Evaluation of effective ion-ion potentials in aqueous electrolytes

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We present high-accuracy simulation data for ion-ion radial distribution functions in NaCl aqueous electrolyte. From the data we evaluate ion-ion effective potentials via inverse Monte Carlo simulation procedure. Alternatively, we first evaluate effective direct correlation functions and then obtain effective potentials using the hypernetted-chain (HNC) approximation. Both methods are in excellent agreement, indicating that HNC approximation performs well with effective ion-ion potentials in aqueous solutions.

I. EFFECTIVE POTENTIALS

Even the most common electrolyte solutions defy simple and accurate description, mainly because the aqueous solvent has a very complicated structure. This leads to the widespread use of the primitive model, where aqueous structure is included only through the high dielectric constant of the continuous background medium. However, that model is inaccurate when solute separations are comparable to the molecular diameter of water and when solvent structure and geometry are important. In practice, all situations involving approach and binding of macromolecules or colloidal particles belong to this class.

The classical McMillan-Mayer theory [1,2] of solutions provides a natural way to proceed beyond the limitations of the primitive model. A solution is described with a reference system (usually the aqueous solvent) and a system of solute particles interacting via *n*-particle potentials of mean force. In applications of the McMillan-Mayer theory one normally approximates *n*-particle potentials of mean force with a sum of pairwise terms (Kirkwood approximation for the *n*-particle correlation function) expressing the problem in terms of the ion-ion potentials of mean force

$$V_{ij}^{pmf}(r) = -k_B T \ln[g_{ij}(r)], \qquad (1)$$

where $g_{ij}(r)$ are the radial distribution functions. If the reference solution in the McMillan-Mayer theory is a uniform electrolyte, pairwise approximation (1) for the potentials of mean force $V_{ij}^{pmf}(r)$ is screened by other ions and for large separations the potentials do not reduce to the Coulomb form. Perhaps for this reason, the McMillan-Mayer theory in its original form has seldom been applied to electrolyte solutions. A notable exception is the work by Friedman [3] who consistently promoted the use of empirical ion-ion potentials in aqueous solutions.

The McMillan-Mayer theory is easily generalized to nonuniform problems, for example, electrolyte solutions near charged surfaces [4]. We [5,6] and others [7,8] have recently applied this method to electrical double layer problems with encouraging results. In the course of that work we noticed a

need for more accurate effective ion-ion potentials, which is the motivation for the present study.

The theory of solutions was further developed by Adelman [9,10], who derived exact expressions for effective direct correlation functions $c_{ij}^{eff}(\mathbf{r})$ that formally satisfy normal Ornstein-Zernike equations

$$h_{ij}(\mathbf{r}) = c_{ij}^{eff}(\mathbf{r}) + \sum_m \rho_m \int d\mathbf{r}' c_{im}^{eff}(\mathbf{r}-\mathbf{r}') h_{mj}(\mathbf{r}'). \quad (2)$$

$h_{ij}(\mathbf{r}) = g_{ij}(\mathbf{r}) - 1$, and ρ_m are the solute densities. Adelman also defined effective pair potentials, that can be expressed as [11]

$$\beta V_{ij}^{eff}(\mathbf{r}) = -\ln[g_{ij}(\mathbf{r})] + h_{ij}(\mathbf{r}) - c_{ij}^{eff}(\mathbf{r}) + b_{ij}^{eff}(\mathbf{r}). \quad (3)$$

The effective bridge functions $b_{ij}^{eff}(\mathbf{r})$ are functionals of $h_{ij}(\mathbf{r})$ and ρ_i and $\beta = 1/k_B T$. Just like the effective direct correlation functions, the effective potentials describe the average interaction of two ions in the presence of the solvent. They have the correct asymptotic behavior because $c_{ij}^{eff}(\mathbf{r}) \sim -\beta q_i q_j / \varepsilon_\rho r$ where the effective dielectric constant ε_ρ depends on the concentrations. However, because of the difficulty in evaluating $c_{ij}^{eff}(\mathbf{r})$ from the first principles Adelman's formalism was also seldom used.

