. (6) and is equal to

$$\Delta\phi = \frac{c}{N}\left\langle \frac{\partial}{\partial c}[H(c)/kT] \right\rangle \tag{7}$$

and can be evaluated from the average difference of the two Hamiltonians corresponding to two different concentrations.

To calculate the chemical potential [and the activity coefficient according to Eq. (4)], we can write

$$\mu = \frac{\partial}{\partial N}F(c)\bigg|_V = \frac{\partial}{\partial N}F(c)\bigg|_c + \frac{1}{V}\frac{\partial F(c)}{\partial c}\bigg|_N = \mu_0 + \Delta\mu, \tag{8}$$

where μ_0 is the chemical potential for a concentration-independent Hamiltonian which can be obtained by standard free energy calculation methods, for example, the particle insertion. The correction to the chemical potential due to explicit concentration dependence of the Hamiltonian is

$$\Delta\mu = \frac{1}{V}\frac{\partial F(c)}{\partial c}, \tag{9}$$

and it can be calculated from the free energy difference of the two Hamiltonians, corresponding to two different concentrations.

Since we have carried out the calculations of the effective potentials at very different concentrations, we can only roughly estimate the correction terms $\Delta\phi$ and $\Delta\mu$. However, the dependence of the effective potentials on salt concentration is weak, almost below the statistical error and we can expect the correction terms to be small. Based on this, we have performed calculations of the osmotic and activity coefficient for each set of the effective potentials, corresponding to different concentrations, by assuming these to be concentration independent [i.e., we have calculated the terms ϕ_0 and μ_0 according to Eqs. (6) and (8)].

The simulation is carried out by the Metropolis Monte Carlo method for 200 ion pairs. The box size was determined by the ion concentration in each case. Since the original effective potentials are obtained for distances less than half of the box length in the MD simulations, we allow them to become Coulombic potentials with dielectric constant $\varepsilon = 78$ at larger distances. The long range part of the Coulombic potential was taken into account by the Ewald method. The osmotic pressure was determined by Eq. (5) and the excess chemical potential was calculated by insertion or deletion of an ion pair in the frame of the expanded ensemble method [14].

The calculations are carried out for six sets of effective potentials, obtained at different concentrations in corresponding molecular dynamics runs (see Table I). The results are presented in Tables II and III. The agreement with experimental results is almost perfect for concentrations less than $1M$. Some deviations are observed at high concentrations. These deviations seem to have a random character and do not represent concentration- or size-dependent trends, which can be observed for RDFs and effective potentials. This is because the osmotic and especially the activity coefficients are very sensitive to the interaction potentials at high salt concentration. Our test simulations at $5M$ show that an increase of the Na-Na potential by only $0.02kT$ for interionic distances of 6–8 Å will lead to about 10% increase in the activity coefficient. The uncertainty in effective potentials comes mainly from the statistical error in calculations of RDF in MD simulations. Precise determination of ion-ion

TABLE II. Osmotic coefficients, calculated for six sets of effective potentials (see Table I). $\Delta\phi$ is evaluation of correction due to concentration dependence of effective potentials. Experimental results are from [20]. For more details, see the text.

			Run	number				
Concentration (M)	1	2	3	4	5	6	$\Delta\phi$	Experiment
0.01	0.969	0.970	0.97	0.97	0.968	0.967		
0.03	0.951	0.953	0.95	0.95	0.949	0.945		
0.1	0.93	0.93	0.93	0.93	0.926	0.915	<0.01	0.93
0.3	0.91	0.92	0.91	0.92	0.91	0.90		0.92
0.6	0.91	0.90	0.92	0.92	0.91	0.90	0.05	0.92
1	0.92	0.91	0.94	0.94	0.93	0.91		0.94
1.5	0.93	0.92	0.96	0.97	0.98	0.93	± 0.05	0.96
2	0.96	0.94	0.99	1.02	1.00	0.95		0.98
3	1.04	1.0	1.08	1.13	1.13	0.99	-0.1	1.05
5	1.25	1.12	1.29	1.43	1.41	1.14	-0.2	1.2

RDF is a very difficult task because of the low number of ions in the solution and their slow diffusion. In fact, even after several nanoseconds of simulation the statistical error may be about 5% [6]. This may correspond to an uncertainty in effective potentials of about $(0.05-0.1)kT$ units. This uncertainty, however, influences the osmotic and activity coefficients only at high concentrations.

