Solubility of KF and NaCl in water by molecular simulation

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The solubility of two ionic salts, namely, KF and NaCl, in water has been calculated by Monte Carlo molecular simulation. Water has been modeled with the extended simple point charge model (SPC/ E), ions with the Tosi-Fumi model and the interaction between water and ions with the Smith-Dang model. The chemical potential of the solute in the solution has been computed as the derivative of the total free energy with respect to the number of solute particles. The chemical potential of the solute in the solid phase has been calculated by thermodynamic integration to an Einstein crystal. The solubility of the salt has been calculated as the concentration at which the chemical potential of the salt in the solution becomes identical to that of the pure solid. The methodology used in this work has been tested by reproducing the results for the solubility of KF determined previously by Ferrario et al. [J. Chem. Phys. 117, 4947 (2002)]. For KF, it was found that the solubility of the model is only in qualitative agreement with experiment. The variation of the solubility with temperature for KF has also been studied. For NaCl, the potential model used predicts a solubility in good agreement with the experimental value. The same is true for the hydration chemical potential at infinite dilution. Given the practical importance of solutions of NaCl in water the model used in this work, whereas simple, can be of interest for future studies. © 2007 American Institute of Physics. [DOI: 10.1063/1.2397683]

I. INTRODUCTION

The knowledge of the physical and chemical properties of ionic solutions is of great interest from a geological and biological perspective.¹ Whereas experimental studies provide useful macroscopic information, molecular simulation can offer a microscopical picture of the solution. There are a number of simulation studies of ionic salts. The majority of them deal with the determination of the properties of the pure solution.^{2–11} However, the possible phase transitions of the mixture are also of interest, especially when the solution is in contact with a solid phase. When the pressure is fixed, the phase diagram of water-salt solutions present, at low temperatures, a eutectic point.¹² In the eutectic point, two coexistence lines meet. The first one determines the equilibrium composition of the solution when in contact with pure ice. This line is the branch of interest when studying colligative properties of water (i.e., the depression of the freezing point of water by the addition of salt). There is an increasing interest in studying the equilibrium between ice and salt solutions.^{13,14} It is obvious that to study colligative properties from simulation, knowledge of the melting point of ice for the used water model is needed. In the last two years, we have established the melting point of a number of water models^{15–18} so that one may anticipate that the determination of the depression of the melting point in salt solutions will be an active area of research in the future. The second coexistence line that emerges from the eutectic point determines the solubility of the pure salt in water. It is striking to realize that

there is only one previous paper estimating the solubility of a pure salt in water by computer simulation. The seminal work of Ferrario *et al.*¹⁹ illustrates that it is possible to determine the solubility of ionic salts by computer simulation. Obviously, the knowledge of the solubility of a certain model of salt in water is needed before performing kinetics studies of the crystallization of the solute in water^{20,21} or of the dissolution of the salt.^{22,23} In all these studies, it would have been convenient—or even necessary—to know the solubility and the degree of saturation of the model selected; mainly if crystallization in a supersaturated solution is studied.^{20,21} The assumption that the solubility of the model is the same as that of the real salt is not necessarily true.¹⁹

In the present work we calculate, from computer simulation, the solubility of KF and NaCl in water. The choice of these two salts is motivated by several reasons. Since the only solubility determined previously is that of KF it seems obvious to test the programs and methodology used in this work by comparing with the only previously published result. The choice of NaCl as the second salt to be studied is motivated by the practical interest of studying water solutions of sodium chloride. The potential model used in this work for KF and NaCl is of the same type. Water is described by the extended simple point charge (SPC/E) model, the ion-ion interactions are described by the Tosi-Fumi potential,²⁴ and water-ion interactions are described by the Smith-Dang model.^{25–28} The choice of this type of potential can be explained by the fact that we did not want to use a different type of force field for NaCl in water than that used for KF in water. Moreover, since Ferrario et al.¹⁹ used these kinds of interactions for the KF system, we basically follow their approach.

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The solubility of a certain salt in a given solvent is reached when its chemical potential in solution equals the chemical potential of the solid. The Einstein crystal method proposed by Frenkel and Ladd²⁹ has become a standard procedure to compute the chemical potential of solids numerically.^{15,30} The chemical potential of ions in solution has been determined in a number of simulation studies.^{31–37} In most of the cases, the chemical potential at infinite dilution was obtained by computing the free energy difference between the solvent with an ionic pair and the pure solvent. Nevertheless, there is not a great consensus yet in the procedure to be followed in these calculations. Some authors choose to insert simultaneously the ionic pair in order to preserve the system electroneutrality,³² while others prefer to avoid the interaction between the ions by inserting them separately.³⁷ Among the last ones, some utilize a neutralizing uniform background to keep the system electroneutral^{37,38} and some others do not explicitly mention to have done anything in this respect.^{31,33} Besides, on some occasions, a finite size correction is applied to the calculations,³⁷ while some other times it is not.

Extending these techniques to concentrated solutions, Ferrario and co-workers calculated the solubility of KF in water.¹⁹ In their work, the chemical potential of KF in solution was calculated at different concentrations as the sum of the contributions of K⁺ and F⁻, computed separately by means of thermodynamic integration between the solution and the solution with an extra ion. They made use of a homogeneous neutralizing background in order to compensate the charge of the extra ion that is inserted in the solution. In this work we present a new methodology to compute the chemical potential of the salt in the solution. The Gibbs free energy of the whole solution is computed for several salt concentrations keeping constant the number of water molecules. This is done by performing thermodynamic integration and transforming the solution (solvent and solution) into a pure Lennard-Jones (LJ) fluid. Electroneutrality is preserved when doing this thermodynamic integration. Once the total Gibbs free energy of the solution is known, then the solute chemical potential is obtained simply by determining the slope of the Gibbs free energy versus the number of ionic pairs in solution (at constant number of solvent molecules).

The aim of this work, on the one hand, is to test the accuracy of the selected potential model in predicting the solubility of the NaCl. It is not necessarily true that the SPC/E and the Tosi-Fumi models, which describe fairly well water and alkali halides, respectively, are also good models to simulate salt aqueous solutions. On the other hand, the value of the maximum solubility of the NaCl solution model can be of great interest for many computational studies, for instance, in the analysis of the crystallization of NaCl in the supersaturated solution.²⁰ Furthermore, with this work we establish a general methodology for the calculation of solute chemical potential and solubility.

The article is organized as follows. In Sec. II, the model selected to simulate ionic aqueous solutions is described. In Sec. III, simulation details and the method to compute the free energy of the solid phase and of the solution will be

TABLE I. Parameters of the Born-Mayer-Huggins-Tosi-Fumi model for ionion interactions, as taken from Table I of Ref. 43.

Salt	Interaction	A_{ij} (kJ/mol)	$\rho_{ij} (\text{\AA})$	C_{ij} (kJ Å ⁶ /mol)	D _{ij} (kJ Å ⁸ /mol)
	Na ⁺ -Na ⁺	40 870	0.317	101	48
NaCl	Na+-Cl-	121 075	0.317	674	837
	Cl ⁻ -Cl ⁻	336 259	0.317	6986	14032
	K^+-K^+	146 278	0.338	1463	1445
KF	K^+-F^-	50 508	0.338	1174	1265
	FF-	16 350	0.338	1120	1325

described. In Sec. IV the results of this work will be presented, and in Sec. V the main conclusions of this work will be discussed.