While the exact solution theory cannot be constructed with only the pairwise ion-ion terms, Eq. (3) represents the best pairwise potential approximation based on the knowledge of two-particle correlation functions [12]. In practice, this pairwise potential can be determined from the available correlation functions via an inverse Monte Carlo (MC) simulation as described in several recent works by Lyubartsev and Laaksonen [13–15]. They first performed a full molecular simulation of an aqueous ionic solution obtaining the ion-ion correlation functions. The correlation functions were then used in a separate inverse Monte Carlo simulation of a system consisting of only ions interacting via effective potentials. The effective potentials were continuously adjusted until the procedure reproduced the correlation functions obtained from the initial simulation with the molecular solvent.

TABLE I. Simulation parameters.

Run no.	Concentration (M)	No. of H_2O	No. of ion pairs	Average box size (Å)	Density (g/cm^3)
1	0.5	1964	18	38.97	1.022
2	1	1950	36	39.02	1.041

As we are dealing with rather dilute solutions $b_{ij}^{eff}(\mathbf{r})$ is expected to be small and short-ranged. We therefore propose to use Eq. (3) with $b_{ij}^{eff}(\mathbf{r})=0$ [amounting to an *effective* hypernetted-chain (HNC) approximation], evaluate $c_{ij}^{eff}(\mathbf{r})$ from $h_{ij}(\mathbf{r})$ from Eq. (2) and find the effective potentials $V_{ij}^{eff}(\mathbf{r})$ without the need for the inverse Monte Carlo simulation.

II. COMPUTATIONAL DETAILS

The molecular simulations that provide input ion-ion distribution functions are most often performed for a cubic periodic system using Ewald potentials. We performed molecular dynamics simulations of aqueous NaCl solution at two concentrations: 0.5 M and 1 M. The essential simulation parameters are given in Table I. The molecular models and the simulation procedure were the same as in previous works [13,14], however, the present simulations were performed in a larger box over a substantially longer time. Briefly, the flexible simple point change water model [16] and Smith-Dang parameters [17] for ions ($\sigma_{Na}=2.35$ Å, $\varepsilon_{Na}=0.544 kJ/M$, $\sigma_{Cl}=4.4$ Å, $\varepsilon_{Cl}=0.419$ kJ/M) were employed. The constant temperature–constant pressure molecular dynamics algorithm [18] was used to keep temperature $T=298$ K and pressure 1 atm. The system was equilibrated during 0.5 ns (of which first 100 ps at fixed volume) and then averages were collected during 10 ns. The Ewald summation method was used to include long-range electrostatic interactions. The simulation software used was MDYNAMIX package [19].

The second simulation method used in this work was inverse MC calculation applied to obtain effective potentials from the radial distribution functions. Details were reported in earlier work [13,15]. The inverse procedure used the same system size and parameters, with electrostatic interaction again described by the Ewald potential. Practically, the ion-ion potential was decomposed into Coulombic and short-range parts. The Coulombic part was treated in the simulations by the Ewald method, while the short-range part was varied in the course of the inverse MC procedure. The dielectric constant of the Coulombic part was determined from the condition that the short-range potential goes to zero at large separations as fast as possible. We defined in this way the effective dielectric constant as $\varepsilon=79$ for 0.5 M concentration and $\varepsilon=78$ for 1 M, though variation of ε within five units does not noticeable change the results.

