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E. Schwegler

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First-Principles Simulations of Aqueous Solutions

Eric Schwegler

Lawrence Livermore National Laboratory, Livermore, CA 94550

E-mail: schwegler@llnl.gov

Abstract. The importance of water in many areas of science has motivated an enormous number of experimental and theoretical investigations. In this paper, we review several recent examples where first-principles molecular dynamics simulations coupled with large scale computing has enabled important insight into the unique properties of water in a variety of systems, including pure liquid water, the solvation of ions and hydrophobic solutes and nanoscale confined systems such as water inside carbon nanotubes.

1. Introduction

Advances in both experimental techniques and theoretical methods have resulted in the discovery of a wide range of fascinating new properties of materials. However, in many instances, experimental measurements and simple models are insufficient for a complete understanding of the emerging new phenomena at a microscopic level. In such cases, the combination of first-principles molecular dynamics (FPMD) with large-scale computations have proven to be extremely useful for resolving experimental ambiguities and for predicting the properties of materials where measurements do not yet exist.

One particular area where FPMD simulations have proven to be particularly useful is in examining the properties of liquid water and its interaction with a various solutes. These simulations, which treat electronic degrees of freedom quantum mechanically within density functional theory (DFT) and ionic motion classically, have allowed for important insights into the properties of aqueous solutions under a variety of thermodynamic conditions. Quantum simulation techniques combined with significant increases in available computer power have pushed the computational simulation of water to an exciting stage. Simulations can now be used both to make genuine predictions directly comparable with experiment as well as to establish the accuracy of newly developed classical potentials, which are critical for accessing much longer time scales and much larger systems.

In the following, we briefly review our recent use of FPMD to examine the properties of water in a number of different systems, including simulations of pure liquid water, the solvation of hydrophilic and hydrophobic solutes in water, and water confined to a nanoscale environment.

2. First-Principles Molecular Dynamics

Molecular dynamics has been used for decades to investigate dynamical properties of molecules, solids, and liquids by numerical simulations. In the standard approach, which is usually referred to as classical molecular dynamics, one must provide in advance a model potential for determining the interatomic interactions. In contrast, FPMD-based approaches do not require any empirical or fitted interatomic potentials as input because the interactions between atoms are computed directly from the

electronic structure of the system “on-the-fly” at every time step in the simulation. In particular, the underlying methods that are used are based on finding numerical solutions to the fundamental laws of quantum mechanics in an approximate, yet non-empirical manner. These methods have a distinct advantage over semiempirical or classical simulation approaches in that they can provide a quantitatively accurate description of chemically active species in realistic environment.

The typical FPMD simulation approach is based on the use of a planewave/pseudopotential implementation of density functional theory to describe the electronic structure, and with the MD carried out with either a Car-Parrinello (CP) approach [1], where the electronic and ionic degrees of freedom are coupled by a Lagrangian, or the Born-Oppenheimer (BO) approach, where the electronic wave functions are fully relaxed to the ground state at each time step. In either case, the main computational step is centered on solving the Kohn-Sham equations [2], which involves heavy use of numerical linear algebra methods and three-dimensional Fourier transforms. We refer the interested reader to Ref. [3] for a recent discussion of the challenges involved in massively parallel implementations of FPMD within the context of the Qbox code [4].

Although first-principles techniques offer distinct advantages over empirical models in terms of accuracy and predictive power, the methods are quite computationally expensive and often require significant computational resources just to simulate a moderate sized system for short periods of time. In the standard implementation, the cost of simulations involving N atoms grows as N^3 , which quickly limits the size of systems that can be treated with a reasonable computational cost. For instance, we recently performed a series of first-principles molecular dynamics simulations of a water-filled carbon nanotube involving over 1,600 valence electrons. For this rather large system, a 20 ps long trajectory (1 ps = 10^{-12} s) required approximately 1.2M CPU hours on the Thunder computing platform [5].

3. First-Principles Simulations of Liquid Water

In order to better understand the level of accuracy that can be achieved with DFT-based techniques for the calculation of the properties of liquid water it is helpful to examine the importance of the various approximations that are needed to carry out the simulations. To this end, we have performed a series of long-time scale simulations of water where a number of approximations were tested by varying the density functional employed, the fictitious electron mass used in the CP approach, the system size and the use of CP versus BO approaches.