The corrections due to concentration dependencies of the effective potentials can be calculated in principle by Eqs. (7) and (9). Because the effective potentials are calculated at well separated concentrations and because of statistical errors, we can only give a rough estimate of the derivatives in Eqs. (7) and (9). We have estimated the possible corrections to the osmotic and activity coefficients by calculating the energy and the free energy differences from Hamiltonians derived at different concentrations. Because of statistical uncertainty, we can only speak about an upper bound to the corrections due to concentration dependencies of effective potentials. These values are listed in Tables II and III. One can see that possible corrections are of the same magnitude as the fluctuations due to the uncertainties in the RDF calculations. The true values of the corrections may be even lower.

IV. DISCUSSION

While going from the full atomic model of the ion-water system to the hydrated ion model with effective potentials, we reduce the description of the system by removing unimportant (solvent) degrees of freedom. The exact Hamiltonian of the reduced system, which reproduces all canonical averages for important degrees of freedom $\{x_i, i=1,\ldots,n\}$, is obtained by averaging over the other degrees of freedom $\{x_i, i=n+1,\ldots,N\}$:

$$-\beta H^*\{x_i\}_{i=1,\ldots,n} = \ln \int \prod_{j=n+1}^{N} dx_j \times \exp(-\beta H\{x_i, x_j\})_{i=1,\ldots,n;j=n+1,\ldots,N}. \tag{10}$$

The basic underlying approximation of the effective potential approach is the replacement of H^* in Eq. (10) by a sum of pair potentials $H_{\mathrm{eff}}=\Sigma_{i>k}U(r_{ik})$. The Hamiltonians H^* and H_{eff} produce the same RDF, but they do not necessarily coincide. One can prove, however, that among Hamil-

TABLE III. Activity coefficients, calculated for six sets of effective potentials (see Table I). $\Delta\lambda$ is evaluation of correction due to concentration dependence of effective potentials. Experimental results are from [21]. For more details, see the text.

				Run number				
Concentration (M)	1	2	3	4	5	6	$\Delta\lambda$	Experiment
0.001	0.964	0.963	0.965	0.964	0.964	0.965		0.965
0.003	0.942	0.943	0.943	0.943	0.942	0.94		0.94
0.01	0.90	0.896	0.905	0.902	0.898	0.89		0.903
0.03	0.84	0.838	0.845	0.842	0.843	0.835		0.845
0.1	0.77	0.765	0.772	0.78	0.771	0.76	<0.01	0.78
0.3	0.70	0.69	0.72	0.71	0.70	0.68		0.71
0.6	0.65	0.64	0.67	0.66	0.67	0.64	0.05	0.67
1	0.64	0.62	0.66	0.66	0.67	0.62		0.66
1.5	0.63	0.61	0.67	0.69	0.70	0.61	± 0.05	
2	0.63	0.61	0.68	0.72	0.73	0.62		0.67
3	0.65	0.62	0.75	0.84	0.85	0.65	-0.1	
5	0.85	0.72	1.05	1.25	1.29	0.83	-0.2	0.87

tonians with only pair interactions, there is a single Hamiltonian producing a given set of RDFs [4].

Moreover, it can be shown that this particular Hamiltonian gives maximum configurational entropy among all the Hamiltonians reproducing the same RDF. The proof is given in the Appendix. It is often assumed that the maximum entropy principle corresponds to a ''best guess'' when the amount of information about a system is limited. In our case, the ''limited information'' is our RDF (pair correlation function), compared to a full N-particle distribution function. The maximum entropy principle simply means here that the effective potentials, obtained by inverting the RDF, generate in some sense the most typical set of configurations, consistent with the given RDF.

In general, the effective potential H^* contains also three- and higher-order terms, which cannot be reduced to the effective pair potentials. This part of the Hamiltonian, $H^* - H_{\mathrm{eff}}$, leads to possible differences in three- and higher-order correlation functions. The possible effect of the irreducible three-body interactions is discussed in the literature in connection with the problem of uniqueness of the reverse Monte Carlo simulations [5,15,16]. The reverse Monte Carlo method, originally suggested in 1988 by McGreevy and Pusztai [17], uses the RDF as an input parameter and produces a set of configurations for further analysis, though not reconstructing the interaction potential. This method has since then widely been used for analysis of disordered structures [18,19]. The problem is, to what extent pair correlations can be used to determine higher-order correlations. It was shown in [15] that for atomic liquids, like liquid argon or molten salt, equality of RDFs implies strong similarity of local arrangement of particles. For liquid water it was found [16] that, by starting from the experimental atom-atom RDF, the reverse Monte Carlo method reproduces orientational correlation functions rather well, although for some other multiparticle correlations it yields more disordered structures.