III. RESULTS AND DISCUSSION

A. Radial distribution functions

Ion-ion distribution functions obtained after spherical averaging are shown in Fig. 1. They generally agree well with the results obtained earlier [13,14] with smaller system sizes, shorter run times, and slightly different concentrations. Some differences can still be observed. Particularly, there is a significant difference in the first peak of the Na-Na and Cl-Cl radial distribution functions, as well as the clear oscillatory behavior in the 8–12 Å separation region, which was not
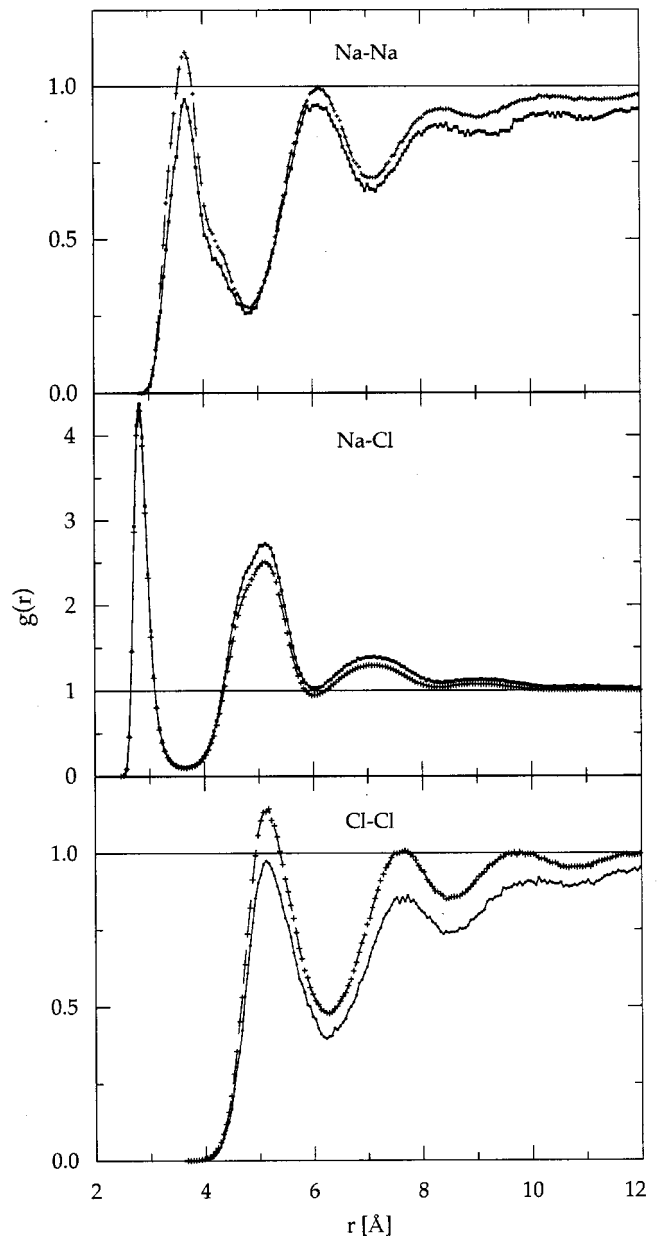

FIG. 1. Radial distribution functions for ion pairs in aqueous NaCl electrolyte. Continuous line, 0.5 M; dashed line, 1 M.
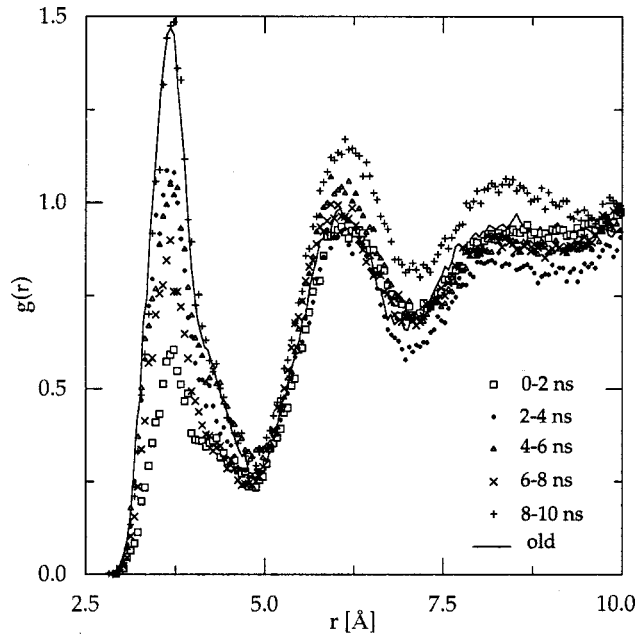
FIG. 2. Na-Na radial distribution functions in 0.5 M NaCl electrolyte obtained over five consecutive 2 ns segments of the molecular dynamics trajectory (the initial 0.5 ns of the simulation was disregarded). The old data from Ref. [14] for the 0.55 M electrolyte, 38.7 Å box size, and 2 ns simulation time are also presented.

apparent in the previous simulations. It was noticed earlier [14] that convergence of the ion-ion distribution functions in molecular dynamics (MD) simulations is very slow, due to relatively low statistics of ion pairs and their slow diffusion.

