


Molecular dynamics simulation of lithium fluoride in aqueous solutions at different temperatures 300 K – 360 K

Abdelkbir ERROUGUI ¹ * and Asmaa BENBIYI ¹

¹Laboratory Physical Chemistry, Catalysis and Environnement, Faculty of Sciences Ben M'Sik,
Hassan II University of Casablanca, Morocco.

 <https://orcid.org/0000-0001-9972-7522>

Abstract. Lithium metal is one of the most promising anodes for rechargeable batteries due to its large capacity, but its performance is plagued by high chemical reactivity, forming an unstable Li–electrolyte interface. Lithium fluoride has been recently touted as a promising material to improve this interface. Computer simulation of lithium in fluoride aqueous solution has an important tool in understanding the structural and dynamical characteristics of ionic complexes. In this investigation, the structural and dynamical properties of supersaturated LiF systems have been studied by molecular dynamics simulations at different temperatures range from 300 K up to 360 K using SPC/E water model and the ions which are modeled as charged Lennard-Jones particles. The cartesian positions of each atom of lithium chloride aqueous solution are recorded at every time step of the trajectory. Therefore, the analysis of data requires to calculate the radial distribution functions (RDF) describing the structural and dynamical properties of the water and Li⁺ and F⁻ ions, such as the coordination numbers, interparticle distances, self-diffusion coefficients and dielectric constants at various temperatures.

Keywords: Molecular Dynamics; Hydration number; Self-diffusion coefficient; Dielectric constant; Lithium Fluoride; Energy.

* Corresponding author: a_errougui@yahoo.fr

1 Introduction

Lithium fluoride possesses some unique properties, including high mechanical strength [1], low solubility [2], a wide electrochemical stability window (0 to 6.4 V vs. Li) [3, 4], and low calculated barriers to Li diffusion [5], which suggests that LiF may enable homogeneous Li⁺ flux and suppress dendrites. Consequently, the prevalence of fluoride combined with its attractive properties has led to the suggestion that LiF is a particularly beneficial phase for Solid Electrolyte Interphases [6, 7].

Molecular dynamics (MD) have been established as a powerful and valuable method to investigate the molecular structure of liquids. However, computer simulation of fluorinated salts has an important tool in understanding the dynamics of condensed phases at the molecular level. The development of the fluorine chemical industry is increasing and there is an increasing demand for fluorite. In fact, the hydration properties of fluorinated compounds are relevant to many natural processes and industrial applications [8-12].

The hydration numbers of Li⁺ were considered to be dependent on salt concentrations, with higher salt concentrations resulting in lower hydration numbers. Many structural studies of solutions of alkali metal salts are devoted to hydrated complexes of lithium ions. A large number of works have been undertaken to identify the structure forming and structure breaking properties of ions [13, 14].

The dynamical properties of the alkali fluoride aqueous solutions are of great interest for the knowledge and better understanding of the physico-chemical processes governing industrial, environmental and energetic processes. The analysis of literature of lithium fluoride in aqueous solutions shows a deficiency of data at various temperatures.

The outline of this paper is the following. The simulation details of the MD simulations are given in section 2. The computed structural properties, self-diffusion coefficients and dielectric constants are determined in section 3. The conclusion and final remarks are presented in section 4.

2 Simulation details

Equilibrium molecular dynamics (MD) simulations of lithium in fluoride aqueous solution have been investigated using the GROMACS package [15]. The density of the system is adjusted to reflect the composition of the specific solution being simulated. Coulombic interactions were evaluated with the smooth PME method [16]. NPT simulations were fixed at 1 bar with Parrinello-Rahman pressure coupling [17]. The MD calculation is executed for 3 000 000 steps using 0.1 fs for one time step. In all simulations, we used the simple three-site extended single point charge (SPC/E) model [18] for the water molecules because of its performance combined with a reasonable

description of structure and dynamic properties, which is known to also give an appropriate description of several solution properties. The ion-ion and the ion-water interactions are represented by a combination of Coulombic and LJ potentials [19]. The potential can be written in general as:

$$U_{ij}(r) = \frac{q_i q_j}{r_{ij}} + 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

Where q_i is the charge of the i th atom (or ion). The Lennard-Jones parameters σ_{ij} and ϵ_{ij} are obtained by using the combination rules $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$. The values of the potential parameters q_i , σ_{ij} and ϵ_{ij} for water, Li⁺ and F⁻ ions are summarized in Table 1.

