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# A potential model for sodium chloride solutions based on the TIP4P/2005 water model

A. L. Benavides,<sup>1</sup> M. A. Portillo,<sup>2</sup> V. C. Chamorro,<sup>2</sup> J. R. Espinosa,<sup>2</sup> J. L. F. Abascal,<sup>2</sup> and C. Vega<sup>2</sup>

<sup>1</sup>*Departamento de Ingeniería Física, División de Ciencias e Ingenierías, Universidad de Guanajuato, Loma del Bosque 103, Col. Lomas del Campestre, CP 37150 León, Mexico*

<sup>2</sup>*Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain*

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Despite considerable efforts over more than two decades, our knowledge of the interactions in electrolyte solutions is not yet satisfactory. Not even one of the most simple and important aqueous solutions, NaCl(aq), escapes this assertion. A requisite for the development of a force field for any water solution is the availability of a good model for water. Despite the fact that TIP4P/2005 seems to fulfill the requirement, little work has been devoted to build a force field based on TIP4P/2005. In this work, we try to fill this gap for NaCl(aq). After unsuccessful attempts to produce accurate predictions for a wide range of properties using unity ionic charges, we decided to follow recent suggestions indicating that the charges should be scaled in the ionic solution. In this way, we have been able to develop a satisfactory non-polarizable force field for NaCl(aq). We evaluate a number of thermodynamic properties of the solution (equation of state, maximum in density, enthalpies of solution, activity coefficients, radial distribution functions, solubility, surface tension, diffusion coefficients, and viscosity). Overall the results for the solution are very good. An important achievement of our model is that it also accounts for the dynamical properties of the solution, a test for which the force fields so far proposed failed. The same is true for the solubility and for the maximum in density where the model describes the experimental results almost quantitatively. The price to pay is that the model is not so good at describing NaCl in the solid phase, although the results for several properties (density and melting temperature) are still acceptable. We conclude that the scaling of the charges improves the overall description of NaCl aqueous solutions when the polarization is not included. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.5001190>]

## I. INTRODUCTION

Electrolyte solutions are the media in which many essential chemical and biological processes take place. Alkali halide—more precisely NaCl—solutions with some accompanying ions at lower concentrations are the basic component of environments like the physiological serum or seawater. The behavior of NaCl solutions is then a determinant in many of the physico-chemical properties of these liquids. Molecular simulation has proven to be useful in the investigation of the properties of many physical systems. Once the underlying force field is validated, it may be used to shed light under conditions where experiments are not easily accessible. Besides, numerical simulation provides information about microscopic properties that cannot be directly measured experimentally. This is particularly interesting in the case of electrolyte solutions because the experimental data are obtained for the system as a whole but they are often partitioned into terms of single-ion contributions, sometimes presented as “experimental” values. The advantage of computer simulation is that, in addition to the global properties of the solution, the individual ionic contributions could in principle be evaluated<sup>1</sup> (although it is not clear if this can be done unambiguously<sup>2</sup>). On the downside, the validity of results obtained via

numerical simulation is bound to the quality of the underlying force field.

The simulation of electrolyte solutions dates back several decades and, in recent years, it has received increasing interest. Former research was based on implicit solvent models.<sup>3–6</sup> The rise in computational power led to reliable water models and to the development of a number of force fields based on an explicit treatment of the solvent.<sup>7–16</sup> Improved force fields make a more realistic approach to the behavior of ionic solutions, hence the increasing number of papers recently devoted to this topic.<sup>17–35</sup> The development of a force field for these systems implies the optimization of the parameters of the water-water, ion-ion, and ion-water interactions. The first choice to be made is to select the water model. It is not clear whether the rest of the interactions can be optimized independently of the water model. It seems reasonable that the water model should somehow affect the rest of the interactions. However, it has also been shown that the use of a good water model does not deteriorate the quality of the results when used together with ion models developed either independently or for a specific water force field.<sup>30,36,37</sup> This is in fact an indication of the primary importance of the water-water interactions in aqueous solutions. The presence of charged ions would suggest the use of a polarizable water model. It is then surprising that, although the

prediction for some properties is improved, the overall performance of polarizable force fields seems to be quite similar to that of non-polarizable ones.<sup>8,38,39</sup> This could be due to the fact that, until very recently, polarizable water models were probably not fine-tuned. The situation may change in the coming years since the development of very accurate polarizable water models<sup>40–43</sup> is stimulating its use for the simulation of ionic solutions.<sup>33,39,44</sup> At the moment, non-polarizable force fields seem to be a cost-effective representation of the interactions in aqueous solutions.<sup>33</sup> Thus it seems interesting to explore the limits of non-polarizable force fields in describing the properties of this type of system before introducing a more elaborate description.

Leaving aside the simulation of biomolecular solutions (often making use of standard packages with force fields based on TIP3P, a rather poor<sup>45</sup> water model), SPC/E<sup>46</sup> is currently the more common choice for the water interactions in electrolyte solutions. Although SPC/E gives a fairly accurate description of the water properties,<sup>47</sup> it fails in some of its predictions.<sup>47</sup> In particular, the result for the temperature of maximum density at ambient pressure is too low, which disqualifies its use in the investigation of the effect of the ionic concentration on the density of the solution. Despite its great success,<sup>45,47</sup> no force field for electrolyte solutions has been built upon TIP4P/2005.<sup>48</sup> In a few cases, it has been used together with ionic interactions parametrized independently or tuned for a different water model.<sup>30,36,37</sup> The goal of this work is to develop a force field for aqueous sodium chloride solutions based on the TIP4P/2005 water model.

It seems clear that the ion-ion interactions in the solution may be similar to those in the ionic crystal. This could provide a more or less direct way to parametrize the ionic interactions. Many years ago, Tosi and Fumi adopted a generalized Huggins-Mayer form for the Born repulsive energy.<sup>49</sup> The Tosi-Fumi (TF) model in general predicts good densities and lattice energies of alkaline halides, but it is unable to reproduce the phonon dispersion curves. Besides, simplified functional forms, such as the 12-6 Lennard-Jones (LJ) potential, have the advantage that the same functional form may be used for all the molecular interactions in the solution.<sup>50</sup> However, until recently, the evaluation of some important solid properties (in particular, the calculation of the free energy) was perceived as too complex. Only the position of the peaks of the radial distribution functions (rdfs) was used in the parametrization of the ion-ion interactions in the solution. Recently, some properties of the solid alkali halide crystal have been evaluated using the ion-ion interactions optimized for the corresponding dissolved salt. For instance, Aragonés *et al.*<sup>51</sup> have calculated the melting temperature of NaCl using the parameters proposed by Smith and Dang<sup>8</sup> and by Joung and Cheatham.<sup>11</sup> These models overestimate the experimental melting temperature by about 20%. The difference is significant though the predictions could also be interpreted as satisfactory considering that the interaction parameters were tuned using only the aqueous solution properties.

For the ion-water interactions, early parametrizations were mainly based on the ion hydration free energies and the first peaks of the ion-water rdfs<sup>52</sup> (for a summary of the target properties used to parametrize electrolyte solutions, see Table I

of Ref. 11 and the review of Nezbeda *et al.*<sup>53</sup>). In recent years, additional properties like osmotic pressure, activity coefficients, and Kirkwood-Buff integrals<sup>54–61</sup> or dynamical properties have been used to parametrize and/or validate the force fields.<sup>13,22,33,62–67</sup> Systematic comparisons of the predictions for a variety of properties have shown the limitations of these models.<sup>17,24,68,69</sup> Transferability problems or the failure of the Lorentz-Berthelot rules for mixed interactions<sup>69–71</sup> could be expected to a certain extent. More indicative of the failure of the force fields are the disparate results for the salt solubility or the systematic deviations from the experiment for several dynamic properties such the viscosity or the diffusion coefficients.

Yethiraj<sup>24</sup> and co-workers have calculated the water self-diffusion coefficient for several non-polarizable and polarizable force fields. They concluded that none of the models tested were able to reproduce the experimentally observed trend for the concentration dependence of the diffusion coefficient. The simulation results are in all cases decreasing functions of concentration, while the experimental values may have a positive or a negative slope. They concluded that the “form” of the interaction potentials (not the specific values of the potential parameters) has to be re-examined. Similar conclusions were reached by Kann and Skinner.<sup>30</sup> However, these authors were able to present a rather novel alternative to the “form” of the interaction potential consisting in a simple scaling of the ionic charges. Basic chemical intuition seems to prescribe that the ion-ion interactions in the solution should be the same as those in the solid crystal and that the ionic charges are those of the isolated gas-phase ion. This has been recently challenged by Leontyev and Stuchebrukhov.<sup>72</sup> They argue that non-polarizable models do not fully account for the electronic contribution to the dielectric constant. They proposed that the screening effect of the electronic continuum could be effectively included by a simple scaling of the charges, namely,  $q_{\text{eff}} = q/\sqrt{\epsilon_{el}}$ , where  $\epsilon_{el}$  is the high frequency dielectric constant. The Leontyev-Stuchebrukhov approach is gaining increasing acceptance.<sup>16,30,32,35,73–76</sup> Kann and Skinner<sup>30</sup> were able to show that the charge scaling method together with a good-quality water model leads to results in agreement with the experiments for the self-diffusion coefficient of water in a number of electrolyte solutions. Similarly, Yao *et al.*<sup>76</sup> have shown that the inclusion of dynamical charge transfer account for the distinct behavior of the water diffusivity in NaCl(aq) and KCl(aq). In the same spirit, we have recently introduced the idea that the effective charges that provide a good description of the potential energy surface may not be the same as those describing the dipole moment surface.<sup>77,78</sup>

