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Analysis of effect of ion irradiation to liquid surface on water molecule kinetics by classical molecular dynamics simulation

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We analyzed the physical behavior of water molecules to assess the effect of ion bombardment from atmospheric-pressure plasma to a liquid surface by classical molecular dynamics simulation. As the incident ions, O\(^+\) was considered. The number of sputtered water molecules, liquid temperature, and ion penetration depth in liquid were investigated after O\(^+\) ions with kinetic energies of 10 and 100 eV impinged on the liquid surface. The average numbers of sputtered water molecules by ion impact were 0.5 at 10 eV and 7.0 at 100 eV. The sputtering of water molecules depended on the ion penetration depth and near-surface liquid temperature. The sputtering dynamics was discussed in detail. In addition, we presented the effect of an impinging ion on a liquid surface under an external electric field. The result shows that the number of sputtered water molecules increases with increasing electric field strength, which affects the water molecule orientation.

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1. Introduction

Nonthermal atmospheric-pressure plasmas have the advantage that we can easily irradiate various substances such as solid, liquid and biological objects with high-density plasma under atmospheric conditions.\(^{1}\) In particular, plasmas in contact with liquid are promising in the fields of material science,\(^{2-6}\) environment technology,\(^{7,8}\) and medical biology\(^{9}\) as a tool to provide a new reaction field. The phenomena on the molecular scale occurring at the plasma–liquid interface are still not clear. When we operate atmospheric-pressure discharge plasma with a liquid cathode, and analyzed the sputtering yield and polymer surfaces formed by dielectric barrier discharge filaments in air, and showed that the incident ion energy depended on the dielectric constant of the polymer and instantaneously exceeded 100 eV with a high-dielectric-constant material.\(^{10}\) Note that the energy of an incident positive ion depends on the gas composition, pressure, current density, type of discharge, and so on.

In the present work, we report the results of impingement of O\(^+\) ions with kinetic energies of 10 and 100 eV on the water surface in atmospheric-pressure dc discharges with a liquid cathode. The incident ion energy of 10 eV corresponds to a moderate atmospheric-pressure glow discharge, and that of 100 eV corresponds to a more active discharge. The effect of ion impact on the liquid surface is evaluated using the number of sputtered water molecules and the time variation of liquid temperature. We discuss how the energy is transferred from incident ions to surrounding water molecules in liquid. When a voltage is applied to an electrolyte solution, an electric double layer is formed on the surface.\(^{11,12}\) The thickness of the electric double layer depends on the electrolyte concentration and becomes approximately 1 nm at a high electrolyte concentration. When the voltage drop of the double layer with a thickness of 1 nm is 1 V, the electric field becomes 10\(^5\) V\(\cdot\)m\(^{-1}\), which affects the orientation of water molecules. There are many studies on the dipole moment and orientation of water molecules under an electric field,\(^{13-23}\) but no studies on the effect of ion impact on a liquid surface.

Thus, we also investigated the effect of ion impact on a liquid surface under an external electric field. The composition of this paper is as follows. In Sect. 2, the simulation model and calculation method are shown. In Sect. 3.1, the results of liquid dynamics, the number of sputtered water molecules, and the penetration depth of incident ions in liquid are presented. The temporal change in liquid temperature is discussed in Sect. 3.2. In Sect. 3.3, the sputtering mechanism of water molecules caused by ion impact is discussed. The effects of an external electric field on the orientation and behavior of water molecules during ion impact on a liquid surface are described in Sect. 3.4. Finally, conclusions are presented in Sect. 4.

