

Benchmarking polarizable molecular dynamics simulations of aqueous sodium hydroxide by diffraction measurements

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Abstract

Results from molecular dynamics simulations of aqueous hydroxide of varying concentrations have been compared with experimental structural data. First, the polarizable POL3 model was verified against neutron scattering using a Reverse Monte Carlo fitting procedure. It was found to be competitive with other simple water models and well suited for combining with hydroxide ions. Second, a set of four polarizable models of OH⁻ were developed by fitting against accurate ab initio calculations for small hydroxide-water clusters. All these models were found to provide results similar to each other, robustly agreeing with structural data from X-ray scattering. The present force field thus represents a significant improvement over

previously tested non-polarizable potentials. Although it cannot in principle capture proton hopping and can only approximately describe the charge delocalization within the immediate solvent shell around OH^- it provides structural data which are almost entirely consistent with data obtained from scattering experiments.

Introduction

A key element in the validation of computer simulation results is comparison with experimental data. Structural quantities, which are typically the most suitable ones for the purpose, are frequently calculated from molecular dynamics (MD) and Monte Carlo (MC) simulations and then contrasted to their experimental counterparts [1]. It is the radial distribution function (*rdf* or $g(r)$) that is most often used for comparison, even though the *rdf* is not a direct result of diffraction experiments. This is the reason why it is advisable to consider also the primary experimental outcome, the total scattering structure factor (*tssf* or $F(Q)$), wherever possible. A scheme based on the Reverse Monte Carlo (RMC) procedure [2] provides a bridge between diffraction experiments and interaction potential models [3].

A common element of simulation of aqueous solutions is the use of a particular potential model of water, applicability of which should be established. A polarizable 3-site POL3 potential [4] has been employed in our previous studies of aqueous interfaces as a reasonable compromise between simplicity and accuracy and it is this model that is being scrutinized from the structural point of view in the present study. Pure water, being the simplest system considered in this work, can be investigated in great detail. Thus, the primary source of experimental information on the structure, i.e., the *tssf*, is used for validation purposes in a procedure [3], which offers a direct consistency check between experimental data and the potential model. In the next step, results from experiment and simulations are compared for a more complex system – aqueous solution of NaOH [5]. Here, the most robust way of comparison as applied to pure water could not yet be applied although work toward realisation of such a scheme for NaOH solutions is underway. Therefore, here we restrict ourselves to comparisons at the level of *rdfs*.

The principal motivation behind the present study of NaOH_{aq} is the interfacial behavior of hydroxide anion, which has been a subject of a recent controversy [6-8]. Simulations, spectroscopic experiments, and surface tension measurements indicate no or at best weak surface affinity of OH^- [9-13]; in contrast results of zeta potential and titration measurements on air bubbles and oil droplets in water are interpreted in terms of a very strong surface adsorption of hydroxide [14-16]. While potentials employed in these simulations have been tested against *ab initio* calculations, here we compare directly to the experiment.

Methods

MD simulations

We developed and tested four different force fields for OH^- . All models had the same geometry with the O-H distance of 1 Å and polarizability of 2.1 Å³ placed at the oxygen atom [17]. The remaining parameters, presented in Table 1, were optimized against *ab initio* MP2/aug-cc-pVDZ interaction energies of OH^- with four most strongly interacting water molecules (for the employed local minimum geometry see Figure 1) calculated with the program package Gaussian03 [18]. The first force field model, which adopted a charge distribution from the natural population analysis, was taken from our previous paper [17] and is referred as M1. Next two models have modified Lennard-Jones terms on oxygen. The last model has additionally a modified charge distribution, and, consequently, the permanent dipole. Here, the partial charges were calculated using the RESP method after *ab initio* Hartree-Fock calculation in the 6-31g* basis via fitting the electrostatic potential at points selected according to the Merz-Singh-Kollman scheme. After matching the force field and *ab initio* interaction energies for the OH^- (H_2O)₄ cluster for all four models, these were then checked also for an optimal cluster of

hydroxide and three water molecules. The agreement with MP2/aug-cc-pVDZ was excellent for all models. Finally, for water we employed polarizable POL3 model [4].

