Molecular Force Field Development for Aqueous Electrolytes: 2. Polarizable Models Incorporating Crystalline Chemical Potential, and their Accurate Simulations of Halite, Hydrohalite, Aqueous Solutions of NaCl, and Solubility

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Abstract

The current state-of-the-art force fields (FFs) for Na\(^+\) a Cl\(^-\) ions are not capable of simultaneously predicting the thermodynamic properties of the aqueous solution and the crystalline phase. This is primarily due to an oversimplification of the interaction models used but partially also due to the insufficient parametrization of the FFs. We have devised a straightforward and simple parametrization procedure for determining the ion-ion interaction parameters in complex molecular models of NaCl electrolytes which involves fitting the density, lattice energy and chemical potential of crystalline NaCl at ambient conditions. Starting from the AH/BK3 and MAH/BK3 FFs, the parametrization approach is employed to develop a complex and accurate polarizable molecular model for the NaCl electrolyte by parametrizing the ion-ion interactions. The performance of the refined polarizable NaCl FF is assessed by evaluating the different thermodynamic and mechanical properties of the crystal, density of crystalline and molten NaCl along with the melting temperature, properties of aqueous solutions, and the structure and stability of hydrohalite. The simulation results confirm the superiority of the refined FF in comparison with the existing state-of-the-art FFs to accurately predict a wide range of system properties in different NaCl phases, including NaCl aqueous solubility. The refined FF may find applications in the accurate simulations of NaCl electrolytes including inhomogeneous environment, phase equilibria and interfaces, and metastable states. Finally, the parametrization strategy is robust and general, and can be used to devise molecular models for other electrolytes.
1 INTRODUCTION

Sodium chloride and other alkali-halide electrolytes are important in many common, industrial, and biological processes, from simple cooking to advanced power storage or nuclear power technologies. Understanding such processes involves understanding interactions between the Na\textsuperscript{+} and Cl\textsuperscript{−} ions and also between the ions and the molecules of water. These interactions cannot be probed directly by experiments due to their microscopic nature. Computer modeling is thus used to develop molecular interaction models, force fields (FFs), that can be used to simulate the microscopic behavior of both liquid and solid phases, and to predict their thermodynamic, structural and dynamical properties. The accuracy of such computer simulations inevitably depends on the accuracy of the FFs employed, and it reflects our understanding of electrolytes, their solutions, and their hydrates at the microscopic level.

There is a plethora of FFs for Na\textsuperscript{+} and Cl\textsuperscript{−} ions in literature, e.g., see our reviews,\textsuperscript{1,2} and new models continue to be developed.\textsuperscript{3-8} It is thus surprising that there is no FF yielding accurate predictions of thermodynamic properties of both the NaCl aqueous solutions and NaCl crystal (halite). It is common that an electrolyte FF completely fails in predicting some of the key properties. For example, the complex polarizable AH/BK3 FF predicts six times lower aqueous solubility\textsuperscript{9} as compared to experiment, the recent Madrid FF misses the NaCl crystal lattice energy and also the chemical potential both in the solution and solid phases by \(\sim 182 \text{ kJ mol}^{-1}\),\textsuperscript{5} the NaCl/\(\varepsilon\) FF\textsuperscript{3} predicts incorrect concentration dependence of activity coefficient and very low solubility,\textsuperscript{10} and 12 of 13 electrolyte FFs assessed in our previous study\textsuperscript{11} fail to predict of the density of NaCl crystal. One can attribute these problems to oversimplified or incorrect functional forms of interactions employed in the molecular models, e.g., using the Lennard-Jones potential or simple combining rules for short-ranged repulsive forces, neglecting polarizability, considering point distributions of charges, using inaccurate water FFs, and employing charge scaling without applying the electronic continuum corrections. In addition, these problems can also be related to insufficient parametrization of the
FFs, often targeting a limited set of properties and excluding properties that are important for the correct overall behavior of the molecular models; e.g., targeting only properties of infinitely diluted solutions, neglecting energetic and dynamical properties, and phase behavior, and targeting non-reliable experimental data.

In our previous study,\textsuperscript{12} we attempted to develop a new set of parameters for a simple nonpolarizable model based on Lennard-Jones and point charge interactions accompanied by Lorentz-Berthelot rules for NaCl aqueous solutions at ambient conditions. We showed that the model was not able to simultaneously fit the dependence of the chemical potential and density on NaCl concentration over the entire experimentally accessible concentration range, and we thus concluded that more complex models are needed when the concentration dependence of several properties are of interest. The inadequacy of simple nonpolarizable models for electrolyte solutions is also supported by other studies.\textsuperscript{11} For example, it is well known that all nonpolarizable FFs yield too slow dynamics in concentrated solutions unless their charges are scaled down. However, the decrease of charges results in an enormous increase of potential energy.\textsuperscript{5} Furthermore, the simulation studies of electrolytes typically deal with spatially heterogeneous systems, e.g., electrolytes in confined systems such as mineral pores,\textsuperscript{13–15} at solid surfaces with the surface polarizability such as graphene,\textsuperscript{16} where molecular polarizability plays very important roles compared to bulk liquids. Hence, polarizable models should be favored in principle.

The AH/BK3 FF\textsuperscript{17} turned out to be a promising candidate for an advanced model of aqueous electrolyte solutions because it employs complex interaction potentials while also being tractable for a wide range of applications. It considers polarizability, Gaussian distributions of charges, and the Buckingham intermolecular potential. Moreover, the AH/BK3 FF relies on the polarizable BK3 water model\textsuperscript{18} which predicts the majority of the properties of pure water extremely well, e.g., density, self-diffusivity, viscosity, compressibility, permittivity, and chemical potential.\textsuperscript{9} The BK3 FF has its origin in the GCP model of Cummins and coworkers.\textsuperscript{19} The AH/BK3 FF for NaCl yields correct concentration dependence
of density and activity at ambient conditions, and its chemical potential in NaCl aqueous solutions is lower by only $\sim 3.35$ kJ mol$^{-1}$ compared to experiment. However, the AH/BK3 FF has a few drawbacks as it exhibits very strong Na$^+$-Cl$^-$ ion pairing in aqueous solutions and too low chemical potential of NaCl crystal by $\sim 15$ kJ mol$^{-1}$, resulting in unrealistically low solubility, and its temperature dependence of activity coefficients is incorrect. The deficiencies of the AH/BK3 FF are related to its parametrization as its authors did not target any properties of concentrated solutions, and they considered the properties of crystalline NaCl only loosely; e.g., missing the density of NaCl crystal by $\sim 45$ kg m$^{-3}$ and its lattice energy by $\sim 9.3$ kJ mol$^{-1}$.

Later, the parameters of the ion-ion interactions were refitted by Kolafa, yielding the MAH/BK3 FF for NaCl. The MAH/BK3 FF successfully predicts several mechanical properties of the NaCl crystalline phase at ambient conditions, lattice energy, and additional properties at the melting point. However, Kolafa’s explicit interface simulations indicate that the prediction of the NaCl aqueous solubility by the MAH/BK3 FF is too low as compared to experiment by $\sim 40\%$. Our simulations confirmed this low aqueous solubility and showed this is due to a low value of the chemical potential of NaCl crystal by the MAH/BK3 FF when compared to experiment by $\sim 4.4$ kJ mol$^{-1}$. It is puzzling that even the complex polarizable NaCl MAH/BK3 FF, targeting many properties of crystalline phase and including experimental lattice energy, yields too low a value of the chemical potential and aqueous solubility when compared with experiments.

