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ABSTRACT

Molecular dynamics simulations of aqueous electrolytes generally rely on empirical force fields, combining dispersion interactions—described by a truncated Lennard-Jones (LJ) potential—and electrostatic interactions—described by a Coulomb potential computed with a long-range solver. Recently, force fields using rescaled ionic charges [electronic continuum correction (ECC)], possibly complemented with rescaling of LJ parameters [ECC rescaled (ECCR)], have shown promising results in bulk, but their performance at interfaces has been less explored. Here, we started by exploring the impact of the LJ potential truncation on the surface tension of a sodium chloride aqueous solution. We show a discrepancy between the numerical predictions for truncated LJ interactions with a large cutoff and for untruncated LJ interactions computed with a long-range solver, which can bias comparison of force field predictions with experiments. Using a long-range solver for LJ interactions, we then show that an ionic charge rescaling factor chosen to correct long-range electrostatic interactions in bulk accurately describes image charge repulsion at the liquid–vapor interface, and the rescaling of LJ parameters in ECCR models—aimed at capturing local ion–ion and ion–water interactions in bulk—describes well the formation of an ionic double layer at the liquid–vapor interface. Overall, these results suggest that the molecular modeling of aqueous electrolytes at interfaces would benefit from using long-range solvers for dispersion forces and from using ECCR models, where the charge rescaling factor should be chosen to correct long-range electrostatic interactions.

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I. INTRODUCTION

Molecular dynamics (MD) is a very powerful tool to explore the structure and dynamics of aqueous electrolytes at the atomic scale. To simulate large systems over long times, empirical interaction potentials (force fields) are widely used. Liquid water is commonly described with rigid non-polarizable models,^{1,2} and some of them perform quite well. For instance, the SPC/E model³ is rather good at reproducing the dielectric properties of water,^{4–6} and the TIP4P/2005 model⁷ accurately reproduces the structure and dynamics of water over a wide range of temperatures and pressures.^{8–14} However, non-polarizable models for ions in water are less successful at predicting the thermodynamics and dynamics of aqueous

solutions.^{15–17} For instance, most non-polarizable models cannot qualitatively reproduce even the impact some salts have on water self-diffusion,^{18,19} while explicit inclusion of polarizability and/or charge transfer can improve the predictions.^{20–22}

In that context, new non-polarizable models have been developed based on a rescaling of the ionic charges,^{23–36} an approach often referred to as electronic continuum correction (ECC). Originally, the rescaling aims at implicitly describing electronic polarization to improve the description of local ion–water and ion–ion interactions.²⁵ However, the rescaling can also compensate for the underestimated permittivity of water models²⁷ and recover the correct long-range Coulombic interactions. Both motivations suggest different charge rescaling factors, i.e., $1/\sqrt{\epsilon_{el}}$ (with ϵ_{el}

being the electronic permittivity of the solvent) for the local argument²⁵ and $\sqrt{\epsilon_r/\epsilon_r^{\text{exp}}}$ (with ϵ_r being the permittivity of the water model and ϵ_r^{exp} being the experimental value) for the long-range argument.²⁷ In practice, various rescaling factors have been chosen^{23–36} based on the expressions above or simply tuned to optimize the performance of the model. Bare ECC, or ECC complemented with rescaling of the Lennard-Jones (LJ) parameters^{28,31}—referred to as ECC rescaled (ECCR) for “electronic continuum correction rescaled,” indeed provides improved predictions for the structure, dielectric permittivity, and dynamics of bulk aqueous solutions.^{27–30,33–35,37,38}

However, ECC models have been less studied at interfaces.^{39–41} At the water–air interface, the ECC increases the surface affinity of ions and can create an ionic double layer,^{39,40} in line with the predictions of polarizable force fields.^{42–44} Yet, the bare ECC overestimates the anionic surface affinity, an effect attributed to the abrupt change in the electronic part of the relative permittivity across the interface.³⁹ Moreover, the experimentally observed linear increase in the surface tension with respect to ionic concentration is not always recovered.⁴⁰ ECC models can also be applied to liquid–solid interfaces by rescaling the surface charges consistently with those of the electrolyte.⁴¹

