The role of water near charged interfaces: molecular dynamics simulations of biological macromolecules in presence of high intense electric fields

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Abstract

Because of its central role in basically all aspects of science, water is certainly one of the most extensively investigated substances from a theoretical point of view. Moreover, the characterization of liquids and solutions under the effect of external electric fields is a long standing and challenging field of investigation for both theoretical and experimental approaches. In this work the behavior of water near charged interfaces has been evaluated considering two different cases: an ion in aqueous solution and a macromolecule of DNA. The methodology used is based on atomistic simulations, specifically adapted to account for the presence of exogenous electric fields.

1. Introduction

In the study of bioelectromagnetic interaction mechanisms one of the principal hypothesis is that the effects of the interaction at macromolecular scale could be mainly connected to the aqueous environment in close proximity of cell membrane. Therefore it is of great interest to investigate the specific properties of water near charged interfaces, representing highly specific environments with proper characteristics (high intensity local electric fields [1], [2]) very different either from those of bulk water or from those of isolated macromolecules. In this context two different case studies of increasing complexity have been chosen, to evaluate the role of water near charged structures, under the action of an external electromagnetic field. The first one is an ion solvated in aqueous solution and exposed to a high intense electric field, the second one is a fragment of a single strand of DNA composed by a sequence of ten similar nucleotides. In the past analytical methods have been adopted to study water dielectric properties in presence of high intensity static electric fields [3]. Here an approach based on molecular dynamic (MD) simulation [4] is proposed and results obtained are compared with physiological condition of no exposure.

2. Materials and Methods

MD simulations solve Newton's equation of motion for a system of N interacting atoms; the system is followed for some time, with a very small time step, taking care that temperature and pressure remain at the required values. In this context GROMACS, an engine to perform MD simulations and energy minimization, has been used. As a first step, simulations on a box with different sizes, filled with water molecules have been carried out. This approach had the scope to establish an optimized set of simulation parameters, fixing the most suitable force field, water model, cut off-ray for the interaction forces among molecules, number of water molecules and duration of the simulation. As a second step a static E field, of different intensities has been introduced in the simulations either in the case of the single ion or in the one of the DNA. In Fig. 1 are reported the models used for MD simulations for the ion (Fig. 1 (a)) and the DNA (Fig. 1 (b)) respectively. When analyzing the solvated ion, a cylinder of constant height moving at different distances (d) from the ion has been used to evaluate the distribution of water molecules close to the ion, in terms of density and mean dipole moment (Fig. 1 (a)). As for the evaluation of water around DNA a volume of ellipsoidal shape volume of increasing dimensions has been used. In Fig. 1 (c) is reported in red the minimum ellipsoidal volume containing the whole DNA and it is referred as the unitary volume.

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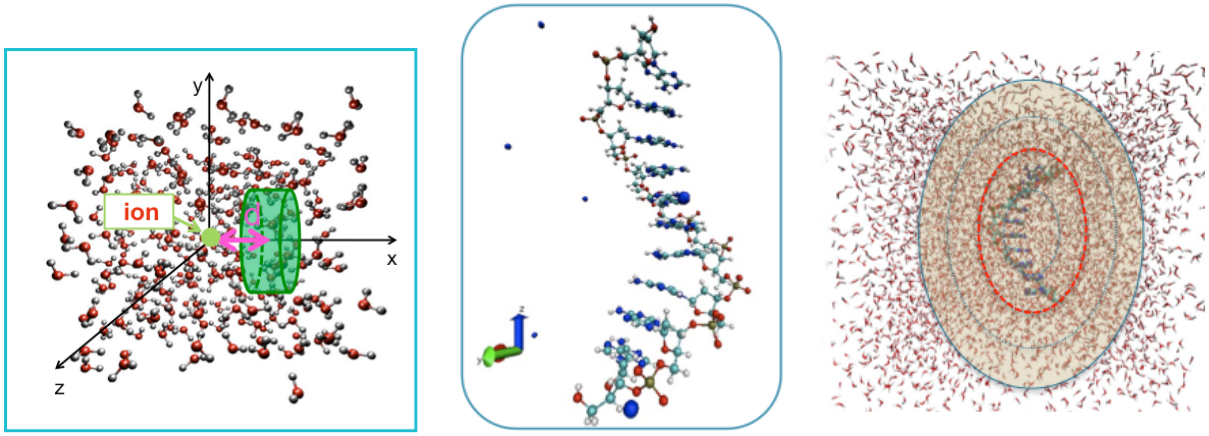
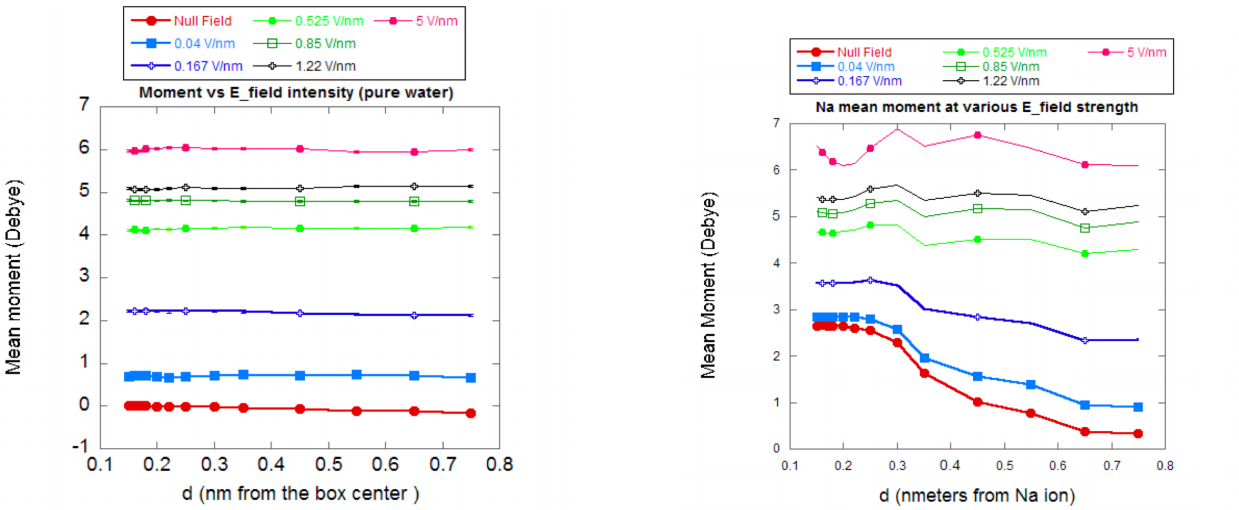