Hence, the aims of this work are the following: (i) to investigate, if and how the NaCl MAH/BK3 FF can be refined to yield correct predictions of the aqueous solubility and chemical potential of the crystal while maintaining accurate predictions of other system properties; (ii) to determine new Na$^+$ and Cl$^-$ FF parameters; (iii) to test the refined NaCl FFs under different conditions, including NaCl aqueous solutions, crystalline NaCl (halite), NaCl·2H$_2$O low temperature crystalline phase (hydrohalite), and NaCl melt; and (iv) to provide insight into the microscopic behavior of NaCl systems and suggestions for possible improvements of FFs for modeling of other alkali-halide electrolytes.
The remainder of the paper is organized as follows: In section 2, we propose a method for fitting the FF parameters of Na\(^+\) and Cl\(^-\) ions, targeting crystalline chemical potential and pressure at specified density and temperature. In section 3, we describe the simulation methodology employed. In section 4, we present our refined NaCl FF and assess its performance at various state conditions and phases. Section 5 provides our conclusions, including suggestions for the possible improvement or development of FFs for other electrolytes.
2 FORCE-FIELDS TARGETING CHEMICAL POTENTIAL AND DENSITY OF HALITE

We argue that, besides different properties of the solution phase, development of any electrolyte FF should always include the chemical potential of crystalline electrolyte, \( \mu_{cr} \), within the set of target properties. Particularly, excluding \( \mu_{cr} \) from the target properties often results in an inaccurate prediction of aqueous solubility, which limits the usability of the FF and may lead to precipitation at low concentrations or spurious behavior in general. We are not aware that considering \( \mu_{cr} \) as the target property has been applied in developing polarizable FFs, which is not surprising as its implementation poses a serious challenge. Calculation of chemical potentials by molecular simulations is a challenging task, always involving tens of separate simulations at different integration stages, in systems of different sizes, and extrapolations to infinite systems. Developing a complex polarizable FF targeting \( \mu_{cr} \) thus relies on a fast converging process that needs to avoid any iterative procedure involving a long sequence of iteration steps; e.g, Newton’s method used by Kolafa comprised of 25 iteration steps.\(^4\) Such iterative approaches would be very time consuming if \( \mu_{cr} \) (typically also its partial derivatives with respect to all the fitted FF parameters are required) was calculated within each of the numerous steps. Moreover, such iterative approaches do not provide further insight into the microscopic behavior of crystalline NaCl. Hence, we have devised a fast converging procedure based on several physical assumptions, which allows us to straightforwardly and easily reparametrize the MAH/BK3 FF to yield correct values of \( \mu_{cr} \) and in addition, also pressure \( P_{cr} \) at the given density of crystalline NaCl, \( \rho_{cr} \), and temperature, \( T \). The fitting procedure can be further extended to target also other properties or properties at different thermodynamic conditions.

**Force-Field Functional Form**

We consider the same functional form of the molecular interactions as the AH/BK3, MAH/BK3, and BK3 FFs, which is briefly summarized below. The AH/BK3 and MAH/BK3 FFs model
the nonpolar interactions between ions by the Buckingham (EXP6) potential

\[
u_{ij}^{\text{EXP6}}(r) = A_{ij} \exp(-B_{ij}|\mathbf{r}_i - \mathbf{r}_j|) - C_{ij}|\mathbf{r}_i - \mathbf{r}_j|^{-6} \tag{1}
\]

where subscripts \(i\) and \(j\) refer to the particles. The electrostatic interaction between ions is modeled by two Gaussian charge distributions per each ion. One of the Gaussian charges is fixed to the center of the ion. The other Gaussian charge is massless and is attached to the center of the ion by a virtual harmonic spring, modeling polarizability by the Drude charge-on-spring approach, where the spring constants are obtained from the particle polarizability, \(\alpha_{ia}\). The interactions between Gaussian charges of different particles converge to the Coulomb potential at long distances but become weaker at short distances due to the overlap of the Gaussians depending on their distribution widths, \(\sigma_{ia}\):

\[
u_{ij}^{\text{GC}}(r) = \frac{1}{4\pi\varepsilon_0} \sum_{a,b} q_{ia}q_{jb} \frac{|\mathbf{r}_{ia} - \mathbf{r}_{jb}|}{|\mathbf{r}_{ia} - \mathbf{r}_{jb}|} \text{erf} \left( \frac{|\mathbf{r}_{ia} - \mathbf{r}_{jb}|}{\sqrt{2(\sigma_{ia}^2 + \sigma_{jb}^2)}} \right) \tag{2}
\]

where subscripts \(a\) and \(b\) refer to the interaction sites of the particles, \(q_{ia}\) are the values of charges, \(\varepsilon_0\) is the permittivity in vacuum, and the summation over \(a, b\) runs over the two charge sites. The BK3 FF models the \(\text{H}_2\text{O}\) molecules as the AH/BK3 and MAH/BK3 FFs and it employs the rigid four-site geometry of the TIP4P model.\textsuperscript{21} The EXP6 interaction sites are considered only for the \(\text{O}\) atoms. The electrostatic interaction is modeled by three massless Gaussian charge distributions attached by virtual harmonic springs to the rigid backbone of the molecule, two charges on the \(\text{H}\) atom sites and one on the \(\text{M}\) site.

**Force-Field Parameters of BK3, AH/BK3 and MAH/BK3 Models**

The interaction parameters of the BK3, AH/BK3 and MAH/BK3 FFs are listed in Table 1. The unlike EXP6 interaction parameters \(A_{ij}\) and \(B_{ij}\) are given by the Kong combining rules\textsuperscript{22}

\[
A_{ij} = \frac{1}{2} \left[ A_{ii} \left( \frac{A_{ii}B_{ii}}{A_{jj}B_{jj}} \right)^{-\frac{B_{ii}}{B_{jj}}} + A_{jj} \left( \frac{A_{jj}B_{jj}}{A_{ii}B_{ii}} \right)^{-\frac{B_{jj}}{B_{ii}}} \right] \tag{3}
\]
\[ B_{ij} = \frac{2B_{ii}B_{jj}}{B_{ii} + B_{jj}} \]  

(4)

where the AH/BK3 FF applies the Kong rules to H$_2$O-H$_2$O, H$_2$O-ion, and ion-ion interactions. In the MAH/BK3 FF, only the ion-ion interaction parameters follow the Kong rules while the H$_2$O-H$_2$O and H$_2$O-ion interaction parameters are identical to those for the AH/BK3 FF, i.e., they are not associated with the ion-ion parameters by any rules. The unlike EXP6 interaction parameters \( C_{ij} \) for all the FFs follow the Berthelot rule

\[ C_{ij} = \sqrt{C_{ii}C_{jj}} \]  

(5)

Therefore, all the FFs have identical H$_2$O-H$_2$O and H$_2$O-ion interactions, and they differ only in the \( A \) and \( B \) parameters for the ion-ion interactions. For further details, see the original papers.$^{4,17,18}$ We note that Kolafa uses a different but equivalent Busing functional form of the same EXP6 interaction potential.

Table 1: The interaction parameters of the BK3, AH/BK3, and MAH/BK3 FFs. The superscript ‘at’ denotes the charge fixed to the atom center and ‘Dr’ denotes the Drude charge attached by the spring to the atom.

| Atom | \( A_{ii} \) (kJ mol$^{-1}$) | \( B_{ii} \) (Å$^{-1}$) | \( C_{ii} \) (kJ Å$^6$ mol$^{-1}$) | \( q^a_{ia} \) (e) | \( q^{Dr}_{ia} \) (e) | \( \sigma_{ia} \) (Å) | \( \alpha_{ia} \) (Å$^3$) |
|------|----------------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|
| BK3$^{18}$ | O | 3.22 · 10$^5$ | 3.56 | 3320 | 0 | 0.584 | 0.4 | 0.36 |
|          | H | | | | | | |
|          | M | | | | 0 | -1.168 | 0.71 | 0.72 |
| AH/BK3$^{17}$ | Na | 8.5 · 10$^{12}$ | 15 | 550 | 11 | -10 | 0.65 | 0.157 |
|          | Cl | 9.4 · 10$^5$ | 3.1 | 8000 | -11 | 10 | 0.96 | 3.5 |
| MAH/BK3$^{4}$ | Na | 1.49132 · 10$^{11}$ | 10.36837 | 550 | 11 | -10 | 0.65 | 0.157 |
|          | Cl | 3.96366 · 10$^4$ | 2.401223 | 8000 | -11 | 10 | 0.96 | 3.5 |