When a system is more concentrated than its solubility limit, the salt may crystallize. Since the nucleation of the solid is an activated process, it may take some time<sup>79</sup> and, thus, the formation of a crystalline phase is clearly detected only in a few cases.<sup>34,80,81</sup> What is often perceived is a strong aggregation denoted by a large number of ion pairs.<sup>50</sup> The problem is particularly important in biomolecular systems because the ion pairing differences (actually due to different solubilities) could be interpreted as ionic selectivity.<sup>82</sup> In fact, this seemed to be a wide concern of the biomolecular

simulations community<sup>83</sup> (yet not always manifested in published reports<sup>11</sup>) and resulted in an increasing acknowledgment of the importance of the ionic solubility of the potential model. The evaluation of the solubility in simulations is not trivial. The pioneering calculation of the solubility of a salt (KF) was performed by Ferrario *et al.*<sup>84</sup> in 2002. Five years passed until Sanz and Vega<sup>85</sup> reported the solubility of KF and NaCl and eight more years until a paper by Paluch *et al.*<sup>86</sup> on NaCl. From then on, the problem has attracted a wide interest<sup>36,37,39,53,70,87–93</sup> and the solubility is increasingly considered as a key property to be accurately described. Recent efforts by the groups of Smith and Nezbeda,<sup>36,53,87</sup> the group of Panagiotopoulos,<sup>90,91</sup> and our group<sup>37,70</sup> have contributed to establishing a consensus on the solubility of a number of force fields and concluding that most of the force fields provide rather poor results in the determination of the solubility. As it can be seen from the above discussion, it is not an easy task to find a good model for salt aqueous solutions able to reproduce most of the previously commented properties. This work represents an effort in this direction. The proposed force field for a NaCl aqueous solution is based on the TIP4P/2005 water model. We test the model for a variety of properties of the solution—equation of state (including the temperatures of maximum density), enthalpy of hydration, radial distribution functions, chemical potential, activity coefficients, solubility, surface tension, diffusion coefficients, and viscosity—and for others relevant to the solid NaCl behavior as well. In order to check the performance of the model, we will compare our results with experimental data and with the predictions of another force field also based on TIP4P/2005 that uses the Joung-Cheatham (JC) parameters for the ionic interactions (JC-TIP4P/2005).<sup>37</sup> This model was presented in our previous work (see Table II of Ref. 37) and it was denoted there as JC-SPC/E-ion/TIP4P/2005. Here we shall denote it simply as JC-TIP4P/2005. The comparison between the results of the model proposed in this work (which uses the concept of charge scaling) and the JC-TIP4P/2005 model (which does not use the concept of charge scaling for the ions) will allow us to establish conclusions on the possible benefits of using the scaling of the charges on the ions since in both cases, the model of water is the same, namely, TIP4P/2005.

The paper is organized as follows. The force field and the interaction parameters are described in Sec. II and the simulation details are given in Sec. III. Results are presented in Sec. IV and a general discussion (Sec. V) closes this work.

## II. A MODEL FOR NaCl AQUEOUS SOLUTIONS

The total potential can be split into three contributions, namely, water-water ( $U_w$ ), ion-ion ( $U_{ion-ion}$ ), and ion-water ( $U_{ion-w}$ ) interactions,

$$U = U_w + U_{ion-ion} + U_{ion-w}. \quad (1)$$

The three contributions are pairwise additive, i.e., the total potential is the sum of the interactions between all possible pairs of particles. As commented in the Introduction, an essential requirement for a force field of electrolyte solutions is to use an appropriate model for the water interactions. Among

non-polarizable water models, TIP4P/2005<sup>48</sup> seems to be an excellent candidate. It consists of a Lennard–Jones (LJ) site placed at the oxygen and three charges located, respectively, at the hydrogens and at a point M positioned along the H–O–H bisector. For the interactions between the ions, we have also chosen the LJ potential in addition to a screened Coulombic term,

$$U_{ion-ion}^{ij} = \frac{C_{12}^{ij}}{r_{ij}^{12}} - \frac{C_6^{ij}}{r_{ij}^6} + \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}}, \quad (2)$$

where  $i$  and  $j$  refer to any of the  $\text{Na}^+$  or  $\text{Cl}^-$  ions,  $r_{ij}$  is the distance between them,  $q_{i,j}$  are the ionic charges, and  $\epsilon_0$  is the vacuum permittivity. The same functions are used to describe the ion-water pair interactions

$$U_{ion-w}^{ij} = \frac{C_{12}^{iO}}{r_{iO}^{12}} - \frac{C_6^{iO}}{r_{iO}^6} + \sum_s \frac{q_i q_s e^2}{4\pi\epsilon_0 r_{is}}. \quad (3)$$

Here,  $i$  refers to an ion ( $\text{Na}^+$  or  $\text{Cl}^-$ ) and O to the oxygen atom of the water molecule  $j$ . The final term includes the sum of the Coulombic contributions between the  $i$  ion and the three charged sites,  $s = 1, 2, 3$ , of the  $j$  water molecule.

In the optimization of TIP4P/2005,<sup>48</sup> we followed a systematic procedure based on the prediction of the target properties using a multidimensional Taylor expansion that requires the knowledge of the values of the properties and their derivatives for the initial set of parameters. The application of the same scheme to ionic solutions is more problematic. The trouble is that we are interested in some target magnitudes (the solubility for instance) that are not easily evaluated in numerical simulations. Hence, the calculation of their derivatives is a prohibitive task. As a consequence, we have used a Taylor expansion for some properties and a trial and error scheme for others. The parameters were obtained as follows. The values of the scaled ionic charge were obtained to reproduce the experimental value of the limiting slope (at high dilution) of the activity coefficient with concentration. The dielectric constant of TIP4P/2005 is below the experimental value, and for this reason, the experimental limiting behavior was recovered when the charge of the ions was scaled to 0.85. We observed that this scaling improved the description of the diffusion coefficient of water in NaCl solutions. A similar reasoning was used by Kann and Skinner<sup>30</sup> who also suggested 0.85 as the ionic charge to be used for TIP4P/2005. To determine the other parameters of the potential, we used as target properties the densities of the NaCl solutions and that of NaCl in the solid phase and the variation of the temperature of maximum in density at room pressure (TMD) with salt concentration. The solubility was also a target property, but since its evaluation is very expensive, we used the difference in chemical potential between the solid and the standard chemical potential of the salt in solution as the target since we have recently shown that the solubility is strongly correlated with this property (see Ref. 94). We used as target properties neither the absolute value of the chemical potential of the solid nor the absolute value of the standard chemical potential of the salt in solution but rather the difference between both values. We should confess though that the entire procedure was rather involved with several back and forth steps (it took two years all together since our initial trials).

TABLE I. Parameters of the new model (the Madrid model) for NaCl solutions in TIP4P/2005 water. For convenience, we provide them in two different formats (using the coefficients  $C_{12}$  and  $C_6$  or using the parameters  $\epsilon_{LJ}$  and  $\sigma_{LJ}$  of the LJ interaction).

Lennard-Jones parameters					
	$C_{12}^{ij}/(\text{kJ/mol nm}^{12})$	$C_6^{ij}/(\text{kJ/mol nm}^6)$	$\sigma_{LJ}/(\text{nm})$	$\epsilon_{LJ}/(\text{kJ/mol})$	$(\epsilon/k_B)/(\text{K})$
Na <sup>+</sup> -Na <sup>+</sup>	$8.32 \cdot 10^{-8}$	$7 \cdot 10^{-4}$	0.221 737	1.472 36	177.086
Cl <sup>-</sup> -Cl <sup>-</sup>	$5.20 \cdot 10^{-5}$	$4 \cdot 10^{-3}$	0.484 906	0.076 923	9.2518
Na <sup>+</sup> -Cl <sup>-</sup>	$2.08 \cdot 10^{-6}$	$3.46 \cdot 10^{-3}$	0.290 512	1.438 89	173.062
O-O	$3.0601 \cdot 10^{-6}$	$3.0798 \cdot 10^{-3}$	0.315 890	0.774 907	93.2011
Na <sup>+</sup> -O	$2.0167 \cdot 10^{-7}$	$8 \cdot 10^{-4}$	0.251 338	0.793 388	95.4240
Cl <sup>-</sup> -O	$9.075 \cdot 10^{-6}$	$1.5 \cdot 10^{-3}$	0.426 867	0.061 983	7.4550
Charges/ <i>e</i>					
$q_{\text{Na}^+} = -q_{\text{Cl}^-}$			0.85		
$q_H = -q_M/2$			0.5564		
H <sub>2</sub> O geometry					
Distance $d_{\text{OH}}$			0.9572 Å		
Distance $d_{\text{OM}}$			0.1546 Å		
$\angle \text{HOH}$			104.52°		

The model parameters are shown in Table I. We have also included the corresponding traditional Lennard–Jones parameters  $\sigma_{LJ}$  and  $\epsilon_{LJ}$  values in two sets of units. This model will be denoted hereinafter as the Madrid model for NaCl in water (after all, it was developed in Madrid and, since the sea is far away, we can only propose approximate models for NaCl solutions).