Our simulations showed that there are negligible differences in the structural properties of the room temperature liquid obtained using different density functionals such as PBE [6] and BLYP [7]; size effects, although not fully negligible when using 32-molecule cells, were found to be rather small. We also found that as long as an appropriate fictitious mass parameter is used in the CP approach, results consistent with BO simulations can be readily achieved.

Overall, we have found that in well-converged DFT simulations of water under ambient conditions, the liquid exhibits significant over-structure and slow diffusion as compared to experimental measurements. Very similar results have been reported by a number of different research groups [8]. A significant fraction of this observed over-structure and slow diffusion is due to the neglect of proton quantum motion in the simulations, which can be effectively accounted for by performing simulations

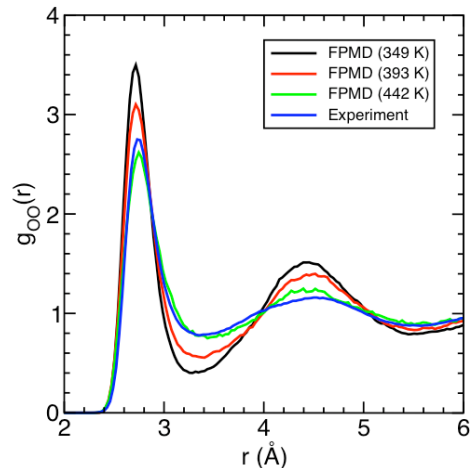


Fig. 1. Oxygen-oxygen radial distribution functions obtained from FPMD simulations of water as a function of temperature in comparison to experimental measurements under ambient conditions [12].

at elevated temperatures. We note that approximately accounting for quantum effects via temperature rescaling is a technique that has been used in a variety of materials other than water [9]. This effect is illustrated in Figure 1, which shows the oxygen-oxygen radial distribution function obtained from FPMD simulations of liquid water at different temperatures in comparison with experimental measurements at ambient conditions. Work is currently underway to directly account the quantum proton motion in our simulations with Feynman path integral sampling techniques [10]. Additional details of these findings can be found in Refs. [11,12].

4. The Rigid Water Approximation

Even with the development of sophisticated codes implemented on massively parallel computers, accurate and well-converged FPMD simulations of water have remained particularly challenging. One of the specific problems encountered in simulations of water is due to the presence of the high-frequency intramolecular modes, *i.e.* the O-H stretch (3200 to 3600 cm^{-1}) and H-O-H bending modes ($\sim 1600\text{ cm}^{-1}$) of water. This is particularly relevant in CP simulations, where one must use a relatively small fictitious mass parameter in order to avoid a direct overlap of ionic and electronic degrees of freedom, which would otherwise lead to severe inaccuracies in the simulation. The use of small values of the fictitious mass necessitates the use of small MD time steps to ensure an accurate integration of the equations of motion. As a consequence, a typical FPMD time step with the CP approach can be less than 0.1 fs , which is at least ten times smaller than what is often used in classical MD simulations of water with empirical interatomic potentials. This poses a severe restriction on the time scales that can be accessed in CP simulations of water.

We note that when using BO dynamics (where the total energy of the system is minimized at each ionic step), it is possible to safely use larger time steps than in CP simulations, because electronic degrees of freedom are not propagated at the same time as ionic coordinates. However, the accuracy required to reduce systematic errors on the ionic forces so as to have conservative dynamics is such that large number of iterations are usually necessary to minimize the Kohn-Sham energy at each ionic step. Therefore, the gain in efficiency obtained with a larger time step is more than counter-balanced by the increased computational time requirement for total energy minimizations.

With the aim of investigating how to increase the integration time step in CP simulations of water and thus access longer time scales, we have carried out calculations using a rigid water approximation. By completely removing the high frequency vibrations and bending modes, the rigid water model allows for much larger values of the fictitious mass, as well as time steps in the CP method. As shown in Figure 2, the use of the rigid water approximation leads to a decrease in the liquid structure as compared to the FPMD simulations of flexible water, which brings the rigid water results into better agreement with experiment. Our results indicate that at least some of the improved agreement is related to the fact that the rigid water model can be considered to be a better representation when the quantum motion of the protons is taken into account. Additional details of these simulations can be found in Ref. [13].