All our MD simulations were performed using the program package Gromacs version 3.3.1 compiled in double precision [19]. A time step of 1 fs was used with a cutoff of 1.1 nm for non-bonded interactions. Long range electrostatic interactions were treated using the Particle Mesh Ewald (PME) method [20]. The systems were simulated in the NpT ensemble with Berendsen temperature and pressure coupling [21] set at 300 K and 1 atm. We modelled systems with four particular compositions - pure water and 1, 2.4, and 4.8 M solutions of NaOH, each containing about 700 water molecules and the corresponding number (for the particular concentration) of Na⁺ and OH⁻ ions.

Reverse Monte Carlo

In order to compare simulation results for the POL3 water model with experimental structural data we have applied a novel approach [3] which combines experimentally determined total scattering structure factor(s) and partial radial distribution functions from molecular dynamics simulations into a single structural model. Such particle configurations may be constructed by the RMC method [22-24]. We require agreement within experimental uncertainties with diffraction data and at the same time inquire how well the potential-based partial rdfs can be reproduced. In this way, it is possible to tell if (or which of) the simulated partial radial distribution functions are consistent with the experimental *tssf*s. Note that this approach, while also being more instructive, is easier to perform than combining *prdfs* from MD simulations to provide the *tssf*s. This is because the size of the simulation box is not important since no Fourier-transform is carried out and there is no difficulty with rigid water models, for

which approximations concerning the intra-molecular part would otherwise be necessary [25].

In the RMC calculations, 2000 flexible water molecules (i.e., 6000 atoms) were employed at the experimental atomic number density of 9.9 \AA^{-3} . According to the protocol described in Ref. [3], the experimental total scattering structure factor of heavy water [26], along with the three (O-O, O-H, and H-H) partial radial distribution functions from a molecular dynamics simulation of bulk POL3 water [4] were used as input data for RMC.

Very recently, a comparison, using a similar protocol, of several water potentials including the POL3 model has been performed by one of us [27]. In that work, the very same conditions for each potential model had to be used in order to facilitate unbiased comparison. As a result of such analysis, the POL3 model performed well in terms of the overall fit, nevertheless, consistency with the experimental data set was not optimal without weighting input *prdfs*. The level of consistency between diffraction experiments and the POL3 water model is improved in this study through systematic optimization of weights of the input data sets while keeping the experimental total scattering structure factor within experimental uncertainties and having the best possible fit to *prdfs* from the MD simulations. In order to find the most appropriate parameters, as well as the finest balance between experiment and the POL3 potential model (via the corresponding simulated *prdfs*), about ten RMC calculations had to be carried out, of which only the best one is reported here.

Experiments: structure factors of pure water

Since the *tssf* ($F(Q)$) has a central role in assessing the quality of the water potential, it is helpful to recall that (focusing here on results from neutron diffraction experiments) it is defined as [28]:

$$G(r) = \sum_{i,j=1}^n c_i c_j \bar{b}_i \bar{b}_j [g_{ij}(r) - 1] \quad (1a)$$

$$F(Q) = \rho_0 \int_0^{\infty} 4\pi r^2 G(r) \frac{\sin Qr}{Qr} dr \quad (1b)$$

In equations (1a) and (1b), c_i and b_i are the molar ratio and the scattering length of species i , $g_{ij}(r)$ are the *pdfs*, $G(r)$ is the total radial distribution function, ρ_0 is the number density and Q is the scattering variable (proportional to the scattering angle); indexes i and j run through nuclear species of the system.

The experimental input information, i.e., the *tssf* for pure heavy water (D₂O) at ambient conditions has been obtained from neutron diffraction experiments conducted at a pulsed neutron source (ISIS Facility, UK) [26]. The neutron scattering amplitudes (the so-called coherent scattering lengths, b) of the deuteron and the oxygen atom are 6.7 and 5.8 fm. Taking into account molar ratios of H and O, this yields the appropriate weighting factors of the O-O, O-H and H-H pair correlations of 0.09, 0.42, and 0.49. Neutron diffraction is a convenient tool for the present measurements since the scattering lengths are independent of Q (and of the scattering angle). Also, the above weighting factors are valid for both Q -space (*tssf*) and r -space (*rdf*) data.