### III. METHODS

Some properties, like the equation of state, radial distribution functions, or enthalpy, for example, can be more or less directly evaluated in molecular dynamics simulations<sup>95,96</sup> and will not be described here. This is not the case of the calculation of the solubility for electrolyte solutions which is not a simple task. Basically, there are two approaches to the problem. In the chemical potential route, the solubility limit is obtained by computing the chemical potential of the salt in the solid phase and in the solution: the solubility limit is the concentration at which both values are identical. The chemical potential of the salt in the solid phase can be evaluated with the Einstein crystal or the Einstein molecule methodologies.<sup>97–100</sup> Thus, the main trouble in the determination of the solubility is the calculation of the chemical potential of the salt in solution. This involves either thermodynamic integration from a reference system<sup>70,101</sup> or, as in the osmotic ensemble, the determination of the species concentrations in the solution as averages over a simulation run performed at the (assumed known) chemical potential of the solid.<sup>87</sup>

An alternative and relatively simple approach is the direct coexistence. In this method, a slab of salt is put in contact with water until equilibrium is reached at constant temperature and pressure.<sup>102</sup> Recently it has been shown that both techniques (when the slab of solid in the direct coexistence simulations is sufficiently thick<sup>39,93</sup>) predict the same values of the solubilities of salts in water. In this work, we shall use the two

techniques to determine the solubility. An advantage of the chemical potential method is that it also enables the determination of the activity of water and the activity coefficient of the salt.

We shall now describe the chemical potential route to the determination of the solubility. The key quantity in this route is the Gibbs free energy of the solution,  $G_{\text{solution}}$ . Since  $G_{\text{solution}}$  is an extensive property, it can be expressed in terms of the chemical potentials and number of molecules of water ( $N_w$ ) and salt ( $N_{\text{NaCl}}$ ) as

$$G_{\text{solution}} = N_w \mu_w + N_{\text{NaCl}} \mu_{\text{NaCl}}. \quad (4)$$

The procedure for the calculation of  $G_{\text{solution}}$  using numerical simulation is straightforward from a theoretical point of view, but its implementation is cumbersome. We give here an overview of the method and refer the reader to previous studies<sup>37,70</sup> for details.  $G_{\text{solution}}$  is related to the Helmholtz free energy,  $A_{\text{solution}}$ , through

$$G_{\text{solution}} = A_{\text{solution}} + p V_{\text{solution}}, \quad (5)$$

where  $p$  is the pressure and  $V_{\text{solution}}$  is the volume of the system. The second term is trivially obtained in the simulations and  $A_{\text{solution}}$  can be split into the ideal and the residual contributions,

$$A_{\text{solution}} = A_{\text{solution}}^{\text{id}} + A_{\text{solution}}^{\text{res}}. \quad (6)$$

The ideal term involves the densities of the different species of the system and other terms coming from internal degrees of freedom, among them the translational contribution that depends on the de Broglie wavelength. A burdensome task is the evaluation of the residual term which is carried out by means of a Hamiltonian integration based on a  $\lambda$ -expansion of the molecular interactions in terms of a reference potential. However, the trouble is compensated because the knowledge of  $G_{\text{solution}}$  facilitates the calculation of the chemical potential



of NaCl in solution,  $\mu_{\text{NaCl}}^{\text{solution}}$ . This paves the way for the determination of a large set of properties of the solution, the activity coefficients and the solubility limit among them.

The chemical potential of NaCl in solution is the derivative of the Gibbs free energy  $G_{\text{solution}}$  with respect to the number of NaCl molecules at constant pressure,  $p$ , and temperature,  $T$ , and the number of water molecules,  $N_w$ ,

$$\mu_{\text{NaCl}}^{\text{solution}} = \left( \frac{\partial G_{\text{solution}}}{\partial N_{\text{NaCl}}} \right)_{T,p,N_w}. \quad (7)$$

Besides,  $\mu_{\text{NaCl}}^{\text{solution}}$  can be written in terms of the molality (i.e., number of moles of NaCl per kilogram of water),  $m$ , and the salt activity coefficient,  $\gamma$ , which is a measure of the deviation of the chemical potential of the salt in the solution from that of the ideal solution at infinite dilution,<sup>103</sup>

$$\mu_{\text{NaCl}}^{\text{solution}} = \mu_{\text{NaCl}}^\dagger + 2RT \ln m + 2RT \ln \gamma, \quad (8)$$

where  $\mu_{\text{NaCl}}^\dagger$  is Henry's law standard chemical potential of the salt. The salt activity coefficient (also referred to as mean ionic activity coefficient) can be described by the following empirical expression, inspired by the Davies equation<sup>104</sup> for experimental data:

$$\ln \gamma = \ln(10) \left[ \frac{-A^* \sqrt{m}}{1 + B\sqrt{m}} + \beta m \right]. \quad (9)$$

The parameter  $A^*$  stems from the Debye-Hückel theory and depends on the charges of the ions  $\lambda_q$  (in electron units), on the relative permittivity of the water model,  $\epsilon$ , and on the temperature as  $A^* = \lambda_q^3 1.824 \times 10^6 / (\epsilon T)^{3/2}$ . Notice that the charges of the  $\text{Na}^+$  and  $\text{Cl}^-$  ions are not one (in electron units), but they are scaled by a factor  $\lambda_q = 0.85$  for the Madrid model (as will be discussed later on). The origin of the  $\lambda_q^3$  term arises from the Debye-Huckel expressions that include a  $|z_+z_-|$  term (which introduces a  $\lambda_q^2$  factor) and another one arising from the contribution of the ionic strength  $I^{1/2}$ . For models where the charges of the ions are one (in electron units),  $\lambda_q = 1$ . The parameters  $B$  and  $\beta$  are typically fitted to the experimental (or simulation) results. On the other hand, the water chemical potential can be expressed as

$$\mu_w = \mu_w^* + RT \ln a_w, \quad (10)$$

where  $\mu_w^*$  is the standard potential of pure water and  $a_w$  is the water activity. Using Eq. (9) and the Gibbs-Duhem relation, the water chemical potential may be expressed as<sup>28</sup>

$$\mu_w = \mu_w^* - 2RTmM_w - RTM_w \ln(10) \left[ \beta m^2 + \frac{2A^*}{B^3 + B^4 \sqrt{m}} + \frac{4A^* \ln(B\sqrt{m} + 1)}{B^3} - \frac{2A^* \sqrt{m}}{B^2} - \frac{2A^*}{B^3} \right], \quad (11)$$

where  $M_w$  is the molar mass of water (in kg/mol).  $\mu_w^*$  can be simply obtained from our simulations by dividing the Gibbs free energy of pure water (i.e., no ions) between the number of molecules of water.

In this work, the thermodynamic integration route to obtain the solution chemical potential was undertaken in two steps: (1) We bring the ionic aqueous solution to an intermediate state by reducing the ionic charges to half of their original values. The ion-water repulsive  $C_{12}$  Lennard-Jones coefficient

was reduced around half of its original value to compensate the ion-water interaction that has been affected by the reduction of the ionic charges. (2) We take the intermediate system described in (1) to a Lennard-Jones one. This way of performing the thermodynamic integration is better than the one used in our previous studies since it guarantees that the free energy changes are smooth along the integration route. Once  $G_{\text{solution}}$  is known, we fit it using the previous equations. Only five parameters are required: the NaCl standard chemical potential  $\mu_{\text{NaCl}}^\dagger$ , the parameters  $A^*$ ,  $B$ , and  $\beta$  of Eq. (9), and the standard chemical potential of water  $\mu_w^*$ . The coefficient  $A^*$  was obtained as mentioned above. The standard chemical potential of water was obtained directly by dividing the Gibbs free energy of pure water between the number of water molecules. The value of  $B$  was fixed to  $1.5 \text{ (kg/mol)}^{1/2}$  and was not optimized (in fact, for most of 1:1 electrolytes, the value of  $B$  when fitting to experimental results is not very different from  $1.5$ <sup>103</sup>). The absolute value of the free energy depends on the particular choice of the internal terms of the atomic/molecular partition function. However, phase equilibria do not depend on mass and the de Broglie wavelength can be arbitrarily fixed. Because of this, in the estimation of the solubility, we set the de Broglie wavelength to  $1 \text{ \AA}$  for simplicity (a detailed discussion can be found in Ref. 101). This will be denoted as reference system 1 or simply ref1. When using the same reference state as used in experiments, we shall denote the results as reference 2 or simply ref2. The conversion from ref1 to ref2 can be done by adding the following constants: for NaCl,  $C_{\text{NaCl}} = 386.8 \text{ kJ/mol}$  and for water,  $C_w = -202.256 \text{ kJ/mol}$ . The reason for this has been explained elsewhere.<sup>37,70</sup> For the model considered in this work, these parameters are given in Table II.