To illustrate the convergence, in Fig. 2 we show the Na-Na distribution function for the 0.5 M NaCl solution averaged over five consecutive 2 ns segments of the MD trajectory. The earlier data for 0.55 M concentration and the box length 38.7 Å, obtained from a 2 ns simulation [14] are also shown for comparison. One can see that at the first peak of the radial distribution function the fluctuations around the average reach the value of 0.4, decreasing to about 0.1 for distances 6–10 Å and less than 0.05 at distances larger than 12 Å. The statistical error of the average radial distribution function may be evaluated by dividing these fluctuations by $\sqrt{5}$. Thus the present data, generated during substantially longer simulation time, show clear improvement in accuracy and resolution. Na-Cl and Cl-Cl distribution functions have similar but somewhat lower fluctuations, while in the case of 1 M concentration the fluctuations are about half as large as those in the 0.5 M case.

Below, we will treat the distribution functions calculated in the MD simulations as "exact" and reconstruct the effective ion-ion potentials by the inverse Monte Carlo simulation or by the hypernetted-chain equation.

B. Change to grand canonical ensemble

As the simulations are performed in the canonical ensemble with relatively small number of ions N, at large separations the radial distribution functions do not approach unity, with the difference being of the order of $1/N$. The
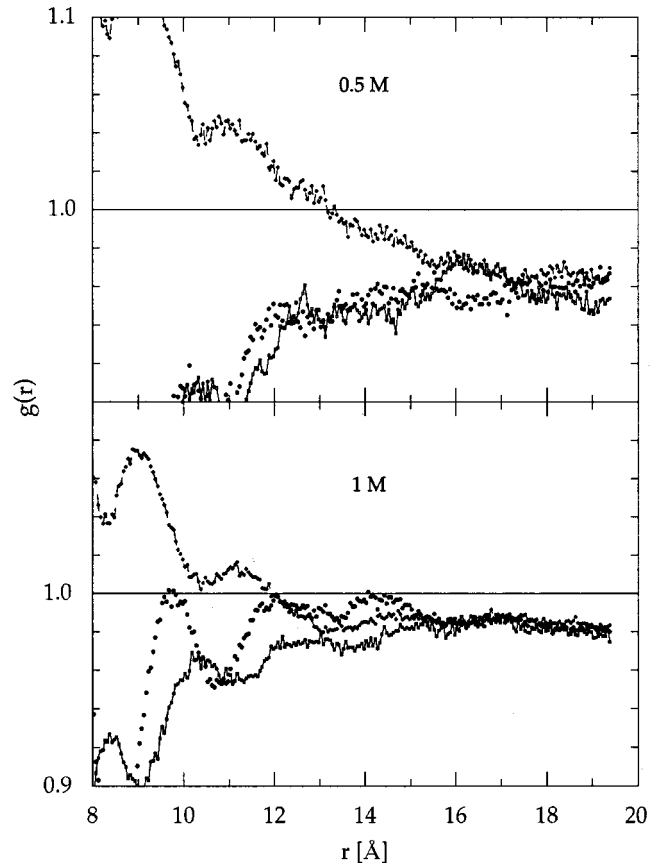

FIG. 3. Behavior of the radial distribution functions shown in Fig. 1 at larger ion-ion separations. Continuous line, Na-Na; dashed line, Na-Cl; separate symbols, Cl-Cl.

direct correlation functions are formally undefined [20] because of the constraint on the number of particles. Before we continue with the calculation we need to convert (approximately) the radial distribution functions to their counterparts in the grand canonical ensemble.

The behavior of all three pairs $g_{ij}(r)$ at large separations is shown in Fig. 3. Note that at both concentrations the two like-ion pairs and the dislike pair all appear to approach the same limiting value. The same behavior has recently been found by Ulander and Kjellander [21] in a Monte Carlo calculation of ion-ion radial distribution functions within the primitive model.

Calculation of the asymptotic behavior of the radial distribution functions of an ionic solution in the canonical ensemble is complicated, as is the calculation of compressibility described in Ref. [22]. But the large-separation behavior of $g_{ij}(r)$ suggests that anion and cation density fluctuations are so strongly coupled that they effectively vary together.

In the first order, and for a single-component system, one estimates the radial distribution function $g(r)$ of the infinite system from its N-particle finite system counterpart as [23]

$$g(r) = g_N(r) + \frac{\kappa_T}{N\kappa_T^0}, \qquad (4)$$

where κ_T is the isothermal compressibility and $\kappa_T^0 = (\rho k_B T)^{-1}$ is its ideal gas value.