II. MODEL POTENTIAL

To study the solubility of an ionic salt in water, a model for the interactions between the ions, a model of water and a model for the interaction between the ions and water are needed. In this work we will use the SPC/E model of water proposed by Berendsen and co-workers.³⁹ Although SPC/E model is not able to mimic real water perfectly (no model actually does), we have decided to use the same model as Ferrario and co-workers in order to compare our results with theirs for the KF solutions. In this model the O-H bond distance is set to 1 Å and the H–O–H bond angle adopts the tetrahedral value. A positive partial charge (with a value of 0.4238e) is located on each of the hydrogen atoms and a negative charge is located on the oxygen. Besides the Coulombic interaction between the charges of two water molecules, an additional LJ interaction exists between the oxygen atoms. The interaction between two water molecules is given by

$$u_{\mathrm{H_2O-H_2O}} = 4\varepsilon_{\mathrm{O-O}} \left[\left(\frac{\sigma_{\mathrm{O-O}}}{r_{\mathrm{OO}}} \right)^{12} - \left(\frac{\sigma_{\mathrm{O-O}}}{r_{\mathrm{OO}}} \right)^{6} \right] + \sum_{l=1}^{3} \sum_{m=1}^{3} \frac{q_l q_m}{4\pi\varepsilon_o r_{lm}}, \tag{1}$$

where *l* and *m* index the point charges *q* of each molecule and O makes reference to the oxygen. The values of $\sigma_{\text{O-O}}$ = 3.1656 Å and $\varepsilon_{\text{O-O}}/k$ =78.2 K are used in the SPC/E potential. The interaction between ions is given by the Born-Mayer-Huggins-Tosi-Fumi potential^{24,40–42}:

$$u_{ij} = A_{ij}e^{-r_{ij}/\rho_{ij}} - \frac{C_{ij}}{r_{ij}^6} - \frac{D_{ij}}{r_{ij}^8} + \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}}.$$
 (2)

The parameters A_{ij} , ρ_{ij} , C_{ij} , and D_{ij} are given in Table I.

Finally, the ion-water cross interaction $(i-H_2O)$ is given by a Lennard-Jones potential plus the electrostatic interaction between the point charges of the water molecule and the ion:

$$u_{i-\mathrm{H}_{2}\mathrm{O}} = 4\varepsilon_{i-\mathrm{O}} \left[\left(\frac{\sigma_{i-\mathrm{O}}}{r_{i\mathrm{O}}} \right)^{12} - \left(\frac{\sigma_{i-\mathrm{O}}}{r_{i\mathrm{O}}} \right)^{6} \right] + q_{i} \sum_{m=1}^{3} \frac{q_{m}}{4\pi\varepsilon_{o}r_{im}}.$$
(3)

The Lennard-Jones parameters for the ion-water interaction are given in Table II. They were obtained by applying Lor-

TABLE II. LJ parameters of the ion-water interaction. They were obtained by applying Lorentz-Berthelot rules to the LJ parameters of the SPC/E model of water (Ref. 39) and to the LJ models of the ions. The LJ parameters of the ions are those proposed in Refs. 25 and 26 for K⁺ and F⁻ and from Refs. 27 and 28 for Na⁺ and Cl⁻.

Interaction	$\sigma_{i\text{-}0}$ (Å)	$\varepsilon_{i-\mathrm{O}}/k_\mathrm{B}~(\mathrm{K})$
K+-O	3.249	62.73
F ⁻ -O	3.143	84.17
Na ⁺ -O	2.758	71.52
Cl ⁻ -O	3.783	62.73

entz Berthelot rules to the LJ parameters of SPC/E water and to the LJ parameters proposed by Smith and Dang for the ions.^{25–28} The total potential energy is obtained by adding up all the pair interactions present in the system.

The same combination of potential models has been used in some other computational studies of ionic aqueous solutions¹⁹⁻²². The SPC/E properly describes many properties of pure liquid water.³⁹ Unfortunately, it describes correctly neither the phase diagram of water nor the melting point.¹⁵ Let us just mention that although SPC/E water may be successful in describing the solubility of certain salts, it will fail in describing the other coexistence line emerging from the eutectic point (i.e., the freezing of ice from dilute salt solutions). This is so because the melting temperature of SPC/E pure water is 215 K, which is about 60 K below the experimental value. The use of other models for solubility studies should be considered in the future. However, at this stage it seems sufficient to show that solubilities can be computed and that qualitative agreement with experimental results can be achieved. For the ion-ion interaction, the use of the Born-Mayer-Huggins-Tosi-Fumi potential is easily justified. This model describes the solid phases reasonably well⁴³ and moreover, it has been shown recently³⁰ to describe correctly the melting point of NaCl. This could guarantee a good estimate of the solid salt chemical potential, which is essential in predicting the solubility. Once two reasonable models are found for the pure substances, a good crossinteraction model is also needed to mimic the mixture. Smith and Dang potential (as derived for ions in SPC/E water) describes fairly well the structure and dynamics of infinitely diluted solutions of NaCl.²⁸ We will study whether this combination of potentials is able to predict the solubility of NaCl and KF in water.

III. SIMULATION METHODOLOGY

The determination of the solubility of a salt requires two types of simulations. First, NpT Monte Carlo (MC) simulations should be performed both for the solid phase and for the water solution. Second, free energy calculations should be performed for the salt in the solid phase and for the solution (at different concentrations of salt) to determine the chemical potential. This is needed since the solubility of a salt in water is just the concentration at which the chemical potential of the salt in the water solution becomes identical to the chemical potential of the salt in the solid:

$$\mu_{AX}^{\text{solid}} = \mu_{AX}^{\text{solution}},\tag{4}$$

where AX represents a generic monovalent salt, which in our particular case is either NaCl or KF. Let us first describe the details of the NpT simulations.

A. NpT simulations

Before performing free energy calculations, NpT Monte Carlo simulations were carried out in order to obtain an equilibrated configuration of the solution and to determine the average density of the system at a certain pressure, temperature, and in the case of the solution, composition.

Let us denote by N_A the number of cations in a certain phase and N_X as the number of anions. Obviously for an AX salt $N_{AX} = N_A = N_X$. Let us denote as N the total number of particles of a certain phase. For the salt in the solid phase $N=N_A+N_X$. For the water solution $N=N_{H_2O}+N_A+N_X$. In this work, the number of water molecules in the solution was fixed to 270. We denote as ρ the number density of particles in the solution per cubic Ångstrom (i.e., N/V with the V expressed in Å³). The number of molecules of salt used, i.e., N_{AX} , ranged from 1 for the most dilute solution, to 280 for the most concentrated one. In this work the solubility at 1 bar and 298 K of NaCl in water, and the solubility at 1 bar and 320 K of KF in water will be determined. The conditions selected for KF are identical to those used by Ferrario et al.,¹⁹ so that it is possible to compare the results of this work with those published previously.

Now we give some details on the simulations of the solid phases. Both, NaCl and KF present a NaCl-like structure in the solid phase. The total number of ions used in the simulations of the solid phase was of N=512. The non-Coulombic part of the potential was truncated at 10 Å and long range corrections to the energy were added by assuming that g(r)=1 beyond the cutoff. The Coulombic part of the potential was treated by using Ewald sums.⁴⁴ The Coulombic part of the potential was truncated in the real space sum at 10 Å and the value of the screening constant α was set to 0.25 Å^{-1} . The number of vectors used in the reciprocal space was of about 1000. Since the NaCl structure is cubic, isotropic NpT simulations were performed for the solid phase. Typically, about 50 000 cycles were used for equilibration and 50 000 cycles for obtaining the averages, where a cycle indicates a trial move per particle plus a trial volume change.