Experiments: sodium hydroxide solutions

1.0, 2.5, and 4.8 M samples of aqueous NaOH were measured for direct comparison with the simulated systems. X-ray scattering measurements were performed at room temperature ($24 \pm 1^\circ\text{C}$), with a Philips X'Pert goniometer in a vertical Bragg-Brentano geometry with a

pyrographite monochromator in the scattered beam using MoK α radiation ($\lambda = 0.7107 \text{ \AA}$). The liquid sample holder had plane-parallel windows prepared from 75 μm thin foils of bi-oriented polypropylene. The scattering angle range of measurement spanned over $1.28^\circ \leq 2\Theta \leq 120^\circ$ corresponding to a range of $0.2 \text{ \AA}^{-1} \leq k \leq 15.3 \text{ \AA}^{-1}$ of the scattering variable $k = (4\pi/\lambda) \cdot \sin\Theta$. Over 100,000 counts were collected by a proportional detector at each of the 150 discrete angles selected in $\Delta k \approx 0.1 \text{ \AA}^{-1}$ steps, in several repeated runs (10,000 counts at each point). The measurement technique and data treatment were essentially the same as in our previous study [29].

Results

Water structure: experiment and simulation

The best results obtained by applying the RMC fitting scheme of Ref. [3] to the POL3 water potential are summarised in Figure 2. It follows from this figure that the consistency with experimental data is very good. In other words, using the POL3 water model it was possible to obtain a fit almost within the experimental error. Nevertheless, full consistency with neutron diffraction data on liquid D₂O (i.e., indistinguishable curves for experimental data and the fit) was not reached for small sections of *prdfs* of POL3 water. More precisely, it is the O-O *prdf*, which may be termed as entirely consistent with available diffraction data, while the O-H and H-H *prdfs* display small deviations. Furthermore, we note that attempts to further improve the quality of the fits to these functions lead to deterioration of the level of consistency with experimental data, which again indicates small inconsistencies between diffraction data and the potential model in question.

Sodium hydroxide solutions: computational results

The hydroxide oxygen (O) – water hydrogen (HW) *pdfs* and integrals thereof (i.e., cumulative sums) are presented in Figure 3 for the four potential models employed. The profiles of *pdfs* are very similar to each other, with the main difference being a small shift in the first peak corresponding to slightly different sizes of the hydroxide oxygens in different force fields. The oxygen atom of hydroxide has 4 - 5 water hydrogens in first solvation shell for all models (Figure 3). Note that the second peak in Figure 3 corresponds to the outer shell of water molecules around OH^- including that weakly hydrogen-bonded to the hydrogen of hydroxide [5, 30, 31]. M2 and M4 turned out to be the most distinct among the four investigated models, therefore, they were employed for further studies of 1, 2.4, and 4.8 M NaOH solutions.

For all the above concentrations we calculated *pdfs* resulting from the M2 and M4 models, as depicted in Figure 4. Although the two models perform similarly, sodium ions interact more strongly with hydroxide and water oxygens (having a higher first peak) within the M4 model compared to the M2 model, with the location of the first maximum being shifted to slightly larger distances. For the distribution of water oxygens around hydroxide oxygens we see a small effect of the slightly larger hydroxide oxygen within the M4 model, otherwise the two potentials perform similarly. There is no visible effect of a particular OH^- model on radial distribution functions between Na^+ and water oxygens (OW) and on the OW-OW distribution for any of the studied concentrations. Such a result is not unexpected since this is a second order effect of the hydroxide potential.

In summary, differences between the investigated models of hydroxide are small. The simulation results are, therefore, robust.

Sodium hydroxide solutions - experimental results:

The *rdfs* obtained from X-ray diffraction experiments are compared to simulated ones in Figure 5. The part of the total structure function, which is relevant to the liquid structure (i.e., that without intramolecular contribution) can be calculated from the *prdfs* according to the equation

$$H(k) = \sum_{\alpha \geq \beta} \sum \frac{(2 - \delta_{\alpha\beta})x_{\alpha}x_{\beta}f_{\alpha}f_{\beta}h_{\alpha\beta}(k)}{M(k)} . \quad (2)$$

Here, f_{α} is the scattering length or scattering factor of the α -notated atom (which depend on k in the case of X-ray diffraction) and x_{α} is the corresponding mole fraction. $h_{\alpha\beta}(k)$ is defined according to the following equation:

$$h_{\alpha\beta}(k) = 4\pi\rho \int_0^{r_{\max}} r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin(kr)}{kr} dr \quad (3)$$

The total *rdf* is then given as the Fourier transform of the structure function.