With respect to density fluctuations in binary electrolytes we will now consider the strong coupling limit where density fluctuations of two components only occur together. For each component of the electrolyte, the compressibility is given as $\kappa_T = (2\phi\rho k_B T)^{-1}$ where ϕ is the osmotic coefficient. The factor of 2 enters because one can only compress both components together.

Using the experimental values [24] of $\phi = 0.92$ for 0.5 M NaCl and $\phi = 0.94$ for 1M NaCl electrolyte, from Eq. (4) we estimate the difference between $g(r)$ and $g_N(r)$ in our simulations as 0.030 and 0.017, respectively. Referring back to Fig. 3 we see that these values are in good agreement with the simulations. Similarly good agreement is obtained with the higher precision simulation of a 2:2 electrolyte in the primitive model [21]. That simulation was performed with the ion radius of 2.3 Å and 20 ion pairs. The osmotic coefficient for 40 mM 2:2 primitive model electrolyte with ion radius 2.1 Å in the HNC approximation can be interpolated from the table IV in Ref. [25] as $\phi = 0.66$. The constant required to change the radial distribution functions to the grand canonical ensemble is then estimated as 0.038 and determined from the simulation as 0.039.

C. Radially symmetrical calculation of effective potentials

The potentials $V_{ij}^{eff}(\mathbf{r})$ in Eq. (3) are the sums of the electrostatic part and the short-range part arising from the structure of the solvent. In simulations that use the Ewald method the electrostatic part is the Ewald potential and we have

$$V_{ij}^{eff}(\mathbf{r}) = V_{ij}^{Ewald}(\mathbf{r}) + V_{ij}^{short}(\mathbf{r}). \qquad (5)$$

In principle, the periodicity of the simulation system will be reflected in all the results. In order to obtain spherically symmetrical effective potentials at some stage in the procedure it will be necessary to perform angular averaging. Normally this is done when radial distribution functions are estimated from system configurations observed during the simulation. Presently we will follow this procedure.

The effective direct correlation functions were obtained from spherically averaged distribution functions, corrected to correspond to the grand canonical ensemble as described above. Beyond the system size limit (19 Å) the distribution functions were assigned the value of one. Ornstein-Zernike equations were solved via Fourier transforms and the resulting direct correlation functions are similar to the functions $g_{ij}(r)$ but have clearly acquired a long-range Coulomb tail (Fig. 4). To obtain accurate values for the functions $c(r)$ inside the ion core requires greater precision in calculation. As they are not needed for this study, we have not attempted such calculations.

The Ewald potential between a pair of ions [26,27] was also spherically averaged and subtracted from the effective potential to obtain $V_{ij}^{short}(\mathbf{r})$. The baseline value of $c(r)$ and $V_{ij}^{short}(\mathbf{r})$ is affected by the small errors at $k=0$ of the Fourier transforms of $g(r)$ and in case of $V_{ij}^{short}(\mathbf{r})$ also by the choice of the additive constant in the Ewald potential. But we know that the solvent contribution to the effective poten-
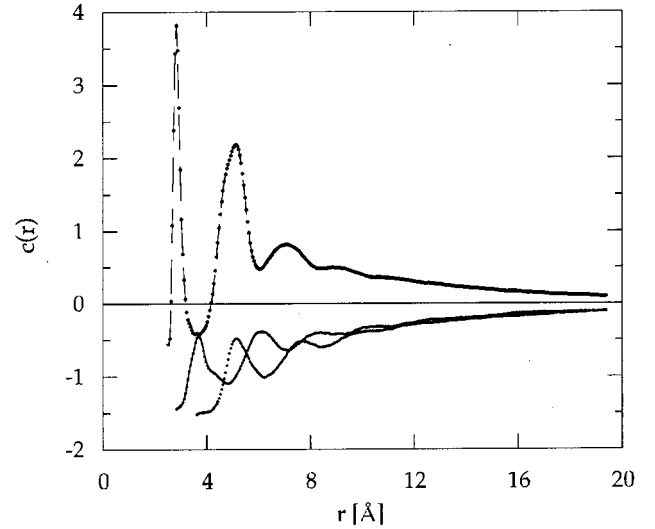

FIG. 4. Effective direct correlation functions for 0.5 M NaCl electrolyte. The accuracy is insufficient to determine a small constant term that needs to be added to each function. Continuous line, Na-Na; dashed line, Na-Cl; separate symbols, Cl-Cl.

tial is short ranged, and can therefore choose the additive constant to ensure that $V_{ij}^{short}(\mathbf{r})$ go to zero at large separations.