Table 1. Lennard-Jones and electrostatic parameters for the ion and water Force Fields [11, 13].

Element	q	$\sigma_{LJ}(\text{\AA})$	$\epsilon_{LJ}(\text{kJ/mol})$
Li ⁺	+1	2.12645	0.07648
F ⁻	-1	2.73295	3.01248
O	-0.8476	3.16549	0.65314
H	+0.4238	1	0

During dynamic simulations, the OPLS-AA force-field [20] was employed to describe the interatomic potentials of the ions and water components. The simulations were performed at various temperatures. The temperature is controlled by a Nosé-Hoover thermostat [21, 22]. The lithium and fluoride ions were added to a cubic (40 × 40 × 40) Å³ simulation box with 2165 water molecules.

The structure of the liquid was characterized by calculating the pair distribution functions (RDFs) of different pairs and the radial coordination numbers. The radial coordination numbers $n_{ij}(r)$ of different ions are obtained by integrating the radial distribution function, an estimate of the number of water molecules surrounding the M⁺ particle between 0 and the distance r_{\min} .

$$n_{ij}(r) = 4\rho_i \int_0^{r_{\min}} r^2 g_{ij}(r) dr \quad (2)$$

Where $g_{ij}(r)$ is pair distribution function for the i - j pair, ρ_i to the minimum of the first peak in the RDF [$g_{ij}(r)$].

The most common quantity to describe the dynamical behavior of a aqueous system is its self-diffusion coefficient D_i . The translational self-diffusion coefficient can be obtained from the long-time limit of the Mean Square Displacement (MSD) by the Einstein relation:

$$D_i = \lim_{t \rightarrow \infty} \frac{\langle |r(t) - r(0)|^2 \rangle}{6t} \quad (3)$$

Where $r(t)$ is the position vector of the centre of mass of the molecule (or ion) at time t .

The dielectric constant of non-polarizable fluids was computed from fluctuations [23] of the total dipole moment $M = \sum_{i=1}^N \mu_i$ in the simulation volume by

$$\epsilon = \frac{4}{3k_B T \langle V \rangle} (\langle M^2 \rangle - \langle M \rangle^2) + 1 \quad (4)$$

Where k_B is the Boltzmann constant and μ_i is the individual dipole moment vector of the molecule. The angled brackets denote the ensemble average.

3 Results and discussion

3.1 Thermodynamical and structural properties

The effect of temperature is a fundamental element in the structural study of aqueous electrolytic solutions. The computed densities, total energy and structural properties of aqueous LiF solutions at different temperatures are presented in Table 2. The calculated density of aqueous lithium fluoride solutions is a decreasing linear function of temperature.

The hydration structural properties for each aqueous ion (Li^+ and F^-) are computed from canonical NVT ensemble molecular dynamics simulations. It is convenient to study the local structure of an electrolyte solution by means of ion-ion, ion-water, and water-water pair correlation or the radial distribution functions. The RDFs for the case of saturated aqueous LiF electrolytes having a molality $m = 0.1 \text{ mol.Kg}^{-1}$ at different temperatures from 300 K to 360 K are presented in Figs. 1-3. The bibliographic study revealed that the effect of temperature has been less often reported for the aqueous LiF system. Increasing temperature for the cases of Li^+-O_w , Li^+-H_w , F^--O_w , F^--H_w , O_w-O_w and O_w-H_w RDFs (Figs. 1-a, 1-b, 2-a, 2-b, 3-a and 3-b) causes to decrease in the height of the first peak. This is due to increment of kinetic energies of water molecules and ions. But for the Li-F radial distribution function it inversely causes to increase.