5. Hydrophilic Solvation of Ions

The aqueous solvation of ions is encountered in a wide range of biological and chemical systems. In particular, the manner in which water solvates alkali cations is relevant to problems such as the

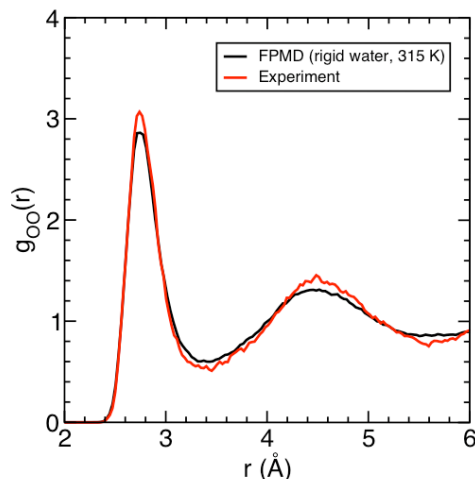


Fig. 2. The oxygen-oxygen radial distribution function from a FPMD simulation of rigid water in comparison with experiment [13].

mechanism of enzymatic catalysis and the structural stability of DNA and RNA. In order to investigate the hydration structure of ions, a variety of experimental techniques can be used. For example, X-ray and neutron diffraction methods have proved to be valuable tools for determining the static structure factors of waters solvating a given ion. However, experimental measurements often yield an incomplete description of ionic solvation, due to, e.g., the lack of suitable isotope substitutions in neutron diffraction experiments, or difficulties in separating the atomic correlations of different species in diffraction data. In many cases, molecular dynamics simulations have emerged as a successful complement to experimental measurements and have led to a greater understanding of the solvation process.

We have carried out first principles molecular dynamics simulations on aqueous solutions of sodium [14], magnesium [15] and calcium [16] cations. The different cation-water radial

distribution functions obtained in these simulations are shown in Figure 3. These simulations provide a rather detailed view of the ion solvation process, and can be used to directly interrogate how the properties of the water molecules are altered due to the presence of the ions. One of the more obvious differences between the different cations is that in the case of sodium, the first minimum in $g_{\text{Na-O}}(r)$ at approximately 3.5 Å is large. This suggests that the first solvation shell around sodium is rather floppy and that the water molecules move rapidly between the first and second solvation shells. In fact, during the rather short timescale of the simulations, numerous exchange events can be observed.

In the case of magnesium and calcium, the height of the first minimum is much smaller, which indicates that the first solvation shell around these ions is more structured than what is found around sodium. In general, the first solvation shells around magnesium and calcium consist of six water molecules in an octahedral arrangement. Because the ions are divalent cations, these six water molecules tend to be strongly oriented with their oxygen atoms closest to the ion and with their hydrogen atoms pointing away. In order to determine if the presence of the ion has a significant effect on the electronic structure of the first solvation shell waters, we examined the properties of the first solvation shell water molecules with the use of maximally localized Wannier functions [17]. Interestingly, what we found is that the first solvation shell waters tend to asymmetrically coordinate with the ion with just one of the lone pair orbitals located on the oxygen atoms, which leads to significant changes in the polarization of the first solvation shell water molecules. This asymmetric orientation gives the water molecules a small "tilt" and only small modifications to hydrogen bonding in agreement with experimental measurements [18,19,20].

6. Hydrophobic Solvation of Small Solutes

The hydrophobic effect plays a central role in processes spanning numerous scientific and technological disciplines, from protein folding to the formation of natural gas hydrates in oil and gas pipelines. We have used a combination of classical and FPMD simulations to probe the impact of small hydrophobic solutes on the local structure of water [21]. In particular, we have recently carried out long time scale FPMD and classical simulations of a benzene molecule in water [22,23]. The solvation of benzene represents an interesting test case for molecular simulations because it involves two quite different interfaces when it is surrounded by water. The equatorial region around the

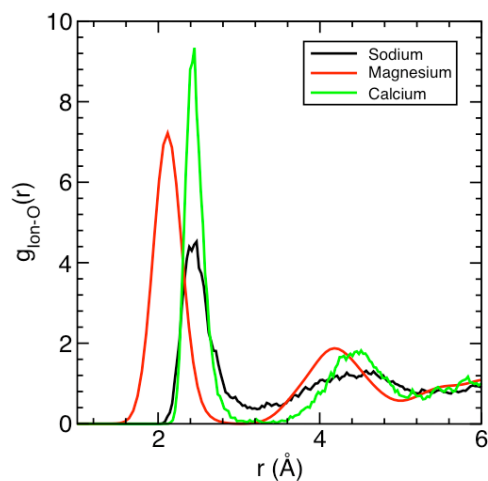


Fig. 3. The ion-oxygen radial distribution functions from FPMD simulations of Na^+ (black), Mg^{2+} (red) and Ca^{2+} (green) solvated in water [14,15,16].