**Unchanged Force-Field Parameters**

To achieve the desired values of target properties without altering other properties, we aim to minimally modify the MAH/BK3 FF, keeping most of the interaction parameters of the
MAH/BK3 and AH/BK3 FFs unchanged. We preserve the total charge magnitudes as there is no reason to scale charges in polarizable models. We also did not modify polarizability, $\alpha_{ia}$, as the values of $\alpha_{ia}$ used in the AH/BK3 FF are plausible. We further kept unchanged all other electrostatic parameters, $q_{ia}^{at}$, $q_{ia}^{dr}$, and $\sigma_{ia}$ because their roles are rather technical, and they affect the behavior of crystalline NaCl only marginally (e.g., Kiss and Baranyai stated that the size of the charge-on-spring is arbitrary, apart from very extreme choices.\textsuperscript{18}), or their changes can be compensated by changes in the short-ranged repulsive exponential interactions. Finally, we did not change the values of $C$ as we argue that the London’s attractions at long distances are negligible compared to strong electrostatic interactions, and they can be compensated by changing the repulsive exponential interactions at short distances. We note that these are just assumptions whose validity will be judged by the parametrization procedure and performance of the refined FF.

**Reparametrized Force-Field Parameters**

We decided to modify the exponential repulsion interactions of the ion-ion interactions by changing the values of parameters $A$ and $B$ for the ions (a similar approach was adopted by Kolafa\textsuperscript{4}). We argue that the exponential repulsion interactions play the key role and they balance strong electrostatic attractions between unlike ions while simultaneously keeping realistic interactions between like ions. We further assume that the exponential repulsion between Na cations is negligible due to the small size of Na\textsuperscript{+} and typical Na\textsuperscript{+}-Na\textsuperscript{+} distances in the NaCl aqueous solutions and crystals. On the other hand, the exponential repulsion between Cl anions may play a role as Cl\textsuperscript{-} is relatively large with respect to Na\textsuperscript{+}. Hence, we focus on the Na\textsuperscript{+}-Cl\textsuperscript{-} and Cl\textsuperscript{-}-Cl\textsuperscript{-} interactions and obtain the Na\textsuperscript{+}-Na\textsuperscript{+} $A$ and $B$ parameters from the Kong rules.

**Relation between Short-Ranged Repulsion Potentials and Crystalline Properties**

We argue that small changes in the exponential repulsion between ions in crystalline NaCl significantly affect the energetic properties and equilibrium density of the crystal phase. Considering a canonical ensemble (given temperature, $T$; volume $V$; number of ion pairs in
the crystal, \( N_{\text{NaCl}} \), the lattice energy, \( U_{\text{cr}} \), and pressure, \( P_{\text{cr}} \), include contributions due to the exponential repulsion, which can be expressed using radial distribution functions, \( g_{ij}(r) \), as

\[
U_{\text{cr}}^{\text{EXP}} = \frac{2\pi N_{\text{NaCl}}^2}{V} \int_{r=0}^{\infty} \sum_{i=\{\text{Na,Cl}\}} \sum_{j=\{\text{Na,Cl}\}} u_{ij}^{\text{EXP}}(r) g_{ij}(r) r^2 dr
\]

\[
P_{\text{cr}}^{\text{EXP}} = -\frac{2\pi N_{\text{NaCl}}^2}{3V^2} \int_{r=0}^{\infty} \sum_{i=\{\text{Na,Cl}\}} \sum_{j=\{\text{Na,Cl}\}} \frac{du_{ij}^{\text{EXP}}(r)}{dr} g_{ij}(r) r^3 dr
\]

In Eqs. (6) and (7), the sums run over two types of ions, and

\[
u_{ij}^{\text{EXP}}(r) = A_{ij} \exp(-B_{ij}|r_i - r_j|)
\]

\[
\frac{du_{ij}^{\text{EXP}}(r)}{dr} = -A_{ij} B_{ij} \exp(-B_{ij}|r_i - r_j|)
\]

are the exponential repulsion potential between the ions and its derivative. Considering the face-centered cubic lattice of the NaCl crystal, one can devise simple formulae which approximate the exponential contributions, \( U_{\text{cr}}^{\text{EXP}} \) and \( P_{\text{cr}}^{\text{EXP}} \), as

\[
\tilde{U}_{\text{cr}}^{\text{EXP}} \approx 6N_{\text{NaCl}} \left[u_{\text{NaCl}}^{\text{EXP}}(2.775 \text{ Å}) + u_{\text{ClCl}}^{\text{EXP}}(3.975 \text{ Å})\right]
\]

\[
\tilde{P}_{\text{cr}}^{\text{EXP}} \approx -\frac{2N_{\text{NaCl}}}{V} \left[(2.775 \text{ Å}) \frac{du_{\text{NaCl}}^{\text{EXP}}}{dr}(2.775 \text{ Å}) + (3.975 \text{ Å}) \frac{du_{\text{ClCl}}^{\text{EXP}}}{dr}(3.975 \text{ Å})\right]
\]

where the values \( r = 2.775 \) and \( 3.975 \text{ Å} \) correspond to the locations of first maxima in \( g_{\text{NaCl}}(r) \) and \( g_{\text{ClCl}}(r) \) as obtained from a molecular simulation using the MAH/BK3 model at an experimental ambient crystal density 2163 kg m\(^{-3}\) and temperature 298.15 K.

**Fitting Crystalline Density and Lattice Energy**

Eqs. (10) and (11) are employed in the parametrization procedure as follows. We start with the interaction parameters of the MAH/BK3 FF and simulate the lattice energy, \( U_{\text{cr}} \), and pressure, \( P_{\text{cr}} \), at \( \rho = 2163 \text{ kg m}^{-3} \) and \( T = 298.15 \text{ K} \). Comparing the simulation values of \( U_{\text{cr}} \) and \( P_{\text{cr}} \) with the experimental (target) values, we evaluate their differences and subsequently
the corresponding values of $\tilde{U}_{cr}^{\text{EXP}}$ and $\tilde{P}_{cr}^{\text{EXP}}$ which are in turn used to find new values of $A_{\text{NaCl}}$, $A_{\text{ClCl}}$, $B_{\text{NaCl}}$, and $B_{\text{ClCl}}$ via Eqs. (10) and (11). Values of $A_{\text{NaNa}}$ and $B_{\text{NaNa}}$ are then obtained via the Kong rules, Eqs. (3) and (4). However, as we fit six parameters, we need six equations. Fitting two properties ($U_{cr}$ and $P_{cr}$ at given $\rho$ and $T$) yields two equations, the Kong rules are another two equations, and we thus need two additional conditions. Keeping the minimal change in the MAH/BK3 FF, we opt to fix the fractions of the energetic and pressure contributions from the $\text{Na}^+\text{-Cl}^-$ and $\text{Cl}^-\text{-Cl}^-$ interactions for the MAH/BK3 FF, i.e.,

$$\theta_U = \frac{u_{\text{NaCl}}^{\text{EXP}}(2.775 \text{ Å})}{u_{\text{ClCl}}^{\text{EXP}}(3.975 \text{ Å})} = 0.79598$$

$$\theta_P = \frac{(2.775 \text{ Å}) \frac{du_{\text{NaCl}}^{\text{EXP}}}{dr}(2.775 \text{ nm})}{(3.975 \text{ Å}) \frac{du_{\text{ClCl}}^{\text{EXP}}}{dr}(3.975 \text{ Å})} = 0.81560$$

If necessary, these two conditions can be modified. For example, one can consider different values of $\theta_U$ and $\theta_P$ or can substitute the conditions by other equations similar to Eqs. (10) and (11), corresponding to additional target values of $P_{cr}$ and $U_{cr}$ at different density and temperature and/or can employ other approximate equations related to different target properties. Our results show that such changes are not necessary unless very accurate predictions of the crystal or melt properties at high temperatures are required.

