

Systematic comparison of force fields for microscopic simulations of NaCl in aqueous solutions: Diffusion and structural properties

MICHAEL PATRA AND MIKKO KARTTUNEN

Biophysics and Statistical Mechanics Group, Laboratory for Computational Engineering, Helsinki University of Technology, P. O. Box 9203, FIN-02015 HUT, Finland

<http://www.softsimu.org/>

We compare different force fields that are widely used (Gromacs, Charmm-22/x-Plor, Charmm-27, Amber-1999, OPLS-AA) in biophysical simulations containing aqueous NaCl. The parameters describing the Lennard-Jones interactions among the Na and Cl ions vary between these force fields. We show that the uncertainties in the microscopic parameters of, in particular, sodium and, to a lesser extent, chloride translate into large differences in the computed radial-distribution functions. In addition, the results also depend on the water model. We have used the SPC, SPC/E, TIP3P and TIP4P models.

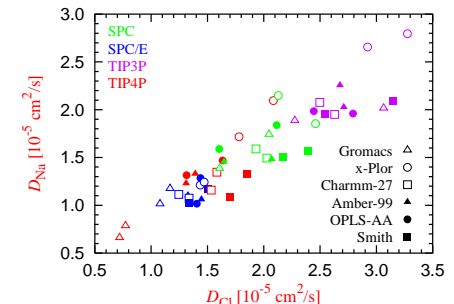
Force fields differ by the Lennard-Jones parameters assigned to the atoms in order to model van der Waals interaction. (There is much less freedom in assigning the particle charges.) There exists a large body of experimental and theoretical knowledge on the properties of water, and differences between water models are comparably small (see table on the right).

For (aqueous) chloride, the differences in the Lennard-Jones parameters are significant, up to 10% for the radius and up to 50% for the depth of the attractive well of the Lennard-Jones interaction, reflecting the lack of high quality experimental input data. For (aqueous) sodium, there seems to be virtually no consensus on its properties.

For each combination of ionic force-field and water model, three simulations with different thermostats were done over a time of 2 ns. (The systems need slightly less than 0.5 ns to equilibrate.) The target temperature was set to 298 K and particle-mesh Ewald (PME) was used for long-range electrostatics. We used the program package Gromacs.

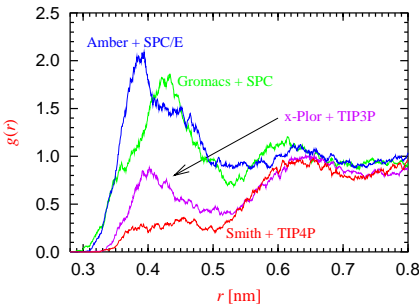
| Gromacs | | | | | x-Plor / Charmm-22 | | | | | | |
|----------|---------------|--------------------------------|-------------------|----------------|--------------------|---------------|--------------------------------|-------------------|----------------|--------|--------|
| Atom | σ (nm) | ϵ_2 (kJ mol $^{-1}$) | ϵ_1 (nm) | ϵ (Å) | Atom | σ (nm) | ϵ_2 (kJ mol $^{-1}$) | ϵ_1 (nm) | ϵ (Å) | | |
| Cl | 0.364 | 1.960 | 10 $^{-4}$ | 0.1094 | 4.680 | Cl | 0.362 | 1.936 | 10 $^{-4}$ | 0.1090 | 4.254 |
| Na | 0.289 | 1.014 | 10 $^{-4}$ | 0.0148 | 2.572 | Na | 0.284 | 1.014 | 10 $^{-4}$ | 0.0100 | 2.727 |
| O (S) | 0.310 | 2.472 | 10 $^{-4}$ | 0.0153 | 3.1655 | O (S) | 0.311 | 2.471 | 10 $^{-4}$ | 0.0151 | 3.1655 |
| O (I) | 0.289 | 2.482 | 10 $^{-4}$ | 0.0159 | 3.1508 | O (I) | 0.291 | 2.493 | 10 $^{-4}$ | 0.0151 | 3.1506 |
| O (H) | 0.289 | 2.554 | 10 $^{-4}$ | 0.0159 | 3.1549 | O (H) | 0.289 | 2.554 | 10 $^{-4}$ | 0.0159 | 3.1549 |
| Cl-Su | 0.364 | 1.960 | 10 $^{-4}$ | 0.0106 | 3.344 | Cl-Su | 0.364 | 1.960 | 10 $^{-4}$ | 0.0106 | 3.344 |
| Cl-O (S) | 0.364 | 1.960 | 10 $^{-4}$ | 0.0106 | 3.344 | Cl-O (S) | 0.364 | 1.960 | 10 $^{-4}$ | 0.0106 | 3.344 |
| Na-O (S) | 0.289 | 1.014 | 10 $^{-4}$ | 0.0106 | 2.851 | Na-O (S) | 0.289 | 1.014 | 10 $^{-4}$ | 0.0106 | 2.851 |
| Cl-O (I) | 0.289 | 1.014 | 10 $^{-4}$ | 0.0106 | 2.851 | Cl-O (I) | 0.289 | 1.014 | 10 $^{-4}$ | 0.0106 | 2.851 |
| Na-O (I) | 0.289 | 1.014 | 10 $^{-4}$ | 0.0106 | 2.851 | Na-O (I) | 0.289 | 1.014 | 10 $^{-4}$ | 0.0106 | 2.851 |
| Cl-O (H) | 0.289 | 1.014 | 10 $^{-4}$ | 0.0106 | 2.851 | Cl-O (H) | 0.289 | 1.014 | 10 $^{-4}$ | 0.0106 | 2.851 |
| Na-O (H) | 0.289 | 1.014 | 10 $^{-4}$ | 0.0106 | 2.851 | Na-O (H) | 0.289 | 1.014 | 10 $^{-4}$ | 0.0106 | 2.851 |