A crucial test of the force field performance at interfaces is to compare its prediction for the surface tension with experimental results.^{30,39,40,45–52} With that regard, previous work has shown that the standard truncation of the Lennard-Jones (LJ) interaction potential can lead to large quantitative differences in the surface tension,⁵³ or even to qualitatively different behaviors of liquids at interfaces.^{47,54–58} Analytical tail corrections are commonly used for the surface tension,⁵⁰ but their implementation can be complex—especially for electrolyte solutions, and there is no guarantee that the structure and dynamics of the interface are correctly predicted by truncated potentials. Alternatively, methods commonly used to compute untruncated Coulomb interactions by calculating the long-range part of the interaction in the Fourier space⁵⁹ can also be applied to LJ interactions.^{48,60} In particular, these approaches successfully predict liquid–vapor surface tension, without requiring *a posteriori* corrections.^{48,60}

In that context, here, we will sequentially investigate two important issues for the description of aqueous electrolytes at the liquid–vapor interface, focusing on sodium chloride. First, we will explore the impact of LJ potential truncation on the liquid–vapor surface tension and show the interest of using a long-range solver for LJ interactions. We will then use such a solver to explore the impact of charge rescaling and identify the best choices to accurately describe the interfacial structure and surface tension of aqueous electrolytes.

II. SYSTEMS AND METHODS

We will use the ECCR model by Benavides *et al.*,³⁰ referred to as the Madrid model from the authors group’s location. This model is based on TIP4P/2005 water; the charge rescaling factor of 0.85 is closer to the value suggested by the long-range argument (0.86) than by the local argument (0.75).

We simulated a liquid film (along the x – y plane) illustrated in Fig. 1, composed of 3500 water molecules. The initial systems

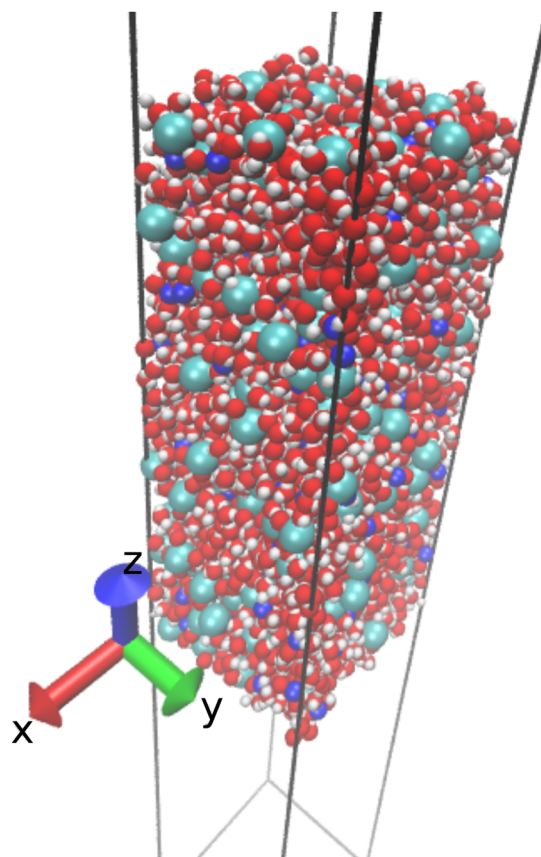


FIG. 1. Snapshot of a typical system: 3500 water molecules, 128 Cl^- ions, and 128 Na^+ ions, corresponding to a 1.6 mol/L system. The box size is $34 \times 34 \times 300 \text{ \AA}^3$, and the system extension in the z axis is around 90 \AA . Periodic boundary conditions are used in the three directions.

were built by using Moltemplate,⁶¹ and we used LAMMPS⁶² to run the simulations. The tested NaCl concentrations were 0.1 mol/L, 0.8 mol/L, 1.6 mol/L, 3.2 mol/L, and 4.2 mol/L. The total box size was $34.5 \times 34.5 \times 300 \text{ \AA}^3$, and the extension of the liquid phase in the z direction was about 90 \AA . Periodic boundary conditions were used along the three directions. The vacuum gap in the z direction was large enough to effectively remove interactions between the system and its periodic images in the z direction. These simulation box values have been widely used in the literature and have been shown to be sufficient to prevent finite size effects.^{47,63} We also tested finite size effects, as detailed in the [supplementary material](#). We integrated the equations of motion using the velocity-Verlet algorithm, with a time step of 2 fs. Long-range Coulombic interactions were treated with the particle–particle–particle–mesh (PPPM) method, a point-grid based Ewald method. Water molecules were held rigid using the SHAKE algorithm.