However due to the approximate nature of Eqs. (10) and (11), the fitting procedure does not directly give a perfect agreement between the simulation and target properties and it was necessary to repeat the parametrization procedure a few times. However, this is a rather easy task as the procedure is fast and quickly converging. We found a very good agreement between the simulation and target values of $U_{cr}$ and $P_{cr}$ within three iterations. We parametrized our refined FF at $\rho = 2163$ kg m$^{-3}$ and $T = 298.15$ K to the target value of $P_{cr} = (1 \pm 10)$ bar. Due to the scattered values of the experimental lattice energy found in literature, we repeated the fitting procedure for several different target values of $U_{cr}$, and we discuss the effects of the choice of the different values for experimental lattice energy below.
Fitting Crystalline Chemical Potential via Lattice Energy

The molar chemical potential of NaCl in the crystal, $\mu_{cr}$, is the molar Gibbs free energy and it consists of $U_{cr}$, the FF-independent kinetic energy, the entropic contribution $-TS$, and the (negligible) pressure contribution $PV$ in one mole of NaCl. The structure of the NaCl crystal in a canonical ensemble only weakly depends on the FF parameters. Therefore, we assume that the same also applies to the entropy and the dependence of $\mu_{cr}$ on $U_{cr}$ becomes approximately linear for different FF parametrizations. Fig. 1 displays the actual dependence of $\mu_{cr}$ on $U_{cr}$ obtained by molecular simulations with different FF parametrizations, i.e., FFs fitted to ambient pressure and different values of $U_{cr}$. Fig. 1 suggests that one can find two FF parametrizations targeting one $P_{cr}$ and two values of $U_{cr}$ at a given density and temperature, obtain their $\mu_{cr}$ by simulations, and subsequently find a value of $U_{cr}$, which gives the desired value of $\mu_{cr}$ by a linear interpolation.

We implemented this approach with the target $U_{cr}$ equal to -780 and -786 kJ mol$^{-1}$ and found the refined FF which yields $\mu_{cr} = -384.01$ kJ mol$^{-1}$, $U_{cr} = -781.5$ kJ mol$^{-1}$ and $P_{cr} = (10 \pm 10)$ bar at $\rho = 2163$ kg m$^{-3}$ and $T = 298.15$ K. The total process comprised of 12 NVT simulations (2 iterations × 3 iteration steps × 2 FFs) to evaluate $P_{cr}$ and $U_{cr}$ and two Frenkel-Ladd simulations to determine $\mu_{cr}$. 

Figure 1: The chemical potential, $\mu_{cr}$, of NaCl crystals at a density of 2163 kg m$^{-3}$ and a temperature of 298.15 K obtained from simulations with different FFs which were fitted to pressure $P_{cr} = (1 \pm 10)$ bar and different values of the lattice energy, $U_{cr}$. The first point on the left corresponds to the MAH/BK3 FF which gives too low $\mu_{cr}$. The fourth point represents our refined FF, which is consistent with the experimental $\mu_{cr}$ equal to -384.024 kJ mol$^{-1}$ and the experimental lattice energy $U_{cr}$ equal to -781.551 kJ mol$^{-1}$ denoted by the open circle. The other symbols denote results of intermediate force fields whose parameters are not necessary to present.
3 SIMULATION METHODS

Crystalline and molten NaCl were simulated using the Multi-Particle Move Monte Carlo (MPMMC) method,\textsuperscript{24,25} periodic boundary conditions and standard Ewald summation for electrostatic interactions. The mechanical properties of crystals (pressure, $P$; bulk modulus, $B$; shear modulus, $G$; isobaric thermal expansion coefficient, $\alpha$) were obtained from canonical ensemble simulations of systems composed of 1372 ion pairs in a cubic simulation cell, or 1400 ion pairs in simulations of rotated crystals for $G$, where the approach of Kolafa\textsuperscript{4} was employed. The values of $B$ were determined from two standalone simulations with a simulation box of density 2163 kg m$^{-3}$ which is uniformly rescaled by $\exp(\pm e)$ in each direction,

$$ B = \frac{P(-e) - P(e)}{6e} \quad (14) $$

where $P(\pm e)$ is the pressure of the expanded/compressed crystal and $e = 0.01$ was used. The values of $G$ were calculated from a simulation with the crystal lattice rotated around the $z$-axis by 45 deg with respect to the simulation cell, with the system size expanded $\exp(e)$-times in the $x$-direction and $\exp(-e)$-times in the $y$-direction,

$$ G = \frac{P_{yy} - P_{xx}}{4e} \quad (15) $$

where $P_{xx}$ and $P_{yy}$ are components of the pressure tensor and $e = 0.00707$. The values of $\alpha$ were evaluated using

$$ \alpha = \frac{P(T + \Delta T) - P(T - \Delta T)}{2B\Delta T} \quad (16) $$

with $\Delta T = 30$ K. In all the cases, the pressure and components of the pressure tensor were simulated using the volume-perturbation method with an optimal $\Delta V$ selected from six different values to avoid any systematic errors due to numerical differentiation. The densities of crystalline and molten NaCl were obtained from simulations in an NPT ensemble with 500 ion pairs and cubic simulation cells. The equivalent isotropic displacement parameters
in crystalline NaCl, $U_{eq}$, were calculated using the equation

$$U_{eq} = \frac{1}{3} \langle u \cdot u \rangle$$  \hspace{1cm} (17)$$

where $u$ is the displacement vector of an ion from its equilibrium position.

The chemical potential of crystalline NaCl, $\mu_{cr}$, was determined using the Frenkel-Ladd integration approach\textsuperscript{26,27} composed of 16 steps gradually changing the interactions of the particles, using 500 and 1372 ion pairs and extrapolating to infinite system size. All the chemical potential values (for both NaCl in the solution phase and crystalline NaCl) presented in this work include the ideal-gas standard chemical potential contributions obtained from the NIST-JANAF tables\textsuperscript{23} as the Gibbs free energies of formation at $P^0 = 1$ bar: for $T = 298.15$ K, $\mu_{\text{Cl}^-}^0 = -240.167$ kJ mol\textsuperscript{-1} and $\mu_{\text{Na}^+}^0 = 574.317$ kJ mol\textsuperscript{-1}; for $T = 373.15$ K, $\mu_{\text{Cl}^-}^0 = -241.580$ kJ mol\textsuperscript{-1} and $\mu_{\text{Na}^+}^0 = 565.462$ kJ mol\textsuperscript{-1}; for $T = 473.15$ K, $\mu_{\text{Cl}^-}^0 = -243.059$ kJ mol\textsuperscript{-1} and $\mu_{\text{Na}^+}^0 = 553.975$ kJ mol\textsuperscript{-1}.

The melting point was determined using the solid-liquid direct coexistence method.\textsuperscript{28} NP\textsubscript{zz} T MPMMC simulations were performed for temperatures ranging from 1000 to 1100 K and with 1000 ion pairs in a rectangular cuboid simulation cell. The width and height of the simulation cell were equal to the size of the cubic simulation cell in the bulk simulations with 500 ion pairs, and the length of the simulation cell was roughly doubled. Initially, one half of the simulation cell was filled with a cubic NaCl crystal, and the rest of the cell was filled by molten NaCl obtained from a separate NP\textsubscript{zz} T simulation at $T = 2000$ K. Melting and crystallization were studied by monitoring total potential energy and density of the system.