2. Simulation method

In atmospheric-pressure dc discharge excited between a metal
anode and liquid water as a cathode, positive ions enter the water surface. In order to assess the effect of irradiating positive ions from plasma to a liquid surface with a nanometer scale, we carried out a classical MD simulation to determine the trajectories of individual molecules. We assumed O$^+$ ions as the irradiation particles from the plasma. The simulation model of O$^+$ ion impingement on a liquid surface is shown in Fig. 1. The rectangular simulation cell has dimensions of $31 \times 31 \times 62 \text{ Å}^3$ and contains 2000 water molecules; thus, its specific weight is 0.998 g cm$^{-3}$. Supposing that the typical current density of atmospheric-pressure dc discharge is $10^{-1}$–$10^{2}$ A cm$^{-2}$, one positive ion travels from the plasma to the liquid surface of the simulation cell in Fig. 1 at intervals of 10 ns–10 μs. Therefore, only one incident ion is considered in the simulation. Vacuum layers that correspond to the gas phase adjoin the top and bottom of the simulation cell, while a periodic boundary condition is applied to the sides of the simulation cell. An incident particle is placed in a vacuum layer at a distance of 30 Å from the top of the liquid surface and impinges vertically on the liquid surface at an initial velocity of 10 or 100 eV. The Verlet algorithm was employed to integrate the classical Newton’s equation of motion with a time step of 1.0 fs. After equilibrating the system at 300 K, the O$^+$ ion entered the liquid surface.

The interaction between water molecules is represented by the extended simple point charge (SPC/E) model. The potential between an O$^+$ ion and a water molecule is not available in the literature to the best of our knowledge. Thus, the potential was determined from the results of quantum chemistry calculation using Gaussian09. Figure 2 shows the potential energy curves for H$_2$O–O$^+$ as a function of the distance between an O$^+$ ion and the O atom of water. We defined the angle between the dipole moment of water and the line connecting O$^+$ with O as $T$ (0–180°). The potential energy curves strongly depend on the orientations of the water molecule and O$^+$ ion because of the electrical polarization of the water molecule. When the distance between O$^+$ and O is smallest ($T=180°$), the potential energy has the most stable form. The most stable distance between O$^+$ and O is 1.8 Å; the potential energy becomes repulsive at an interatomic distance smaller than 1.8 Å and attractive at an interatomic distance larger than 1.8 Å. When $T$ is 30° at which the distance between O$^+$ and H is shortest, the potential energy is highest and is always repulsive because of the strong repulsive Coulomb force. The two-body interatomic potential between a water molecule and an ion is often expressed as the sum of short-range Lennard-Jones (LJ) and Coulomb potential. We also used the same formula for the potential between O$^+$ and a water molecule by fitting the potential curve in Fig. 2 with the following formula by the least-squares method:

$$V_{\text{H}_2\text{O}-\text{O}^+} = 4\varepsilon_0 \frac{q_H q_{\text{O}^+}}{r_{\text{H}_2\text{O}-\text{O}^+}^6} - \frac{1}{4\varepsilon_0} \left( \frac{q_H q_{\text{O}^+}}{r_{\text{H}_2\text{O}-\text{O}^+}} + \frac{q_O q_{\text{O}^+}}{r_{\text{H}_2\text{O}-\text{O}^+}} + \frac{q_{\text{H}_2\text{O}} q_{\text{O}^+}}{r_{\text{H}_2\text{O}-\text{O}^+}} \right).$$  

(1)

Here, $q$ is the charge of H, O, or O$^+$, $r_{a,b}$ is the interatomic distance between atoms a and b, and $\varepsilon_{\text{H}_2\text{O}}$ and $\varepsilon_{\text{O}^+}$ are the LJ energy and size parameters between O$^+$ and the O atom of the water molecule, respectively. The subscripts $\alpha$ and $\beta$ in Eq. (1) are used to distinguish the two H atoms in the water molecule. The angular dependence of the potential curve in Fig. 2 is considered for the interatomic distance in Eq. (1). The LJ potential parameters used in this work are listed in Table I.