The differences between different ionic force fields and water models are visible already in the computed diffusion coefficients. (In the following, we mark the ionic force field by the shape of the symbol, and the water model by the colour).



The diffusion behaviour is dominated, as expected, by the water model. Nonetheless, there also is some influence of the ionic force field.

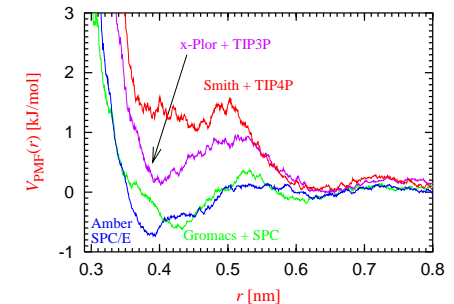
The radial-distribution function $g(r)$ for different force field combinations differ strongly. The figure on the left shows a few typical examples from our collection of computed radial-distribution functions.



$$g(r) = \exp[-\beta V_{\text{PMF}}(r)],$$

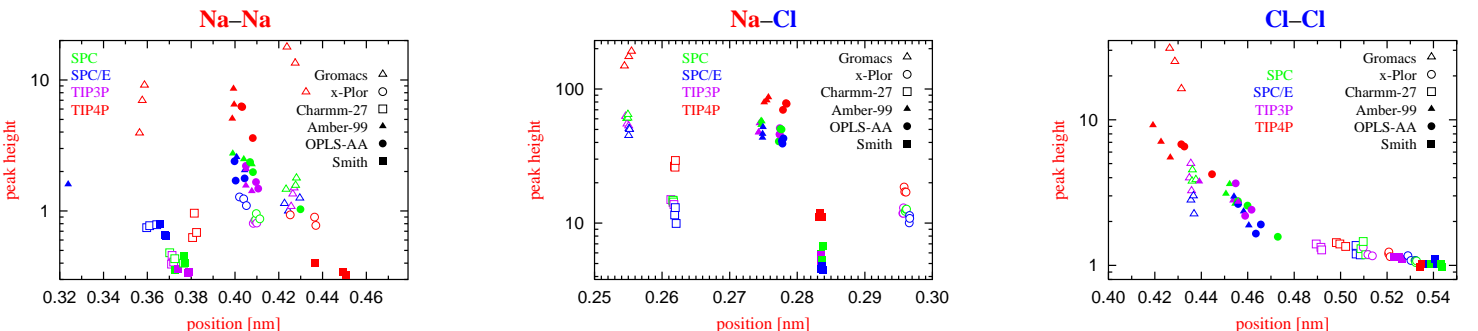
shown in the figure on the right.

Although not immediately visible in the formula, the potential of mean force includes the direct interaction between two particles at fixed positions, and additionally the contribution from having a third particle at a fixed position provided particles 1 and 2 are already fixed. In other words, the potential of mean force includes first order corrections to the pure pairwise potential.



If higher order corrections are included, a different kind of potential is found, termed effective potential. It, too, can be computed from the radial-distribution functions (in a process known as inverse Monte Carlo simulation). Since the qualitative properties of effective potentials and the potentials of mean force are known to be similar, the strong dependence of the potential of mean force on the force field is almost certainly reflected in effective potentials.

To show how much the results for different ionic force fields and water models differ, we have determined the peaks of the radial-distribution function (i. e., their positions and their heights). In the following, we mark the ionic force field by the shape of the symbol, and the water model by the colour.



Please note the following: • The positions of the peaks in the Na-Cl radial-distribution function seem to depend only on the ionic force field, and not on the water model. For the Na-Na and Cl-Cl curves, both choices are important. • A peak height of less than 1 means that the particles are effectively mutually repelling while a peak height of more than 1 means that there is an effectively attractive component. The Na-Cl curve is, as expected, always attractive whereas for the Na-Na and Cl-Cl curves it depends on the ionic force field and on the water model.