The self-diffusion coefficients, $D$, of ions and water in NaCl aqueous solutions were obtained from NPT molecular dynamics (MD) simulations using the Macsimus\textsuperscript{29} simulation package. All MD simulations were performed using a cubic simulation cell with periodic boundary conditions, the Nose-Hoover thermostat and barostat with time constants of 0.3 ps and 1 ps, respectively, integration time step of 1 fs, and Ewald summation for electrostatic
interactions. The self-diffusion coefficients were calculated from the slope of the mean-square displacement as

\[ D = \lim_{t \to \infty} \frac{\langle |r(t) - r(0)|^2 \rangle}{6t} \]  

(18)

The self-diffusion coefficients calculated in cubic simulation cells and periodic boundary conditions linearly depend on the reciprocal length of simulation cell, and either significant finite size corrections must be applied or extrapolations must be performed to obtain self-diffusion coefficients in the thermodynamic limit (infinite systems). In this work, we determined the values of \( D \) by extrapolating simulation \( D_s \), obtained by Eq. (18) and MD simulations with 600, 840 and 1200 H\(_2\)O molecules, to the thermodynamic limit.

The dependence of NaCl chemical potential, \( \mu \), on molality, \( m \), was determined by the Osmotic Ensemble MC (OEMC) method. NaCl aqueous solutions were simulated at constant pressure and temperature [(1 bar, 298.15 K); (1 bar, 373.15 K); (15.5 bar, 473.15 K)], 270 H\(_2\)O molecules, and different prescribed values of \( \mu \) from -400 to -366 kJ mol\(^{-1}\). During the simulations, the concentration converged to the equilibrium value of \( m \). Ions were inserted/removed into/from the aqueous solution by MC steps corresponding to a sequence of 15 processes gradually transforming the fractional particles and changing their coupling parameters using the coupling and staging schemes described in our previous work.

Hydrohalite was simulated as a freestanding finite piece of crystal consisting of 576 ion pairs and 1152 H\(_2\)O molecules in vacuum using the MPMMC method at a constant temperature. Initially, the particles were placed into positions corresponding to the experimental crystal lattice. Neither interaction cut-offs nor the Ewald summation were applied. Periodic boundary conditions were not used because we aim to study the stability of the crystal without imposing any properties of the crystal lattice. In addition, we are not aware of software capable of implementing the complex polarizable FF in monoclinic periodic boundary conditions.
4 RESULTS

New Force-Field Parameters

We applied the fitting procedure described in section 2 to parametrize the ion-ion interactions and the resulting new interaction parameters are listed in Table 2. We opt to combine the new ion-ion interaction parameters with the H$_2$O-H$_2$O and H$_2$O-ion interaction parameters of the AH/BK3 model, summarized in Table 1. The Kong rules are used for the ion-ion interactions independently of the H$_2$O-ion and H$_2$O-H$_2$O interactions.

Table 2: The new force-field parameters for Na$^+$ and Cl$^-$ ions.

| Atom | Buckingham Functional Form | | | Busing Functional Form | | |
|------|---------------------------|----------------|----------------|----------------|----------------|----------------|
|      | $A_{ii}$ (kJ mol$^{-1}$)  | $B_{ii}$ (Å$^{-1}$) | $C_{ii}$ (kJ Å$^6$ mol$^{-1}$) | $q_{ia}^{at}$ (e) | $q_{ia}^{Dr}$ (e) | $\sigma_{ia}$ (Å) | $\alpha_{ia}$ (Å$^3$) |
| Na   | $5.8279474 \cdot 10^{10}$ | 9.7357893     | 550           | 11             | -10            | 0.65           | 0.157          |
| Cl   | $2.3432945 \cdot 10^{4}$ | 2.2547242     | 8000          | -11            | 10             | 0.96           | 3.5            |

Crystalline NaCl at Ambient Conditions

Table 3 lists several properties of crystalline NaCl obtained from simulations with our refined FF and compares them with our simulated values using other state-of-the-art models from literature, Madrid and MAH/BK3 FFs, and also with experiments.
Table 3: Properties of crystalline NaCl at a temperature of 298.15 K and a pressure of 1 bar obtained from simulations with several FFs and experiments: mass density, $\rho_{cr}$; chemical potential, $\mu_{cr}$; lattice energy, $U_{cr}$; bulk modulus, $B$; shear modulus, $G$; isobaric thermal expansion coefficient, $\alpha$.

| FF type          | $\rho_{cr}$ (kg m$^{-3}$) | $\mu_{cr}$ (kJ mol$^{-1}$) | $U_{cr}$ (kJ mol$^{-1}$) | $B$ (GPa) | $G$ (GPa) | $\alpha$ (MK$^{-1}$) |
|------------------|---------------------------|----------------------------|--------------------------|-----------|-----------|----------------------|
| refined FF (this work) | 2163                      | -384.01                    | -781.63                  | 23.5      | 12.5      | 122                  |
| MAH/BK3 FF$^4$   | 2163$^4$                  | -388.34                    | -786.60                  | 25.5      | 12.8      | 117                  |
| Madrid FF$^5$    | 2171$^5$                  | -200.01$^5$                | -607$^5$                 | 41.5      | 16.1      | 92                   |
| Experiment       | 2163$^{34}$               | -384.024$^{23}$            | -781.551$^{23}$          | 25.0(5)$^{35}$ | 12.7(3)$^{35}$ | 119.4$^{36}$         |

We see from Table 3 that the crystalline density, $\rho_{cr}$, obtained at $P = 1$ bar and $T = 298.15$ K, for the refined and MAH/BK3 FFs agrees with the experimental value while the experimental $\rho_{cr}$ is slightly overestimated by the Madrid FF; by $\sim 8$ kg m$^{-3}$ which is rather small compared to many other FFs found in literature.$^{11}$ It is worth mentioning that experimental data are subject to uncertainties and possible lattice defects are neglected in simulations.

The chemical potential of crystalline NaCl, $\mu_{cr}$, reported in Table 3 at $\rho = 2163$ kg m$^{-3}$ and $T = 298.15$ K, agrees with the experimental value only for our FF. For the MAH/BK3 FF, the difference between the predicted and the experimental values of $\mu_{cr}$, $\sim 4$ kJ mol$^{-1}$, is significant, as it causes about a 40% decrease in simulated aqueous solubility when compared with experiment (shown below), which is a serious drawback of the MAH/BK3 FF. For the Madrid model, $\mu_{cr} = -200.01$ kJ mol$^{-1}$ is well above the experimental $\mu_{cr} = -384.024$ kJ mol$^{-1}$. This enormous increase in the chemical potential is a result of weakened electrostatics due to scaled down charges, which also applies in the solution phase. However, the effects of the weakened electrostatics compensate each other mutually in the solution and crystalline phases, and the Madrid model thus predicts the aqueous solubility reasonably well.$^5$ We argue that, despite this compensation, the enormous difference in the chemical potential for the Madrid FF is an undesirable feature of the molecular model and
may adversely affect other system properties.

The comparison of simulation values of the lattice energy with experimental literature data needs to be done with caution. It is typical in the experimental literature that the reported values of the lattice energy actually correspond to the lattice enthalpy, i.e., the enthalpy released when the ions come together from the ideal-gas state to form the NaCl crystal at the given $T$ and $P$. In addition, experimental data found in the literature are rather scattered, e.g., -787.5 kJ mol$^{-1}$, 4-790 kJ mol$^{-1}$, 34 -764 kJ mol$^{-1}$, 35 and -787 kJ mol$^{-1}$ at $T = 298.15$ K and $P = 1$ bar. To transform the lattice enthalpy to $U_{cr}$, one first needs to add the work necessary to compress the ideal gas to the solid density, i.e., 4.955 kJ mol$^{-1}$ $\approx 2RT$; $R$ is the universal gas constant. Second, to ensure consistency with our simulations of the chemical potential, we opt to evaluate the experimental lattice energy, $U_{cr}^{\text{exp}}$, from NIST-JANAF Thermochemical Tables$^{23}$ at $T = 298.15$ K and $P = 1$ bar as

$$U_{cr}^{\text{exp}} = \Delta_f H^0(\text{NaCl, cr}) - \Delta_f H^0(\text{Na}^+, g) - \Delta_f H^0(\text{Cl}^-, g) + 4.955 \text{ kJ mol}^{-1}$$

$$= (-411.120 - 609.343 + 233.954 + 4.955) \text{ kJ mol}^{-1}$$

(19)

$$= -781.551 \text{ kJ mol}^{-1}$$

Table 3 then shows that the experimental lattice energy from Eq. (19) matches $U_{cr}$ obtained by our refined FF. In addition, it further indicates that the refined FF predicts the entropy of crystalline NaCl correctly. Similarly as for $\mu_{cr}$, the MAH/BK3 FF slightly underpredicts $U_{cr}^{\text{exp}}$ while the Madrid model enormously overpredicts $U_{cr}^{\text{exp}}$ due to the weakened electrostatics. We further note that it would be possible to directly fit $U_{cr}^{\text{exp}}$ given by Eq. (19), in turn yielding the correct chemical potential, but this approach was not used because of the scattered values of $U_{cr}^{\text{exp}}$ found in literature.