Table 2. Simulation values of thermodynamical and structural properties of LiF(aq) at various temperatures

LiF systems for $m = 0.1 \text{ mol/kg}$	1	2	3	4
Temperature (K)	300	320	340	360
Volume (nm^3)	64.52	65.29	66.26	67.36
Calculated density (Kg/m^3)	1002.76	991.02	976.42	960.51
E_{tot} (kJ/mol)	-89011.3	-85320.8	-81680.2	-78073.5

Table 2. (Continued)

$r_{\text{min}}(\text{Li}-\text{O}_w)$ (Å)	2.03	2.03	2.03	2.03
Hydration number (n_{Li^+})	4.19	3.77	2.99	2.63
$r_{\text{min}}(\text{F}-\text{O}_w)$ (Å)	2.61	2.61	2.61	2.61
Hydration number (n_{F^-})	6.23	5.52	4.40	3.75
Number Hbonds / Hydrogen	1.788	1.744	1.700	1.653

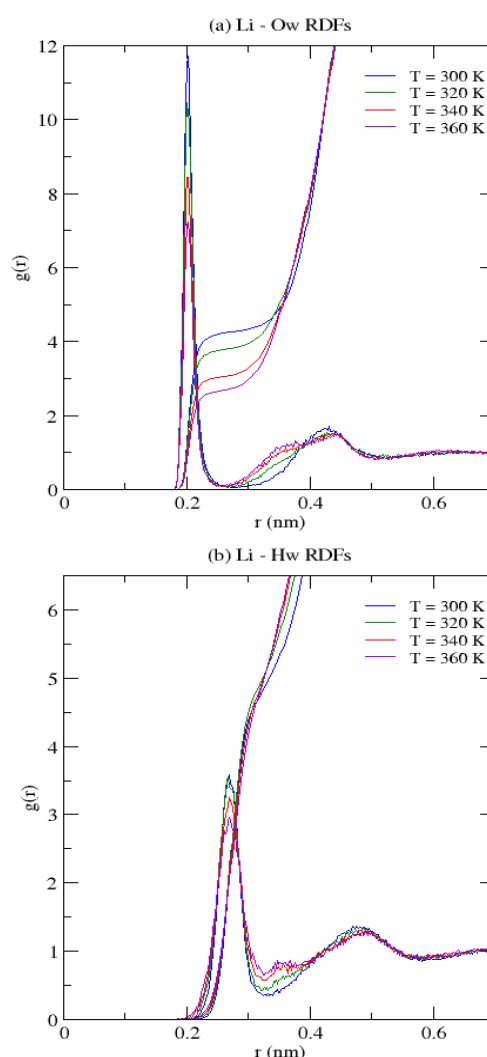


Fig. 1. Radial distribution functions $g_{\text{Li-Ow}}(r)$ and $g_{\text{Li-Hw}}(r)$ for lithium cation at different temperatures.