Once the chemical potential of NaCl in solution is known, the calculation of the solubility limit only requires the evaluation of the chemical potential of NaCl for the solid phase. This can be done with the Einstein crystal methodology.<sup>97,98,101</sup> The solubility limit (usually termed simply as solubility) is the concentration at which both chemical potentials are equal,

$$\mu_{\text{NaCl}}^{\text{solution}} = \mu_{\text{NaCl}}^{\text{solid}}. \quad (12)$$

Most of the simulations have been performed in the isothermal-isobaric  $NpT$  ensemble using the molecular dynamics package GROMACS 4.6<sup>105,106</sup> with a 2 fs time step and a sample size of 555 water molecules. For the calculation of free energies, we used a system made of 270 water molecules in the NVT ensemble as in previous studies.<sup>37,70,85</sup> The self-diffusion

TABLE II. Fit parameters for the solution chemical potential of the Madrid model. The chemical potential is expressed in kJ/mol. Results labeled as ref1 use  $1 \text{ \AA}$  for the thermal de Broglie wavelength. Results labeled as ref2 use the same reference state as used in experiments. The value of  $A^*$  is obtained by multiplying the ionic charges (in electron units) to the third power  $0.85^3 \times 0.803$ , which is the value of  $A^*$  for the TIP4P/2005 model of water when the ionic charges are unity (in electron units). Notice that the value of  $A^*$  from experiments is 0.509, which is close to the value reported here. The units of  $A^*$  and  $B$  are  $(\text{kg/mol})^{1/2}$  and the units of  $\beta$  are kg/mol.

$A^*$	$B$	$\beta$	$\mu_{\text{NaCl},\text{ref1}}^\dagger$	$\mu_{w,\text{ref1}}^*$	$\mu_{\text{NaCl},\text{ref2}}^\dagger$	$\mu_{w,\text{ref2}}^*$
0.493 142	1.5	0.057 605	-596.268	-38.694	-209.471	-240.95

coefficients and surface tension are quite sensitive to finite-size effects. Accordingly, we increased to 5000 the number of water molecules for the runs evaluating the self-diffusion coefficients. For the calculation of the surface tension,  $\sigma$ , we considered a slab of liquid consisting of 6600 molecules of water placed between two empty regions. Long-range electrostatic interactions have been evaluated with the smooth particle mesh Ewald method.<sup>107</sup> The geometry of the water molecules has been enforced using *ad hoc* constraints, in particular, the LINCS algorithm.<sup>108,109</sup> To keep the temperature and pressure constant, the Nosé-Hoover thermostat<sup>110,111</sup> and an isotropic Parrinello-Rahman barostat have been applied<sup>112</sup> with 2 ps relaxation times.

## IV. RESULTS

### A. Equation of state and temperatures of maximum density

The predictions of the model for the density along two isobars are compared to experimental measurements<sup>113–115</sup> in Fig. 1. The slope of the curves closely follows the experimental densities both at 0.1 MPa and 200 MPa. Figure 1 shows that the excellent performance of TIP4P/2005 for the equation of state of water is extensive to NaCl solutions. This idea is reinforced when one realizes that the JC-TIP4P/2005<sup>37</sup> model yields very similar values. In fact, the latter results have not been included in the plot because the outcome of both simulations is almost indistinguishable on the scale of the figure. It also seems interesting to check another force field for NaCl aqueous solutions (the E3B/MP-S model<sup>30</sup>) also based on scaled ionic charges. The reported density of the 1*m* solution at 298 K, 1 bar using the E3B/MP-S model is clearly lower than the experimental value. Although the E3B model underestimates the water density by a small amount (5 kg/m<sup>3</sup>), the deviation of the E3B/MP-S value at 1*m* from the experiment is higher indicating that the model tends to underestimate the density of the NaCl solution.

A more demanding test of the performance of a model is the dependence on salt concentration of the temperatures at which the density attains a maximum (TMD). Results for the location of the maximum in density of the NaCl solution (at 1 bar) are presented in Table III along with the experimental results from Ref. 117.

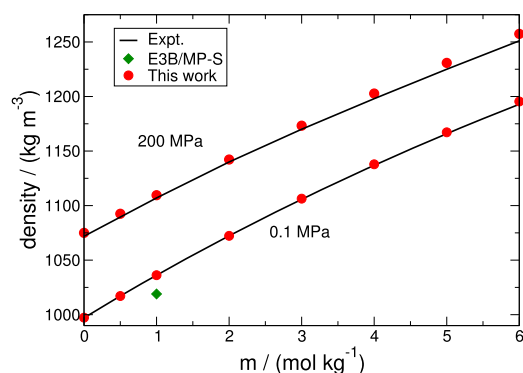


FIG. 1. Density as a function of molality at  $T = 298$  K for the 0.1 MPa and 200 MPa isobars. Experimental results were taken from Refs. 113–115. The diamond corresponds to the result for the E3B/MP-S model.<sup>30</sup>

TABLE III. Temperatures of maximum density (in K) at 0.1 MPa for different solutions of NaCl in water as obtained from simulations (using two different models) and from experiments.<sup>117</sup> The uncertainty in the TMD from computer simulations is about 1 K.

m/(mol/kg)	Expt.	Madrid	JC-TIP4P/2005
0	277.1	278	278
0.5	270.5	270	267
1.0	263.5	262	259
1.5	256.3	254	249

Since TIP4P/2005 essentially matches the experimental result for pure water at 0.1 MPa (at around 277 K), it is clear that the TMD curve for models using TIP4P/2005 for water should converge towards the experimental one at decreasing salt concentrations. It can be seen in Fig. 2 that this is fulfilled as expected. More significantly, the variation of the TMD with the molality of the solution is also in close agreement with the experimental data. Notice that this merit cannot be attributed to the quality of the water model because the departures from the pure water behavior stem from the ion-water interactions. Our results improve considerably upon those obtained with the JC-TIP4P/2005 model (see Fig. 2), suggesting that the outcome of the ion-water interactions is better described by our model. Thus the Madrid model is highly recommended for the study of the properties of supercooled NaCl solutions and it may be very useful in the future to understand the origin of the anomalous behavior of water and NaCl solutions when highly supercooled.<sup>118</sup>

### B. Enthalpies of solution

Consider the process of dissolving  $n$  moles of solid NaCl in 1 kg of water. Assume that the process takes place at constant temperature and pressure. In these conditions, the enthalpy change is

$$\Delta H = \Delta U + p\Delta V, \quad (13)$$

where  $U$  is the change of the potential energy. If the pressure is not too high (at ambient pressure, for instance), the term  $p\Delta V$  is negligible and the enthalpy change is simply  $\Delta H \approx \Delta U$ . Dividing  $\Delta H$  by  $n$ , we get the enthalpy of solution per mol of solute,

$$\Delta h_d \approx (U_{\text{NaCl}(aq)} - U_{\text{H}_2\text{O}}) / n - U_{\text{NaCl}_s}^*, \quad (14)$$

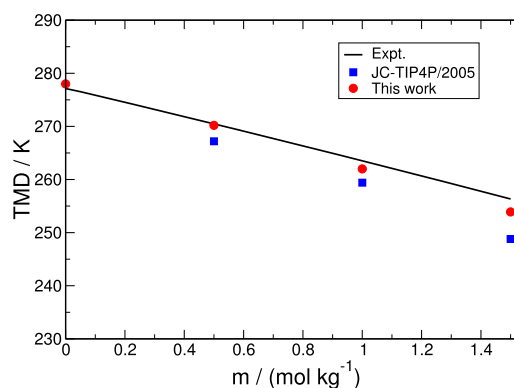


FIG. 2. Temperatures of maximum density at 0.1 MPa.

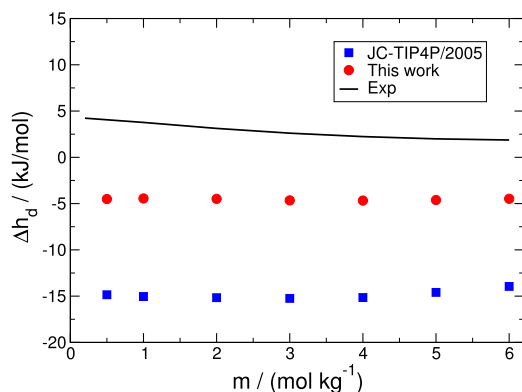


FIG. 3. Enthalpies of solution at ambient conditions. Experimental results were taken from Ref. 119.

where  $U_{\text{NaCl}(aq)}$  is the potential energy of the solution of NaCl in water,  $U_{\text{H}_2\text{O}}$  is the potential energy of pure water, and  $U_{\text{NaCl}_s}^*$  is the potential energy of NaCl per mol of solid NaCl.

The enthalpies of solution (per mol of solute) are shown in Fig. 3 along with the experimental results.<sup>119</sup> The model predicts that  $\Delta h_d$  is negative irrespective of the salt concentration which is opposite to the experimental behavior. Despite that, the model improves the results of the JC-TIP4P/2005 force field, reducing to about a half the departure with respect to the experimental data. Notice also that this magnitude is determined by the difference between two much larger values, the internal energy of the solution and that of its pure components. In practice, these amount to several hundreds of kJ/mol, whereas the final value for  $\Delta h_d$  is of the order of a few kJ/mol. It is finally worth noting that our attempts at improving the predictions for this property always resulted in a magnified deterioration of the solubility. In summary, the final parameters were dictated by a compromise between these conflicting tendencies. In any case, the model correctly predicts that the enthalpy of solution of NaCl in water is very small and the predictions, although not quantitatively correct, are much better than those obtained using other force fields.