In order to evaluate the importance of three-body interactions, we have calculated the three-body correlation functions between the ions from the full molecular dynamics simulations and from the corresponding Monte Carlo simulations with effective potentials and then compared both results. It is, however, rather difficult to illustrate these functions in a two-dimensional figure. To simplify this, we have fixed the distance between the first and second particle corresponding to the first maximum of their RDF, and built a two-dimensional contour map of the density distribution of the third particle. The maxima of this distribution show typical configurations for the three particles. The results for a distribution of Na^+ ions around a NaCl pair, obtained from MD simulations with explicit water and from MC simulations using the effective potential, are shown in Figs. 7(a) and 7(b). One can observe clear structural similarities in positions of the most essential maxima and minima, while there are some differences in the intensities of these maxima. One can notice also that the three-body distributions, obtained from the molecular dynamics simulations, have a more pronounced angular structure. It can be concluded that the effective pair potential reproduces the basic features of the high-order structure, while some details may be somewhat diffuse.

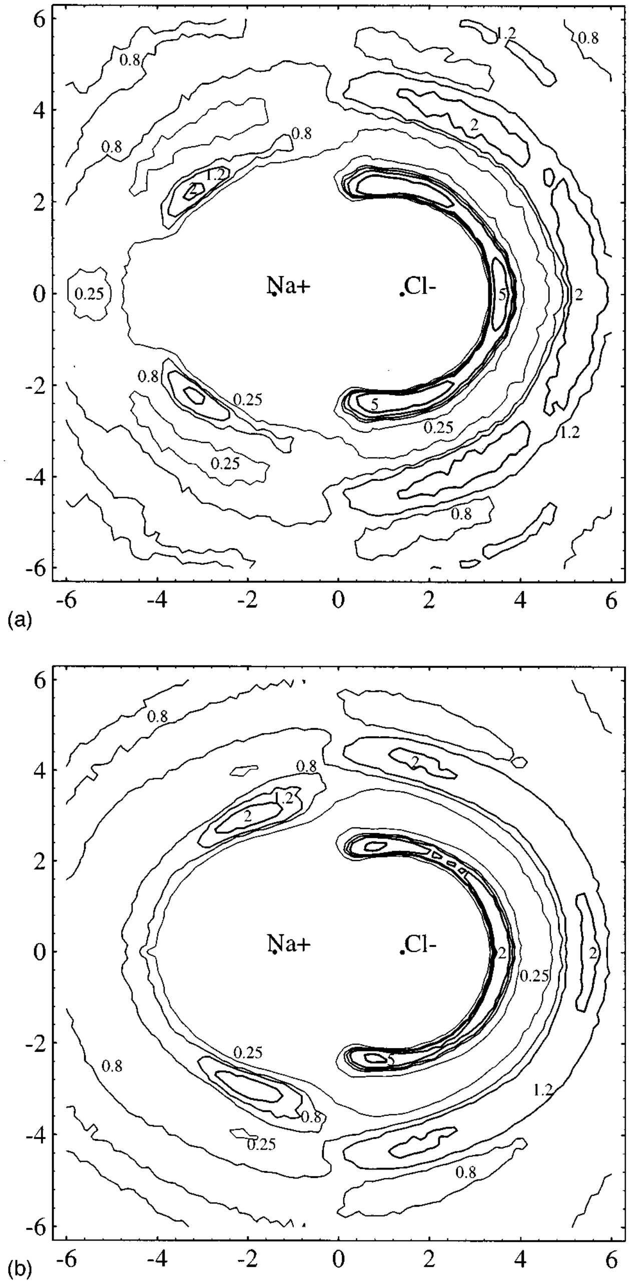

FIG. 7. Density distribution of Na^+ ions around $\mathrm{Na}^+\mathrm{Cl}^-$ ion pair separated at 2.8 Å. (a) From molecular dynamics simulations of ions in water; (b) from Monte Carlo simulation with effective potentials. Levels are drawn at 0.25, 0.8, 1.2, 2, and 5 intensity units.