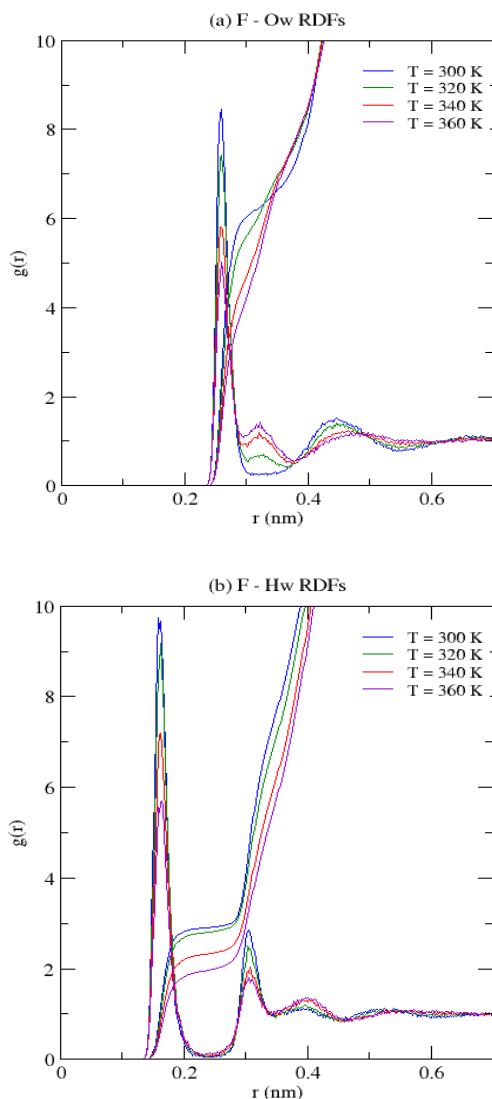


Fig. 2. Radial distribution functions $g_{F-Ow}(r)$ and $g_{F-Hw}(r)$ for fluoride anion at different temperatures.

The first peak of $g_{Li-Ow}(r)$ was at 0.203 nm and the second shell at around 0.433 nm respectively. The magnitude and position of the first peak in Li^+-O_w radial distribution functions agree closely with the previous computer simulations [24-26].

The structural around the fluoride anion can be evaluated by the $g_{F-Ow}(r)$ and $g_{F-Hw}(r)$. Figs. 2-a and 2-b show that the $g_{F-Hw}(r)$ presented two peaks at 0.162 nm and 0.307 nm, respectively. The $g_{F-Ow}(r)$ also presented two peaks, the first peak lay between those of $g_{F-Hw}(r)$ at a distance of 0.261 nm, which indicates that water molecules in the first shell were oriented in such a way that only one hydrogen atom pointed toward the fluoride anion.

The coordination numbers of Li^+ and F^- ions decrease significantly with increasing temperature, which proves the rupture of pairing ions and the increase of separated ones.

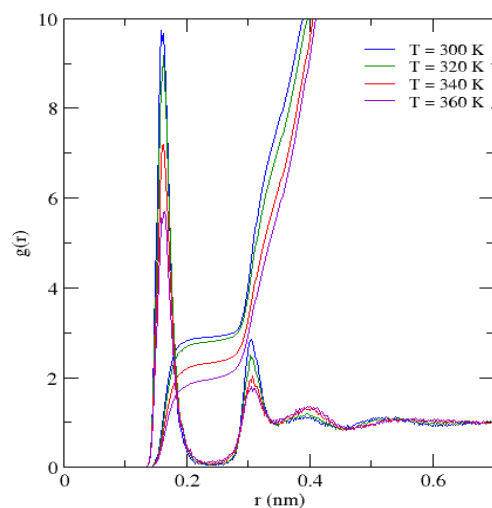


Fig. 3. Radial distribution functions $g_{Li-F}(r)$ at various temperatures.

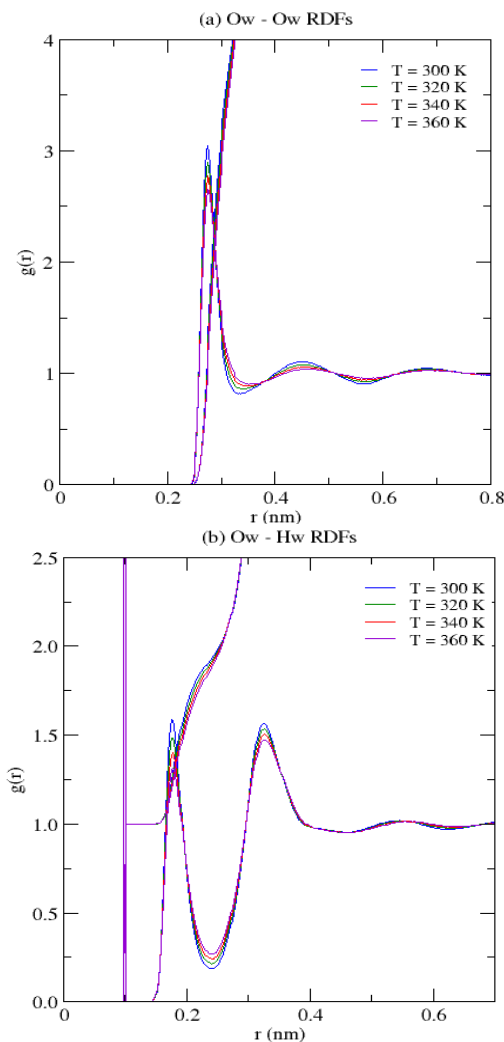


Fig. 4. Radial distribution functions $g_{Ow-Ow}(r)$ and $g_{Ow-Hw}(r)$ for hydrogen bond network as a function of temperature.