(a) (b) (c)

Fig. 1 Models used for molecular dynamics simulations: (a) ion in a box of water molecules; a cylinder is used to evaluate the distribution of water molecules (b) single DNA strand made of a sequence of 10 adenine, in a box of water molecules. Water molecules have been hidden to permit a better view of the macromolecule; (c) ellipsoidal volumes surrounding the DNA macromolecule used to calculate the number of water molecules around the DNA. The red one is the ellipse of unitary volume.

3. Results

First results regard the behavior of water molecules in presence of high intense electric fields, in particular referring to the mean dipole moment of water. As reported in Fig. 2 (a) for a box of pure SPC water the mean moment dipole is constant both at increasing distances from box centre and under the effect of static field at increasing intensities.



(a) (b)

Fig. 2 Mean dipole moment of water molecules present inside the cylinder of constant height moving from the box center in presence of increasing intensity of electric field applied (a) pure water molecules; (b) water molecules and Sodium ion located at the box center.

For a dilute system with a sodium ion the profile of mean moment dipole is not constant anymore (Fig. 2 (b)). An intensity of the field approximately greater than 0.5 V/nm is needed to let the profile to be constant again. This means that lower intensities are not able to overcome the local electric field generated by the charged ion located at the center of the simulating box. With intensities higher than 0.5 V/nm the external field seems to be the only responsible for dipole orientation leading all the microscopic properties of water to reach a bulk value.

When considering a more complex situation as the DNA macromolecule the behavior of water molecules surrounding the single strand can be evaluated through the results reported in Fig. 3. When a 10^7 V/m electric field is applied, it can be observed that for volume fractions lower than one (i.e. 0.5 of volume fraction represents an ellipsoidal volume 50% lower than the minimum volume which contains the DNA macromolecule) there is a depletion of water molecules, indicating a sort of shell around the DNA where water density is lower. Whereas increasing the volume around the DNA (i.e. at volume fraction of 2, which represents an ellipse with a volume twice than the unitary volume) the density in exposed conditions tends to become not distinguishable from the unexposed one.

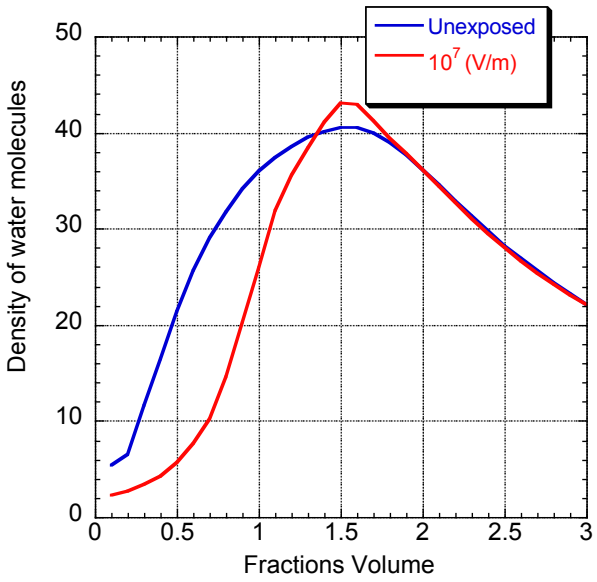


Fig. 3 Density of water molecules reported as a function of an increasing ellipsoidal volume. The volume fraction equal to one corresponds to the minimum volume containing the DNA. Higher values indicate volumes which contain the DNA plus water molecules, lower values are volumes which not contain the whole DNA.

4. Conclusions

Results from classical MD simulations on dilute system allow a direct evaluation of exogenous field influence on water molecules near highly charged regions, like could be the cellular internal or external environment but, in principle, even near binding sites or polar groups. Interestingly, has emerged that exogenous fields with sufficient strength (i.e $> 10^8$ V/m) start a sort of contest with the local field produced by ions (but this supposedly stands even for generic charged or polar groups) that ends up with the overall reorientation of water dipoles when a very high value for the E-field is reached ($>10^9$ V/m). When a more complex situation is considered, as the single strand DNA macromolecule, the applied field tends to create a shell of reduced water density around the molecule, for intensities up to 10^7 V/m.

5. References

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