The initial configuration of the salt solution was obtained from an initial large system of SPC/E water molecules, by selecting randomly some water molecules and transforming them into ions. Since the number of water molecules was fixed to $N_{\rm H_2O}$ =270 in this work, the remaining water molecules were deleted. Several *NpT* runs were then performed between 390 K and the temperature of interest to equilibrate the initial configuration. Once the desired temperature was obtained, then long *NpT* runs were performed. A Monte Carlo cycle consisted of a trial *NVT* move per particle plus an attempt of changing the system volume. In the case of water, rotational moves were also included. The maximum angle of rotation, the maximum modulus of the displacement vector, and the maximum change of volume were adjusted in the equilibration stage in such way that the acceptance of each kind of trial move was between 30% and 40%. The number of cycles used to equilibrate the solution was between 10^5 for the most diluted solutions and 10^6 for the most concentrated ones. The difference in equilibration length was due to the fact that, for high concentrations, the particles in the system do not diffuse easily.⁷ We considered that the system was equilibrated when the density and the internal energy fluctuated around a mean value for more than 50 000 MC cycles. A comparison of the mean value of the density and the internal energy with molecular dynamics simulations of other authors is also a good test to verify that our configurations are sufficiently equilibrated (see discussion later in the text). In our simulations of the solutions, the non-Coulombic part of the potential was truncated at 9 Å and tail corrections were added assuming g(r)=1 beyond the cutoff. Coulombic interactions were calculated with the Ewald sums technique.⁴⁴ The real space cutoff (r_c) was set to 9 Å and the screening parameter in Fourier space to $\alpha = 0.29 \text{ Å}^{-1}$. The number of vectors used in the reciprocal space was of about 600.

B. Free energy calculations

Without any doubt, the determination of the chemical potential of the salt both in the solid and in the solution represents the more difficult part of the determination of the solubility. Different methodologies will be used to determine the chemical potential of the salt in the solid and in the solution.

The chemical potential of the salt in the crystal can be obtained from the Gibbs free energy of the crystal G_{solid} as $\mu_{AX}^{\text{solid}} = G_{\text{solid}}/(N/2)$ (recall that N is the total number of ions in the crystal, so that $N_{AX}=N/2$). Since $G_{\text{solid}}=A_{\text{solid}}+pV_{\text{solid}}$ and the volume V_{solid} of the crystal at a certain temperature and pressure is known from the NpT simulations, the only problem is to compute the Helmholtz free energy A_{solid} . The Helmholtz free energy of the crystal is calculated using the Einstein crystal method first proposed by Frenkel and Ladd.²⁹ The Hamiltonian of the Einstein crystal is given by

$$U_{\rm Ein} = \Lambda_E \sum_{i=1}^{N} (\vec{r}_i - \vec{r}_{io})^2,$$
(5)

where Λ_E is the strength of the spring connecting each ion located in $\vec{r_i}$ to the equilibrium lattice position $\vec{r_{io}}$. In the Frenkel-Ladd method, a reversible path is generated connecting the Einstein crystal—for which the free energy can be computed analytically—with the real crystal. This path is performed in two steps. In the first step harmonic springs are added in addition to the pair potential. The pair potential in this stage is given by

$$U(\lambda) = U + \lambda U_{\rm Ein},\tag{6}$$

where *U* is the energy of the crystal in a given configuration. In the second step the free energy difference between the bare Einstein crystal (with just springs and no interionic interactions) and the system with the interaction given by $U(\lambda = 1)$ is computed by umbrella sampling (see Refs. 45 and 46 for details). It is possible to show that the Helmholtz free

energy of the crystal is given by (Refs. 45 and 46):

$$\frac{A_{\text{solid}}}{Nk_{\text{B}}T} = -\frac{1}{N} \ln \left[\left(\frac{h}{\sqrt{2\pi m k_{\text{B}}T}} \right)^{-3N} \left(\frac{\pi}{\beta \Lambda_{E}} \right)^{3(N-1)/2} V_{\text{solid}} N^{-3/2} \right] \\ -\int_{\lambda=0}^{\lambda=1} \left\langle \frac{U_{\text{Ein}}}{Nk_{\text{B}}T} \right\rangle_{N,V,T,\lambda} d\lambda + \frac{U_{o}}{Nk_{\text{B}}T} \\ -\frac{1}{N} \ln \langle \exp[-\beta(U-U_{o})] \rangle_{\text{Eins}}, \tag{7}$$

where U_0 is the lattice energy of the crystal when the ions stand in their equilibrium lattice position, $\beta = 1/(k_{\rm B}T)$ and V_{solid} is the total volume. The bracket with subindex "Eins" means that the configurations are obtained from simulation of an Einstein crystal, as given by Eq. (5). The bracket within the integral is the average of the spring energy [Eq. (5)] evaluated over an ensemble interacting through the potential given by Eq. (6) for a certain value of λ . The center of mass of the Einstein crystal should be fixed in the simulations. We refer the reader to previous work for further details.^{45–47} The integral of Eq. (7) was evaluated by using about ten values of λ . For simplicity, we shall assume that the mass of the cation is identical to that of the anion and moreover that the value of thermal de Broglie length $h/\sqrt{2\pi m k_B T} = 1$ Å. Although these choices affect the value of the Helmholtz free energy they do not affect the coexistence properties as far as the same choice is done for all phases. Notice also that this choice of the thermal wavelength means that the volume V_{solid} in Eq. (7) should be given in Å³ and the constant Λ_E in $kT/Å^2$.

Let us now describe the procedure used to compute the chemical potential of the salt in the solution. The chemical potential of the salt in solution is obtained from the relation

$$\mu_{AX}^{\text{solution}} = \left(\frac{\partial G_{\text{solution}}}{\partial N_{AX}}\right)_{T,p,N_{\text{H}_2\text{O}}},\tag{8}$$

where G_{solution} is the Gibbs free energy of the solution. In this work, we will use Eq. (8) to compute the chemical potential of the salt in water. In fact, we shall compute the total Gibbs free energy for several amounts of salt while keeping constant the number of water molecules (i.e., $N_{\text{H}_2\text{O}}$ =270). After that we will compute the derivative given by Eq. (8) to obtain the chemical potential of the salt. All that is needed is a procedure to compute the total Gibbs energy of the solution. For a certain composition, the Gibbs energy of the solution G_{solution} is given as

$$G_{\text{solution}} = A_{\text{solution}} + pV_{\text{solution}}.$$
(9)

The term pV_{solution} is obtained from an NpT run for a certain pressure, temperature, and composition. Therefore, a method to compute A_{solution} is needed. The Helmholtz free energy of the solution can be split into a residual and an ideal part: $A_{\text{solution}}=A_{\text{solution}}^{\text{id}}+A_{\text{solution}}^{\text{res}}$. A residual thermodynamic property is defined as the difference between the actual value of the thermodynamic property in the system and that of an ideal gas *at the same temperature, volume, and composition*. The ideal value of the Helmholtz free energy of the solution is given as⁴⁸ : 4

$$\frac{A_{\text{solution}}^{\text{id}}}{Nk_{\text{B}}T} = x_{\text{H}_{2}\text{O}} \ln(\rho_{\text{H}_{2}\text{O}}\lambda_{b,\text{H}_{2}\text{O}}^{3}) + x_{A} \ln(\rho_{A}\lambda_{b,A}^{3}) + x_{X} \ln(\rho_{X}\lambda_{b,X}^{3}) - 1, \qquad (10)$$

where it should be recalled that $N=N_{H_2O}+N_A+N_X$ and the molar fraction of each component is $x_i, x_i = N_i/N$, whereas ρ_i stands for the number density of component *i*: $\rho_i = N_i/V$. For convenience, we shall set the de Broglie thermal wavelength λ_b of all species to 1 Å. This choice implies that the number densities given in Eq. (10) should be given in number of particles per Å³. For this reason, in this work all number densities reported will be given as number of molecules per $Å^3$. The choice made here for the thermal wavelength is consistent with that used for the solid phase. Obviously, the value of the de Broglie wavelength depends on the mass of the particles and the temperature. However, since the goal of this article is to obtain phase equilibria and not absolute values of the free energies, the value of 1 Å will be assigned to all particles. The phase equilibria are not affected by such arbitrary assignment since the de Broglie wavelength, which arises from the contribution of the momenta to the free energy, appears in all phases, and therefore its contribution cancels out when the phase equilibria is considered.