The $g_{Li-F}(r)$ curve shows a pronounced two peaks, the first sharp peaks at 0.195 nm correspond to the presence of contact ion pairs (CIP) and the second peaks at 0.387 nm show the presence of solvent-shared ion pair (SIP). The CIP peaks are also higher with increasing of temperature and the number of water separated ion pairs is found to be less significant for

this saturated solutions. A generally good concordance is obtained by comparing these simulation results with those reported in the literature by Fennell and all [27].

The noticeable effects of the increase of the temperature are a decrease of the first and second peaks maximum of Oxygen – Oxygen RDFs. In Fig 4-a we report the $g_{Ow-Ow}(r)$ of LiF(aq) at various temperatures and saturated molality $m = 0.1$ mol/Kg. They are representative of the effects of the temperature on the structure of water. The position of the second peak of $g_{Ow-Ow}(r)$ moves from $3.29 - 5.66$ Å to $3.56 - 5.84$ Å, which indicates a strong distortion of the Oxygen–Oxygen structure in LiF(aq) system when the temperature is increased. Fig 4-b showed the effect of temperature on the hydrogen bond network. According to this figure, when the temperature of the solution increases, the value of the first peak of RDFs decreases. This could be explained by thermal agitation which makes the water molecules faster and subsequently the breaking of the hydrogen bond. These observations on the effect of temperature are in agreement with those of literature [28, 29].

3.1 Dynamical properties

The new values obtained from the simulation for the dielectric constant and self-diffusion coefficients of water, Li^+ and F^- at different temperatures and saturated molality $m = 0.1$ mol.kg⁻¹ are listed in Table 3. As presented in this table, although there are some exceptions for the ion species, the values of the self-diffusion coefficients increase with increasing temperature. This behavior is more pronounced for the water molecules and less for the ions. This may be related to the strong effect of the columbic forces which are more effective on the ion species. Another interesting result is that the dielectric constant decrease with decreasing temperature.

We notice that our value of the simulated dielectric constant using SPC/E is relatively small compared to that found experimentally for pure water ($\epsilon = 78.5$). However, our results are in good agreement with other studies [30-32].

Table 3. The simulation results for the dynamical properties of water, Li^+ and F^- at various temperatures, the self diffusion coefficient expressed in units of (10^{-9} m²/s).

Temperature (K)	D_w	D_{Li^+}	D_{F^-}	Dielectric constant
300	2.644 ± 0.014	1.188 ± 0.039	1.448 ± 0.062	69.655
320	3.902 ± 0.058	1.931 ± 0.097	1.583 ± 0.033	67.968
340	5.236 ± 0.062	1.794 ± 0.056	2.041 ± 0.062	69.930
360	6.827 ± 0.085	0.845 ± 0.049	1.161 ± 0.056	62.934

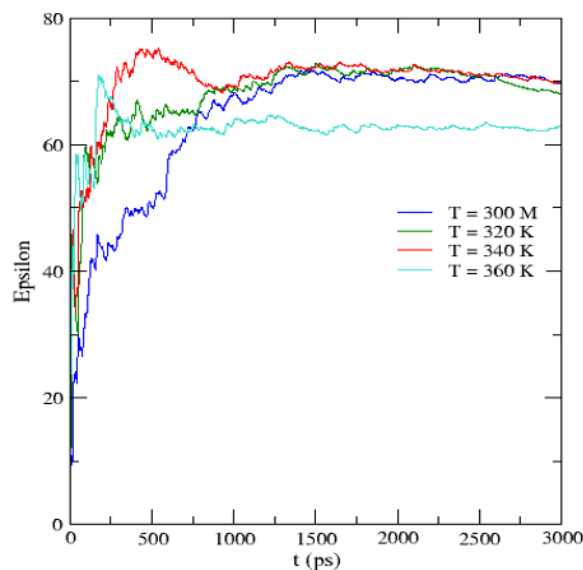


Fig. 5. Dielectric constant of aqueous LiF system as a function of the simulation time at various temperatures.