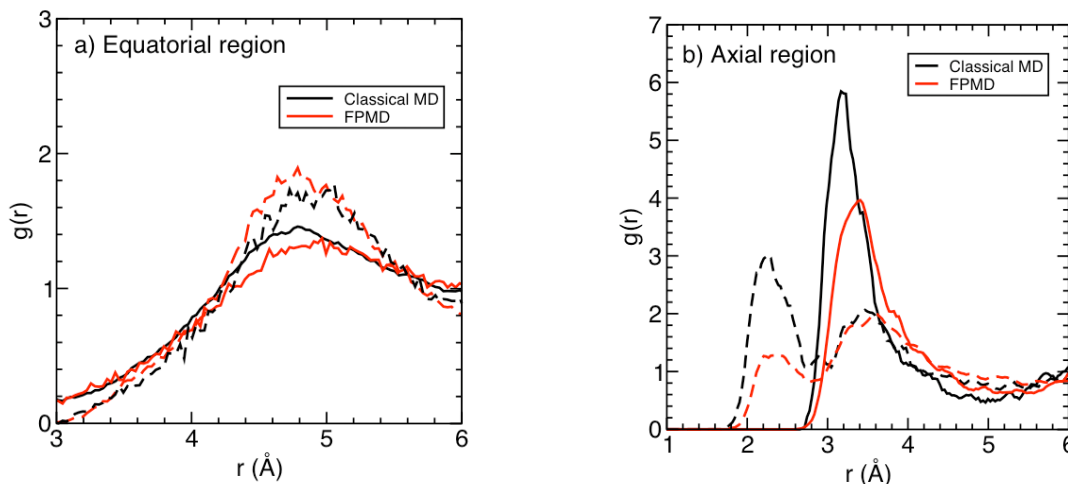


Fig. 4. The benzene-oxygen (solid lines) and benzene-hydrogen (dashed lines) radial distribution functions collected in a) the equatorial region, and b) the axial region around benzene from FPMD (red lines) and classical MD (black lines) simulations.

benzene ring resembles a typical hydrophobic solute, whereas the axial regions near the center of the benzene ring can interact with neighboring water molecules by forming weak π -hydrogen bonds.

In Figure 4, the benzene-oxygen and benzene-hydrogen radial distribution functions around the equatorial and axial regions of benzene obtained from an FPMD and a classical MD simulation are shown. Both simulation approaches find nearly featureless oxygen and hydrogen distributions near the equatorial regions that are peaked at approximately 4.9 Å from the center of the solute. In contrast, the distributions around the axial regions exhibit a noticeable amount of structure. In particular, there is a benzene-hydrogen peak located at approximately 2.3 Å that comes from a slight tendency to form π -hydrogen bonds with nearby water molecules. Although this peak is present in both simulations, the height of the peak is significantly smaller in the FPMD simulation as compared to the classical MD distribution.

The fact that there are similarities between the classical models and the FPMD simulations for the equatorial regions, and significant differences near the axial regions is perhaps not too surprising. In the case of small hydrophobic solutes it is known that the hydrogen bond network mostly persists around the solute - although in a rearranged form [24]. Because the local hydrogen bonds are not broken, the water molecules near the solute see an environment that looks similar to the bulk and as such the classical models tend to work well because these models were originally designed to reproduce the bulk properties of water. However, in cases such as the axial regions around benzene where solute-water interactions become significant, the local environment changes when the water-water hydrogen bonding is no longer preserved. Simple classical models cannot account for these subtle changes in the local environment. We note that a similar breakdown of classical water models should be expected to occur around large hydrophobic solutes and surfaces because it is not possible to preserve the water-water hydrogen bonding around an extended interface [24]. In the case of solvated benzene, the interfacial water molecules in the axial region are weakly bound to the π -electron system of benzene instead of forming water-water hydrogen bonds, which leads to smaller water molecule dipole moments by about 0.15 Debye when compared to the bulk. A similar decrease in the dipole moment of the interfacial waters near the equatorial region of the solute does not occur because water-water hydrogen bonding persists in this region.

