

Structural Arrangement of Water Molecules around Highly Charged Nanoparticles: Molecular Dynamics Simulation

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Molecular dynamics simulations were performed to understand the structural arrangement of water molecules around highly charged nanoparticles under aqueous conditions. The effect of two highly charged nanoparticles on the solvation charge asymmetry has been examined. We calculated the radial distribution functions of the components of water molecules around nanoparticles which have four charge types at two different salt concentrations. Even though the distributions of water molecules surrounding a sodium ion and a chloride ion are hardly affected by the charges of nanoparticles and the salt concentrations, those around highly charged nanoparticles are strongly influenced by the charges of nanoparticles, but hardly by the charges of nanoparticles and salt concentrations. We find that the distributions of hydrogen atoms in water molecules around one highly charged nanoparticle are dependent on the magnitude of the nanoparticle charge.

Key Words : Nanoparticle, Electrostatic interactions, Radial distribution function

Introduction

In a typical human cell, it is estimated there are 100 trillion water molecules and several thousand different proteins. Water and proteins play crucial roles in many metabolic processes, photosynthesis, and enzyme function.¹⁻⁷ Recent researches have revealed the structure and function of internal water molecules in proteins. For examples, hydrogen-bonded water molecules play an important role in the proton-pumping activity of *Gloeobacter rhodopsin*.

Water causes a greenhouse effect because water vapor, tiny water droplets in clouds, and ice clouds absorb solar radiation.⁸⁻¹⁶ In particular, water clusters (clusters of water molecules including water dimers) act as greenhouse gases. Many studies on water clusters have been carried out not only to investigate the role of water clusters in biological and chemical systems but also to understand the nature of hydrogen bonding.^{8-11,13-28} Coleman and Spael²⁹ studied the evaporation from water clusters containing singly charged ions to examine the effect of the presence of ions on the evaporation of water droplets.

Charged nanoparticles hold great promises for biomedical applications such as drug delivery, gene therapy, and anti-cancer treatments due to their physicochemical properties. Charged nanoparticles in aqueous media interact with others through van der Waals dispersion forces and electrostatic interactions. Recent experiments³⁰ and theoretical studies³¹⁻³³ reported charge-dependent asymmetry near surfaces of charged colloidal systems. Gonzalez-Mozuelos and Olvera de la Cruz³¹ studied how the effective renormalized charges of nanoparticles affect the asymmetric charge distribution of water molecules by using the dressed interaction site theory. They reported the strong dependence of the effective renormalized charge of the nanoparticles on the sign of the

bare charge. However more detail information between highly charged nanoparticles and the other small molecules should be examined. In this work, we present simulations on highly charged nanoparticles under aqueous conditions. Especially the radial distribution functions of small atoms around highly charged nanoparticles are obtained in order to understand the effect of two charged nanoparticles in aqueous media.

Model and Simulation

Constant temperature and volume molecular dynamics (NVT) simulations of two highly charged nanoparticles under aqueous conditions were performed using LAMMPS software package.³⁴ Two highly charged nanoparticles were separately positioned in a simulation box whose size is $15 \times 15 \times 15$ nm. The initial distance between two nanoparticles is 7.5 nm so that those can't interact directly with each other. The simulation box was replicated periodically in x, y, and z directions. The aqueous solution with NaCl salt contains 109,660 and 111,689 water molecules. Five cases of highly charged nanoparticles for each salt concentration of 0.1 M and 1.0 M are considered. Two kinds of nanoparticles are defined as NP and MP. Each nanoparticle has a charge of either -8 , -5 , 5 , or 8 . The specific conditions of simulation systems are given in Table 1. The Nosé-Hoover thermostat with a time constant of 0.1 ps was employed to regulate the temperature. SPC/E (extended simple point charge) water model is used and the interaction potential for all pairs is given by

$$\beta u_{ij(r)} = \beta u_{ij}^{LJ}(r) + \frac{l_B}{r} q_i q_j \quad (1)$$

Table 1. System information

Salt concentration (M)	Case	Number			Charge	
		Water	Na ⁺	Cl ⁻	NP	MP
1.0	C _{5,-5}		2,015	2,015	5	-5
	C _{8,-5}		2,015	2,018	8	-5
	C _{5,-8}	109,660	2,018	2,015	5	-8
	C _{5,5}		2,015	2,025	5	5
	C _{-5,-5}		2,025	2,015	-5	-5
0.1	D _{5,-5}		201	201	5	-5
	D _{8,-5}		201	204	8	-5
	D _{5,-8}	111,689	204	201	5	-8
	D _{5,5}		201	211	5	5
	D _{-5,-5}		211	201	-5	-5