### C. Ion-ion radial distribution functions

Figure 4 (top) shows the  $\text{Na}^+-\text{Cl}^-$  radial distribution function at 1m and 5m concentrations. The height of the first peak, corresponding to contact ion pairs (CIP), is lower than that of the second maximum, corresponding to solvent-separated ion pairs (SSIP). The positions of the CIP and of the following rdf minimum are similar to those of the Smith-Dang model<sup>62</sup> although the latter model exhibits a much larger peak, probably due to a stronger ionic association indicative of a reduced solubility. The positions of the first maxima and minima are quite independent of the molality. The effect of the concentration is significant at distances beyond the second maximum of the  $\text{Na}^+-\text{Cl}^-$  rdf. The  $\text{Cl}^- - \text{Cl}^-$  and  $\text{Na}^+ - \text{Na}^+$  radial distribution functions are displayed in Fig. 4 (middle and bottom panels, respectively). Again, the first extrema of the rdf's are located at approximately the same positions in both solutions and the structure is enhanced in the more concentrated solution. It is to be noticed that the extrema of the unlike-charged and the like-charged ion correlation functions are not coupled in the 5m solution. For instance, the first maximum of the  $\text{Cl}^- - \text{Cl}^-$

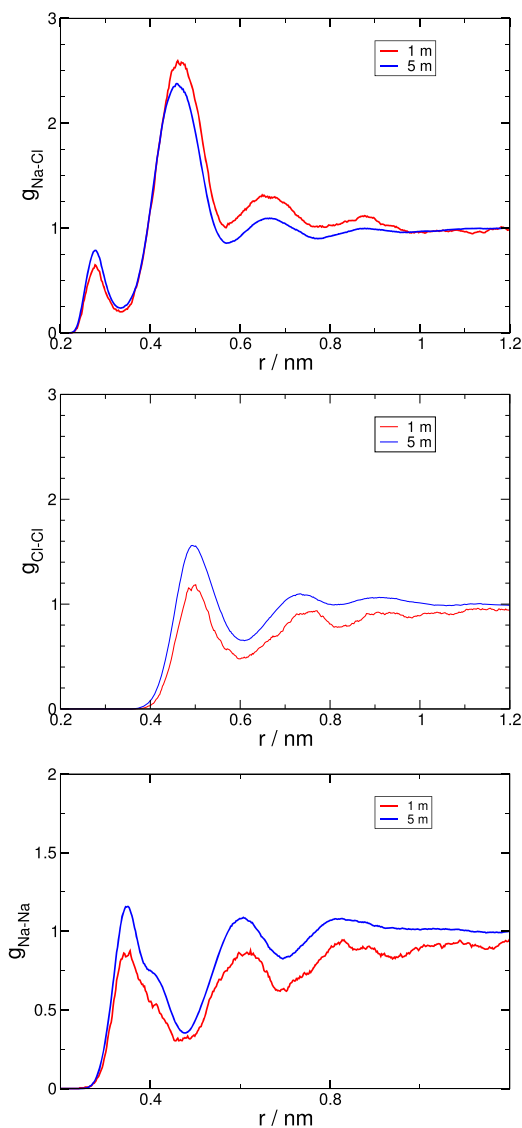


FIG. 4. Radial distribution functions at 1m and 5m concentrations. Top:  $\text{Na}^+-\text{Cl}^-$ ; middle:  $\text{Cl}^- - \text{Cl}^-$ ; bottom:  $\text{Na}^+ - \text{Na}^+$ .

pair correlation function is located at a distance between the SSIP and the following minimum of the  $\text{Na}^+-\text{Cl}^-$  curve. This ordering is significantly different from that of the crystal which exhibits layers of alternating charges.

We have also computed the oxygen-ion distribution functions. For a 1m solution, the maximum is located at 2.25 Å for the  $\text{Na}^+-\text{O}$  distribution function and at 3.10 Å for the  $\text{Cl}^- - \text{O}$  distribution functions, respectively. These results compare reasonably well with the experimental values<sup>30,52</sup> which are 2.36 Å and 3.19 Å, respectively, although they seem to be somewhat lower by about four per cent. From the water-ion distribution functions, it is possible to calculate the number of water molecules in the first coordination shell of each ion. These coordination numbers (CN) are shown in Fig. 5. Both the  $\text{Cl}^- - \text{H}$  and the  $\text{Na}^+ - \text{O}$  CN's are weakly dependent on concentration with  $\text{CN}(\text{Cl}^- - \text{H}) > \text{CN}(\text{Na}^+ - \text{O})$ . This is in accordance with the results from neutron diffraction experiments<sup>120</sup> though the slope of the  $\text{CN}(\text{Na}^+ - \text{O})$  curve is smaller than the experimental one. Besides, the extrapolated values at infinite dilution are in good agreement with the experiment.



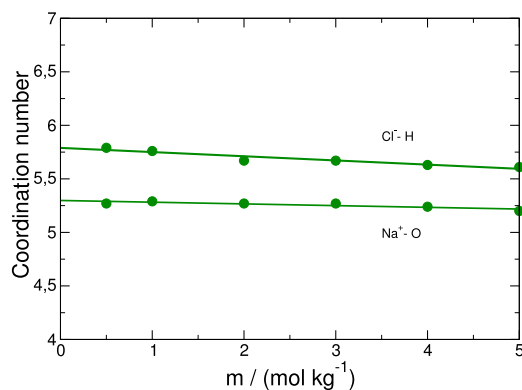


FIG. 5. Average coordination numbers of  $\text{Na}^+\text{--O}$  and  $\text{Cl}^-\text{--H}$  as a function of the concentration.

#### D. Water activity, osmotic pressure, and salt activity coefficients

The water activity (more precisely  $RT \ln a_w$ ) is shown in Fig. 6 (left panel). The performance of our model is clearly better than that of JC-TIP4P2005. In fact, our results are in nearly quantitative agreement with the experimental ones. Closely related to the water activity is the osmotic pressure<sup>121</sup>  $\Pi = RT \ln a_w / \bar{v}_{\text{H}_2\text{O}}$ , where  $\bar{v}_{\text{H}_2\text{O}}$  is the partial molar volume of water. Thus, to correctly predict the osmotic pressure, both the water activity and partial volume should be predicted accurately. We have evaluated  $\bar{v}_{\text{H}_2\text{O}}$  as a function of the concentration and found that its concentration dependence is small. Thus a pre-requisite to evaluate  $\bar{v}_{\text{H}_2\text{O}}$  accurately is that the water model provides a good description of the density of pure water (and also of the variation of density with concentration in the solution). Therefore one can anticipate that models which provide a correct description of the activity of water and of the density of the solution along all the range of concentrations should provide a good description of the osmotic pressure  $\Pi$ . In fact, this is the case, and in Fig. 6 (right panel) the osmotic pressure is presented as a function of the concentration of the salt. As can be seen, the agreement with the experiment is quite good. The scaling of the charges significantly improves the variation of the activity of water with the salt concentration and, in consequence, that of the osmotic pressure as well.

The salt activity coefficient is presented in Fig. 7. The curve of our model follows closely the experimental data<sup>103</sup> at the infinite dilution limit. This is because the scaling of the ionic charges approximately compensates the departure of the permittivity of TIP4P/2005 with respect to the experimental value for pure water. For TIP4P/2005 at 298.15 K,

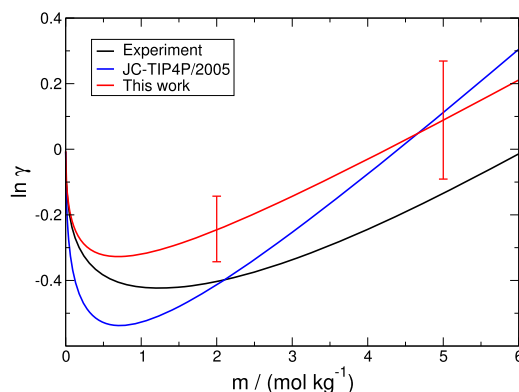


FIG. 7. Mean ionic activity coefficient as a function of molality. Vertical lines represent the uncertainty in the activity coefficient (due to the uncertainty in the standard chemical potential of the salt) at two different concentrations. Experimental results were taken from Ref. 103.

$A^* = 0.803 \text{ (kg/mol)}^{1/2}$  when the ionic charges are one (in electron units). Since the scaled charges in our model are  $\lambda_q = 0.85$ , the slope at infinite dilution is 0.493, close to the predictions of the Debye-Hückel limiting law,  $0.509 \text{ (kg/mol)}^{1/2}$ .

However, both curves begin to separate from each other at low concentrations. Interestingly, at intermediate concentrations, the slopes of the experimental and the simulation results are again quite similar. In this way, at high salt concentrations, the simulation and the experimental curves run parallel to each other. Overall, the predictions of our model are quite satisfactory along the whole range of salt concentrations. On the contrary, the JC-TIP4P/2005 model leads to much steeper curves: it predicts too negative  $\gamma$  values at low salt concentrations and too large (positive) results at high concentrations. Notice that our values of the activity coefficient have large error bars (mainly due to the uncertainty in the determination of the standard chemical potential of the salt, which is typically of 0.6 kJ/mol). Thus the estimated error in  $\ln(\gamma)$  is about 0.10 at 2m and about 0.18 at 5m. In any case, it seems that the activity coefficients of the Madrid Model, although close to the experiment, are slightly high.

#### E. Properties of solid NaCl

Since the model is intended for aqueous solutions, the properties of solid NaCl may not be fully optimized. In particular, the implementation of the scaling charges is in contradiction with the accepted ionic interactions in the crystal, so we must accept the lack of transferability of our force field to the solid state. Nevertheless, it seems interesting to investigate the extent of the anticipated failure of our model in this case.

