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Properties of the polarizable MARTINI water model: A comparative study for aqueous electrolyte solutions

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ABSTRACT

The coarse-grained MARTINI approach is nowadays used for the simulation of charged systems. A robust and valid water model to reproduce electrostatic screening effects in addition to hydration properties is therefore of crucial importance. We study the properties of the polarizable MARTINI water model in the presence of varying sodium chloride concentrations to test the validity of the approach. The numerical findings are compared to results that are obtained by a Kirkwood–Buff based atomistic force field in combination with the SPC/E water model. An acceptable agreement between both approaches and experimental results is observed for dynamic properties like ionic conductivities, diffusion coefficients and the dielectric constants when a rescaling approach is used. Slighter deviations can be observed for the mass density as well as for the local surrounding of the ions which can be related to the spherical geometry of the polarizable MARTINI water beads. We highlight agreements and differences and discuss the corresponding consequences.

1. Introduction

Over the last years, the application of coarse-grained MARTINI models [1,2,3,4] for the simulation of various systems has emerged rapidly. While originally intended to study the behavior of lipid bilayers [1], recent developments also include molecular topologies and force fields for DNA, proteins and polymers [3,4,5,6,7]. The success of the MARTINI force field becomes reasonable with regard to the broad range of applicability and the significant acceleration of simulation time by the introduction of an efficient coarse-graining scheme [4]. In contrast to simple bead-spring models (refs. [8,9,10] and references therein), which often neglect atomistic details, the MARTINI force field follows a top-bottom strategy. Herewith, polar, apolar, neutral and charged species are introduced and the interaction strength is parameterized according to partitioning coefficients [2].

With regard to the simulation of biological systems, it has been discussed that the properties of aqueous solutions have important consequences for most chemical processes and the solvation of macromolecules [11]. Even for coarse-grained force fields and specifically the MARTINI approach, a reliable description of the solvent is therefore of crucial importance. With regard to this point, the originally introduced MARTINI water approach models a group of four water molecules by one coarse-grained uncharged bead and has been mainly introduced to reproduce hydrophilic and hydrophobic effects [2]. In combination with the desire to use the MARTINI force field for DNA, proteins and polymer/polyelectrolyte solutions which are often highly charged, the need for a novel water model which better reflects electrostatic interactions has grown constantly. Specific features of this model should at the best include the inherent screening of electrostatic interactions which has been artificially achieved in the original unpolarizable MARTINI water model by the introduction of a short-range electrostatic interaction function [1,2,4]. The development of the novel polarizable MARTINI water approach has been finally accomplished by Yesylevskyy et al. [12] where the details of the model rely on properties introduced for polarizable Drude particles. The underlying strategy is therefore closely related to the inclusion of polarization effects in classical atomistic force fields [13,14].

In line with the MARTINI water approach, the last years have also seen an enormous increase in the development of additional polarizable and efficient coarse-grained water models (see refs. [15,16] for an overview). Unfortunately, like for most coarse-grained strategies, the applicability of these models is limited to specific classes of systems. In contrast, recent studies with the polarizable MARTINI water model include ion permeation through pores [12], polymers in an aqueous solution [6] and more refined studies of pore formation in lipid bilayers [17].

The aim of this article is to test the validity of the polarizable MARTINI water approach for charged MARTINI coarse-grained systems. Therefore we have simulated broad concentration ranges of aqueous sodium chloride solutions to study water characteristics like the dielectric constant, radial distribution functions and the diffusion behavior. Our results indicate that the polarizable water model reproduces most of these crucial properties in acceptable agreement with atomistic force field results and experimental findings when a rescaling approach is used. Stronger deviations can be observed for properties which are

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related to the structural order of the solution. We highlight differences as well as agreements and discuss the resulting consequences. In addition, we also studied the influence of full electrostatic interactions via the PME method in contrast to the originally proposed shift function approach which introduces a smooth cutoff for electrostatic interactions.

The paper is organized as follows. All simulation details are discussed in the next section and the results are presented in Section 3. We conclude and summarize in the last section.

2. Simulation details

2.1. Coarse-grained MARTINI molecular dynamics simulations

For the details of the polarizable MARTINI water model, we refer the reader to the original publication [12]. Here we shall only mention that a polarizable MARTINI water bead consists of three particles (a central uncharged particle W and two oppositely charged particles WP and WM). The model strongly relies on properties that have been introduced for polarizable classical all-atom force fields in terms of Drude particles [13,14].