The results are shown in Fig. 5. They agree with the results obtained from the same input data using the inverse Monte Carlo simulation so well that the differences would hardly be observable in the figure (see Fig. 6). Both data sets in tabular form as well as the input values of $g_{ij}(r)$ are available from the author's internet site [28].

D. Anisotropic calculation of the effective potentials

As the simulation system consists of a periodic cubic lattice, the ion-ion distribution functions $g_{ij}(\mathbf{r})$ are anisotropic. The effective ion-ion potentials $V_{ij}(\mathbf{r})$ calculated via Eq. (3) are then also anisotropic, reflecting the symmetry of the simulation system. However, for a bulk ionic fluid simulation it can be expected that the short-range part of the potential $V_{ij}^{short}(\mathbf{r})$ is less affected by the anisotropy because it does not extend beyond the edges of the simulation cell.

The evaluation of effective potentials from the anisotropic ion-ion distribution functions $g_{ij}(r)$ is also interesting because of its possible use in physically anisotropic situation, such as the interaction of two ions in the presence of a wall or a macromolecule. In order to test the procedure and possibly also improve the accuracy of calculated effective potentials we have attempted to calculate the effective potentials using the anisotropic ion-ion distribution functions $g_{ij}(r)$ evaluated over the whole periodic simulation cell.

The effective direct correlation functions were obtained via discrete Fourier transforms of large data sets containing the functions $h_{ij}(\mathbf{r})$ defined on the cube with 198 points in each direction. The effective potentials $V_{ij}(r)$ were then obtained from Eq. (3) with the functions $b_{ij}^{eff}(\mathbf{r})$ set to zero.
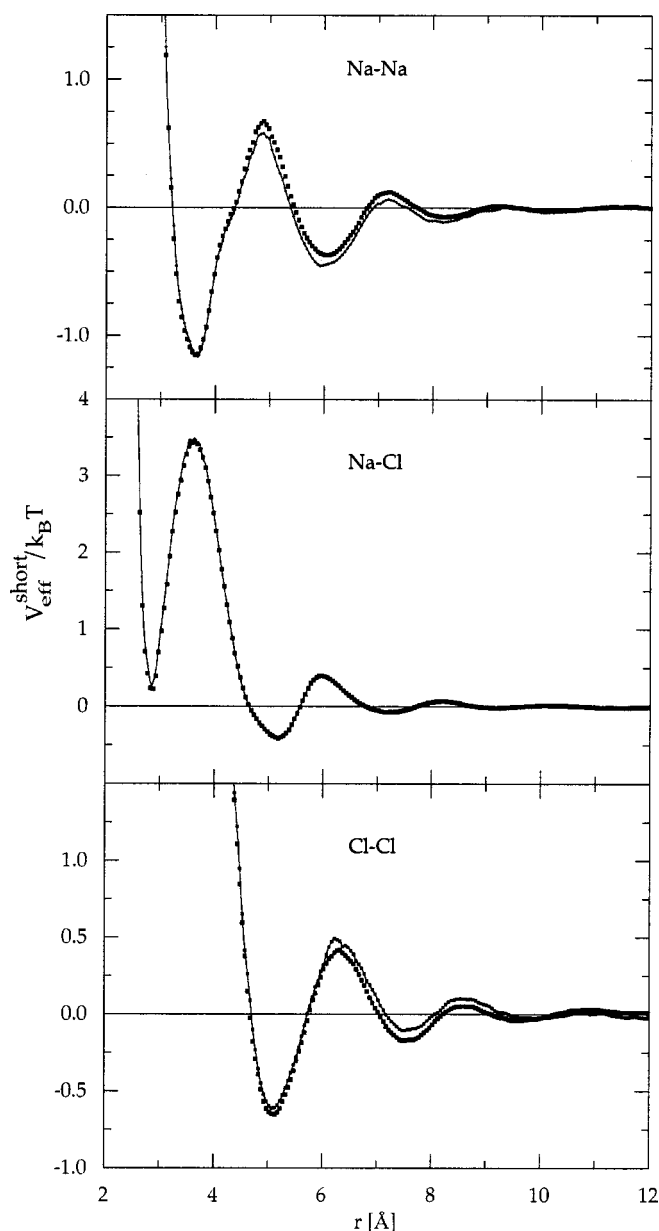
FIG. 5. Short-range part of the effective potential between ion-ion pairs in aqueous NaCl electrolyte. Continuous line, 0.5 M; separate symbols, 1 M. In subtracting Ewald potential we assumed dielectric constant of 79 and 78 for 0.5 M and 1 M solution, respectively.