When a cathode sheath is facing the liquid surface, a strong electric field penetrates into the liquid. In other words, a double layer is formed in the liquid. The strong electric field in the double layer contributes to the orientation of water molecules. Therefore, the effect of an external electric field on the behavior of water molecules was studied. The additional force $F_i$ induced by the external electric field $E$ is

$$F_i = q_i E,$$

(2)

where $q_i$ is the charge of each atom. The static electric field was always applied along the vertical direction (z-axis).
of the simulation cell. The MD simulation was performed under different external electric fields of $0, 2.0 \times 10^8$, and $2.0 \times 10^9$ V·m$^{-1}$ to investigate the effect of the external field on the structure and dynamics of water. We defined the angle between each dipole moment of water, $m_{pi} = (m_{pxi}, m_{pyi}, m_{pzi})$, and each electric field vector, $E = (0, 0, -E)$, as $\theta_i$. The orientation of each water molecule is expressed by $\cos \theta_i$ as

$$\cos \theta_i = \frac{-m_{pzi}}{|m_p|}.$$  \hspace{1cm} (3)

3. Results and discussion

3.1 Behavior of incident ion and liquid after ion bombardment

Figures 3(a) and 3(b) show typical snapshots of the simulation results at ion irradiation with energies of 10 and 100 eV. After ion impact on the liquid surface, water molecules are ejected from the surface; however, most ejected water molecules are brought back to the liquid by the attractive force of the liquid surface. Some water molecules with sufficient energy to overcome the attractive force from the liquid surface evaporate. At 10 eV ion impact on the liquid surface, the structure of the water surface changes slightly. When an ion with an energy of 100 eV impinges on the liquid surface, water molecules are pushed out of the liquid surface and temporarily form a hollow structure at ion impact. At 10 ps, most ejected water molecules are brought back to the liquid surface and then the hollow structure disappears. At an ion irradiation energy of 10 eV, sputtered water molecules exist as monomers in the gas phase since the number of ejected water molecules is small. At an ion irradiation energy of 100 eV, the number of ejected water molecules increases, and the water molecules exist as dimers, trimers, and clusters formed by hydrogen bonds between water molecules, which is the same as the result obtained by Nikiforov.\textsuperscript{13) The impinging ion was surrounded by roughly 3–4 water molecules.

Figure 4 shows the distribution of penetration depths of impinging ions with kinetic energies of 10 and 100 eV for 20 calculations. If an impinging ion bounces off the liquid surface and cannot penetrate into the liquid, we consider the penetration depth to be 0 Å. The incident ions with a high energy of 100 eV are sometimes reflected at the liquid surface without penetrating into the liquid. This is because the hydrogen atoms in the water molecules repel the incident ions owing to a strong repulsive Coulomb force. At low ion irradiation energies, even if the hydrogen atoms of the water molecules are facing the O$^+$ ion, the water molecules rotate to reduce the repulsive force very rapidly within 0.03 ps. In contrast, the incident high-energy ions approach the water molecules before the water molecules start to rotate; thus, a strong repulsion pushes the incident ions away at high velocities.

Table II shows the average number of sputtered water molecules and the average and maximum penetration depths of impinging ions from the liquid surface. The ion penetration depth at 10 eV has a high probability around the mean value of 7.0 Å. At 100 eV ion energy, the average ion penetration depth is nearly twice ($\approx 15.0$ Å) as deep as that at 10 eV and has a wide distribution.

Figure 5 shows the relationship between the average number of sputtered water molecules and the penetration...
depth of incident ions. When the penetration depth of incident ions is less than 5 Å, the average numbers of sputtered water molecules are 1.0 for 10 eV ion irradiation and 23 for 100 eV ion irradiation. With increasing ion penetration depth in the liquid, the number of sputtered water molecules decreases. The water molecules ejected into the gas phase are not from deep in the liquid but from near the surface. Thus, the position where the incident ion transfers its kinetic energy to the surrounding water molecules is more important for the sputtering of water molecules. An example of the energy loss of incident ions in a liquid is shown in Fig. 6. The ion penetration depth and the number of sputtered molecules are 14.5 Å and 2 for case 1, and 21.7 Å and 7 for case 2, respectively. Since the ion in case 2 loses more energy near the gas–liquid interface, the number of sputtered water molecules is larger than that in case 1.