Table 2. Values of the Lennard-Jones Parameters

	$\beta\epsilon_i$	σ_i (Å)
O	0.26066	3.1656
H	0.16782	0.60
Na ⁺	0.21820	2.35
Cl ⁻	0.16780	4.40
NP	1.67785	15.00
MP	1.67785	15.00

$$u_{ij}^{LJ}(r) = 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^6 \right) \quad (2)$$

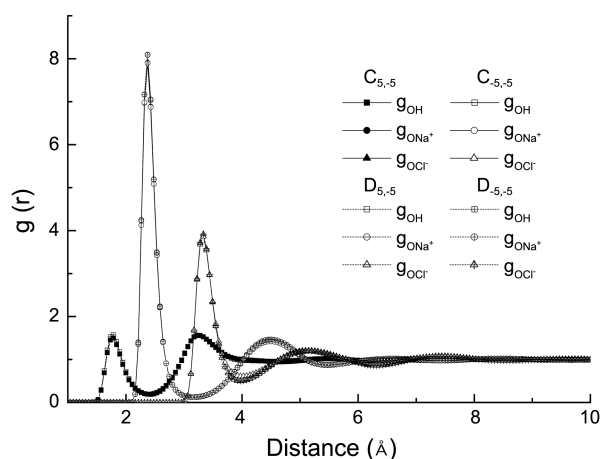
for $i, j = \text{O, H, Na}^+, \text{Cl}^-, \text{NP, and MP}$, where l_B is the Bjerrum length, q_i is the charge of the each atom and is the Lennard-Jones pair potential. The Lennard-Jones parameters are given by the values in Table 2. The charges of the water molecules are given by $q_o = -2q_H = -0.8476$, and r is the distance between two atoms. Simulations of charged nanoparticles under aqueous conditions with two ion types were performed for 3 ns for equilibration after a short pre-equilibration. Following the equilibration procedure, 3 ns MD simulations were carried out for the equilibrium properties. All simulations were performed at 298.15 K.

Results and Discussion

In order to understand the effect of highly charged nanoparticles under aqueous conditions on the structural arrangement of water molecules, radial distribution functions are calculated. We determined the radial distribution function by calculating the distance between all atom pairs.

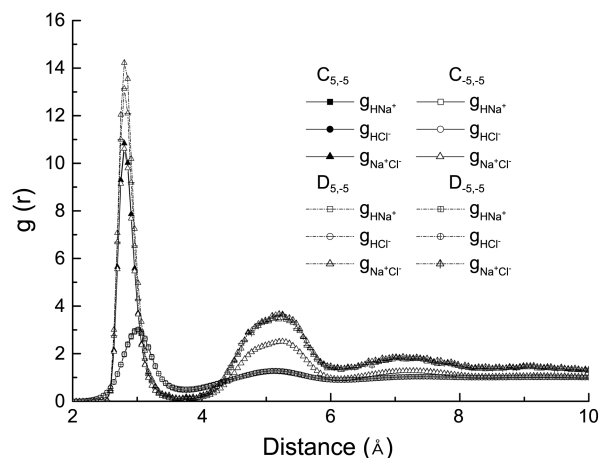
Water molecules distribute around nanoparticles, free sodium ions and chloride ions. Water radial distribution functions³⁵ with salts and temperature dependence³⁶ on water structure had been discussed. In this work, we discuss how the distributions depend on the sign of the bare charge of nanoparticles and the magnitude of the nanoparticle charge. The effect of distributions of water molecules on salt concentrations is also examined.

