



# Solvation structure and dynamics of Li<sup>+</sup> ion in liquid water, methanol and ethanol: A comparison study



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## ABSTRACT

Car–Parrinello molecular dynamics was performed on Li<sup>+</sup> in water, methanol and ethanol. Structural and dynamical properties of Li<sup>+</sup> were studied and compared with experimental data. Excellent agreement was obtained with the experimental data for the structure of the first solvation shell. The results show the Li<sup>+</sup> has a more stable tetrahedral coordination in water and methanol than that in ethanol. The diffusion of water in its first solvation shell was rather slow. Compared to water and methanol, the ethanol in the first solvation shell diffuses slower. The decay of orientational profiles of the solvent molecules in the solvation shell shows slower relaxation for first and second rank correlations compared to bulk water and methanol. The decay of orientational correlations for solvation shell molecules shows faster relaxation compared to that of bulk ethanol. Spectral of bound solvent molecules are compared to those of the bulk. Reasonable agreement is obtained with experiments.

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## 1. Introduction

The solvation structure and dynamics of ions in polar solvent are an important topic of current interest in chemical physics fields [1]. Structural features of the solvation shell have been studied in many computer simulations [2–4] and experimental techniques [5,6]. Tielrooij et al. [7] studied the effect of ions on water using the fs-IR spectroscopy and terahertz DR spectroscopy. They studied dissolved salts containing various combinations of ions with different charge densities, and observed dynamic hydration effects that extend well beyond the first structural solvation shell. However, experimental determination of a detailed microscopic structure of solvation shells around ions is difficult. Classic computer simulation techniques, such as molecular dynamics or Monte Carlo can provide detailed and statistically reliable information on structure and dynamical properties of solvent molecules around the ions. While, these classic simulation methods rely on the quality of the interaction force fields. Milek and his co-workers [8] reported on the development of force-field parameters for accurately modeling lithium and hydroxide ions in ethanol in solution. The results show that ion–solvent interaction model parameters for aqueous solution cannot be simply transferred to organic solvents or even

their mixtures with water. These force field functions may be parameterized by fitting the results from available experimental data [9] or quantum chemical calculations [10,11]. However, the validation of empirical potentials in the liquid phase condition is difficult.

In this work, water, methanol and ethanol are selected as model fluid molecules. Compared with non-polar solvent, the strongly polar molecules, such as water, occur by hydrogen bonding. Water represents a strongly polar molecule while methanol and ethanol are intermediate between nonpolar and strongly polar molecules. Alcohols might be expected to show behavior which is intermediate between these extremes. Methanol is the smallest molecule characterized by both a hydrophilic and a hydrophobic group and it is widely used as a solvent. However, the number of computational studies on the structural and dynamical properties of the liquid [12–15] and its ionic solutions [16–18] is limited. On the other hand, the interest in methanol has also grown as a possible fuel cell component in the past few years [19–21]. Therefore, the comprehension of the liquid methanol properties and its interactions with ions and simple molecules is becoming important. The ethanol molecule has a stronger hydrophobic group than that of methanol, which maybe has a significant effect on the structure of solution. Ethanol has distinct solvation properties, and it is easily soluble as its polar hydroxyl group can participate in the hydrogen bonded network and the hydrophobic ethyl group is relatively big.

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Consequently, the understanding of the ethanol properties and its interactions with  $\text{Li}^+$  ion is very interesting.

*Ab initio* molecular dynamics (AIMD) simulations have been shown to be a valuable tool to gain microscopic insight into some solution systems [22,23]. In recent years, the Car–Parrinello molecular dynamics (CPMD), based on the density-functional theory (DFT), is one of the more popular alternatives. The CPMD technique has been successfully applied in simulations of both pure water [24–26] and ions in water [27–30] as well as many other systems of chemical interest [31–33]. The essence of *ab initio* molecular dynamics consists in calculating the forces between the nuclei are determined ‘on the fly’ from quantum chemical calculations at each time step, rather than fixing the potential at the outset of the simulation. The AIMD could, in principle, provide information about the microstructure and dynamics of molecules on a theoretically sound basis. In addition, this information can be used for derivation of more reliable effective liquid state potential functions for classical molecular simulations [34].

Liu et al. [35] investigated the hydration structure and coordination of  $\text{K}^+$  solvation in water at different temperatures using Car–Parrinello molecular dynamics. The results of RDFs show that the perturbation of  $\text{K}^+$  on the water structure is strong in the first hydration shells, while it is mild outside of this region in bulk liquid.