After the incident ion penetrates into the liquid, it moves until the kinetic energy is almost lost. The kinetic energy of the incident ion is relaxed within 0.5–1.0 ps. The trajectory of the incident ion depends on how the ion receives the repulsive force from the water molecules. The ion trajectory in the liquid was classified roughly into three patterns, as shown in Fig. 7. In Fig. 7(a), an incident ion receives the repulsive force from the water molecules in the vertical direction against its travelling direction. The horizontal ion trajectory near the liquid surface caused the sputtering of a large number of water molecules. Thirty molecules were sputtered in this example. In Fig. 7(b), the ion trajectory reaches deeper without receiving strong repulsive force. In this case, there were no sputtered water molecules. Figure 7(c) shows the trajectory of the ion reflected at the liquid surface without penetrating into the liquid. In this case, 90 water molecules were sputtered.

3.2 Liquid temperature after ion impact

After ion bombardment on the liquid surface, the liquid temperature locally increases since the kinetic energy of impinging ion is transferred to the liquid. We investigated the liquid temperature after ion bombardment with energies of 10 and 100 eV on the liquid surface to clarify the heat transfer mechanism. To clarify the change in liquid temperature as a function of depth from the liquid surface, the simulation cell was separated into six layers, as shown in Fig. 8. The layers were named layers A to F from the surface. Figure 9(a) shows the change in liquid temperature when the penetration depth of the incident ion is 6.5 Å and the number of sputtered water molecules is 30. After ion impact on the liquid surface, the temperature of layer B, which corresponds to the ion penetration depth, increases immediately. The temperature of layer B exponentially decays with a decay constant of 1 ps since water molecules move from layer B to layer A. At 6 ps,
the liquid temperature is almost relaxed with temperature increase of 100–200 K from the initial value of 300 K near the liquid surface. Irradiation energy is transferred to layer D within sub-ps; however, it requires tens of picoseconds to transfer the heat to layers E and F. Figure 9(b) shows the change in liquid temperature when the penetration depth of the incident ion is 27.5 Å and the number of sputtered water molecules is zero. In this case, a rapid increase followed by a decrease in liquid temperature was confirmed in layer C, while the temperature change in layer B was found to be not very large. This indicates that the liquid temperature near the surface plays a more important role than that at greater depths.

3.3 Detailed sputtering mechanism of water molecules

When the kinetic energy of a water molecule in a liquid overcomes the attraction force from the surrounding molecules, the water molecule is sputtered or evaporated. An ion entering the water disturbs the stable arrangement of hydrogen-bonded water molecules in the liquid. Some water molecules that receive a repulsive force from neighboring water molecules in a liquid move away or rotate. The new molecular arrangement again causes the interaction between molecules, and the potential is successively distorted. Finally, the water molecule at the gas–liquid interface is pushed out into the gas. Figure 10 shows a typical example of the sputtering of water molecules by ion irradiation. After ion penetration into the liquid, the incident O⁺ receives a repulsive force from the H atoms of the water molecule near the interface and changes its travelling direction [Fig. 10(a)]. The O⁺ ion repulsively interacts with the H atoms of water molecule 1 [Fig. 10(b)], then water molecule 1 rotates very rapidly [Fig. 10(c)]. The H atoms of water molecule 1 rapidly approach the O atom of water molecule 2. Water molecule 2 receives a rightward force and pushes out water molecule 3 [Figs. 10(d)–10(f)]. Then, water molecule 3 is released into the gas phase at 0.4 ps. The effect of the strong Coulomb interaction is due to the dipole moment of the
A water molecule and the rapid molecular rotation is distinctive in the sputtering of liquid-phase water molecules by ion impact.