Figure 1 shows the distribution functions between pairs of

**Figure 1.** Oxygen-hydrogen, oxygen-sodium ion, and oxygen-chloride ion radial distribution functions at two different salt concentrations.

water molecules (g_{OH}) and oxygen atoms in water molecules around free sodium and chloride ions (g_{ONa^+} and g_{OCl^-}). As one would expect, the first peaks for the distributions are located at the van der Waals radii of two atoms. The oxygen atoms in water molecules have a clear affinity toward the sodium ions. These distributions are hardly affected by the charges of nanoparticles and salt concentrations.

In Figure 2, the distribution functions for the hydrogen atoms in water molecules surrounding a sodium and a chloride ion (g_{HNa^+} and g_{HCl^-}) have been shown. Figure 2 also illustrates the distributions of the sodium ion-chloride ion at two different concentrations. In these systems, water molecules and two salt ions might be affected by two nanoparticles with charges either $q_{\text{NP}} = 5$ and $q_{\text{MP}} = -5$ or $q_{\text{NP}} = -5$ and $q_{\text{MP}} = -5$. However the hydrogen-salt ion distributions are hardly affected by the charges of nanoparticles and salt concentrations. Even though, for the distribution functions ($g_{\text{Na}^+\text{Cl}^-}$) between salt ion pairs, the positions of the peaks are hardly affected, but the heights of the first maxima

**Figure 2.** Hydrogen-sodium ion, hydrogen-chloride ion, and sodium ion-chloride ion radial distribution functions at two different salt concentrations.

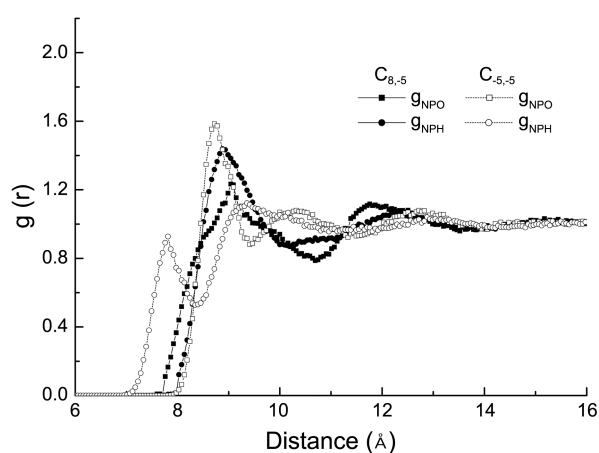


Figure 3. Radial distribution functions of the oxygen atoms and hydrogen atoms in water molecules around one nanoparticle with charges either $q_{NP} = 8$ or $q_{NP} = -5$ at 1.0 M salt concentration.

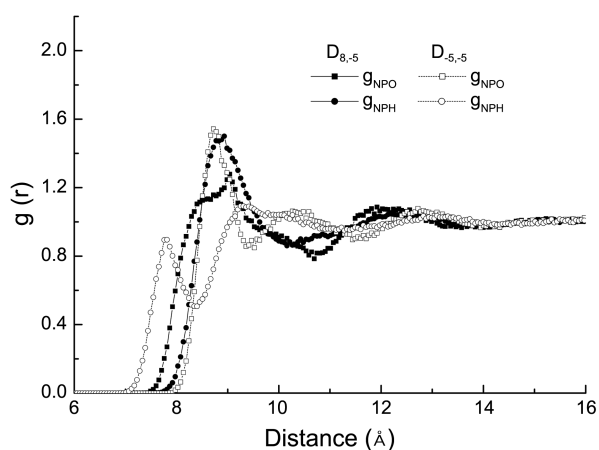


Figure 4. Radial distribution functions of the oxygen atoms and hydrogen atoms in water molecules around one nanoparticle at 0.1 M salt concentration.

are lowered at high concentration. Interestingly, when both nanoparticles are negatively charged, the distributions are lowered than those of other systems after the position of the first minima. This difference is attributed to affinity of sodium ions toward the negatively charged nanoparticles.