4 Conclusion

The computer simulations are able to give quantitative information on the dynamics of aqueous electrolytes. We have investigated the structural and dynamical properties of lithium fluoride salt solution at various temperatures ranging from 300 to 360 K by using a SPC/E water model in combination with the OPLS-AA force-field to describe the ion-ion, ion-water and water-water interactions in solution. The results may therefore be used with some confidence in predicting coordination numbers and ion-water geometries for those systems.

The reliability of these force-field parameters has been validated here by comparison of our results with those available in the literature from of molecular simulations and spectroscopic experimental techniques. The hydration structure and dynamical properties of LiF aqueous system are so influenced by the temperature and chemical nature of counterion.

We found that the dielectric constant values decreases as the temperature increases. This is due to increment of kinetic energies of water molecules and ions.

References

- [1] C. Monroe, J. Newman, The effect of interfacial deformation on electrode position kinetics. *J. Electrochem. Soc.* A880–A886, 151(2004).
- [2]. J. Jones et al., Thermodynamic of LiF dissolution in alkyl carbonates and some of their mixtures with water. *Fluid Phase Equilib.* 62–68, 285 (2009).
- [3]. W. D. Richards et al., Interface stability in solid-state batteries. *Chem. Mater.* 266–273, 28 (2016).
- [4]. Y. Zhu, X. He, Y. Mo, Origin of outstanding stability in the lithium solid electrolyte materials: Insights from thermodynamic analyses based on first-

principles calculations. *ACS Appl. Mater. Interfaces*. 23685–23693, 7 (2015).

[5]. Y. Ozhables, D. Gunceler, T. A. Arias, Stability and surface diffusion at lithium electrolyte interphases with connections to dendrite suppression. *ArXiv:1504.05799*, (22 April 2015).

[6] K. D. Collins, G. W. Neilson, J. E. Enderby, Ions in water: Characterizing the Forces that Control Chemical Processes and Biological Structure, *Biophys. Chem.* 95-104, 128 (2007).

[7] B. Morel, B. Duperret, Uranium and fluorine cycles in the nuclear industry, *J. Fluorine. Chem.* 7–10, 130 (2009).

[8] I. Ponsot, R. Falcone, E. Bernardo, Stabilization of fluorine-containing industrial waste by production of sintered glass-ceramics, *Ceram. Int.* 6907–6915, 39 (2013).

[9] H. Li, B. J. Teppen, D. A. Laird, C. T. Johnston, S.A. Boyd, Effects of Increasing Potassium Chloride and Calcium Chloride Ionic Strength on Pesticide Sorption by Potassium- and Calcium-Smectite, *Soil Science Society of America Journal*. 1889-1895, 70 (2006).

[10] D. E. Galvez-Aranda, J. M. Seminario, Simulations of a LiF Solid Electrolyte Interphase Cracking on Silicon Anodes Using Molecular Dynamics, *Journal of The Electrochemical Society*. A717-A730, 165 (2018).

[11] S. Choudhury, L. A. Archer, Lithium Fluoride Additives for Stable Cycling of Lithium Batteries at High Current Densities, *Advanced Electronic Materials*. 1500246, 2 (2016).

[12] M. He, R. Guo, G. M. Hobold, H. Gao, B. M. Gallant, The Intrinsic Behavior of Lithium Fluoride in Solid Electrolyte Interphases on Lithium, *Applied Physical Sciences*. 73-79, 117 (2020).