All simulations have been performed by using the GROMACS 4.6.1 software package [18,19,20]. A pre-equilibrated polarizable MARTINI water system can be downloaded at the web page of the project [21]. It consists of a simulation box with the dimensions $(5.22371 \times 8.24551 \times 4.85631)\ \mathrm{nm}^3$ in which 1824 polarizable MARTINI water beads have been inserted. In order to model electrolyte solutions with different concentrations, we have removed water molecules and replaced them by the corresponding equal number of sodium and chloride ion beads with the force field parameters given in refs. [2,4]. The number of $\mathrm{Na}^+\mathrm{Cl}^-$ ion pairs varies between 0 and 360, which corresponds to a maximum concentration of 3.24 mol/L. The temperature in all simulations was $T = 298$ K and periodic boundary conditions were applied in all directions. After energy minimization, first a run of 20 ns under NVT ensemble conditions was performed followed by a NPT ensemble run of 40 ns. The time step was 10 fs for both simulation runs. After equilibration, a production run of 900 ns (NPT ensemble) was performed with a time step of 20 fs. It has to be noticed that for too large time steps in MARTINI simulations several artifacts like temperature drifts or energy fluctuations can be observed [22,23]. However, for our chosen parameter set it has been shown that reasonable results can be obtained [24]. In the NVT equilibration, temperature was controlled by a Berendsen thermostat [25] with a characteristic time interval of $\tau = 1$ ps. In the NPT simulations, the temperature coupling was achieved by a velocity rescaling technique [26] and the pressure was controlled by a Berendsen barostat [25] with the characteristic time interval $\tau = 3$ ps, a reference pressure of 1 bar and a compressibility of $3 \times 10^{-5}\ \mathrm{bar}^{-1}$. The used thermostats and barostats have been chosen with regard to the original parameterization scheme [12,21]. The neighbor lists had a range of 1.2 nm and were updated each 10 time steps. The cut-off radius for Lennard–Jones interactions was 1.2 nm and the corresponding function was smoothly shifted to zero after 0.9 nm. For the evaluation of the electrostatic interactions, the PME method [27] as well as the originally introduced shift function approach [12] were used. In terms of the shift function method, all electrostatic interactions were shifted to zero for distances larger than the cut-off radius of 1.2 nm. The direct space cut-off radius of the PME method was 1.2 nm and the spacing of the Fourier grid was 0.12 nm. The background dielectric constant was $\epsilon_B = 2.5$ for both the shift function and the PME method as it was also originally proposed [12].

It should be noted, that the introduction of an efficient phenomenological 4:1 mapping scheme for the MARTINI approach has been discussed in the original literature [2,12]. The mapping scheme can be motivated with regard to the ratio of charged to dipolar particles, e.g. ions and the surrounding water molecules in the first hydration shell. Indeed, this rescaling approach is of crucial importance for dynamic properties like diffusion constants as well as ionic conductivities. Nevertheless, a more detailed derivation of this mapping scheme is missing. In the following, we will use scaled effective concentrations for the study of all dynamic properties.

2.2. Atomistic molecular dynamics simulations

For the atomistic simulation of a NaCl solution, we have used the parameters of the Kirkwood–Buff force field (KBFF) introduced in ref. [28] which can be downloaded at the corresponding web page [29] in combination with the SPC/E water model [30]. The initial simulation box had the same dimensions as in the MARTINI simulations and identical salt concentrations were used. The temperature in all simulations was $T = 298$ K and periodic boundary conditions were applied in all directions. After energy minimization, first a run of 100 ps under NVT ensemble conditions with a time step of 1 fs was performed followed by a NPT simulation of 20 ns. Temperature coupling in the NPT simulations was achieved by a Nosé–Hoover thermostat with a characteristic time interval of $\tau = 0.5$ ps. The pressure was controlled by a Parrinello–Rahman barostat with a characteristic time interval $\tau = 4$ ps, a reference pressure of 1 bar and a compressibility of $4.5 \times 10^{-5}\ \mathrm{bar}^{-1}$. The reason for choosing different thermostats and barostats as compared with the MARTINI simulations can be motivated with regard to a more accurate modeling of the thermodynamic NPT ensemble. The neighbor lists had a range of 1.2 nm and were updated each 5 time steps. The cut-off radius for the Lennard–Jones interactions was 1.2 nm. The PME method [27] was used with a direct space cut-off radius of 1.2 nm for the evaluation of the electrostatic interactions. The spacing of the Fourier grid was 0.12 nm.

All non-bonded parameters for the species considered in this study are presented in Table 1. It has to be noted that the diameters of the ions do not resemble the real size of the atoms [28]. In addition, the identical diameter ($\sigma = 0.47$ nm) of MARTINI beads, regardless of being water or ion particles is evident. Hence, it is therefore inherently questionable if the correct hydration behavior in addition to accurate ion pairing properties is reproduced by the MARTINI approach. Noteworthy, it has been discussed in ref. [2], that the first hydration shell in combination with the central ion is modeled by one coarse-grained MARTINI bead which can be interpreted as an explanation for the identical cation and anion diameters. Although being a rough approximation, it was shown that the resulting coordination numbers are in good agreement with atomistic models at distances larger than 0.6 nm [1].

3. Simulation results

In the following section we present the numerical results for the polarizable MARTINI water model with the PME method in contrast to the shift function approach and the corresponding values for the Kirkwood–Buff based atomistic force fields. With regard to the presented structural details of the solution, we specifically focus on salt concentrations of

Table 1

Non-bonded Lennard–Jones 6–12 and partial charge parameters for the considered species in the atomistic model (KBFF), the SPC/E water model (SPC/E), the MARTINI approach (MARTINI) and the polarizable MARTINI water model (WATER). The Lennard–Jones parameters ϵ are presented for interactions between like-wise atoms or beads. More details and additional information on the MARTINI force field can be found in ref. [2].

Species	Model	ϵ [kJ/mol]	σ [kJ/mol]	$q[\lvert e \rvert]$	Reference
Na^+	KBFF	0.3200	0.2450	1.0000	28
Cl^-	KBFF	0.4700	0.4400	−1.0000	28
O	SPC/E	0.6506	0.3166	−0.8476	30
H	SPC/E	0.0000	0.0000	0.4238	30
Na^+	MARTINI	5.0000	0.4700	1.0000	2
Cl^-	MARTINI	5.0000	0.4700	−1.0000	2
WP	WATER	0.0000	0.0000	0.4600	11
WM	WATER	0.0000	0.0000	−0.4600	11
W	WATER	4.0000	0.4700	0.0000	11