Figures 3 and 4 show the distributions of the oxygen atoms and hydrogen atoms in water molecules around one nanoparticle with charges either $q_{NP} = 8$ or $q_{NP} = -5$. At the high salt concentration, the first peaks of the oxygen-nanoparticle radial distribution functions are located at 9.09 Å and 8.72 Å, respectively. The first peaks of the hydrogen-nanoparticle radial distribution functions are located at 8.88 Å and 7.81 Å, respectively. The second peak of the distribution functions of hydrogen atoms in water molecules around one nanoparticle with charge $q_{NP} = -5$ are located at 9.36 Å. This second peak becomes higher than the first peak. In case of nanoparticle with $q_{NP} = -5$, hydrogen atoms are oriented toward the oppositely charged nanoparticle. But the distributions of hydrogen atoms in water molecules around one nanoparticle with $q_{NP} = -5$ indicate that only one of two

hydrogen atoms in water molecules in the first solvation layer is oriented toward the oppositely charged nanoparticle. So the height of the second peak is higher than that of the first. This might be attributed to the energetic effect of hydrogen bond formation between water molecules and/or the entropic restrictions due to the anisotropic shape of water molecules.

In Figure 4, the first peaks of the oxygen-nanoparticle radial distribution functions are located at 9.04 Å and 8.72 Å, respectively. The first peaks of hydrogen-nanoparticle radial distribution functions are located at 8.93 Å and 7.81 Å, respectively. The second peak of the distribution functions of hydrogen atoms in water molecules around one nanoparticle with charge $q_{NP} = -5$ are located at 9.25 Å. Comparing with the positions of the peaks at high salt concentration, their positions at low salt concentration remain almost invariant. That means the hydrogen-salt ion distributions are hardly affected by the salt concentrations. In case of nanoparticle with charge $q_{NP} = 8$, the first peaks of the hydrogen distributions locate a little bit closer those of the oxygen distributions from the nanoparticle.

However the broad distributions of oxygen atoms and the shift to shorter distance show that oxygen atoms in water molecules have a stronger affinity with respect to hydrogen atoms in water molecules. While only water molecules distribute in the first solvation layer of the nanoparticle with charge $q_{MP} = -5$, chloride ions are also found in the first solvation layer of the nanoparticle with charge $q_{MP} = 8$ (Figure 5). So the water molecules near the first solvation layer interact with both the oppositely charged nanoparticle and the likely charged chloride ions.

In Figures 6 and 7, radial distribution functions of the oxygen atoms (g_{MPO}) and hydrogen atoms (g_{MPH}) in water molecules around one nanoparticle with charges either $q_{MP} =$

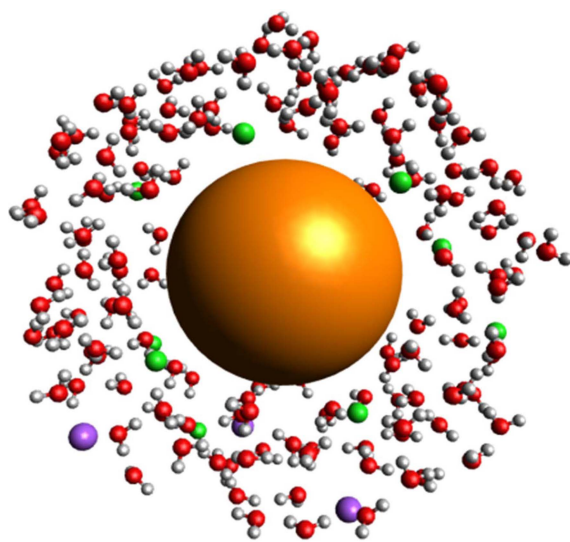


Figure 5. Snapshot of the arrangement of water molecules surrounding one nanoparticle with charge $q_{MP} = 8$. A nanoparticle, oxygen atoms, hydrogen atoms, sodium ions, and chloride ions are colored in orange, red, white, purple, and green, respectively. Some water molecules are shown for clarity.