The system was equilibrated during ca. 3 ns, and the production run lasted for 100 ns. We calculated the surface tension γ from the difference of normal and tangential pressures, as detailed in the

supplementary material,

$$\gamma = \frac{L_z}{2} \left[p_z - \frac{1}{2} (p_x + p_y) \right], \quad (1)$$

where p_i is the average pressure along direction $i = x, y, z$ and L_z is the total box size along the z direction normal to the two interfaces. Experimentally, the surface tension increases linearly with respect to the ionic bulk concentration; the surface tension gain between 0.1 mol/L and 4.2 mol/L is around 7 mN/m for NaCl at room temperature.^{64,65}

III. EFFECT OF LONG-RANGE DISPERSION INTERACTIONS

As discussed in the Introduction, the standard procedure of truncating LJ interactions at a distance of ca. 1 nm, and possibly applying analytical tail corrections, has been challenged recently for heterogeneous systems.^{47,53–55,58} Therefore, we have tested here the impact of the truncation procedure. First, we have computed the surface tension of pure SPC/E and TIP4P/2005 water using various cutoffs (note that we used a simple cutoff scheme without any smoothing) and an Ewald based method—PPPM—presented in Refs. 48 and 60—to treat the LJ interaction. As detailed in the supplementary material, for truncated LJ interactions, the surface tension seems to converge at a high cutoff value. For pure water, the interfacial density profile is well approximated by an hyperbolic tangent shape, for which analytical tail corrections can be derived,^{66,67} providing satisfying results since the corrected surface tension reaches a plateau. For both SPC/E and TIP4P/2005 water, using the PPPM method fixes the LJ cutoff dependence. Moreover, for the pure water system, results obtained using PPPM and using cutoffs with tail corrections matched quantitatively. Still, the surface tensions obtained with the PPPM method are ca. 2 mN/m larger than the ones obtained using the largest cutoff (17 Å) without tail correction. This highlights the fact that the long-range part of the LJ potential—naturally taken into account through the PPPM method—has a significant impact, and even a large cutoff misses some relevant interaction for this heterogeneous system.

We then tested the effect of the long-range part of dispersion interactions in the presence of salt, by comparing the results obtained with the cutoff and PPPM methods, using the Madrid model of NaCl in water. Note that for an aqueous electrolyte solution, no simple tail correction can be written due to the complex ion distribution at the interface so that here we only considered the raw simulation results. At low salt concentration, the surface tension obtained with the cutoff method is smaller than the one using the PPPM method, see Fig. 2. This is consistent with the results obtained for pure water (see Fig. 1 of the supplementary material). As shown by the force field developers,³⁰ the surface tension increases smoothly with the salt concentration, in contrast with previous results obtained with another ECC model.⁴⁰ Surprisingly, when the salt concentration increases, the increase in the surface tension is higher with the cutoff method than with the PPPM method, see Fig. 2. Importantly, this effect could bias comparisons of the surface tension dependency on the salt concentration with experiments, which are commonly used as a test of the quality of aqueous electrolyte force fields. Here, for instance, cutoff simulations