 $A_{\text{solution}}^{\text{res}}$ was obtained by means of thermodynamic integration in the *NVT* ensemble from the solution to a Lennard-Jones reference fluid (LJ,ref) for which the residual free energy is known.⁴⁹ In the thermodynamic path, both the molecules of water and the ions of the system are transformed into LJ particles. The thermodynamic path is generated by using a coupling parameter λ :

$$U(\lambda) = \lambda U_{\text{LJ,ref}} + (1 - \lambda)U, \qquad (11)$$

where λ varies from 0 to 1 along the integration path. The residual free energy of the solution is then obtained as

$$A_{\text{solution}}^{\text{res}} = A_{\text{LJ,ref}}^{\text{res}} + \Delta A = A_{\text{LJ,ref}}^{\text{res}} + \int_{0}^{1} \langle U - U_{\text{LJ,ref}} \rangle_{N,V,T,\lambda} d\lambda.$$
(12)

The volume used in these NVT simulations is just the average volume of the system obtained in the NpT runs. The integrand is evaluated at several points between $\lambda = 0$ and $\lambda = 1$. We have evaluated the integrand at eight points of λ , distributed between 0 and 1 according to a Gaussian quadrature. Each of these NVT simulations consisted of 10 000 cycles of equilibration plus 20 000 of averaging, in the case of NaCl solutions, and of 20 000 plus 30 000 in the KF solution. The final configuration of the run for a certain value of λ was used as the initial configuration of the next run. In Fig. 1 the integrand is plotted as a function of λ for three different solutions of NaCl and for other three of KF. As can be seen in the plot, the higher the salt content, the bigger the free energy difference between the LJ fluid and the solution. Notice also that there is no divergence of the integrand in the integration limits. Such a divergence may appear when going for instance from a solution to an ideal gas, but it does not appear when going from the solution to the LJ reference fluid. For the NaCl solution with 20 ionic pairs, the integrand was computed in the forward (increasing the value of λ) and



FIG. 1. Top, integrand of the transformation of NaCl solutions at 298 K and KF solutions at 320 K into a Lennard-Jones fluid. Bottom, integrand of the transformation of the NaCl solution with 20 NaCl molecules into a Lennard-Jones fluid. We show the comparison between the integration in the direction solution-Lennard-Jones (forward) with the integration in the direction Lennard-Jones-solution (backward).

in the backward (decreasing the value of λ) directions. As can be seen in Fig. 1, no significant differences were found in the integrand, although it was necessary to perform longer runs for small values of λ to equilibrate the system when the integration was done in the backward direction. To test the accuracy of our integration method, we decided to compute for a few selected solutions the integral of Eq. (12) using 32 values of λ instead of 8. We found that the integral was modified by an small amount of about 0.2%. That means that our choice of eight values of λ to perform the integral is quite reasonable, since it provides accurate results and still keeps the computational effort within reasonable limits. A rough estimate of the effect on the solubility of numerical uncertainties in determining the integral of Eq. (12) yields an uncertainty in the solubility of about 10% (in the direction of decreasing the solubility of the salt). The residual free energy of the Lennard-Jones fluid $(A_{LJ,ref}^{res})$ was taken from the work of Johnson and co-workers.⁴⁹ In order to avoid phase transitions along the integration path, the choice of ε and σ of the reference LJ fluid must be done with care. The value of the Lennard-Jones parameters of the reference fluid, σ_{ref} and ε_{ref} , have been chosen in such way that the reference LJ system is a dense fluid at the temperature and density at which the integration is carried out. For NaCl and KF solutions, the value $\varepsilon_{\rm ref}/k_{\rm B}$ =78.2 K was used (i.e., the same as the oxygens in the SPC/E model). With this choice, the temperatures T=298 K and T=320 K correspond to a reduced temperatures

TABLE III. Free energy calculations for NaCl and KF. All contributions to the free energy are presented. ΔA_1 is the free energy difference between the alkali halide crystal without and with harmonic springs that couple each ion to its lattice position (both situations with the center of mass fixed) and it corresponds to the second term on the right-hand side of Eq. (7). ΔA_2 is the free energy difference between the Einstein crystal with and without the interatomic interactions (again, both situations with the center of mass fixed) and it corresponds to the last two terms on the right-hand side of Eq. (7). A_{A_2} is given in particles per \hat{A}^3 . The number density is that obtained from an NpT run at p=1 bar and the temperature indicated in the table. Notice that in the simulations it is possible to have a solid as a mechanically stable phase even at temperatures slightly higher than the melting point (Ref. 59).

Salt	$T\left(\mathrm{K} ight)$	ρ	$A/Nk_{\rm B}T$	$\Delta A_1/Nk_{\rm B}T$	$\Delta A_2/Nk_{\rm B}T$	Ν	$\Lambda_E/k_{\rm B}T({\rm \AA}^{-2})$	$A_{\rm Eins}/Nk_{\rm B}T$
NaCl	1074	0.0388	-41.8	-6.27	-43.1	1000	500.	7.61
NaCl	1074	0.0388	-41.8	-6.25	-43.1	512	500.	7.61
NaCl	298	0.0438	-153.1	-6.26	-156.9	512	2500.	10.02
KF	320.	0.0521	-149.4	-6.13	-149.4	512	2000.	9.68

of $Tk_{\rm B}/\varepsilon_{\rm ref}$ =3.8 and $Tk_{\rm B}/\varepsilon_{\rm ref}$ =4.1, respectively. The value of $\sigma_{\rm ref}$ was selected such that the reduced density, i.e., $\rho\sigma_{\rm ref}^3$, was around 1. For this reason, the value $\sigma_{\rm ref}$ =3.14 Å was chosen for the NaCl solutions and the value $\sigma_{\rm ref}$ =2.84 Å was used for the solutions of KF.

Once G_{solution} has been computed for several compositions (i.e., number of molecules of salt N_{AX} while keeping the number of molecules of water $N_{\text{H}_2\text{O}}$ =270 constant), the chemical potential μ_{AX} can be obtained from Eq. (8).

IV. RESULTS

We shall start by presenting the values of the free energies of the solid phase. This is done in Table III. The free energy for the KF and NaCl salts are presented. Most of the free energy calculations were done with N=512. However, for the NaCl we also performed free energy calculations for N=1000. In the system with N=1000, the potential was truncated at the same distance as in the smaller system. As can be seen, the free energies obtained for both system sizes are practically identical. For this reason, no system size effects have been observed for a given truncation of the potential. For the NaCl system we calculated the free energy for two different temperatures, T=298 K and T=1074 K, both at the pressure p=1 bar by using the Einstein crystal methodology. By using the thermodynamic relation

$$\frac{G(T_2,p)}{Nk_{\rm B}T_2} - \frac{G(T_1,p)}{Nk_{\rm B}T_1} = -\int_{T_1}^{T_2} \frac{H(T)}{Nk_{\rm B}T^2} dT,$$
(13)

one can compute the Gibbs free energy at $G(T_2 = 298 \text{ K}, 1 \text{ bar})/(NkT_2)$ provided the free energy at $G(T_1 = 1074 \text{ K}, 1 \text{ bar})/(NkT_1)$ is known and that the enthalpy of the system along the isobar p=1 bar is known. By using thermodynamic integration, we estimated that $G(T_2 = 298 \text{ K}, 1 \text{ bar})/(NkT_2)=-153.2$, which is in excellent agreement with the value -153.14 obtained via the Einstein crystal calculation. Remind that at the thermodynamic conditions of this work $G \approx A$. As an additional check, we have also computed the melting temperature of the NaCl model, obtaining $T_m = 1046(15)$, which agrees well with the values $T_m = 1064(14)$ of Anwar *et al.*³⁰ and $T_m = 1050(3)$ of Mastny *et al.*⁵⁰ As can be seen, all tests performed on our free energy calculations were passed satisfactorily. The value of

the chemical potential obtained for the NaCl solid at T=298 K and p=1 bar is $\mu_{\text{NaCl}}(298$ K, 1 bar)= -758.9 kJ/mol. The value of the chemical potential for the KF solid at T=320 K and p=1 bar is $\mu_{\text{KF}}(320$ K, 1 bar)= -794.8 kJ/mol. Notice that the contribution of the pV term to Gibbs free energy of the solid is quite small, so that the main contribution to G by far is that of the Helmholtz free energy.