The mechanical properties $B$, $G$ and $\alpha$ obtained from our FF also agree rather well with experimental values, as seen in Table 3; differences between our and the experimental values are less than 5%. Our simulation results for $B$, $G$ and $\alpha$ exhibit almost the same accuracy
as those obtained using the MAH/BK3 model which was developed by directly targeting the mechanical properties of crystalline NaCl. The performance of the Madrid FF is rather poor with about 66%, 27%, and 23% deviations from experimental $B$, $G$, and $\alpha$, respectively.

In addition for our refined FF, we evaluated equivalent isotropic displacement parameters, $U_{eq}$, for both the ions. Our results, 0.0203 Å$^2$ and 0.0178 Å$^2$ respectively for Na$^+$ and Cl$^-$ ions, are in excellent agreement with experimental data, $^{38}$ 0.0201(8) Å$^2$ and 0.0174(5) Å$^2$, respectively.

**Density of Crystalline and Molten NaCl, and Melting Temperature**

Fig. 2 shows the dependence of density on temperature for crystalline NaCl and its melt, obtained by NPT MC simulations at $P = 1$ bar with our refined FF compared to experiments and simulation results for other FFs.

Regarding comparison of results obtained by the refined FF with experiments in Fig. 2, we see that the density of crystalline NaCl is very well predicted over the entire temperature range. It is worth mentioning that the experimental values of the density suffer from different systematic errors due to different experimental techniques used. There is a difference between the experimental NaCl crystal density $^{34}$ 2163 kg m$^{-3}$ and the NaCl crystal density obtained from experimental lattice constant $^{39}$ 2176 kg m$^{-3}$ at ambient conditions, possibly caused by defects in real crystals. In this work, we adopted the experimental density of 2163 kg m$^{-3}$ and considered no crystal defects. Our simulation results are in excellent agreement with the experimental data of the NBS Monograph 167 $^{40}$ which are not plotted in Fig. 2 because they would completely overlap our simulation data. Our results are only slightly lower than the densities obtained from the lattice constant data of Pathak and Vasavada. $^{39}$ The experimental data of Rao et al. $^{36}$ exhibit a suspicious decrease between 300 and 350 K and seem to be too low. For molten NaCl, our FF yields only slightly lower density and the same slope when compared with the experimental data of Jaeger, $^{41}$ whereas the experiments of Kirshenbaum et al. $^{42}$ exhibit a weaker dependence on temperature. A possible minor inaccuracy of the refined FF in the molten phase is not surprising as we parametrized our refined
FF to properties at ambient conditions only. Our explicit crystal-melt phase equilibrium simulations result in the melting temperature of 1025(5) K, which is close to the experimental 1073.9 K.\textsuperscript{34} We note that the explicit crystal-melt simulations may suffer from finite size and hysteresis effects. If desired, the high-temperature behavior of our FF can be improved, e.g., by considering high-temperature target properties instead of Eqs. (12) and (13). However, this would need to be performed with caution as the experimental high-temperature properties often suffer from large uncertainties.

Regarding comparison with other FFs in Fig. 2, we see that the MAH/BK3 FF yields almost identical results compared to the refined FF in both phases. The AH/BK3 FF underpredicts the density over the entire temperature range. The Madrid FF yields an accurate prediction under ambient conditions, however, its density deviates to lower values with increasing temperature. Very low predictions of density in the molten phase for the Madrid and AH/BK3 FFs indicate incorrect ion-ion interactions.
Properties of NaCl Aqueous Solutions

Fig. 3 shows the density of NaCl aqueous solution as a function of concentration $m$, obtained by NPT MC simulations at ambient conditions. The density predicted by our refined FF exhibits excellent agreement with experiment\textsuperscript{43} for molality $m < 4$ mol kg$^{-1}$, and it is only slightly lower at higher concentrations. Our simulation results for the AH/BK3 and MAH/BK3 FFs completely overlap those from the refined FF whereas the results for the Madrid FF\textsuperscript{5} overlap with experiment, which indicates that the origin of the minor inaccuracy in the solution density at the higher concentrations is most likely caused by the H$_2$O-H$_2$O or H$_2$O-ion interactions which are the same for all the studied polarizable FFs.
Figure 3: The density of NaCl aqueous solution, $\rho$, as a function of molality, $m$, at a temperature of 298.15 K and a pressure of 1 bar. Key: NPT simulations with the refined FF, symbols and black solid line; experiment,\textsuperscript{43} black dotted line; Madrid FF,\textsuperscript{5} blue solid line. The values of $\rho$ for the Madrid FF\textsuperscript{5} overlap with the experimental curve. Our results of $\rho$ for the AH/BK3 and MAH/BK3 FFs overlap with the curve for the refined FF.

Fig. 4 displays the static dielectric constant (relative permittivity), $\varepsilon_s$, of the NaCl aqueous solution as a function of concentration, obtained by NPT MC simulations at ambient conditions. The predicted values of $\varepsilon_s$ agree within statistical uncertainties with experimental data\textsuperscript{44} for $m < 4$ mol kg\textsuperscript{-1}, and they seem to deviate towards lower values at higher concentrations. Similarly to the solution density, the simulation results of $\varepsilon_s$ for the MAH/BK3 FF (not shown here) overlap those from our refined FF, suggesting that the small inaccuracy at higher concentrations is likely due to the H\textsubscript{2}O-H\textsubscript{2}O or H\textsubscript{2}O-ion interactions.
Figure 4: The static dielectric constant, $\varepsilon_s$, of NaCl aqueous solution as a function of molality, $m$, at a temperature of 298.15 K and a pressure of 1 bar. Key: NPT MC simulations with the refined FF, symbols and solid line; experiment, dotted line.

Fig. 5 presents the concentration dependence of the NaCl chemical potential in NaCl aqueous solution, $\mu$, obtained by the OEMC simulations, and the chemical potential of crystalline NaCl, $\mu_{cr}$, obtained by the Frenkel-Ladd method, at three different thermodynamic conditions: $T = 298.15$ K and $P = 1$ bar; $T = 373.15$ K and $P = 1$ bar; and $T = 473.15$ K and $P = 15.5$ bar.