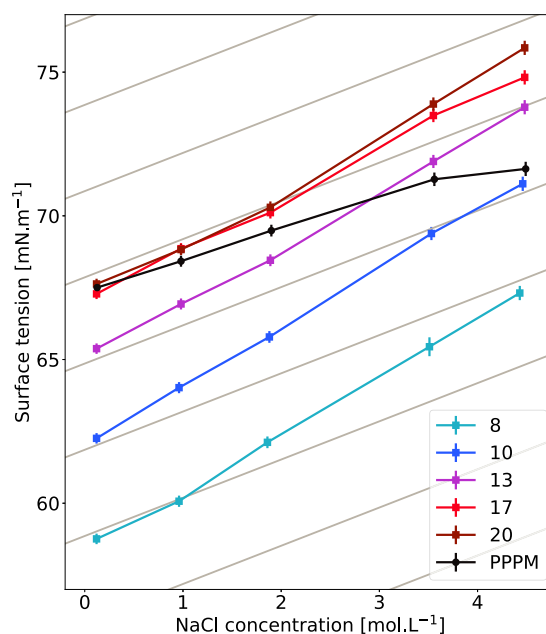


FIG. 2. Surface tension of the Madrid model of aqueous NaCl as a function of NaCl concentration, using truncated LJ interactions with different cutoffs (squares), or untruncated LJ interactions with the PPPM method (black circles). Since no analytical correction is used, the surface tension for pure water increases with an increase in cutoff. The error bars correspond to a 95% confidence level (see the supplementary material for more details). For comparison, the gray tilted line array indicates the experimental gain.⁶⁴

predict higher increases in the surface tension with respect to experiments, while PPPM predicts a lower one so that the model could be validated or not depending on how long-range LJ interactions are treated. The PPPM method has the advantage to be consistent for any system and does not require any post-processing treatment. Therefore, this approach will be used in the following.

IV. EFFECT OF CHARGE RESCALING

A good starting point to explore the effect of charge rescaling at an interface is to fix the LJ parameters (here, we are using those of the Madrid model) and modify only the charges at a given concentration, 3.2 mol/L. The resulting surface tensions, surface excess (SE), and density profiles are shown in Fig. 3, which highlights the dramatic impact of ionic charge. For a $\pm e$ charge, Cl^- and Na^+ are identically depleted from the interface and fully solvated [see the bottom part of Fig. 3(b)]. These observations are consistent with other non-polarizable MD simulations using fully charged ions.^{68,69} When the charge is decreased, the ions increasingly adsorb at the interface, with adsorption peaks growing and moving toward the surface. The ions also organize in a “double layer,” where the Cl^- adsorption peak is closer to the surface than the Na^+ peak. This ionic double layer is an expected feature of the NaCl water–air system, which is retrieved using polarizable classical MD.^{42–44,70}

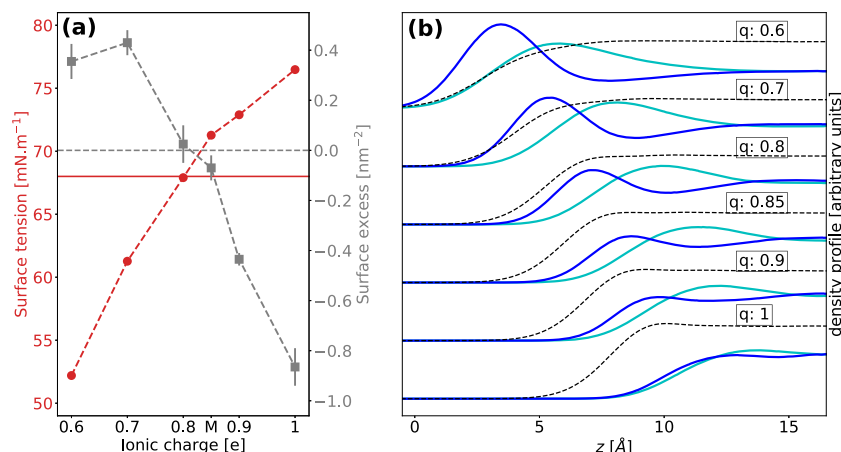


FIG. 3. Effect of ionic charge rescaling on the surface tension, surface excess, and density profiles of a 3.2 mol/L NaCl solution with Madrid's VdW parameters and the TIP4P/2005 water model. (a) Left axis and red circles: surface tension vs ionic charge; the red horizontal full line represents the computed surface tension of pure water, 68 mN/m; according to the experimental surface tension gain as a function of concentration, the expected value for the surface tension at 3.2 mol/L is 72 mN/m–73 mN/m; note that the error bars are within the symbols. Right axis and gray squares: surface excess (SE) vs ionic charge; the gray dashed line is the zero SE value; experiments indicate a negative SE since the surface tension gain is positive with respect to the ionic concentration, see Eq. (2); “M” on the abscissa stands for the original Madrid parameters: an ionic charge of ± 0.85 . (b) Density profiles of water (black dashed lines), Cl⁻ (blue dark lines), and Na⁺ (cyan light lines) for different ionic charges. Water density profiles have been normalized to appear on the same scale as the ionic density profiles.