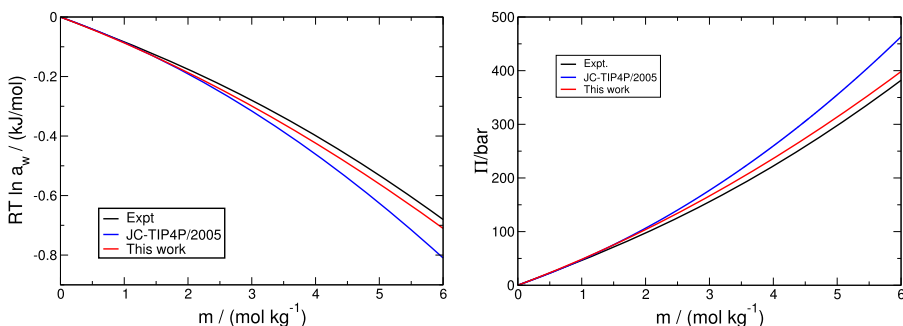


FIG. 6. Water activity (left panel) and osmotic pressure (right panel) as a function of molality.

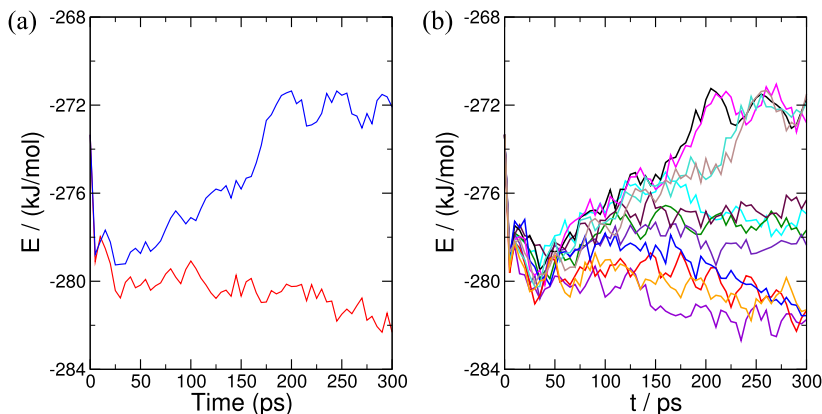


FIG. 8. Trajectories (at 0.1 MPa) showing the evolution of a system containing the liquid in contact with solid NaCl. (a)  $T=1024$  K and  $T=1022$  K (upper and lower curves, respectively); (b) twelve trajectories with different seeds at 1023 K.

The solid properties evaluated include the equation of state at ambient conditions, the melting temperature, and the lattice and free energies.

The calculated density at 298.15 K, 0.1 MPa is  $2171 \text{ kg/m}^3$  which is close to the experimental value,  $2165 \text{ kg/m}^3$ . We have also evaluated the lattice energy (by performing energy minimization). Our result for the lattice energy is  $-607 \text{ kJ/mol}$ , which is noticeably different from the experimental value,  $-789 \text{ kJ/mol}$ . The poor performance is an obvious effect of the charge scaling. Since  $(-789 \times 0.85^2) = -570 \text{ kJ/mol}$ , the model only corrects a minimal part of the energy loss due to the scaling. The melting point (at 0.1 MPa) has been obtained using the liquid–solid direct coexistence method<sup>122–125</sup> for a system of 2000 particles (1000 ions of each type). Figure 8(a) suggests that the melting temperature is 1023 K. Since the melting is a stochastic process for small systems, we have performed 12 additional simulations with different seeds at 1023 K [Fig. 8(b)]. We observe that some systems melted after 300 ps, while other seeds produce the crystallization of the starting configuration. In four of the simulations, the energy remained constant along the run, indicating that the solid–liquid interface did not change substantially. Thus, the melting temperature of our system is 1023 K, which may be compared to the experimental value, 1074 K. The agreement is quite satisfactory. This may be viewed as a surprising result considering the rather poor performance for the lattice energy of the solid. However notice that the scaling of the charges also affects the liquid properties, so its impact on the melting point is not so dramatic.

For the calculation of the free energy of solid NaCl, we start from the value reported by Aragonés *et al.*<sup>70</sup> for the JC model, namely,  $-384.1 \text{ kJ/mol}$  (ref2) at 298 K. Then we evaluate the free energy difference between our model and the JC model by means of Hamiltonian integration using GROMACS with 21  $\lambda$  values. This difference amounts to  $184.1 \text{ kJ/mol}$  so that  $\mu_{\text{NaCl}}^{\text{solid}} = -200.01 \text{ kJ/mol}$  (ref2) for our model. This result is sensibly different from the experimental one,  $-384.0 \text{ kJ/mol}$  (ref2). We may then say that the scaling of the charges produces a noticeable degradation of the energetic properties of the solid although the departures for other properties are much less important. Notice however that the low value of  $\mu^{\text{solid}}$  is the outcome of scaled ionic charges and that the ion–water interactions in the solution will also be affected by the scaling. Thus it is still possible to have reasonable values of the solubility even though the absolute values of the chemical potentials deviate

from the experiment. In fact we have recently shown<sup>94</sup> that it is the difference between the solid and standard state chemical potentials that matters when describing the solubility.

## F. Solubility

For the solubility calculations, we needed the densities at different concentrations. We have obtained them from NpT runs for all the concentrations considered ( $N_{\text{NaCl}}$  between 0 and 25). These densities are well represented by the following third-order polynomial:

$$\rho = r_0 + r_1 N_{\text{NaCl}} + r_2 N_{\text{NaCl}}^2 + r_3 N_{\text{NaCl}}^3. \quad (15)$$

The coefficients  $r_i$  are presented in Table IV. The free energy averages for this model obtained from thermodynamic integration of 4 independent runs are presented in Table V.

In Fig. 9 the chemical potential of NaCl in the solution is represented as a function of the concentration. The curve

TABLE IV. Coefficients for the polynomial fit to the number density  $\rho = N/V$  (given in particles per  $\text{\AA}^3$ ) as a function of the number of NaCl molecules used in the solubility calculations for the new model considered in this work.

$r_0 \cdot 10$	$r_1 \cdot 10^3$	$r_2 \cdot 10^5$	$r_3 \cdot 10^7$
0.333 451 752	0.122 924 096	-0.146 496 832	0.116 753 103

TABLE V. Densities, free-energies, and chemical potentials for the Madrid model at 298 K and 0.1 MPa at the concentrations considered for the solubility calculations. All the solutions have 270 water molecules.  $N_{\text{NaCl}}$  stands for the number of molecules of NaCl in the system.  $G_{\text{solution}}$  is given in kJ per mol of simulation boxes. The number density  $\rho = N/V$  is given in particles per  $\text{\AA}^3$  where  $N = N_w + 2N_{\text{NaCl}}$ .

$N_{\text{NaCl}}$	$\rho$	$G_{\text{solution}}$	$m$ (mol $\text{kg}^{-1}$ )	$\mu_{\text{NaCl,ref2}}^{\text{solution}}$ (kJ $\text{mol}^{-1}$ )
0	0.033 345 2	-10 447.38	0.000	$-\infty$
1	0.033 466 6	-11 058.05	0.206	-218.68
2	0.033 585 3	-11 662.10	0.411	-215.43
5	0.033 924 6	-13 461.07	1.028	-210.91
12	0.034 629 5	-17 624.03	2.466	-206.00
15	0.034 898 8	-19 400.99	3.083	-204.57
17	0.035 068 9	-20 583.25	3.494	-203.73
20	0.035 311 1	-22 352.14	4.111	-202.57
22	0.035 464 8	-23 531.27	4.521	-201.86
25	0.035 685 1	-25 295.39	5.138	-200.87

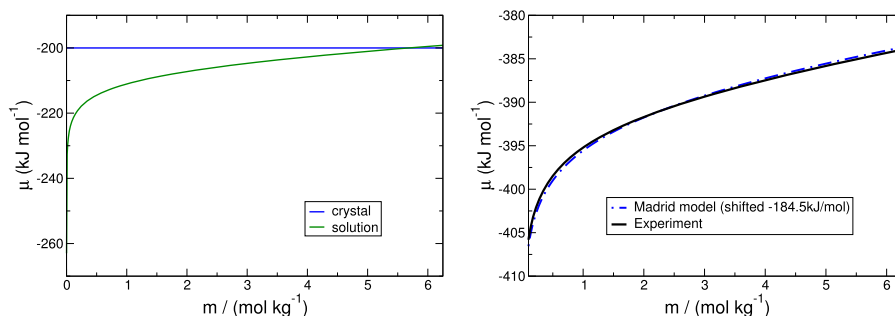


FIG. 9. Left panel: Chemical potential of the Madrid model of NaCl in the solid phase and in the solution (using reference 2). For the solid NaCl chemical potential, we have obtained a value of  $\mu_{\text{NaCl}} = -200.01$  kJ/mol (ref2). Right panel: Chemical potential of NaCl in solution as obtained from experiments (solid line) and from the Madrid model (dashed-dotted line) after applying a shift of  $-184.5$  kJ/mol to the values of the model shown in the left panel. Notice that although the Madrid model fails to describe the experimental values of the chemical potential (and this is the reason of the shift), it is still able to describe the changes in the chemical potential of the salt with its concentration.

crosses the line of the chemical potential of solid NaCl (using the same reference system) at a molality  $m = 5.7(3)$  mol/kg close to the experimental value of the solubility limit of NaCl ( $m = 6.14$  mol/kg). In the right panel of Fig. 9, the chemical potential of NaCl in solution for the Madrid model is compared to the experimental results. As it can be seen, the model is able to describe the variation of the chemical potential with the concentration of the salt. However, it was necessary to apply a shift to the chemical potential of the Madrid model as the use of scaled charges prevents obtaining correct absolute values of the chemical potential of the salt in water.