First, we discuss comparison of results for the refined FF with experiments shown in Fig. 5. We see that $\mu_{cr}$ simulation results (solid horizontal lines) are in an excellent agreement with experiment not only at ambient conditions (see Table 3) but also under elevated temperatures. At 373.15 K and 1 bar, the $\mu_{cr}$ simulation result of $-377.19$ kJ mol$^{-1}$ agrees with $-377.152$ kJ mol$^{-1}$; at 473.15 K and 15.5 bar, the result of $-367.58$ kJ mol$^{-1}$ can be compared with the experimental value of $-367.634$ kJ mol$^{-1}$ for 473.15 K and 1 bar. The simulated $\mu(m)$ results (filled symbols) are only slightly shifted with respect to the experimental curves (dotted curves) depending on temperature: they are shifted to lower values at 298.15 K; they are shifted to higher values at 473.15 K; and they are in an ex-
cellent agreement with experiment at 373.15 K. Simultaneously, the $\mu(m)$ results faithfully follow the shape of the experimental $\mu(m)$ curves over the entire concentration range. This indicates that the refined FF predicts both NaCl and H$_2$O activity rather well, and it only slightly misses the standard state chemical potential values.$^9$ To demonstrate the agreement between our simulation data and experimental activity coefficient, we show $\mu(m)$ plots (solid curves) obtained using fixed experimental values of activity coefficients$^{45}$ (which fix the experimental shape of the curves) and the standard chemical potentials used as free parameters fitted to our $\mu(m)$ simulation data (which shifts the curves along the $\mu$-axis trying to match the simulation data). We see that all our simulation data lie within their statistical errors on these curves, which means that the whole set of the $\mu(m)$ data obtained by the simulations of the refined FF is consistent with experimental activity coefficients. Nevertheless, we do not present activity coefficient plots as their evaluation from our $\mu(m)$ simulation data would be subject of large uncertainties. Solubility results for the refined FF ($m$ at the intercept of the $\mu(m)$ curve and the $\mu_{cr}$ value) exhibit relatively small deviations from experimental values due to the shift of the $\mu(m)$ curves: 7.0(4) mol kg$^{-1}$ vs. experimental 6.144 mol kg$^{-1}$$^{146}$ at 298.15 K and 1 bar; 6.8(6) mol kg$^{-1}$ vs. experimental 7.973 mol kg$^{-1}$$^{145}$ at 473.15 K and 15.5 bar (it is not clear what pressure was applied in the experiment at 473.15 K); and an excellent agreement of 6.7(6) mol kg$^{-1}$ vs. experimental 6.680 mol kg$^{-1}$$^{145}$ at 373.15 K and 1 bar. The concentration-independent shifts of the $\mu(m)$ curves along with the slight deviations of the solubility values by our refined FF are primarily caused by the ion-H$_2$O interactions, modeled using the AH/BK3 FF, and can thus be corrected by refitting parameters of the ion-H$_2$O interactions. However, this is beyond the scope of this work.

Second, we discuss comparison with other FFs shown in Fig. 5. We see that $\mu_{cr}$ results$^{20}$ both for the AH/BK3 FF (long-dashed horizontal lines) and for the MAH/BK3 FF (short-dashed horizontal lines) substantially underpredict experimental values. The $\mu(m)$ results for AH/BK3$^{20}$ (open symbols) are consistent with our results (short-dashed curve), and they underpredict the experimental $\mu(m)$ curves at all thermodynamic conditions. Furthermore,
in contrast to the refined FF, the $\mu(m)$ results for the AH/BK3 FF at high concentrations obviously divert from the shape of the experimental $\mu(m)$ curves to lower values, indicating decreasing activity coefficients.\textsuperscript{20} Solubility of the AH/BK3 FF is strongly underpredicted under all considered thermodynamic conditions primarily due to the very low $\mu_{cr}$ values. The differences between the $\mu(m)$ curves for the refined FF and those from the AH/BK3 FF are due to the very strong Na-Cl ion pairing exhibiting by the AH/BK3 FF.\textsuperscript{9} In contrast to the refined FF, the strong Na-Cl ion pairing in the AH/BK3 model is observed even at very low concentrations and it is responsible for the affecting $\mu$ even in dilute solutions. The strong ion pairing of the AH/BK3 FF seems to be spurious, reflects the very low value of $\mu_{cr}$, and can be accompanied by a qualitative restructuring in the solution phase such as formation of ion clusters. For the MAH/BK3 FF, we performed a simulation at one state point (filled black square), and the simulation result matched the $\mu(m)$ curve from our refined FF. This indicates that the chemical potential in the NaCl aqueous solution is insensitive to the details of ion-ion interactions unless a very strong ion pairing appears and it also suggests that the entire $\mu(m)$ curves for the refined and MAH/BK3 FFs are very similar. The simulation state point for the MAH/BK3 FF corresponds to $\mu = \mu_{cr} = -388.34$ kJ mol\(^{-1}\) (short-dashed horizontal line) which leads to the aqueous solubility of the MAH/BK3 model at 298.15 K and 1 bar, 4.2(3) mol kg\(^{-1}\), which is comparable with the value of 3.7(3) mol kg\(^{-1}\) obtained by Kolafa using the explicit interface simulations,\textsuperscript{4} but which is well below the experimental solubility of 6.144 mol kg\(^{-1}\). Regarding comparison with the Madrid FF, as already mentioned, its chemical potential values both in the crystalline and solution phases are much higher, completely out of the range shown in Fig 5. Hence, the Madrid chemical potential results are not shown in Fig. 5.
Figure 5: The NaCl chemical potential in NaCl aqueous solution, $\mu$, as a function of molality, $m$, and the chemical potential in the NaCl crystalline phase, $\mu_{cr}$, at different thermodynamic conditions. The curves are for $\mu$ in the solution phase and horizontal lines are for $\mu_{cr}$ in the crystal. Key: OEMC/Frenkel-Ladd simulations with the refined FF, filled symbols and solid curve/line; MAH/BK3 model, square and short-dashed line; AH/BK3 model, open symbols and long-dashed curve/line; experimental data, dotted curve/line. Colors denote thermodynamic conditions: 298.15 K and 1 bar, black; 373.15 K and 1 bar, red; 473.15 K and 15.5 bar, blue. The values of $\mu_{cr}$ for the refined FF and experiment overlap. The $\mu$ curves for the refined FF and experiment at 373.15 K overlap.

Fig. 6 shows the concentration dependence of the self-diffusion coefficients, $D$, for H$_2$O and ions in NaCl aqueous solution at $T = 298.15$ K and $P = 1$ bar as obtained with our refined FF. Self-diffusion is strongly affected by the system size and we thus show results for different box sizes. We approximated our simulation $D_s$ by a linear fit and extrapolated the linear fits to the thermodynamic limit. The values of $D_{H_2O}$ and $D_{Na^+}$ increase with increasing system size whereas the values of $D_{Cl^-}$ decrease with increasing system size, resulting in crossing the Cl$^-$ and Na$^+$ lines in Fig. 6d at $m = 3.8$ mol kg$^{-1}$. Our extrapolated $D_s$ show that $D_{H_2O}$ of pure water (the BK3 water model), as in other simulation studies, agrees within statistical uncertainties with experimental $D_{H_2O}$. As NaCl concentration increases, $D_{H_2O}$ decreases since NaCl acts as the structure maker. For the refined FF, the decrease in $D_{H_2O}$ with increasing $m$ is faster compared to experimental data but slower.
than that observed for nonpolarizable FFs. This indicates that the refined polarizable FF partially alleviated an inherent deficiency of the too fast decrease of $D_{\text{H}_2\text{O}}$ with increasing $m$ for nonpolarizable models of aqueous salt solutions.\textsuperscript{48} At infinite dilution, simulation $D_{\text{Cl}^-}$ underpredicts the experimental limiting diffusion coefficient by $\sim 0.33 \cdot 10^{-5}$ cm$^2$ s$^{-1}$ whereas experimental $D_{\text{Na}^+}$ is only marginally underpredicted (by less than $\sim 0.1 \cdot 10^{-5}$ cm$^2$ s$^{-1}$) with the refined FF.