In principle, the difference of the three-body correlation functions can be used to derive a three-body effective potential, quite in the same manner as for pair correlations. Needless to say, the calculation of the three-body potentials is computationally much more demanding and also outside the objective of the present work. The main purpose of the effective potential approach is to create a tool for constructing simplified models for simulations on a larger scale for cases for which the solution is found to be beyond the capacity of the current computer resources.

The present paper shows that the effective potential approach works well for electrolyte systems, reproducing not only structural, but also the thermodynamical properties. The important outcome from this study is that the osmotic and activity coefficients can be obtained without adjustable parameters such as hydration radii and are in good agreement with experiment. The paper also shows an example of using the effective potentials for larger scale simulations and obtaining new information, the osmotic and activity coefficients, which are practically impossible to derive directly from the full-atomic molecular dynamics simulations at present. We plan to present several applications using effective potentials in future.

ACKNOWLEDGMENTS

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APPENDIX: MAXIMUM ENTROPY FOR A SYSTEM WITH FIXED RDF

Configurational entropy of an N-particle system is defined as

$$S=-\int dx_1\cdots dx_N\rho(x_1,\ldots,x_N)\ln\rho(x_1,\ldots,x_N), \tag{A1}$$

where $\rho(x_1,\ldots,x_N)$ is the N-particle distribution function.

We look for a distribution function $\rho(x_1,\ldots,x_N)$ which provides maximum entropy at the condition that the pair distribution function of the system is fixed. In other words, we need to find maximum of the functional (A1) with constraints:

$$\Phi_1=\int dx_1\cdots dx_N\rho(x_1,\ldots,x_N)-1=0, \tag{A2}$$

$$\Phi_{2,ik}(r)=\int dx_1\cdots dx_N\delta(|x_i-x_k|-r)\rho(x_1,\ldots,x_N)-4\pi r^2\rho_{ik}(r)=0. \tag{A3}$$

The first constraint, Eq. (A2), is simply a normalization condition for the distribution function. Equation (A3) is actually a set of functional constraints for the total distribution function $\rho(x_1,\ldots,x_N)$ thereby fixing the RDF between all the pairs of particles. To find an extremum of the functional (A1) with constraints (A2) and (A3) we use the Lagrange formalism. Namely, we find an extremum of the extended functional:

$$S^*[\rho,\lambda_1,\lambda_2]=S+\lambda_1\Phi_1+\sum_{i,k}\int dr\lambda_{2,ik}(r)\Phi_{2,ik}(r), \tag{A4}$$

where λ_1 and $\lambda_{2,ik}(r)$ are the Lagrange multipliers. For S^* we apply the standard criteria of an extremum:

$$\frac{\delta S^*}{\delta\rho}=0, \tag{A5}$$

$$\frac{\partial S^*}{\partial\lambda_1}=0, \tag{A6}$$

$$\frac{\delta S^*}{\delta\lambda_2}=0. \tag{A7}$$

The last two equations are equivalent to the constraint conditions (A2) and (A3). Now we calculate functional derivative (A5):

$$\begin{aligned}\frac{\delta S^*}{\delta\rho}&=\frac{\delta}{\delta\rho}\int dx_1\cdots dx_N\rho(x_1,\ldots,x_N)\left[-\ln\rho(x_1,\ldots,x_N)+\lambda_1+\sum_{i,k}\int dr\lambda_{2,ik}(r)\,\delta(|x_i-x_k|-r)\right]\\&=-\ln\rho(x_1,\ldots,x_N)+\lambda_1+\sum_{i,k}\lambda_{2,ik}(|x_i-x_k|)-1.\end{aligned}$$

Setting this expression to 0, we find that the total distribution function must satisfy

$$\rho(x_1,\ldots,x_N)=\exp\left(\lambda_1-1+\sum_{i,k}\lambda_{2,ik}(|x_i-x_k|)\right). \tag{A8}$$

On the other hand, in the canonical ensemble the total distribution function is expressed as

$$\rho(x_1,\ldots,x_N)=\exp[-\beta H(x_1,\ldots,x_N)]. \tag{A9}$$

Comparing Eqs. (A8) and (A9), we can see that the Hamiltonian of the system is expressed as a sum of pair potentials.

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