Polarization effects are generally believed to be important for aqueous solutions and these effects also vary with thermodynamic state of the solutions. Molina and co-workers [36] reported the dipole polarizabilities of a series of ions in aqueous solutions calculated by first principles. The environmental effects are important for  $\text{Cs}^+$  and a series of anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ ). It reduced the polarizabilities in aqueous solutions with respect to their gas phase values. Tazi et al. [37] presented a new polarizable force field for aqueous ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Cl}^-$ ) derived from *ab initio* calculations. The calculated structural, dynamic, and thermodynamic properties are in good agreement with the available experimental data. A light ( $\text{Nd}^{3+}$ ), a middle ( $\text{Gd}^{3+}$ ), and a heavy ( $\text{Yb}^{3+}$ ) lanthanide aqueous ion were studied, using *ab initio* based flexible and polarizable models for the water–water and the water–ion interactions [38]. A relatively small effect of the polarizability of the ions on the solution properties are observed. Yu et al. [39] developed the polarizable models based on classical Drude oscillators for a large set of monatomic ions including cations of the alkali metals ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$ ) and alkaline earth elements ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ ) and halide anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ).

Pratihari et al. [40] carried out Car–Parrinello molecular dynamics simulations of lithium atom solvation in a water–ammonia mixture. The structure of the primary shell of lithium and the distribution functions in bulk were studied. It is found that only water molecules are present in the primary solvation shell of lithium and the coordination number is mostly 4. Rowley and co-workers [41] performed molecular dynamics simulations of the solvation of  $\text{Na}^+$  and  $\text{K}^+$  in liquid water using the Drude polarizable force field, a QM/MM DFT model, a QM/MM MP2 model, and a CPMD model. The DFT QM/MM and CPMD simulations tended to predict less steep peaks in the RDF and smaller coordination numbers than the MP2 QM/MM and Drude models. Millik et al. [42] reported a first principles molecular dynamics study of structural and dynamical properties of aqueous ionic solutions for different densities under supercritical conditions. Both the coordination and hydrogen bond numbers of the anion are found to be somewhat smaller than the results of classical studies, especially so for the solution of lower density.

In this paper, we report results from Car–Parrinello molecular dynamics simulation of  $\text{Li}^+$  in water, methanol and ethanol. Particular attention has been paid to the structure of the first solvation

shell and to the dynamical properties of the ions and of the solvent molecules. The computational methods are described in Section 2 and our results are discussed in Section 3. The Section 3 is subdivided into various subsections on structural and dynamical properties. Finally, our conclusions are summarized in Section 4.

## 2. Computational methods

We performed *ab initio* molecular-dynamics simulations using the CPMD code [43] for the present simulations. Constant volume *ab initio* molecular dynamics (AIMD) has been performed on solutions containing a single ion and either 32 water molecules or 25 methanol or 25 ethanol molecules in cube boxes applied with periodic boundary conditions in all three directions. The size of cubic boxes is 9.89 Å for water, 11.93 Å for methanol and 13.60 Å for ethanol, respectively. The initial configurations for the CPMD are extracted from a previous trajectory of a classical simulation. In order to be able to use a relatively larger time step, the hydrogen atoms of solvent are fully substituted by deuterium. The ionic motions are less affected by this choice [44]. The Kohn–Sham formulation of DFT is performed to calculate the electronic structure. In the DFT calculations, we use the gradient-corrected BLYP exchange correlation functional. The type of the functional has been used previously to study the liquid water [45] which the structure and dynamics properties were described very well. In the liquid methanol and ethanol, the hydrogen bonds are the dominant interactions as in liquid water. In this work, Martins–Troullier [46] pseudopotentials have been used along with Kleinman–Bylander [47] decomposition for the C and O atoms. We chose the Von Barth–Car pseudopotential for the H atoms [48]. The choice has been shown to give good results for pure liquid methanol [49,50]. The metal ions are taken into account using Goedecker pseudopotential [51]. The electronic states are expanded in a plane-wave basis have been truncated at 70 Ry. The time step in the numerical integration of the equation of motions is 5 a.u. (0.12 fs). A fictitious mass of 800 a.u. is assigned to the electronic degrees of freedom.

The initial configuration for the *ab initio* simulation is taken from a classical molecular dynamics simulation that was run for 1 ns using empirical OPLS potentials. We perform 3 ps of thermalization of this system at 300 K by velocity scaling, and then, 10 ps of free dynamics to make the systems equilibrated. Finally, 32 ps in the NVE ensemble is run, storing the cell dipole every five steps and the atomic coordinates and velocities every step during this production phase of the simulation run for our structural and dynamical analyses.

## 3. Results and discussion

### 3.1. Structure properties

It is generally recognized that obtaining a reliable set of radial distribution function (RDF) has to be an essential prerequisite to understand the structure properties of systems at the atomic level. In Fig. 1, the radial distribution functions for Li–O distances, together with their integration number are reported for the three systems.

The running integration numbers were determined as

$$n(r) = \frac{4\pi N}{V} \int_0^r g(r)r^2 dr$$

where  $N$  is the number of oxygen atoms, and  $V$  is the volume of the simulation cell.

The most distinguished feature is the sharp first maximum of  $\text{Li}^+$ –O and  $\text{Li}^+$ –H RDFs. The amplitude of the  $\text{Li}^+$ –O RDF in the first

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