In Fig. 6d, we also compare simulation $D_s$ for our refined FF with $D_s$ for the Madrid model\textsuperscript{5} which were obtained from simulations containing 5,000 H$_2$O molecules and with finite-size corrections applied only to data at infinite dilution. By considering that the finite-size corrections of $D_s$ are relatively small in simulations with 5,000 H$_2$O molecules, the comparison, in overall, indicates that the refined FF captures the self-diffusivity of the NaCl aqueous solution with comparable accuracy. Specifically for both the FFs, $D_s$ at infinite dilution are almost identical and the $D_{\text{H}_2\text{O}}(m)$ curves seem to have the same slope.
Figure 6: Self-diffusion coefficients, $D$, for H$_2$O and ions in the NaCl aqueous solution as a function of molality, $m$, at a temperature of 298.15 K and a pressure of 1 bar. Panels (a)-(b) present $D$s determined from the mean-square displacements by NPT MD simulations using the refined FF with different numbers of water molecules: (a) 600, (b) 1200. Panel (c) illustrates the $D$ system size dependence ($L$ is the size of the rectangular simulation cell) for a selected concentration of 0.463 mol kg$^{-1}$. Panel (d) shows a comparison of the extrapolated $D$s to the thermodynamic limit with experimental data and with the simulation results of Benavides et al. for the Madrid FF.$^5$ Key: $D_{H_2O}$ by the refined FF, plus symbols and solid lines; $D_{Cl^-}$ by the refined FF, asterisks and dashed lines; $D_{Na^+}$ by the refined FF, crosses and dotted lines; experimental $D_{H_2O}$,$^{47}$ filled circles; experimental $D_{Na^+}$,$^{34}$ filled triangle; experimental $D_{Cl^-}$,$^{34}$ filled diamond; $D_{H_2O}$ by the Madrid FF, open circles; $D_{Na^+}$ by the Madrid FF, open triangles; $D_{Cl^-}$ by the Madrid FF, open diamonds. Finite-size corrections to $D$s were not applied for the Madrid FF at finite concentrations.

**Structure and Stability of Hydrohalite**

Finally, we performed simulations of hydrohalite at $T = 105$ and 256 K with our refined FF. Fig. 7 displays a snapshot of the interior of the equilibrated simulated crystal close to
its center of mass and compares it with the experimental structure.\textsuperscript{49} Overall, there are no observed differences between the simulated and experimental structures and the values of the lattice constants, obtained without considering possible finite-size effects by an analysis of the interior of the simulated crystal at $T = 105$ K. Simulation values $a = 6.36(2)$ Å, $b = 10.02(2)$ Å, $c = 6.50(2)$ Å, $\alpha = 89.9(2)^{\circ}$, $\beta = 112.6(2)^{\circ}$, and $\gamma = 89.9(2)^{\circ}$, reasonably agree with experimental values $a = 6.3313$ Å, $b = 10.1178$ Å, $c = 6.5029$ Å, $\alpha = 90^{\circ}$, $\beta = 114.407^\circ$, and $\gamma = 90^\circ$.\textsuperscript{49} The simulated crystal, similarly as in experiments, was stable at both the temperatures. This is a strong evidence that the refined FF captures faithfully the behavior of the real NaCl in different phases. It also suggests that crystalline hydrates may play an important role in a possible further adjustment of FFs, as their properties are inevitably sensitive to the ion-H$_2$O interactions and still can be relatively easily interpreted in comparison with the complex behavior of aqueous solutions. Further studies of the thermodynamic and structural properties of hydrohalite using polarizable FFs require significant methodological development, particularly to avoid the potentially strong finite-size effects, which are beyond the scope of this work.

Figure 7: The structure of hydrohalite at a temperature of 105 K. Panel (a) shows the experimental structure\textsuperscript{49} and panel (b) presents a snapshot of the interior of a crystal simulated in vacuum using our reparametrized FF. Key: O, red; H, white; Na$^+$, blue; Cl$^-$, cyan.
5 CONCLUSIONS

We have shown that it is possible to straightforwardly and relatively easily reparametrize the ion-ion short range repulsion contributions of the AH/BK3 and MAH/BK3 NaCl FFs to yield experimental values of the crystal density, chemical potential, and lattice energy at ambient conditions. Our parametrization procedure employs several simple assumptions involving the radial distribution functions in the NaCl crystal and their approximate analytical relations to pressure and lattice energy, and another relation between the energy of the crystal and its chemical potential. These relations not only facilitated fast convergence of the iterative process within the parametrization procedure but also provided further insight into the microscopic behavior of the systems. The procedure can be generalized or further extended by additionally devised relations either based on statistical mechanics (e.g., exponential contributions to mechanical properties such as B, G and α), thermodynamics (e.g., targeting energy and pressure values at multiple state points to fit B and α indirectly), mechanics and geometry (e.g, substituting the constant r values in Eqs. (8) and (9) by geometrical rules to target crystals at different densities).

An example in which the procedure provides an important insight into crystalline electrolytes are the approximate relations for the exponential contributions to the lattice energy and crystal pressure, Eqs. (10) and (11). These relations show that simultaneous fitting of the density and energy of the crystal for simple molecular models based on Lennard-Jones (LJ) potential would fail. For the simple models, it is impossible to meaningfully change the derivative and value of the repulsive part of the LJ potential at particle separations corresponding to the nearest neighbors without unrealistically altering the London’s attractions. In contrast to the LJ potential, the Buckingham potential allows simultaneous fitting of both the density and energy of the crystal via a change of its interaction parameters A and B; cf. Eqs. (8) and (9).

The resulting NaCl FF can be viewed as a refinement of the MAH/BK3 FF of Kolafa for the ion-ion interactions, which adopts the original AH/BK3 FF of Kiss and Baranyai.
for the H$_2$O-H$_2$O and H$_2$O-ion interactions. The refined FF provides excellent predictions of the system properties in aqueous solutions, anhydrous NaCl crystal and melt, and an accurate structure of hydrohalite. The performance of the refined FF is superior to the existing state-of-the-art FFs since no significant disagreement between the simulation and experimental results were found for a wide range of system properties, which does not apply to other FFs (The Madrid FF yields extremely high chemical potential and lattice energy, and incorrect mechanical properties of crystal; the AH/BK3 FF has very low solubility, low crystal density, very low crystal chemical potential, and very low lattice energy; the MAH/BK3 FF has low chemical potential of crystalline NaCl and low NaCl lattice energy). Relatively small discrepancies between the simulation and experimental data were observed for the self-diffusivity in the aqueous solutions with errors comparable with those for other state-of-the-art FFs.

As regards general development or improvement of the molecular models for electrolytes, we provide several suggestions:

- It is desirable to include the salt chemical potential in both the solution phase and crystal as a target property in the development of electrolyte FFs.

- The Buckingham potential is preferred to the LJ potential as the Buckingham potential allows targeting both the density and energy of the crystal while for the LJ potential, it leads to spurious London’s attractions.

- Development of the electrolyte FFs requires critical assessment of existing experimental (target) data since they may be rather scattered or misleading, e.g., the mismatch in experimental values of NaCl lattice energy/enthalpy which affects the NaCl aqueous solubility by 40%.

- Our results for water self-diffusivity are similar to those of the Madrid FF which uses the scaled charges. Although both the models improved prediction of the water self-diffusivity when compared with nonpolarizable models they still exhibit faster decrease
in the water self-diffusivity upon an increase of the salt concentration when compared with experiments. This indicates that the slower water self-diffusivity in the nonpolarizable models is not only caused by approximative treatment of polarizability but it may be also related to other features of the models, e.g., the TIP4P water geometry employed in both the BK3 and Madrid water models.

- Our simulations of hydrohalite suggest a way to parametrize electrolyte molecular models by targeting the properties of hydrates. The experimental microscopic properties of hydrates such as lattice constants or atomic displacement parameters are readily available, they are directly related to the interactions of ions with water molecules, and they can be obtained from molecular simulations relatively easily. This can find applications for example in the development of an accurate Li$^+$ FF where properties of different LiCl hydrates can be utilized.

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accurately predicted by refined polarizable force field

halite

density, energy,
chemical potential,
atomic displacement,
mechanical properties

hydrohalite

stability,
structure,
lattice constants

aqueous solution

NaCl chemical pot.,
H₂O chemical pot.,
density, solubility,
static permittivity

accurately predicted by refined polarizable force field