As described in Ref. [29], classical non-polarizable potentials cannot appropriately describe the interaction between the water and hydroxide anion. The agreement between experiment and simulations employing either of the present polarizable potentials is significantly better (Figure 5). From the experimental point of view, the M2 and M4 polarizable potential models are indistinguishable.

Discussion and Conclusions

In order to validate polarizable force fields for aqueous hydroxide solutions it is imperative to check first the employed water model. Comparison with neutron scattering results shows that from the point of view of the static structure the POL3 potential model of liquid water is certainly competitive in comparison with other commonly used water potentials considered

recently [27]. In this work, it is demonstrated that the already quite favorable level of consistency with experiment reported in Ref. [27] can further be improved using the RMC procedure. That is, from the structural point of view, the POL3 water model represents an appropriate choice for the purpose of simulating bulk water properties. In more detail, the description of the O-O correlation function is excellent, while there are small discrepancies for the O-H and H-H pair correlation functions (Figure 2). For the latter *prdfs* quantum nuclear effects, which are not considered or are at best only implicitly accounted for in the present classical simulations, may come into play.

Having validated the water force field we proceeded with testing four polarizable models for hydroxide. All these models are constructed in similar way differing somewhat in the values of oxygen Lennard-Jones parameters and/or the partial charges. They are fitted against accurate *ab initio* calculations on small hydroxide-water clusters, which makes them also consistent with the employed POL3 water model. These four OH⁻ models provide aqueous structural data which are very similar to each other and are in a semi-quantitative agreement with the *prdfs* obtained from X-ray data. The present models thus represent a major improvement over a non-polarizable force field employed for comparison with structural data previously [29]. Clearly, classical MD simulations cannot describe proton hopping and can only partially capture fine structural subtleties connected with the partial charge delocalization of hydroxide over the water solvation shell [5, 32]. Nevertheless, structural features of the present polarizable model of aqueous hydroxide are in a good agreement with experiment despite the relative simplicity (and, consequently, computational efficiency) of the employed force field.

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Table 1: The oxygen parameters for the four employed potential models for hydroxide. There are no Lennard-Jones parameters on the hydroxide hydrogen, the charge of which is deduced from that on the oxygen and from the overall -1 e charge of the ion.

	q [e]	σ [nm]	ϵ [kJ/mol]
M1	-1.35	0.373	0.652704
M2	-1.35	0.384	0.4184
M3	-1.35	0.367	0.8368
M4	-1.20	0.384	0.652704

Figure captions:

Figure 1: Geometry of the *ab initio* local minimum of a cluster containing OH⁻ and four water molecules, used for optimizing the polarizable potentials.

Figure 2: RMC modelling the (a) O-O, (b) O-H, and (c) H-H partial radial distribution functions from MD simulation of bulk water using the POL3 water potential [4] and neutron diffraction experimental data on pure heavy water [26]. Color coding: (a)-(c) black lines: input partial rdf's from MD simulations; red lines: RMC and (d): black line: experimental total scattering structure factor; red line: RMC.

Figure 3: Partial radial distribution functions (full lines) and corresponding cumulative sums (dashed lines) for hydroxide oxygen and water hydrogen in 1 M solution of NaOH using the four different models of OH⁻.

Figure 4: Partial radial distribution functions for sodium (Na⁺), and oxygens on hydroxide (O) and water (OW) at a) 1 M, b) 2.4 M, and c) 4.8 M NaOH solution. The blue color stands for model M2, while the model M4 is plotted by red color.

Figure 5: Comparison of total radial distribution functions obtained from the experiment (circles), from MD simulations using a non-polarizable model (black line), and a polarizable model for MD (red line).