We now present results of the NpT runs for the solutions. Let us first discuss if the models used in this work are able to describe the experimental densities.^{51,52} In Fig. 2 the density of the solutions as obtained from our simulations is compared with experimental data and with simulations performed by other authors. As can be seen, the comparison between our simulation results and those of Ferrario and co-workers¹⁹ is satisfactory. For the case of NaCl, the agreement with the experimental data is quite good for low concentrations of salt, but it deteriorates a bit at higher concentrations. This is in agreement with the results of Brodholt,¹⁰ who studied the density of NaCl in SPC/E using a model quite similar to that used in this work (the only difference being that ion-ion interactions were of LJ type instead of the Tosi-Fumi type). The model used to simulate KF solutions gives densities always higher than the experimental ones. In Fig. 2 we also show the comparison between experiment and simulation for the partial molar volume of the salt in KF and NaCl solutions at 298 K. For the case of NaCl solutions the model is able to predict the correct partial molar volume at low concentrations. At higher concentrations the agreement deteriorates and the model prediction is too high. For KF solutions the prediction of the model is always lower than the experimental value. To test further the performance of our NpT simulations, we have compared our average potential energy of KF solutions at 1 bar and 298 K with the results of Laudernet and co-workers' (Fig. 3). The agreement is very satisfactory and, along with the comparison shown in Fig. 2, it gave us confidence in our NpT simulations.

Let us now present the results for the Gibbs free energy of the solutions. The results for the free energy calculations of the KF and NaCl solutions at 320 and 298 K, respectively, are given in Tables IV and V. All the terms that contribute to the total free energy are specified [see Eqs. (9) and (12)].

In Fig. 4, the Gibbs free energy of the solution is plotted



FIG. 2. Top: density versus molality for NaCl solutions at 298 K and KF solutions at 320 and 298 K. We compare our simulation results with experimental data (Refs. 51 and 52) and with simulation results of Ferrario *et al.* (Ref. 19). At right: partial molar volume of the salt as a function of molal concentration for KF and NaCl solutions at 298 K. The experimental partial molar volumes were obtained through the derivative of a cubic fit to experimental data of volume of solutions with 1000 g of water (Ref. 52) versus the molality.

as a function of the number of ionic pairs present in the system (with a fixed number of water molecules). We fitted the numerical values of the Gibbs free energies of the solution G_{solution} to a polynomial. The chemical potential of the salt is just the first derivative of G_{solution} with respect to N_{AX} . We used a second-degree polynomial function to fit the



FIG. 3. Potential energy of KF aqueous solutions at 298 K and 1 bar obtained with our simulations (circles) and with the simulations of Laudernet and co-workers (Ref. 7) (squares). In order to compare both sets of numbers directly, the energy has been normalized as Laudernet *et al.* did; i.e., counting the number of molecules in the system as the number of water molecules plus the number of ionic pairs. (Note that in the rest of the paper we have normalized with the number of water molecules plus the number of ions).

TABLE IV. Free energy of KF solutions at 320 K and 1 bar. All the solutions have 270 water molecules. Energies are given in kJ/mol. The number density $\rho = N/V$ is given in particles per Å³. The A_{LJ} term is the sum $A_{LJ,ref}^{res} + A_{Solution}^{red}$.

NVE	Galution	$-\Delta A$	ALL	рV	0	<i>M</i> (mol/l)	m (mol/kg)
- · KF	- solution		LJ	P ·	r	()	(
80	-76 212	-72 676	-3537	0.62	0.0420	13.0	16.5
90	-84 326	-80 649	-3678	0.64	0.0424	14.1	18.5
100	-92 490	-88 665	-3825	0.66	0.0426	15.1	20.6
110	-100 622	-96 645	-3978	0.69	0.0428	16.0	22.6
120	-108 674	-104 540	-4135	0.71	0.0430	16.8	24.7
130	-116 726	-112 431	-4296	0.74	0.0431	17.6	26.7
140	-124 819	-120 362	-4458	0.77	0.0432	18.3	28.8
150	-132 868	-128 250	-4619	0.79	0.0433	18.9	30.8
160	-140 956	-136 181	-4776	0.82	0.0434	19.5	32.9
180	-156 997	-151 920	-5078	0.87	0.0435	20.7	37.0
200	-173 016	-167 640	-5377	0.92	0.0437	21.7	41.1
220	-188 977	-183 302	-5676	0.98	0.0438	22.5	45.2
240	-204 946	-198 970	-5977	1.03	0.0439	23.3	49.4
260	-220 829	-214 548	-6282	1.08	0.0439	24.0	53.5
280	-236 703	-230 112	-6592	1.14	0.0440	24.6	57.6

curves. A linear fit cannot be used since it would lead to a chemical potential of the salt independent of the concentration, which obviously is an incorrect result. The values of the fit are

$$G_{\text{solution}}(N_{\text{KF}}) = -10840 - 821.70N_{\text{KF}} + 0.054N_{\text{KF}}^2,$$
 (14)

$$G_{\text{solution}}(N_{\text{NaCl}}) = -10202 - 784.64N_{\text{NaCl}} + 0.492N_{\text{NaCl}}^2,$$
(15)

where G_{solution} is given in kJ/mol (i.e., the Gibbs free energy for an Avogadro number of solutions of N particles each). These fits describe our data quite well. We shall not assign any physical meaning to the coefficients of the fit. Notice that the polynomial form is used to fit G_{solution} for finite concentrations well away from the infinitely dilute limit. The results for the chemical potential of KF and NaCl in water as a function of the molality are presented in Fig. 5. The value of the chemical potential for the solid is also presented in

TABLE V. Free energy of NaCl solutions at 298 K and 1 bar. All the solutions have 270 water molecules. Energies are given in kJ/mol. The number density $\rho = N/V$ is given in particles per Å³. The A_{LJ} term is the sum of $A_{LJ,ref}^{res} + A_{Solution}^{red}$.

						М	т
$N_{\rm NaCl}$	$G_{\rm solution}$	$-\Delta A$	$A_{\rm LJ}$	pV	ρ	(mol/l)	(mol/kg)
12	-19 563	-17 908	-1655	0.51	0.0346	2.34	2.47
15	-21 857	-20 158	-1700	0.52	0.0348	2.89	3.08
17	-23 394	-21 679	-1716	0.52	0.0349	3.24	3.50
20	-25 678	-23 924	-1755	0.53	0.0351	3.76	4.11
22	-27 208	-25 432	-1776	0.54	0.0352	4.09	4.52
25	-29 536	-27 746	-1790	0.54	0.0353	4.58	5.14
27	-31 039	-29 198	-1841	0.55	0.0354	4.90	5.55
30	-33 286	-31 416	-1871	0.56	0.0355	5.36	6.17
32	-34 827	-32 915	-1912	0.56	0.0355	5.65	6.58
37	-38 560	-36 568	-1993	0.58	0.0356	6.36	7.61
40	-40 793	-38 737	-2056	0.59	0.0356	6.76	8.23

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FIG. 4. Gibbs free energy of solutions containing 270 water molecules and N_{AX} ionic pairs at p=1 bar. The plot on the top shows the results obtained for KF solutions at 320 K and the bottom one for NaCl at 298 K.