[13] H. L. Song, C. R. Jayendran, Molecular dynamics simulation of ion mobility. 2. Alkali metal and halide ions using the SPC/E model for water at 25 °C, *J. Phys. Chem.* 1420-1425, 100 (1996).

[14] Sameer Varma, Susan B. Rempe, Coordination Numbers of Alkali Metal Ions in Aqueous Solutions, *Biophysical Chemistry*. 192–199, 124 (2006).

[15] B. Hess, C. Kutzner, D. van der Spoel, and E. Lindahl, GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation, *J. Chem. Theory Comput.* 435-447, 4 (2008).

[16] U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, L. G. Pedersen, A smooth particle mesh Ewald method, *J. Chem. Phys.* 8577-8593, 103 (1995).

[17] M. Parrinello, A. Rahman. Polymorphic transitions in single crystals: A new molecular dynamics method, *J. Appl. Phys.* 7182-7190, 52 (1981).

[18] H. J. C. Berendsen, J. R. Grigera, T. P. Straatsma, The missing term in effective pair potentials, *J. Phys. Chem.* 6269-6271, 91 (1987).

[19] D. Corradini, M. Rovere, P. Gallo, A route to explain water anomalies from results on an aqueous solution of salt, *J. Chem. Phys.* 134508-1/134508-5, 132 (2010).

[20] G. A. Kaminski, R. A. Friesner, J. Tirado-Rives, W. L. Jorgensen, Evaluation and Reparametrization of the OPLS-AA Force Field for Proteins via Comparison with Accurate Quantum Chemical Calculations on Peptides, *J. Phys. Chem. B.* 6474-6487, 105 (2001).

[21] S. Nosé, A molecular dynamics method for simulations in the canonical ensemble, *Mol. Phys.* 255-268, 52 (1984).

[22] W. G. Hoover, Phys. Canonical Dynamics: Equilibrium phase-space distributions, *Phys. Rev. A.* 1695-1697, 31 (1985).

[23] M. Neumann. Dipole moment fluctuation formulas in computer simulations of polar systems, *Molecular Physics*. 841-858, 50 (1983).

[24] Sheng-Bai Zhu and G. Wilse Robinson. Molecular Dynamics Study of an Aqueous LiF Solution. *Z. Naturforsch.* 221 – 228, 46a (1990).

[25] L. Zhang, S. Yan, R. I. Cukier and Y. Bu. Solvation of Excess Electrons in LiF Ionic Pair Matrix: Evidence for a Solvated Dielectron from Ab Initio Molecular Dynamics Simulations and Calculations, *J. Phys. Chem. B.* 3767-3772, 112 (2008).

[26] I. S. Joung and T. E. Cheatham. Determination of Alkali and Halide Monovalent Ion Parameters for Use in Explicitly Solvated Biomolecular Simulations, *J. Phys. Chem. B.* 9020–9041, 112 (2008).

[27] C. J. Fennell, A. Bizjak, V. Vlachy and K. A. Dill. Ion Pairing in Molecular Simulations of Aqueous Alkali Halide Solutions, *J. Phys. Chem. B.* 6782–6791, 113 (2009).

[28] K. Ibuki and P. A. Bopp. Molecular dynamics simulations of aqueous LiCl solutions at room temperature through the entire concentration range, *J. Mol. Liquids*. 56-63, 147 (2009).

[29] R. W. Impey, P. A. Madden, I. R. McDonald. Hydration and Mobility of Ions in Solution. *J. Phys. Chem.* 5071-5083, 87 (1983).

[30] M. R. Reddy and M. Berkowitz. The dielectric constant of SPC/E water, *Chem. Phys. Letters*. 173-176, 155(1989).

[31] G. Raabe and R. J. Sadus. Molecular dynamics simulation of the dielectric constant of water: The effect of bond flexibility, *J. Chem. Phys.* 23450, 134 (2011).

[32] D. Saric, M. Kohns and J. Vrabec. Dielectric constant and density of aqueous alkali halide solutions by molecular dynamics: A force field assessment, *J. Chem. Phys.* 164502, 152 (2020).