Figure 1:

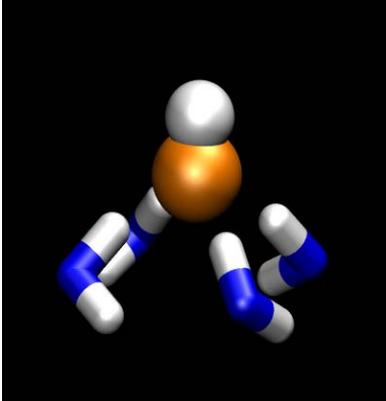


Figure 2 :

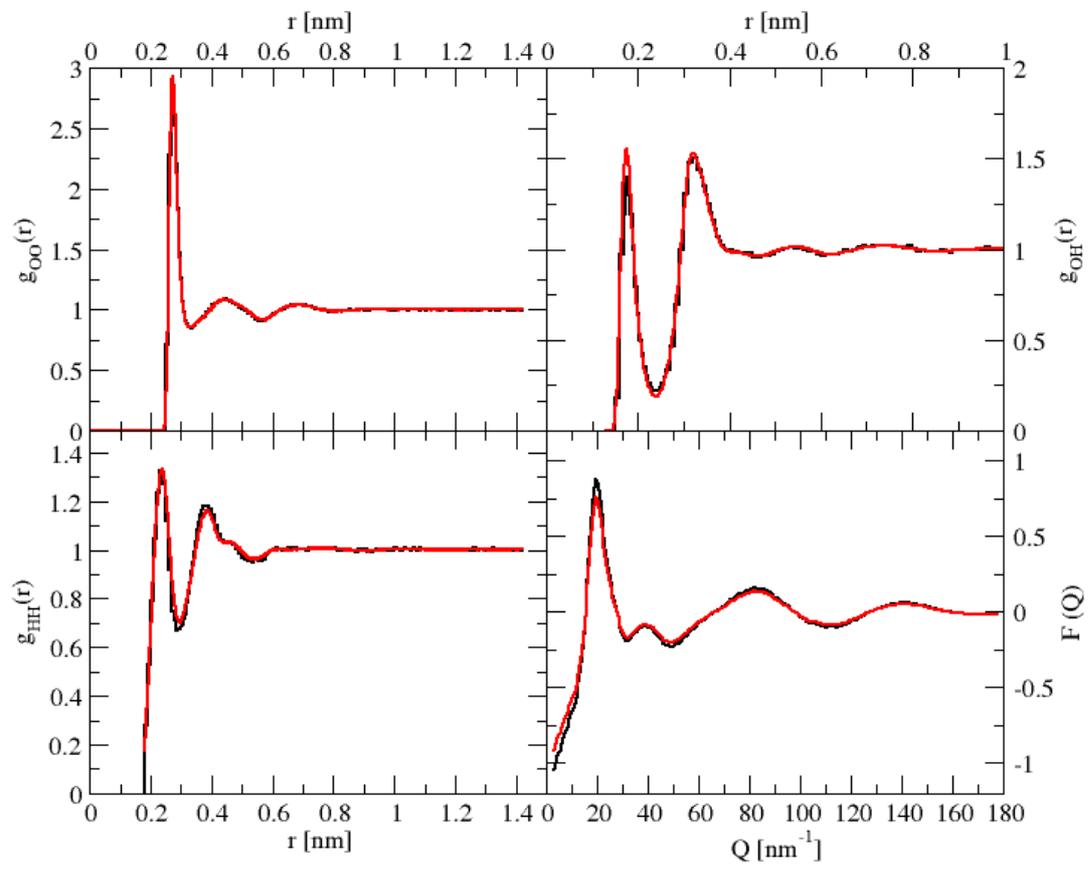


Figure 3:

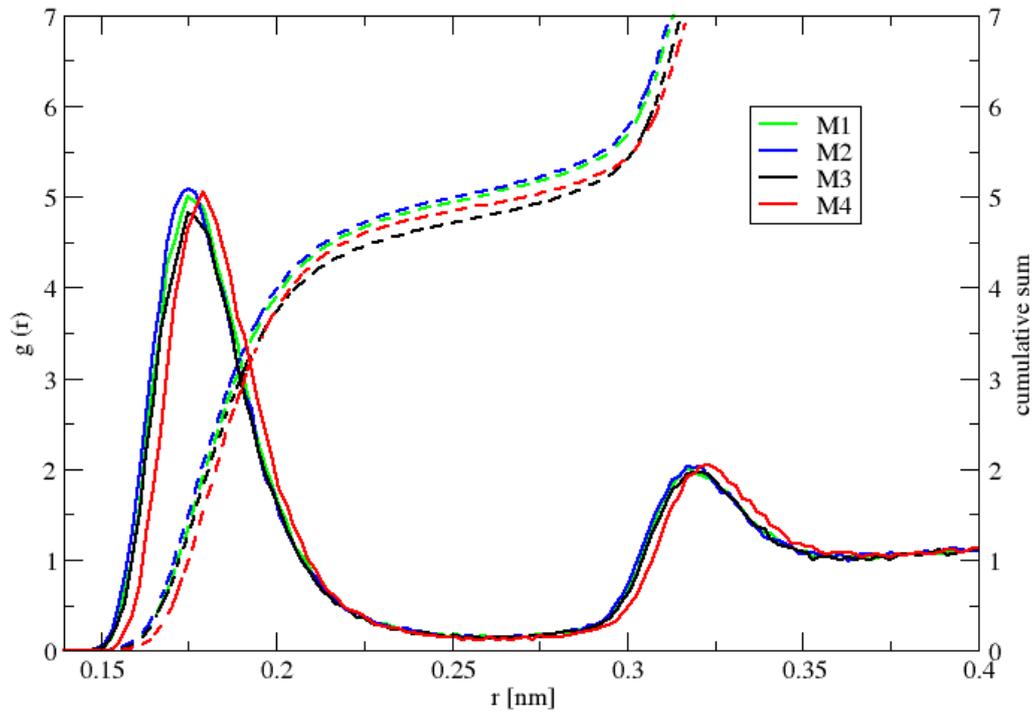


Figure 4a:

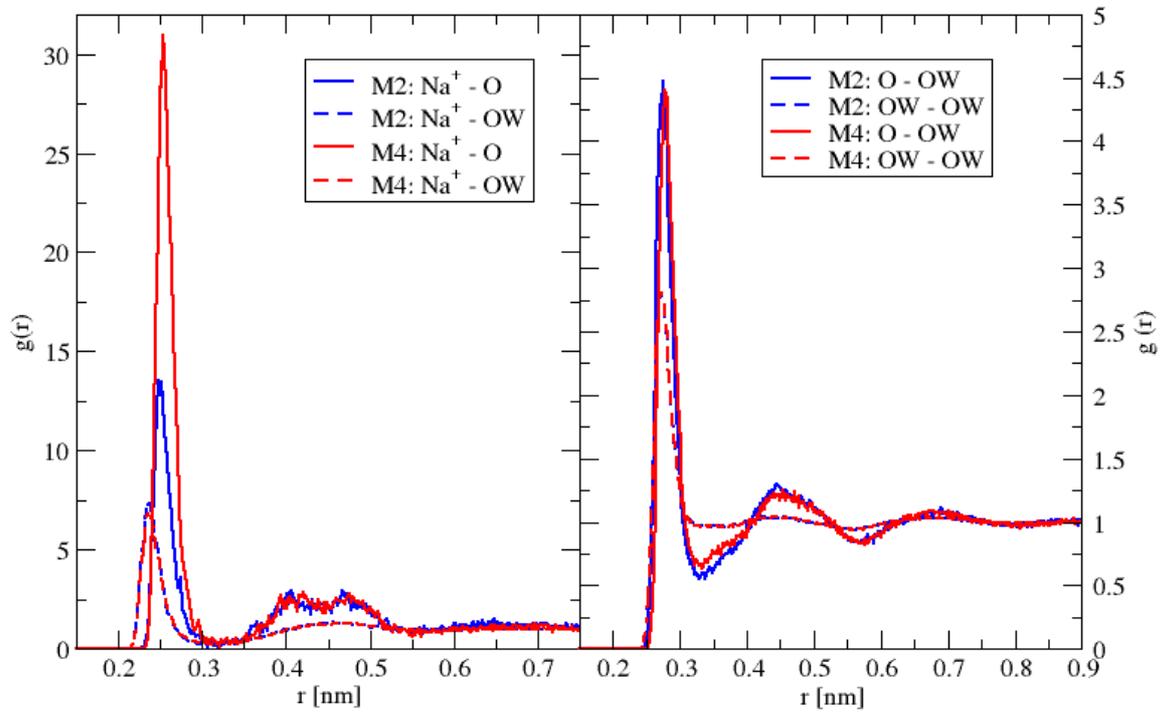


Figure 4b:

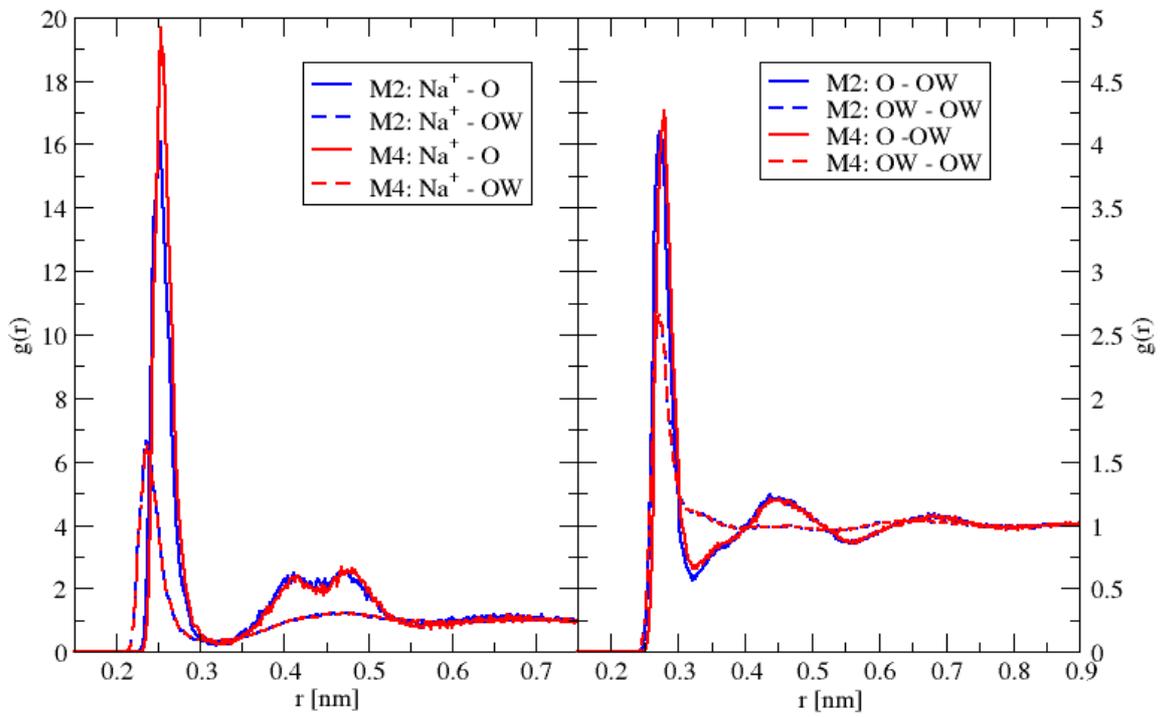


Figure 4c:

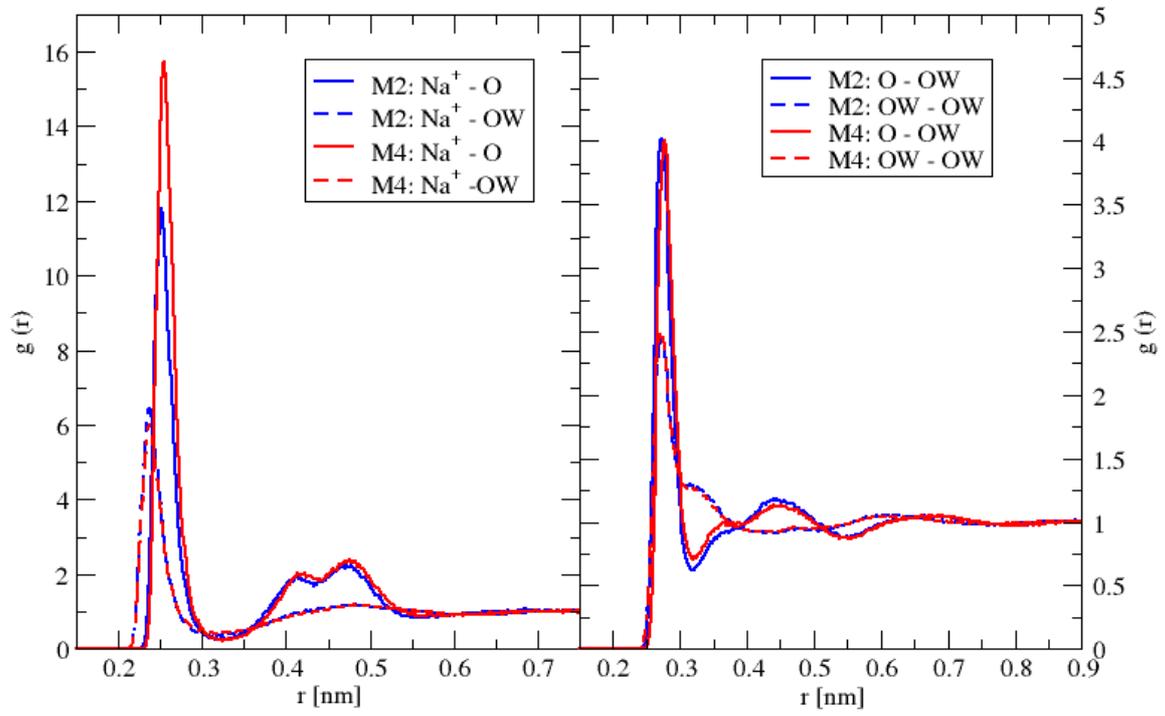
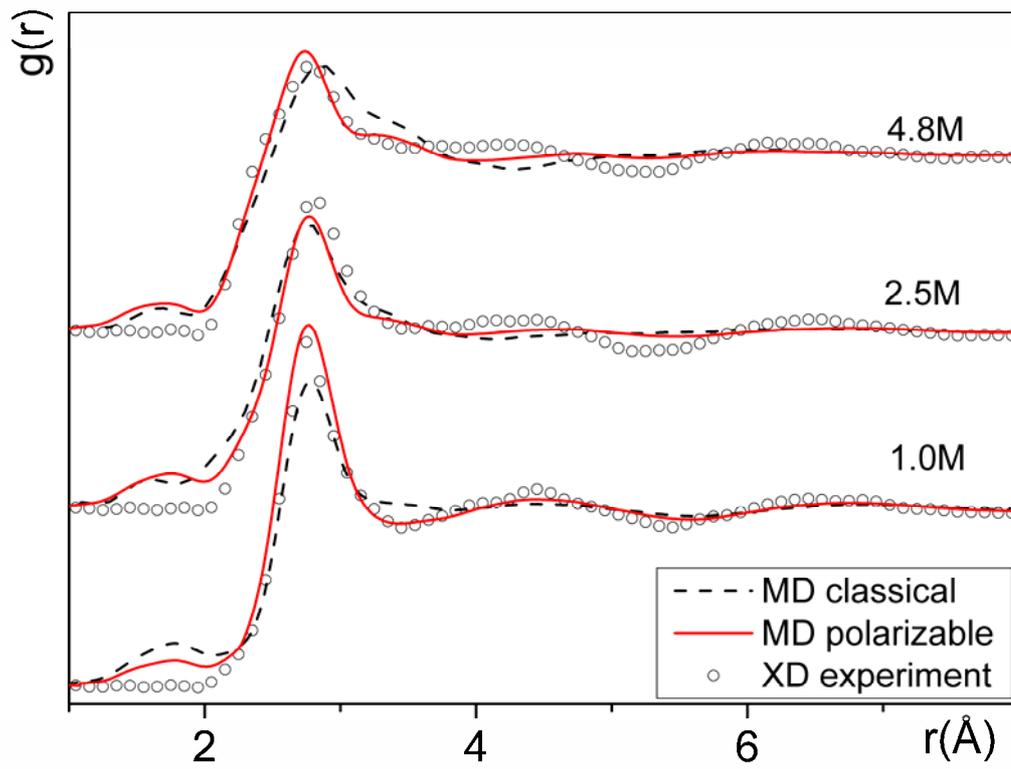


Figure 5:



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