Fig. 5 as an horizontal line. The intersection point between this line and the solute chemical potential corresponds to the solubility of the salt. Notice the linear variation of the chemical potential of the salt in the solution. This is a consequence of the use of a second-order polynomial for G_{solution} . One may wonder if the use of a polynomial of higher order would modify this physical image (a linear increase of the chemical potential with the concentration). For KF we have also fitted G_{solution} to a cubic form. The value of the chemical potential obtained from this cubic fit is also presented in Fig. 5. As can be seen, the difference with the results of the second order polynomial are quite small and the value of the solubility is hardly affected by the choice of the polynomial. For this reason, a second-order polynomial will be used to fit G_{solution} . More evidence of the convenience of the quadratic fit is obtained from the square root of the mean quadratic deviation (i.e., the square root of the average quadratic deviation between the tabulated results and the results of the fit). It changes from 193 to 23 when going from the linear fit to the second-order polynomial, but it decreases only to 22 when going to the cubic fit. The quadratic deviation, therefore, also justifies the use of a second degree polynomial. A similar analysis was performed for the NaCl solution where again the cubic fits provides a marginal improvement over the quadratic fit. Therefore, we considered the second-degree polynomial to be a good approximation. In that case, the chemical potential of the solute varies linearly with the number of ionic pairs in the solution. We found that this is indeed a very good approximation for concentrated solutions-at least for

FIG. 5. In the top, the chemical potential of KF in solution as a function of the molality. The different curves correspond to different orders of the fit $G_{\text{solution}}(N_{\text{KF}})$. The horizontal dashed line is the solid chemical potential. In the bottom, the same is plotted for the NaCl solutions, but only the line coming from a quadratic fit to $G_{\text{solution}}(N_{\text{NaCl}})$ is shown.

the salts considered in this work. Obviously, for dilute solutions, the variation of the chemical potential with salt concentration is not linear, as will be discussed later on for the NaCl solution.

We discuss now the value of the solubility found in this work for the two considered salts. The value of the solubilities are presented in Table VI. Let us start by discussing the results for KF. In the saturated KF solution there are almost as many molecules of salt as water molecules. KF is probably one of the salts with the higher solubility. For this reason it is a rather difficult salt to study. Ferrario *et al.*¹⁹ obtained the chemical potential of the KF as a function of the molarity of the salt. We also present the chemical potential of the salt as a function of the molarity. This is done in Fig. 6. As it can be seen the increase of the chemical potential of KF with molarity is not linear but presents a certain curvature. This is due to the fact that the change in density of KF with

TABLE VI. Solubilities of KF and NaCl as obtained in this work and from experiment. Simulations results from Ferrario (Ref. 19) are also included.

Salt	$T(\mathbf{K})$	Source	М	т
KF	320	This work	24(3)	51(6)
KF	320	Ferrario	26	
KF	320	Experiment	17	
NaCl	298	This work	4.8(7)	5.4(8)
NaCl	298	Experiment	5.4	6.14



FIG. 6. Chemical potential of the ionic pair in solution versus the molar concentration (continuous line). The dashed horizontal line represents the solid chemical potential. In the top the results for KF solutions at 320 K and 1 bar are represented; in the bottom for NaCl at 298 K and 1 bar. The crossing point determines the solubility of the model.

salt concentration is not linear, as was presented before. The dashed horizontal line of Fig. 6 is the chemical potential of the salt in the solid phase. Again, the crossing point corresponds to the solubility, which for the KF model amounts to 24(3)M, which is in fairly good agreement with the data of Ferrario *et al.*; namely, 26*M*. The experimental value of the solubility of real KF in water (as taken from the paper of Ferrario) is of 17*M*. As can be seen, the model describes only qualitatively the solubility of KF in water. This is more clearly visible on a molality scale since the solubility of real KF in water is 24m, whereas that of the model is of 51(6)m. Due to the small size of the fluoride ion, its interactions with the protons could be too strong, since for the SPC/E model no LJ interaction site is located on the hydrogens.

In Fig. 6 the chemical potential of NaCl is presented as a function of the molarity of the solution. Again a certain curvature is observed, which is due to the non linear dependence of the density on the number of molecules of salt. The NaCl solubility is 4.8(7)M, which comprises the experimental value 5.416M (see Ref. 53) within its error. When given in terms of molality, the solubility of the NaCl model as obtained in this work is of 5.4(8)m, which is in good agreement with the experimental⁵³ value 6.144m. Taking into account that solubility varies in orders of magnitude between different salts, the prediction of the model is surprisingly good. The model has also been able to predict that, as is the case experimentally, KF solubility is higher than NaCl one.

The model of NaCl aqueous solution predicts quite

TABLE VII. Gibbs free energy—in kJ/mole of solutions—of KF solutions with 270 water molecules and the indicated number of ionic pairs (N_{KF}) at 1 bar and different temperatures.

		G _{solution} (kJ/mol)	
$N_{\rm KF}$	298 K	260 K	230 K
100	-92 840	-93 510	-94 100
120	-109 040	-109 740	-110 340
140	-125 190	-125 900	-126 520
160	-141 350	-142 080	-142 710
180	-157 410	-158 190	-158 860
200	-173 440	-174 230	-174 910
220	-189 410	-190 210	-190 910
240	-205 390	-206 210	-206 920

nicely the experimental solubility. It seems to be about 10% below the experimental value (although the experimental value of the solubility is within the error bar of our estimate). For KF the results are worse. In fact the model of KF overestimates significantly the solubility. Further work is needed to understand why the agreement was better for NaCl than for KF. In any case the determination of the solubility is a difficult test to pass since it requires, a good water model, a good model for the salt (i.e., providing good values of the chemical potential of the salt), and a good model for the cross interaction between the salt and the water. In order to build an accurate potential to mimic solutions, one should first start from accurate potentials for the pure solute and the pure solvent separately. It would only then be worthwhile to try to fit the parameters of the interaction water-ion to predict the experimental solubility.

It is not very costly to calculate the Gibbs free energy of a solution at any temperature once it is known at one point, as illustrated by Eq. (13). We have performed NpT simulations of several KF solutions at 1 bar pressure and temperatures ranging from 320 to 230 K (the freezing point of SPC/E water is of 215 K, so that these temperatures are well above the melting point of the model). This provided us with a function $H(T)/Nk_{\rm B}T^2$ for each solution. With Eq. (13) we have calculated the Gibbs free energy for the solutions at different temperatures (see Table VII). The same has been done for the KF salt in the solid phase. The values of the chemical potential of the KF crystal for T=298 K, T=260 K, and T=230 K were found to be -795.6, -797.05, and -798.3 kJ/mol, respectively. The solubility can now be calculated for each temperature as described previously for KF solutions at 320 K. The results are shown in Table VIII. As can be seen, the simulations have been able to capture the increase of solubility with temperature, which is also ob-

TABLE VIII. Calculated solubility of KF in water for different temperatures at 1 bar.