7. Water Confined to the Nanoscale

While the properties of bulk liquid water and simple aqueous solutions have been extensively investigated, much less is known about water confined at the nanometer scale, where conventional

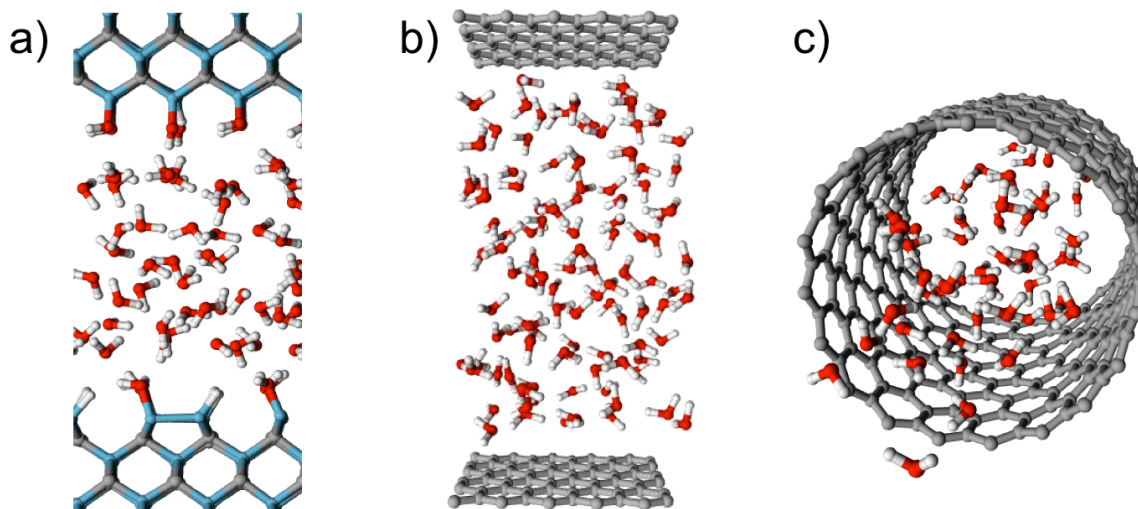


Fig. 5. FPMD simulations of water confined by a) hydroxylated silicon carbide surfaces [26], b) graphitic sheets, and c) a (19,0) carbon nanotube [27].

experimental probes (*e.g.* neutron diffraction and X-ray scattering) are difficult to use and accurate simulations become extremely challenging. Equilibrium properties, phase transformations and molecular mobility of water have all been observed to change upon confinement, however a thorough characterization of these changes is still missing.

A number of theoretical studies using both molecular dynamics and Monte Carlo techniques have been carried out to address some of the issues involved in confined water [25]. However, it should be noted that the existing simulations have all been based on empirically derived classical potentials. As previously mentioned, because these potentials are usually designed to reproduce the properties of bulk water, it is unclear whether they can accurately describe confined states of water that presumably involve complex interfacial regions. Furthermore, as we found near the axial region around benzene, subtle electronic effects can play an important role in understanding the behavior of both water-water and water-solute interactions, which are effects that cannot be captured with simple classical potentials.

We are currently using FPMD simulations to examine how the properties of water change when confined to the nanoscale. As illustrated in Figure 5, our simulations have been designed to address specific issues such as confinement length scale, dimensionality of the confining media, interface effects such as hydrophobic versus hydrophilic surfaces, and the influence of confinement on ion solvation processes.

In the cases of one and two-dimensional confinement by hydrophobic surfaces, our simulations indicate that there is a noticeable spatial ordering of the interfacial water molecules and an overall enhancement of density oscillations that persist for approximately 5 Å away from the surface. For the water molecules closest to the surface, we find a moderate increase in hydrogen bond donors and a specific orientational ordering that leads to an enhancement of four-fold hydrogen bonded ring structures relative to the bulk liquid water. Overall, our results indicate that the majority of changes that occur when water is confined are limited to small regions near the interface and that the liquid quickly recovers its bulk-like properties at moderate distances away from the surface. More specific details from these simulations can be found in Refs. [26,27].

8. Conclusions

We have reviewed several recent examples of the use of FPMD to examine the properties of water in a variety of different systems, including pure liquid water, the solvation of ions and hydrophobic solutes and nanoscale confined systems such as water inside carbon nanotubes. In each case, we highlighted the advantages of using an FPMD approach over less computationally expensive classical methods, especially when dealing with complicated interfacial systems where a high degree of transferability and predictive power is required.

9. Acknowledgments

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