In order to quantify this structural behavior, we have computed the surface excess (SE), denoted as Γ_s , for the different charge rescaling (see the [supplementary material](#) for more details), which is plotted in Fig. 3(a). The SE is related to the evolution of the surface tension γ with respect to the solute activity a_s through Gibbs' thermodynamic theory of interfaces,

$$\Gamma_s = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln a_s} \right)_T, \quad (2)$$

with R being the gas constant and T being the temperature. For NaCl, γ increases with the salt concentration, so that Γ_s is negative, with an experimental value on the order of -0.5 nm^{-2} , see Ref. 43.

Classical polarizable models^{39,43,71} provide correct SE values, while standard non-polarizable ones predict too negative values.⁴³ In Ref. 39, an ECC approach with a $\pm 0.75e$ ionic charge (chosen based on short-range arguments) predicts a positive SE of 0.06 nm^{-2} for a concentration of ca. 0.8 mol/L and thus a negative surface tension gain with respect to the ionic concentration. Our results are fully consistent with the previous ones: for an ionic charge of $0.6 e$ – $0.8 e$, the SE is positive and the surface tension gain is negative, while for a $\pm e$ charge, the SE is very negative and leads to the highest surface tension gain.

The original Madrid force field, with an ionic charge of $\pm 0.85 e$, predicts values very close to the experimental ones. Of course, one can attribute this success to the additional work done for the vdW parameterization since the Madrid model belongs to the ECCR class. As pointed out in Ref. 41, rescaling the vdW parameters helps obtaining better results also at interfaces. However, for these kind of systems, we would like to argue that the rescaling factor should be chosen based on the long-range argument (i.e., correcting long-range Coulomb interactions), as is the case for the Madrid model, and not on the short-range one. To that aim, we will use a simple

mean field model inspired by Ref. 69. Ionic density profiles $\rho_{\pm}(z)$ at the liquid–vapor interface follow a Boltzmann distribution: $\rho_{\pm}(z) = \rho_0 \exp\{-\beta U_{\pm}(z)\}$, where ρ_0 is the bulk ionic density, $\beta = 1/(k_B T)$, and $U_{\pm}(z)$ is the potential felt by the ion. This potential can be decomposed as follows: $U_{\pm}(z) = \pm eV(z) + U_{\pm}^{\text{solvation}}(z) + U_{\pm}^{\text{image}}(z)$, where $V(z)$ is the electrostatic potential, $U_{\pm}^{\text{solvation}}(z)$ represents the interaction with the solvent, and $U_{\pm}^{\text{image}}(z)$ is an image charge potential acting on ions near the dielectric interface located at $z = 0$, as described by Onsager–Samaras theory,⁷²

$$U_{\pm}^{\text{image}}(z) = \left(\frac{\epsilon_r - 1}{\epsilon_r + 1} \right) \frac{q^2 \exp[-2z/\lambda_D]}{16\pi\epsilon_0\epsilon_r z}, \quad (3)$$