<i>T</i> (K)	m (mol/kg)
320	51.3
298	50.4
260	49.5
230	48.9



FIG. 7. Solubility (in mol/kg) as a function of temperature of KF aqueous solutions at 1 bar. The model predictions are represented with circles and the experimental data with squares (Ref. 57).

served in experimental results. This is illustrated in Fig. 7. The agreement with the experimental solubilities is rather poor. Nevertheless, the slope of the change of solubility with temperature seems to be in good agreement with experiment. The kink observed in the experimental curve at low temperatures is due to the fact that $KF(H_2O)_2$ is formed at low temperatures instead of KF. In this work no attempt has been done to compute the solubility of $KF(H_2O)_2$. It is good to know that the model is able to capture the increases of solubility of KF with temperature.

We have also done an analysis of the influence of the model parameters over the solubility. Given that SPC/E model is a reasonable water model (although it can be improved⁵⁴), and that the Tosi-Fumi parametrization seems to describe accurately the properties of pure NaCl,³⁰ we have focused our attention in the interaction water-ion. In particular, we have done an estimation of the solubility of two newly conceived models: one in which the parameter σ of the cross-interaction water-Cl⁻ has been decreased in 0.5 Å with respect to the original model, and another one in which the same has been done with the interaction water-Na⁺. The free energy of the modified model $G(N, p, T, \lambda=1)$ is related to the free energy of the original one $G(N, p, T, \lambda=0)$ by

$$G(N, p, T, \lambda = 1) - G(N, p, T, \lambda = 0)$$
$$= \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{N, p, T, \lambda} d\lambda,$$
(16)

where $U(\lambda) = (1-\lambda)U_0 + \lambda U_1$ is a linear combination between the potential energy of the original model (U_0) and the potential energy of the modified one (U_1). The parameter λ varies from 0 to 1 along the integration of Eq. (16), such that when $\lambda=0$ the system is governed by the original model and when $\lambda=1$ the sampling of configurations is dictated by the modified one. The numerical integration of Eq. (16) requires the evaluation of the integrand, by NpT simulations, at several values of λ , which in our case were distributed between 0 and 1 according to a Gauss quadrature. In this way, we have calculated the free energy of several NaCl solutions at 1 bar and 298 K for both the modified models. The chemical potential of the solid is not affected by the change of the ion-water interaction since the ion-ion interaction is the same

TABLE IX. Free energy of NaCl solutions (in kJ/mol of solutions with 270 water molecules) at 1 bar and 298 K after modifying the value of σ for LJ the interactions Cl⁻-O and Na⁺-O.

N _{NaCl}	G _{Cl⁻-0}	$G_{\mathrm{Na}^{-}\mathrm{-O}}$
10	-19 340	-19 450
15	-23 830	-24 020
20	-28 410	-28 570
25	-32 980	-33 140
30	-37 180	-37 600
35	-41 570	-42 130
40	-45 890	-46 440

as before (i.e., the Tosi-Fumi potential) and in the solid only ion-ion interactions are present. The results are given in Table IX. From this data, and following the same procedure as we did with the original model, we have calculated the solubility of the solutions modeled with the modified interaction parameters. For the case of the change in the interaction Cl⁻-O, a solubility of 17m has been found, while after the modification of Na⁺-O interactions, the solubility changed to 24m. The value of these solubilities have a large error, since they are out of the range of concentrations in which the fit of the Gibbs free energy has been done. Nevertheless, they can serve us perfectly for a qualitative analysis. The solubility predicted by the original model was 5.4m. Either for Cl⁻ or for Na⁺, a decrease in the ionic diameter (when interacting with water) has meant an increase of solubility. This is the expected behavior, since the hydration of the ions is favored if water can get closer to them. The solubility has been more affected in the case of the modification of the Na⁺-O interaction than in the Cl⁻-O one. This study provides a rough estimate of the change of solubility with these potential parameters, which could be used as an initial guess for a model whose solubility was the experimental one; but this is beyond the scope of this work.

Let us finish this paper by discussing the possibility of computing activity coefficients and properties of the salt at infinite dilution by using computer simulation. For this purpose we shall consider the NaCl solution. In a thermodynamic treatment of 1:1 electrolytes in water the chemical potential of the salt is given by

$$\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^0 + 2RT \ln(m\gamma), \qquad (17)$$

where μ_{NaCl}^0 is the chemical potential of the salt in the standard state and *R* is the gas constant 0.008 314 kJ/(mol K). The activity coefficient γ for a certain concentration can be easily obtained from Eq. (17) provided that μ_{NaCl} and μ_{NaCl}^0 are known. When the concentration of the salt is moderate or high, it is a good approximation to assume that the total Gibbs free energy of the mixture for a fixed amount of water (and therefore the chemical potential of the salt) can be approximated by a polynomial expression. However, this is not a good approximation for very dilute solutions. It is necessary to determine an expression for the total Gibbs free energy of the mixture in the limit of highly diluted solutions. We shall now work out such a expression. We shall assume that the activity coefficient of the salt is given by

$$\ln(\gamma) = -1.174 \frac{\sqrt{m}}{1 + \sqrt{m}} + bm.$$
(18)

Equation (18) is just the Debye-Huckel theory for a salt in water at room temperature and pressure (for a 1:1 electrolyte the ionic strength is just the molality of the salt) plus a linear correction term given by bm, which is commonly used in semiempirical theories of activity coefficients.⁵⁵ Equation (18) is expected to be valid for diluted solutions. By replacing Eq. (18) into Eq. (17) one obtains

$$\mu_{\text{NaCl}} = \mu_{\text{NaCl}}^{\circ} + 2RT \ln(m) + 2RT \left(-1.174 \frac{\sqrt{m}}{1+\sqrt{m}} + bm \right),$$
(19)

This equation contains two unknowns; namely, μ_{NaCl}^0 and the constant *b*. The chemical potential of water and the chemical potential of the salt are related through the Gibbs-Duhem equation since

$$N_{\rm H_2O}d\mu_{\rm H_2O} + N_{\rm NaCl}d\mu_{\rm NaCl} = 0.$$
⁽²⁰⁾

By integrating the Gibbs Duhem equation from m=0 to m and assuming that the chemical potential of the solute is given by Eq. (19) one obtains for the chemical potential of water:

$$\mu_{\rm H_2O} = \mu_{\rm H_2O}^0 - \frac{W_{\rm H_2O}RT[-1174\sqrt{m} + 250b(m^2 + m^{5/2}) - 87m + 500m^{3/2} + 1174(1 + \sqrt{m})\ln(1 + \sqrt{m})]}{2.5 \times 10^5(1 + \sqrt{m})},\tag{21}$$

where $W_{\rm H_2O}$ is the molecular weight of water. The Gibbs free energy of a solution of NaCl in water is given by

$$G = N_{\rm H_2O} \mu_{\rm H_2O} + N_{\rm NaCl} \mu_{\rm NaCl}.$$
(22)