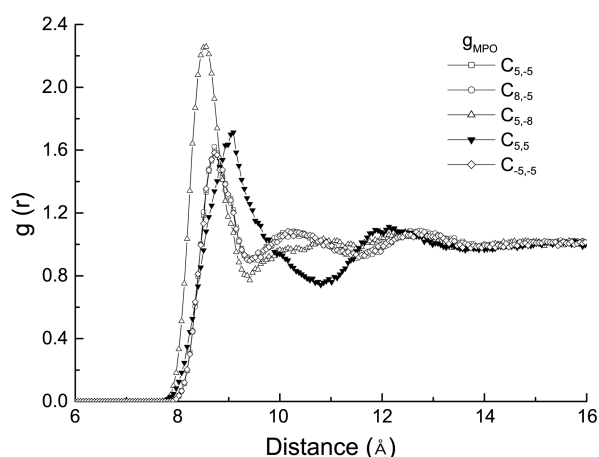


Figure 6. Radial distribution functions of the oxygen atoms in water molecules around one nanoparticle with charges either $q_{MP} = -8$, $q_{MP} = -5$, or $q_{MP} = 5$ at 1.0 M salt concentration.

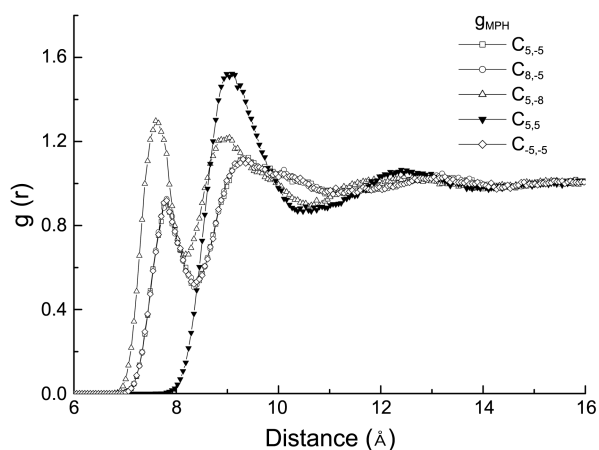


Figure 7. Radial distribution functions of the hydrogen atoms in water molecules around one nanoparticle with charges either $q_{MP} = -8$, $q_{MP} = -5$, or $q_{MP} = 5$ at 1.0 M salt concentration.

-8 , $q_{MP} = -5$, or $q_{MP} = 5$ have been shown. We compared the radial distribution functions of the oxygen atoms and hydrogen atoms in water molecules around one nanoparticle with charges either $q_{MP} = -8$, $q_{MP} = -5$, or $q_{MP} = 5$. The first peaks of the hydrogen distributions are shifted to shorter distance and increase in height as the nanoparticle charge becomes more negative. The oxygen distributions show similar behavior to those of the hydrogen atoms, but simulations show rather weaker effect between oxygen atoms and one charged nanoparticle.

Gonzalez-Mozuleos and Olvera³¹ suggested the positively charged nanoparticles have larger solubility than negatively charged nanoparticles in the absence of short ranged attractions among nanoparticles. If we consider two nanoparticles with different charges under aqueous conditions, water molecules have weaker affinity toward the positively charged nanoparticle with respect to the negatively charged nanoparticle. The distributions of the water molecules around highly charged nanoparticles are hardly affected by salt concentrations (data not shown here).

Conclusion

Molecular dynamics simulations were performed on highly charged nanoparticles under aqueous conditions. Nanoparticles with different charges at two different salt concentrations are considered to examine the structural arrangement of water molecules around highly charged nanoparticles. In order to study a charge dependence of the structural arrangement of water molecules around highly charged nanoparticles, radial distribution functions of the oxygen atoms and hydrogen atoms in water molecules are calculated. The oxygen-salt ion and hydrogen-salt ion distributions are hardly affected by the charges of nanoparticles and salt concentrations. Oxygen atoms and hydrogen atoms in water molecules are oriented toward the oppositely charged nanoparticles. However, only one of two hydrogen atoms in water molecules in the first solvation layer is oriented toward the nanoparticle with charge $q = -5$. Water molecules have weaker affinity toward the positively charged nanoparticle with respect to the negatively charged nanoparticle. The distributions of the water molecules around highly charged nanoparticles are hardly affected by the salt concentrations.

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