with ϵ_0 being the vacuum permittivity, ϵ_r being the solvent relative permittivity, q being the ionic charge, and $\lambda_D = \sqrt{\epsilon_0\epsilon_r k_B T / (2q^2\rho_0)}$ being the Debye length. Here, it is important to note that the solvent relative permittivity involved is the bulk value far from the interface. This potential identically pushes both cations and anions inside water. From Eq. (3), it is clear that choosing the rescaled ionic charge to correct for the permittivity of the water model in bulk, i.e., $q = e\sqrt{\epsilon_r/\epsilon_r^{\text{exp}}}$, will also adequately correct the image potential. Indeed, because water (and water models) have a very large ϵ_r , the error induced by the water model in the prefactor $(\epsilon_r - 1)/(\epsilon_r + 1)$ —not corrected by the rescaling procedure—is minimal. For instance, for TIP4P/2005 water at room temperature, $\epsilon_r \approx 60$, while $\epsilon_r^{\text{exp}} \approx 80$, corresponding to an error in the prefactor of around 1% only. This explains why a rescaling of $\pm 0.85 e$ for the TIP4P/2005 water model provides a structure—and, in particular, a SE—close to the expected one at the interface, while this rescaling has been originally designed for bulk systems. In contrast, when no rescaling is applied, the image potential is too strong, which leads to very negative SE, and with a

rescaling of $\pm 0.75 e$, the image potential is too weak, letting the ions go too far toward the vapor side—leading to too positive SE.

Beyond the image potential, the detailed ion distribution will be controlled by the other terms in the potential felt by the ions, $\pm eV(z) + U_{\pm}^{\text{solvation}}(z)$. With that regard, our simulations show that using an ECCR approach, as done for the Madrid force field, captures correctly the distribution predicted by polarized force fields—and, in particular, the formation of a double layer. To understand this result, one should note that, in practice, charges and LJ interaction parameters in ECCR models are tuned empirically to accurately describe the local environment of ions, i.e., first neighbor ion–ion and ion–water interactions. While the parameterization is performed in bulk, one can expect that the first neighbor interactions should also be fairly described at interfaces, even though the ion hydration shells are different.

V. CONCLUSIONS

We have shown that similar surface tensions are found using the cutoff and PPPM methods for pure water and dilute salts, reaching quantitative agreement when adding tail corrections. In contrast, at high salt concentration, where no simple tail correction can be written due to the complex ion distribution at the interface, the cutoff method leads to a larger surface tension increase than the one obtained using the PPPM method. Hence, we recommend giving special attention to this aspect for heterogeneous systems because it may lead to a qualitative difference in the interfacial structure, which cannot be corrected by any post-simulation routine, and because it may bias comparison of force field predictions with experiments. Currently, many MD softwares provide a long-range implementation of dispersion interactions, which does not involve a large computational cost or can even speed up the calculation.⁶⁰ Therefore, we suggest using an Ewald based method for the long-range dispersion term when dealing with electrolyte solutions at liquid–gas interfaces.

Using such a long-range solver, we reconsidered the impact of the ionic charge rescaling procedure implemented in recent non-polarizable force fields of aqueous electrolytes on the surface tension and liquid–vapor interfacial structure. With an ECCR force field, we obtained a linear gain of surface tension with respect to the ionic concentration, close to the experimental value. We then showed that the charge rescaling factor has a dramatic impact on the local structure in this saline water interfacial system. In particular, we found that a charge rescaling based on short-range arguments ($q = \pm 0.75 e$) leads to a positive surface excess, while a negative value is expected. We explained that the long-range-motivated charge rescaling factor ($q = \pm 0.85 e$) should be preferred for heterogeneous systems since this correction also applies to the image charge potential acting on the ions at interfaces with a dielectric contrast. Finally, we showed the rescaling of LJ parameters in the ECCR approach, while originally tuned to capture local first neighbor ion–water and ion–ion interactions in bulk, and also fairly predicted the formation of an ionic double layer, consistently with polarizable force field results.

We hope that more ECCR models with a charge rescaling factor based on the long-range argument will be established: even if extra work is needed regarding the van der Waals parameters, significant gains for both homogeneous and heterogeneous systems can be expected compared to a usual non-polarizable force field

and at a computational cost lower than the one of polarizable force fields. With that regard, it would be quite interesting to explore in future work how the results obtained here for a NaCl solution would extend to other salts³⁵ in order to further assess the importance of long-range LJ interactions and the applicability of ECCR models to interfaces.

SUPPLEMENTAL MATERIAL

See the [supplementary material](#) for computation of the surface tension of pure water with truncated and untruncated Lennard-Jones interactions, box size convergence, surface tension calculation, surface dividing altitude, and surface excess measurement.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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