We have recently proposed<sup>94</sup> that the solubility correlates with the difference  $\mu^{\text{solid}} - \mu^\ddagger$ . Figure 10 shows this correlation for the calculated solubilities of different models for NaCl solutions. It can be seen that a smooth line connects these data irrespective of the quality of the predictions. In this plot, we have also presented the same correlation for the experimental solubilities of a few 1:1 salts with the halite structure. The latter curve has the same shape of the former one albeit a bit shifted towards high solubilities. This seems to indicate that the correlation is a general trend of these solutions and that the NaCl force fields show a small but systematic deviation from

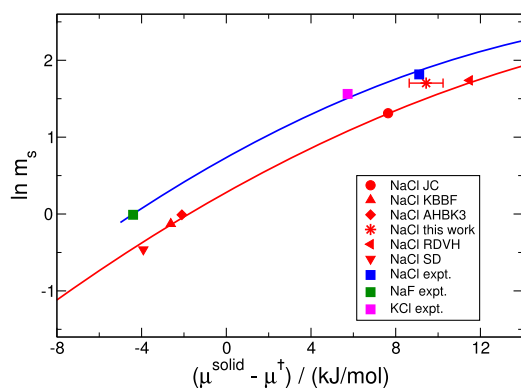


FIG. 10. Logarithm of the solubility,  $m_s$ , in molality units as a function of  $\mu^{\text{solid}} - \mu^\ddagger$ . Red symbols represent the calculations for different NaCl force fields labeled as follows: JC: Joung and Cheatham;<sup>11</sup> KBBF: Weerasinghe and Smith;<sup>62</sup> RDVH: Reiser *et al.*;<sup>31</sup> SD: Smith and Dang;<sup>8</sup> AHBK3: Kiss and Baranyai.<sup>40,44</sup> All of these models, with the exception of AHBK3 (a polarizable model), use SPC/E water as a solvent. The squares represent the experimental data for NaCl (blue), KCl (magenta), and NaF (green). The red star shows the result of the Madrid model (the horizontal line represents our uncertainty in  $\mu^{\text{solid}} - \mu^\ddagger$  which is of about 0.8 kJ/mol).

the experimental trend. The results for the Madrid model are between the experimental curve and that obtained for models that do not use the concept of charge scaling. Since our estimated error for the difference in chemical potentials of the solid and the standard state is of about 0.8 kJ/mol (0.2 arising from the uncertainty in the solid chemical potential and 0.6 kJ/mol arising from the uncertainty in the standard state chemical potential), it is difficult to conclude whether the results of the Madrid model are closer to the experimental or to that obtained for models without charge scaling. In any case, they seem to be located between both sets of results. Results from Fig. 10 also confirm that even for models with charge scaling, the solubility is mostly determined by  $\mu^{\text{solid}} - \mu^\ddagger$ .

We have also determined the solubility from the direct coexistence simulations using the setup denoted as E in Ref. 93. Results are shown in Fig. 11. In one simulation, the initial value of the concentration was of  $6.5m$ , and in the other, it was of  $4.8m$ . Both solutions evolve with time and the direct coexistence technique suggests a value of the solubility of about  $5.7(2)m$ , which is consistent with the value obtained from the chemical potential route  $5.7(3)m$ . Thus, the model provides a reasonable value of the solubility of NaCl in water. The number of ionic pairs per ion of the model at this concentration (i.e.,  $5.7m$ ) is 0.16 (see Ref. 37 for details about how to evaluate the number of ionic pairs). For the JC-TIP4P/2005 model,

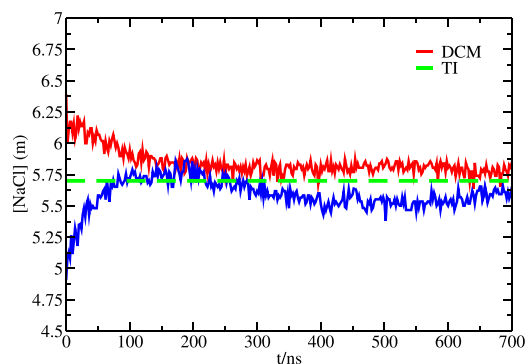


FIG. 11. Solubility of the Madrid model of NaCl in water as obtained in this work from direct coexistence simulations. The setup denoted as E in Ref. 93 was used. The solubility limit obtained from this method is  $5.7(2)m$ . The horizontal line is the solubility evaluated in this work using free energy calculations,  $5.7(3)m$ . The experimental value is  $6.14m$ .<sup>103</sup>

the number of ionic pairs at the solubility limit ( $3.49m$ ) was 0.08.

The solubility of the Madrid model is close to the experimental result. This is in contrast with most of the force fields that predict a quite low solubility. For instance, the Smith-Dang model has a solubility of about  $0.65m$ , and the Joung-Cheatham model (in SPC/E water) has a solubility of  $3.7m$ . The solubility of the JC-TIP4P/2005 model based on the same water model as that of this work but does not use the concept of charge scaling has a solubility of  $3.49m$ . Thus again the concept of charge scaling improves the description of the solubility.

### G. Surface tension

It is well known that most salts produce a small increase of the surface tension of water,  $\sigma$  (except maybe at concentrations below  $0.001m$  where some authors have reported a decrease of  $\sigma$ , which is known as the Jones-Ray effect<sup>126–128</sup>). There are a few reports of the surface tension of electrolyte solutions calculated using computer simulations.<sup>129–134</sup> This is probably because this property represents a demanding test for a force field and it is rarely included in the target properties investigated to check its performance.<sup>133</sup> It is believed that the polarizability may play an important role in the surface tension of saline water. In particular, it has been shown that the structure of the interface can be altered drastically by the particular choice of the dissolved salt.<sup>129</sup> However, most polarizable models are unable to reproduce the salt concentration dependence of the surface tension of NaCl aqueous solutions<sup>132,134</sup> [nevertheless, good results have been reported by Chen and Smith<sup>135</sup> for the Kirkwood-Buff Force Field (KBFF)].

For the calculation of  $\sigma$ , we considered a slab of liquid consisting of 6600 molecules of water placed between two empty regions. For a planar interface perpendicular to the  $z$  axis,  $\sigma$  is given by<sup>136</sup>

$$\sigma = \frac{L_z}{2}(\bar{p}_N - \bar{p}_T), \quad (16)$$

where  $\bar{p}_N$  and  $\bar{p}_T$  are the macroscopic normal and tangential components of the pressure tensor defined in terms of the volume average of their local component counterparts. The truncation of the potential is known to significantly affect the interfacial properties.<sup>137</sup> Long-range corrections to deal with this problem have been proposed (see the recent review by

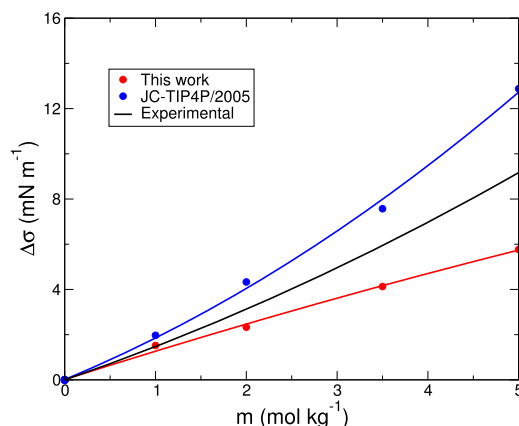


FIG. 12. Surface tension of NaCl aqueous solutions relative to that of pure water evaluated with identical simulation conditions.

Ghoufi *et al.*<sup>134</sup>), but their implementation is not simple, especially in the case of electrolyte solutions. It is to be expected that the corrections are not too dependent on the concentration. This suggests that a proper magnitude to compare with experimental data is the increase of  $\sigma$  with respect to that of pure water. Another advantage of this procedure is that it allows one to examine the performance of the force field irrespective of the quality of the predictions of the solvent model (notice however that this would not be necessary for TIP4P/2005 which gives an excellent prediction for surface tension of pure water<sup>138</sup>). Figure 12 shows the surface tension of NaCl aqueous solutions relative to that of pure water. For concentrations below  $2m$ , the estimates of the Madrid model are close to the experimental values. However, at higher concentrations, the model underestimates the increase in  $\sigma$  seen in experiments. In contrast, the JC-TIP4P/2005 force field overestimates the increase of  $\sigma$ , most notably at high salt concentrations. Curiously, the magnitudes of the departures of JC-TIP4P/2005 and our model with respect to the experimental data are quite similar but have opposite signs.