After subtracting the Ewald potential from the anisotropic $V_{ij}(\mathbf{r})$ the short-range part was expected to be almost isotropic. However, the procedure appears difficult for several reasons. The full distribution functions are not as accurate as the spherical averages, and even longer simulation times would be required for satisfactory accuracy.

Another aspect of the simulation of ionic systems that requires more detailed study became apparent upon investigation of anisotropic data sets. The periodic system with long-range interaction facilitates correlations between more than two ions, and thus leads to unexpected slight preferences of each ion to be in a particular positions within the simulation cell.
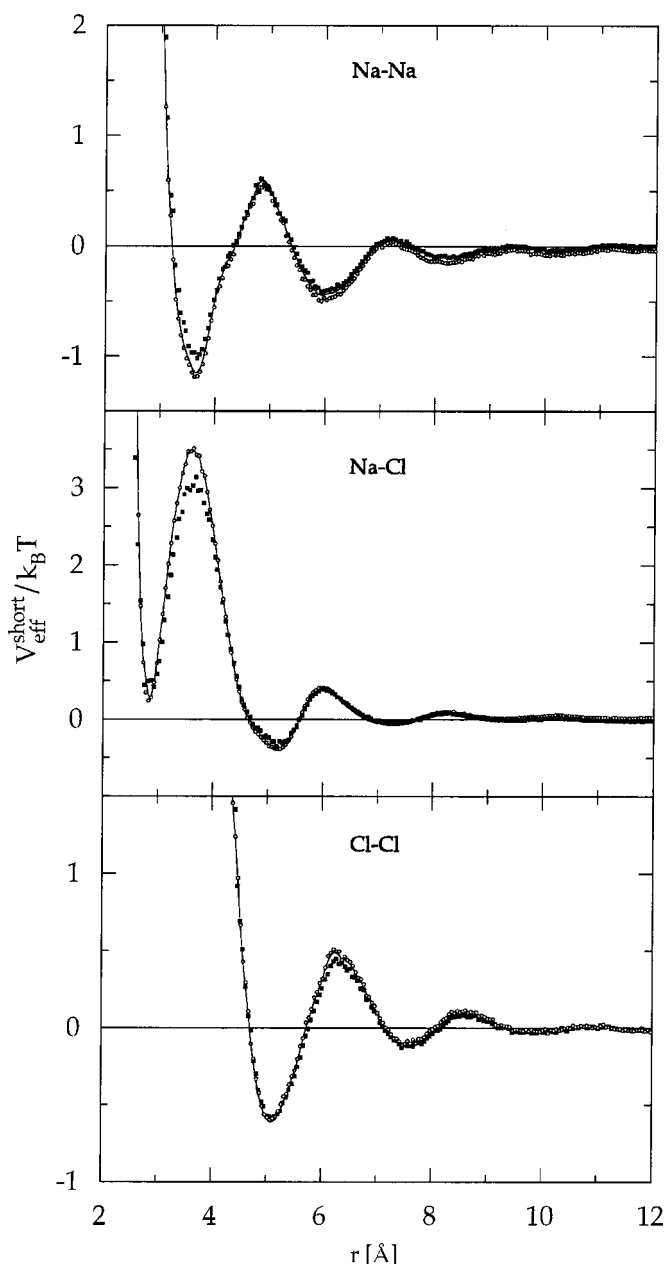

FIG. 6. Short-range part of the ion-ion effective potentials in 0.5 M NaCl electrolyte evaluted with different methods. Open symbols, inverse MC simulation, continuous line, spherical HNC; closed symbols, HNC with anisotropic correlation functions of the simulation cell.

The short-range effective potential obtained in the anisotropic calculation was spherically averaged at the end of the calculation. It is shown in Fig. 6 together with the results obtained from spherically averaged input data. The results indicate that the anisotropic calculation is feasible although at the present stage it appears less accurate. It gives values very close to the other two methods but drifts away from zero at large r. Judging by the drift, the short-range potential calculated with this method is not as good as that obtained after spherical averaging. Possible source of error may be inadequate approximation in changing to grand canonical en-

samble using spherically symmetrical Eq. (4) or a need for corrections between periodic and nonperiodic quantities [29].