3.4 Behavior of liquid water under external electric field
As shown in the previous section, the orientation of water molecules is an important factor that characterizes the sputtering or evaporation of liquid water. The orientation of water molecules can be controlled by an external field. Actually, the electric field in the double layer in electrolysis exceeds $10^8 \text{V}\cdot\text{m}^{-1}$ and reaches $10^9 \text{V}\cdot\text{m}^{-1}$ in a high-concentrion electrolyte. Even at the liquid interface facing the plasma, a high electric field is expected. Therefore, we investigated the effect of the orientation of liquid water molecules with an external static electric field on the liquid water dynamics under ion irradiation from the plasma to the liquid surface. The applied external fields were $2.0 \times 10^8$ and $2 \times 10^9 \text{V}\cdot\text{m}^{-1}$ in the vertical direction ($z$-direction).

Figure 11 shows the orientation distribution of 2000 water molecules determined using Eq. (3). The behavior of the liquid with a field strength of $2.0 \times 10^9 \text{V}\cdot\text{m}^{-1}$ is almost the same as that without an external field because the interaction among water molecules is stronger than the electric field force. For the field strength of $2.0 \times 10^9 \text{V}\cdot\text{m}^{-1}$, many water molecules are oriented along the direction of the electric field. Since H atoms of water molecules receive a downward force from the electric field, water molecules cannot rotate easily. When the O$^+$ ion comes close to the H atoms of water molecules in the liquid, water molecules rotate to reduce the repulsive force at a lower electric field. At the high field strength of $2.0 \times 10^9 \text{V}\cdot\text{m}^{-1}$, water molecules tend to receive a repulsive force and are released into the gas phase because of the restriction of water molecule rotation. Figure 12 shows an example of the dynamics of water molecules during ion irradiation with an energy of 10 eV. The average number of sputtered water molecules increases from 0.5 without an external field to 1.8 with an electric field of $2.0 \times 10^9 \text{V}\cdot\text{m}^{-1}$. At ion irradiation with an energy of 100 eV and an external field of $2.0 \times 10^9 \text{V}\cdot\text{m}^{-1}$, too many water molecules were evaporated and, therefore, sputtering yield could not be defined. It is suggested that a strong electric field causes the higher sputtering yield of water molecules.

4. Conclusions
In atmospheric-pressure discharge plasma with a liquid cathode, ions accelerated by cathode fall hit the liquid surface. Both the physical and chemical effects of positive ion irradiation to a liquid surface should be clarified. Therefore, we investigated the physical behavior of water molecules at the plasma–liquid interface to assess the effect of ion irradiation from atmospheric-pressure plasma to the liquid interface by classical molecular dynamics simulation. As incident ions, O$^+$ ions with kinetic energies of 10 and 100 eV were considered. On the basis of a simulation model, we visualized the trajectory of an incident ion in a liquid, and the energy transfer and sputtering of water molecules. The following results were obtained from the simulation.

(1) The average numbers of sputtered water molecules were 0.5 at 10 eV and 7.0 at 100 eV. At the same incident ion
energy, the number of sputtered water molecules is larger at a small penetration depth because the kinetic energy of the incident ion is delivered to water molecules near the liquid surface. The mean and maximum penetration depths for ion impingement with an energy of 100 eV were 15 and 27.5 Å, respectively. This fact suggests that an ion-induced liquid-phase reaction starts from a narrow region from the liquid surface.

(2) An ion entering the water disturbs the stable arrangement of hydrogen-bonded water molecules in the liquid. Potential distortion occurs successively, and finally, the water molecules at the gas–liquid interface are released into the gas as sputtered molecules. The effects of a strong Coulomb interaction due to the dipole moment of a water molecule and the rapid molecular rotation are distinctive in the sputtering of water molecules by ion impact.

(3) We investigated the effect of the orientation of liquid water molecules with an external electric field on the liquid water dynamics under ion irradiation from the plasma to the liquid surface. An electric field larger than approximately $10^9$ V m$^{-1}$ accelerated the sputtering of water molecules.

In a real plasma–liquid interface, ion irradiation also induces chemical reactions, which is the next subject to be investigated.

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24) Gaussian09, Revision B.01 (Gaussian, Inc., Wallingford, CT, 2010).