According to this, for sufficiently dilute solutions of NaCl in water, the total Gibbs energy will be given by Eq. (22), where μ_{NaCl} is given by Eq. (19) and $\mu_{\text{H}_{2}\text{O}}$ is given by Eq. (21). The analytical expression for G contains three unknowns; namely, $\mu_{H_2O}^0$, μ_{NaCl}^0 , and the constant b. We have computed the Gibbs free energy for diluted solutions of NaCl. The values of the Gibbs free energy were fitted to Eq. (22) so that the value of the three constants $\mu_{H_2O}^0$, μ_{NaCl}^0 , and b were obtained from the fit. In Table X we present the results for the Gibbs free energy of dilute NaCl water solutions obtained by the same procedure used for concentrated solutions. After performing the fit, we obtained $\mu_{\text{NaCl}}^0 = -768.95 \text{ kJ/mol},$ $\mu_{\rm H_2O}^0 = -38.091 \text{ kJ/mol},$ b = -0.040 79 kg/mol. Let us see if the value obtained compare well with previously published results. For pure SPC/E water, we have computed the chemical potential at T=298 K and p=1 bar in previous work. The value obtained in this work $\mu_{\rm H_2O}^0 = -38.091 \text{ kJ/mol}$ compares quite well with the value of our previous work on the phase diagram of water. In fact, in our previous work on the phase diagram of SPC/E we obtained for the free energy of SPC/E model the values -40.85, -38.09, and -35.68 kJ/mol for the temperatures 225, 298, and 443 K, respectively. As can be seen for T=298 K, the results of this work agree quite nicely with those of our previous work. For a salt, the chemical potential of the reference state μ_{NaCl}^0 is the chemical potential of a virtual state with molality 1, but with a residual chemical potential given by the infinite dilution limit $\mu_{\text{NaCl}}^{\text{res}}(m=0)$. According to this,

$$\mu_{\text{NaCl}}^{0} = \mu_{\text{NaCl}}^{\text{res}}(m=0) + 2RT \ln\left(\frac{N_{\text{Av}}}{10^{27}}\right).$$
 (23)

The second term on the right-hand side of Eq. (23) is the ideal term (in molecules per Å³ for an ideal 1*m* solution). From Eq. (23) we have obtained $\mu_{\text{NaCI}}^{\text{res}}(m=0) = -732 \text{ kJ/mol}$. This value is in excellent agreement with the residual chemical potential at infinite dilution obtained by Lynden-Bell *et al.*³³ for the same model used in this work, which amounts to -730 kJ/mol. Let us now turn to the point of whether the model is able to describe the experimental results for NaCl in water. It is common to tabulate experimentally the so-called hydration chemical potential. The hydration chemical potential of the reference state in the solution and the chemical potential of the reference state in the gas (i.e., a

TABLE X. Free energy of NaCl solutions at 298 K and 1 bar. All the solutions have 270 water molecules. Energies are given in kJ/mol. The number density $\rho = N/V$ is given in particles per Å³. The A_{LJ} term is the sum $A_{\text{LJ,ref}}^{\text{res}} + A_{\text{solution}}^{\text{id}}$.

N _{NaCl}	$G_{\rm solution}$	$-\Delta A$	$A_{ m LJ}$	pV	ρ	<i>M</i> (mol/l)	m (mol/kg)
1	-11 067	-9 546	-1521	0.49	0.0334	0.20	0.20
2	-11 845	-10 313	-1533	0.49	0.0336	0.41	0.41
3	-12 616	-11 074	-1543	0.49	0.0337	0.61	0.62
4	-13 399	-11 845	-1554	0.49	0.0339	0.81	0.82
5	-14 171	-12 624	-1548	0.49	0.0340	1.01	1.03
7	-15 698	-14 108	-1590	0.50	0.0342	1.40	1.44
10	-18 016	-16 392	-1624	0.51	0.0344	1.97	2.06
12	-19 563	-17 908	-1655	0.51	0.0346	2.34	2.47
15	-21 857	-20 158	-1700	0.52	0.0348	2.89	3.08

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FIG. 8. Activity coefficient of NaCl in water as obtained in this work from computer simulation (solid line), and as obtained from experiment (dashed line). Experimental results were taken from Refs. 57 and 58.

mole of NaCl molecules in an ideal gas at the same T and p than the solution). The hydration chemical potential μ_{hyd}^0 of the model can be obtained as

$$\mu_{\text{hyd}}^{0} = \mu_{\text{NaCl}}^{\text{res}}(m=0) + 2RT \ln(RT/pV_0), \qquad (24)$$

where V_0 is 1 dm³ and p=1 bar. Therefore, $2RT \ln(RT/pV_0)$ has a value of 15.915 kJ/mol. The value obtained in this work for $\mu_{hyd}^0 = -714$ kJ/mol is in excellent agreement with the experimental value: $\mu_{hyd}^{0,exp} = -720$ kJ/mol.⁵⁶

Let us now compare the values of the activity coefficients obtained in this work with the experimental values.^{57,58} Recall that to compute γ (for a certain composition) the values of μ_{NaCl} and μ_{NaCl}^0 are needed. We have already shown that $\mu_{\text{NaCl}}^0 = -768.95 \text{ kJ/mol}$. The values of μ_{NaCl} will be obtained by differentiating G_{solution} with respect to N_{NaCl} . For dilute solutions we shall use Eq. (22) along with Eqs. (19) and (21) to describe G. When this is done, μ_{NaCl} is simply given by Eq. (19). For concentrated solutions we shall use Eq. (15) for G. We fail to obtain a unique equation able to describe G correctly at low and high concentrations of salt. For this reason, we will use two different expressions for G, one working quite well at low concentrations of salt and another working quite well for concentrated solutions. The values of the activity coefficient of NaCl in water, for the model used in this work, are presented in Fig. 8 along with the experimental results.^{57,58} As can be seen, the model describe only qualitatively the variation of the activity coefficient with salt concentration. It seems that the solubility of NaCl in water is underestimated by the model mostly due to an slightly higher value of the chemical potential of the reference state, and by a too sharp increase of the activity coefficient at high concentrations (although of course it would be necessary to establish more clearly if the chemical potential of the solid is properly described by the model). It should be recognized that the evaluation of activity coefficients is a very demanding calculation from a computational point of view containing many possible sources of error. For this reason we estimate that the typical error of the activity coefficient determined in this work is of about 15%. To the best of our knowledge, this is the first time the activity coefficient has been obtained for a salt close to the solubility limit, in a model with explicit treatment of the water molecules. A subproduct of the calculations of this work is the variation of the chemical potential of water by adding small amounts of salt. In fact this is given by Eq. (21). When a similar analysis to that performed in this work would be done at temperatures close to the melting point of the solvent, then it would be possible to determine the depression of the melting point of a model of water by the addition of salt (notice that SPC/E water would not be particularly useful for this purpose since its melting point is T=215 K), but other models with higher melting points, as, for instance, TIP4P/Ice¹⁸ or TIP4P/2005⁵⁴ could be studied.

V. SUMMARY AND CONCLUSIONS

We have calculated, by means of molecular simulation, the equilibrium solid-solution for two ionic salts: NaCl and KF. We have calculated the solid chemical potential with the Einstein crystal technique. We have developed a new methodology to compute the chemical potential of the salt in the solution. The methodology is relatively straightforward and can be easily implemented. Even though it was applied to ionic solutions of water, it is general and valid for any type of solution. We have obtained that, as is the case in nature, KF solubility is much higher than that of NaCl. The prediction of NaCl solubility is, within the error of the method, in agreement with the experimental value. However, the prediction of the model is not so good for the KF case, as reported previously.¹⁹ The overestimation of the solubility of the KF model is compatible with a bad parametrization of the pure salt model, that underestimates the melting point. Nevertheless, it cannot be discarded that ion-water interaction has also some influence. We observe a decrease of solubility when decreasing temperature for KF aqueous solutions. This is in qualitative agreement with what occurs experimentally, although a quantitative comparison was not possible. As expected, decreasing the ion size in the interaction ion-water provoked an increase of the solubility predicted for NaCl solutions. The fact that water molecules can come closer to the ions yields a more energetically favored hydration. We have also done an estimation of the solvation chemical potential of NaCl at infinite dilution. We obtained good agreement with the residual chemical potential obtained by other authors for the same model³³ and with the experimental value of the hydration chemical potential.⁵⁶ Also the activity coefficient for NaCl in water has been computed. It appears that the model is able to describe only qualitatively the variation of the activity coefficient of the salt with its concentration. The work of Ferrario et al.¹⁹ and this one illustrates how it is possible indeed with current resources and methodologies to use computer simulations to determine the solubility of an ionic salt in water.

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