IV. CONCLUSION

Liquid state closure approximations are normally tested by evaluating radial distribution functions from the model potentials and comparing the results with simulations. In the present case we proceeded in the opposite direction, evaluating the effective potentials from ion-ion distribution functions and comparing the results with inverse MC simulations. The excellent agreement proves that HNC is a very good approximation to use with the effective potentials between ions in aqueous solutions. Just like a primitive model electrolyte, the effective ionic fluid is normally not a dense fluid and this conclusion was therefore naturally expected.

The agreement described of course does not quantify how accurate is the two-particle effective potential description of ion interaction in the aqueous solvent. This has been tested earlier [14] using simulation methods, where activity and osmotic coefficients of a solution were evaluated from the effective potentials. Similar testing can now be more easily performed using variants of the HNC approximation. But the most interesting problems to be explored in the future relate to the behavior of ions in aqueous solutions near the surfaces. The confirmation of the accuracy of HNC approximation in work with the effective potentials is important for such future applications.

ACKNOWLEDGMENTS

[1] J.E. Mayer, *Equilibrium Statistical Mechanics* (Pergamon, Oxford, 1968).

[2] T.L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956).

[3] H.L. Friedman, Annu. Rev. Phys. Chem. **32**, 179 (1981).

[4] S. Marčelja, Langmuir **16**, 6081 (2000).

[5] S. Marčelja, Nature (London) **385**, 689 (1997).

[6] R. Kjellander, A.P. Lyubartsev, and S. Marčelja, J. Chem. Phys. **112**, 8939 (2001).

[7] Y. Burak and D. Andelman, Phys. Rev. E **62**, 5296 (2000).

[8] F. Otto and G.N. Patey, J. Chem. Phys. **112**, 8939 (2000).

[9] S.A. Adelman, Chem. Phys. Lett. **38**, 567 (1976).

[10] S.A. Adelman, J. Chem. Phys. **64**, 724 (1976).

[11] J.S. Høye and G. Stell, J. Chem. Phys. **102**, 2841 (1995).

[12] G. Stell, in *Equilibrium Theory of Classical Fluids*, edited by H.L. Frisch and J.L. Lebowitz (Benjamin, New York, 1964), p. II-223.

[13] A.P. Lyubartsev and A. Laaksonen, Phys. Rev. E **52**, 3730 (1995).

[14] A.P. Lyubartsev and A. Laaksonen, Phys. Rev. E **55**, 5689 (1997).

[15] A.P. Lyubartsev and A. Laaksonen, J. Chem. Phys. **111**, 11 207 (1999).

[16] K. Toukan and A. Rahman, Phys. Rev. B **31**, 2643 (1985).

[17] D.E. Smith and L.X. Dang, J. Chem. Phys. **100**, 3757 (1994).

[18] G.J. Martyna, M.E. Tuckerman, D.J. Tobias, and M.L. Klein, Mol. Phys. **87**, 1117 (1996).

[19] A.P. Lyubartsev and A. Laaksonen, Comput. Phys. Commun. **128**, 565 (2000).

[20] J.D. Ramshaw, Mol. Phys. **41**, 219 (1980).

[21] J. Ulander and R. Kjellander, J. Chem. Phys. **114**, 4893 (2001).

[22] J.C. Rasiah and H.L. Friedman, J. Chem. Phys. **48**, 2742 (1968).

[23] For example, Ref. [2], Appendix 7.

[24] B.E. Conway, *Electrochemical Data* (Elsevier, Amsterdam, 1952).

[25] J.C. Rasiah, J. Chem. Phys. **56**, 3071 (1972).

[26] S.W. de Leeuw, J.W. Perram, and E.R. Smith, Proc. R. Soc. London, Ser. A **373**, 27 (1980).

[27] F. Figuerido, G.S. Del Buono, and R.M. Levy, J. Chem. Phys. **103**, 6133 (1995).

[28] http://www.fos.su.se/physical/sasha/effpot

[29] L.R. Pratt and S.W. Haan, J. Chem. Phys. **74**, 1864 (1981).