### H. Dynamic properties

The self-diffusion coefficient of water,  $D_w$ , in sodium chloride solutions of different concentrations has been evaluated in systems containing 5000 water molecules using the Einstein relation. The dependence of  $D_w$  with the salt concentration is displayed in Fig. 13 for our model and for

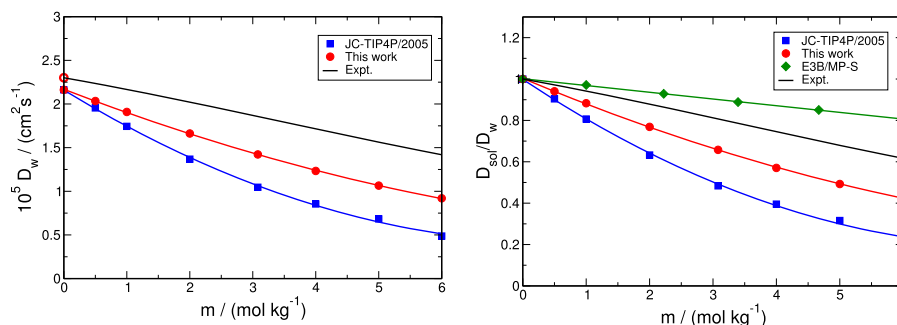
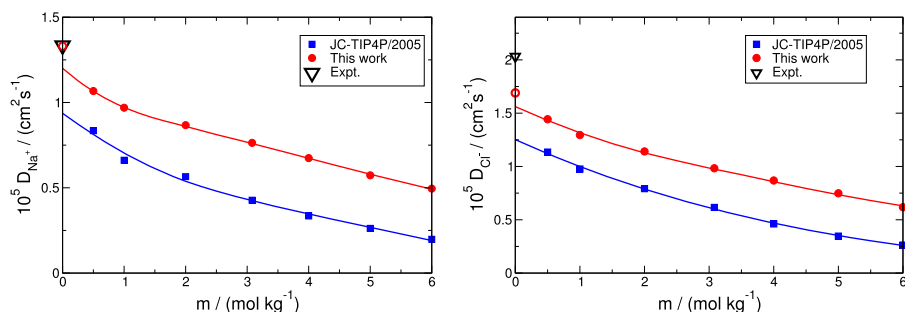


FIG. 13. Self-diffusion coefficient of water as a function of molality (left panel) as obtained from computer simulations using 5000 molecules of water. The open red circle represents the value of pure water (TIP4P/2005) after including the finite-size correction proposed by Yeh and Hummer.<sup>140</sup> Right panel: self-diffusion of water scaled by its value in pure water. Data for the E3B/MP-S model are taken from Ref. 30 and experimental results are taken from Ref. 139.





the JC-TIP4P/2005 model and compared to the experimental results.<sup>139</sup> In Fig. 13 we have also included the results for pure water (see the open circle in the left panel) after including the finite-size correction proposed by Yeh and Hummer.<sup>140</sup> Since the predictions of TIP4P/2005 are quite accurate for the pure solvent, the variation of  $D_w$  with salinity is a good test of the influence of the ions in the dynamics of the system. Both force fields qualitatively predict the slowing down of the water molecules at increasing salt concentrations. However, the dependence on the molality is too large for JC-TIP4P/2005. Our model reduces the departures from the experiment to about one half and is closer to provide semiquantitative predictions. We have also included the predictions of the E3B/MP-S model. Its performance is marginally better than that of our model, but it underestimates the decrease of the diffusion coefficient with salt concentration.

The self-diffusion coefficients of the ions  $\text{Na}^+$  and  $\text{Cl}^-$  are presented in Fig. 14. The ionic diffusivities seem to decrease more abruptly at low salt concentrations, while the dependence at high salt concentrations seems to be linear. At infinite dilution, the predictions of both models are below the experimental value taken from Ref. 141. However, in line with the results for the diffusion of water molecules, our model substantially improves on the departures observed in the JC-TIP4P/2005 calculations. The improvement is particularly important for the diffusion of the  $\text{Na}^+$  ions. In fact, at infinite dilution, our model predicts a value for  $D_{\text{Na}^+}$  very close to the experimental one (and in agreement with the experimental value when including the Yeh and Hummer correction<sup>140</sup>). For  $\text{Cl}^-$  the predictions are reasonable but certainly below the experimental values. In any case, our results for the diffusion coefficient of the ions at infinite dilution are comparable to those

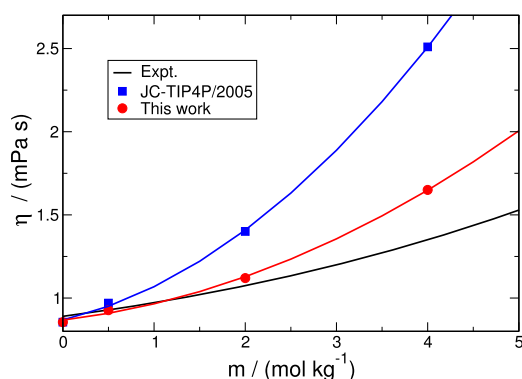


FIG. 15. Shear viscosity as a function of molality. Experimental results were taken from Ref. 143.

obtained by the best models (see, for instance, Table IX of Ref. 30).

The Green-Kubo formula relates shear viscosity to the autocorrelation function of the off-diagonal components of the pressure tensor  $P_{\alpha\beta}$ ,

$$\eta = \frac{V}{kT} \int_0^\infty \langle P_{\alpha\beta}(t_0) P_{\alpha\beta}(t_0 + t) \rangle_{t_0} dt. \quad (17)$$

For details of the calculations, see Ref. 142. The variation of  $\eta$  with the salt concentration is shown in Fig. 15 along with the experimental results.<sup>143</sup> Since TIP4P/2005 essentially matches the experimental value of the shear viscosity of liquid water, both models give excellent predictions at low salt concentrations. Although JC-TIP4P/2005 gives the correct sign of the change with concentration, the curve is steeper and quickly deviates from the experimental one. Our model gives quantitative predictions up to  $2m$  but, at higher concentrations, the performance deteriorates.

## V. CONCLUDING REMARKS

In this work, we have reported the predictions of a new model for NaCl aqueous solutions. Since our model is based on the accurate TIP4P/2005 water model, its performance at low salt concentrations is excellent. It should be more demanding, in principle, to describe the variation of the properties when the salt concentration is changed. The slope of the Debye-Hückel limiting law depends on the dielectric constant of the solvent, which is just one of the few liquid properties for which TIP4P/2005 gives only a fair prediction. However, the scaling of the ionic charges compensates for this flaw and our model also yields an excellent result for the slope.

As the concentration increases, the performance of the model is quite reasonable. The results for most of the properties investigated are in almost quantitative agreement with the experimental data up to a relatively high concentration (say, about  $2m$ ). The enthalpy of solution is probably the more important exception to this rule. We have already mentioned that its value comes from the difference of two internal energies, each amounting two orders of magnitude larger than the final outcome. The increase in the mean ionic activity with concentration at high molalities is in good agreement with the experimental trend. This is in contrast with the results of most of the force fields where the activity coefficient increases too quickly with the concentration of the salt. It seems that the concept of charge scaling significantly improves the prediction of the activity coefficient at high concentrations. For intermediate concentrations, we observe deviations of the activity

FIG. 14. Self-diffusion coefficients of  $\text{Na}^+$  and  $\text{Cl}^-$  as a function of molality as obtained from computer simulations using 5000 molecules of water. The open red circle represents the value of the Madrid model at infinite dilution after including the finite-size correction proposed by Yeh and Hummer.<sup>140</sup> The experimental values at infinite dilution<sup>141</sup> are indicated by an inverted triangle.

coefficient with respect to the experimental value. This deviation should be taken with care, though, as it may be affected by the large uncertainty (i.e., 0.6 kJ/mol) in the determination of the standard state chemical potential of the salt. In any case, it seems that the activity coefficient of the Madrid model, although close to the experimental results at medium and high concentrations, is somewhat higher.

The solid properties are certainly largely influenced by the charge scaling. Since the model is not intended for the solid state, its performance may be termed as acceptable. A major problem would be that the deficiencies of the solid could significantly affect the resulting solubility limit. However, this is not the case and the predicted solubility of the model essentially matches the experimental value. Despite the good predictions commented in previous paragraphs, the strongest point of the new model is its ability to provide satisfactory results for other properties for which all previous models failed dramatically.<sup>24,131,133</sup> None of the models previously developed were able to account for the self-diffusion coefficients or the viscosity of the NaCl(aq) system. In fact, our attempts to improve these properties also resulted in a clear failure until we introduced the scaling of the charges.

The scaling of the charges may seem to be in contradiction with many properties of ionic salts like NaCl. Certainly, this appears to be true for the properties of the crystal. But nothing indicates that the same might also hold for their aqueous solutions. Pure water shows strong evidence of a significant charge transfer, and quantum calculations of water clusters indicate that the hydrogen bond is strongly cooperative. The same seems to be true for ions in water.<sup>76</sup> Unfortunately, atomic charges cannot be unambiguously assigned in *ab initio* calculations (it is not a measurable parameter in quantum mechanics), so we must accept them as an effective parameter. Effective models aiming at describing liquid water always use atomic charges larger than those required to reproduce the well-known value of the dipole moment of the molecules in the gas phase. In other words, the charges for the liquid need to be “scaled” (in non-polarizable force fields) with respect to the accepted values reproducing well-known magnitudes of the gas phase. Similarly, the addition of ions to liquid water disrupts the water structure and the resulting effective interaction might be represented by a scaling of the ionic charges. In summary, even if the work of Leontyev and Stuchebrukhov<sup>72</sup> provides some theoretical foundation to the ionic charge scaling, we prefer to view it as a necessity in order to provide a satisfactory description of the *effective* ionic interactions in aqueous solutions. It is likely that the model used in this work (keeping the ion-ion and ion-water interactions<sup>144</sup>) could be used in combination with the E3B model of water proposed by Skinner and co-workers as this model which includes three-body forces uses TIP4P/2005 as a reference for the two-body interaction.<sup>116</sup> In the future, we want to extend the application of the methodology based on charge scaling presented in this work for NaCl to other electrolytes in TIP4P/2005 water.

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