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Citation	Journal of Physics D: Applied Physics, 55(15), 15LT01 https://doi.org/10.1088/1361-6463/ac48ad
Issue Date	2022-01-20
Doc URL	http://hdl.handle.net/2115/87715
Type	article (author version)
File Information	Shirai_Man_rev_clear1.pdf



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Effect of atmospheric-pressure plasma irradiation on surface tension of water

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November 2021

Abstract. We have shown that measuring the surface tension is a useful scheme to examine the plasma-liquid interface in real-time. The surface tension was measured using a method based on the dispersion relation of an acoustic capillary wave excited on the water surface. The surface tension gradually increased with time, when the water surface was irradiated with the outside region of the spatial afterglow of an atmospheric-pressure plasma. The Marangoni effect associated with the localized increase in the surface tension was observed during the plasma irradiation. The surface tension decreased after the termination of the discharge. A correlation was found between the transient decrease in the surface tension and the variation of the OH radical density in the gas phase. No increase in the surface tension was observed in the solution containing a trapping agent for liquid-phase OH radicals. These experimental results suggest that OH radicals act to increase the surface tension. However, the behavior of the surface tension cannot be explained perfectly by considering only the action of OH radicals.

1. Introduction

The interaction between plasma and liquid finds applications in various fields such as materials processing, medicine, agriculture, and water treatment [1–6]. Many studies have been reported on the chemical effects induced by the transport of active species from the plasma to the liquid surface [7–10]. Active species such as radicals, ions, and hydrated electrons, that contribute to reactions at the plasma-liquid interface, are short-lived, and it is difficult to examine their behaviors in real-time. The measurement of the hydrated electron density at the plasma-liquid interface has been reported [11, 12], but it may be a delicate measurement since the plasma-liquid interface usually vibrates. A relatively simple method to detect active species at the plasma-liquid interface in real-time is to use chemiluminescence. The authors have confirmed that the luminol chemiluminescence can be used for detecting OH radicals in liquid interacting with a plasma [13, 14]. However, this method has an experimental limitation in that the

liquid is needed to be alkaline. In addition, this method does not apply the separated detection of a single chemical, since the luminol chemiluminescence is induced by both OH and O₂⁻. A method to investigate the molecular orientations at the interface is the sum-frequency generation vibrational spectroscopy [15–17]. This method utilizes two-dimensional nonlinear optical effects to enable selective vibrational spectroscopy at the interface, and has the potential for investigating the vibrational nature of water molecules at the plasma-liquid interface [18]. However, it has been difficult to adopt this method to the investigation of the plasma-liquid interaction, because it requires expensive equipment and an experimental environment where the water surface is stationary.

In this study, we focus on the surface tension as a new indicator of the plasma-liquid interface. To date, we can find no works which report the effect of the plasma irradiation on the surface tension of a liquid. The surface tension is an important parameter for understanding the hydrodynamic behavior of the liquid surface. In addition, since the surface tension is determined by the interaction potential between molecules just below the gas-liquid interface, it is highly likely that the surface tension is affected by the transport of chemical species, the heat transport, and the sheath electric field [19]. To measure the surface tension using a non-contact manner, we constructed a system that generates an acoustic capillary wave on the water surface. We determined the surface tension at the plasma-water interface based on the dispersion relation of the acoustic capillary wave.

2. Experimental procedure

All the experiments were carried out in the laboratory atmosphere. The temperature in the laboratory at the time of the experiment was 23 °C and the humidity was 45%. Figure 1 shows the experimental apparatus for the in-situ measurement of the surface tension at the plasma-water interface. The principle of the measurement is based on the fact that the dispersion relation of an acoustic capillary wave is dependent on the surface tension σ such that

$$\sigma = \frac{\rho\omega^2}{k^3}, \quad (1)$$

where ω and k are the angular frequency and the wavenumber of the capillary wave, respectively, and ρ is the weight density of water [20–22]. The acoustic capillary wave was excited on the water surface by putting a needle into the water. The needle was mechanically connected to an acoustic horn which was vibrated at a frequency of $\omega/2\pi = 200 - 600$ Hz. The water surface with the capillary wave was irradiated with a He-Ne laser beam obliquely. The diffraction pattern was caused by the periodic structure of the capillary wave, and the wavelength of the capillary wave was deduced with the help of the theory of the optical diffraction.

This measurement method cannot be successful if the periodic structure on the water surface is disturbed by the plasma. In this experiment, in order to minimize the

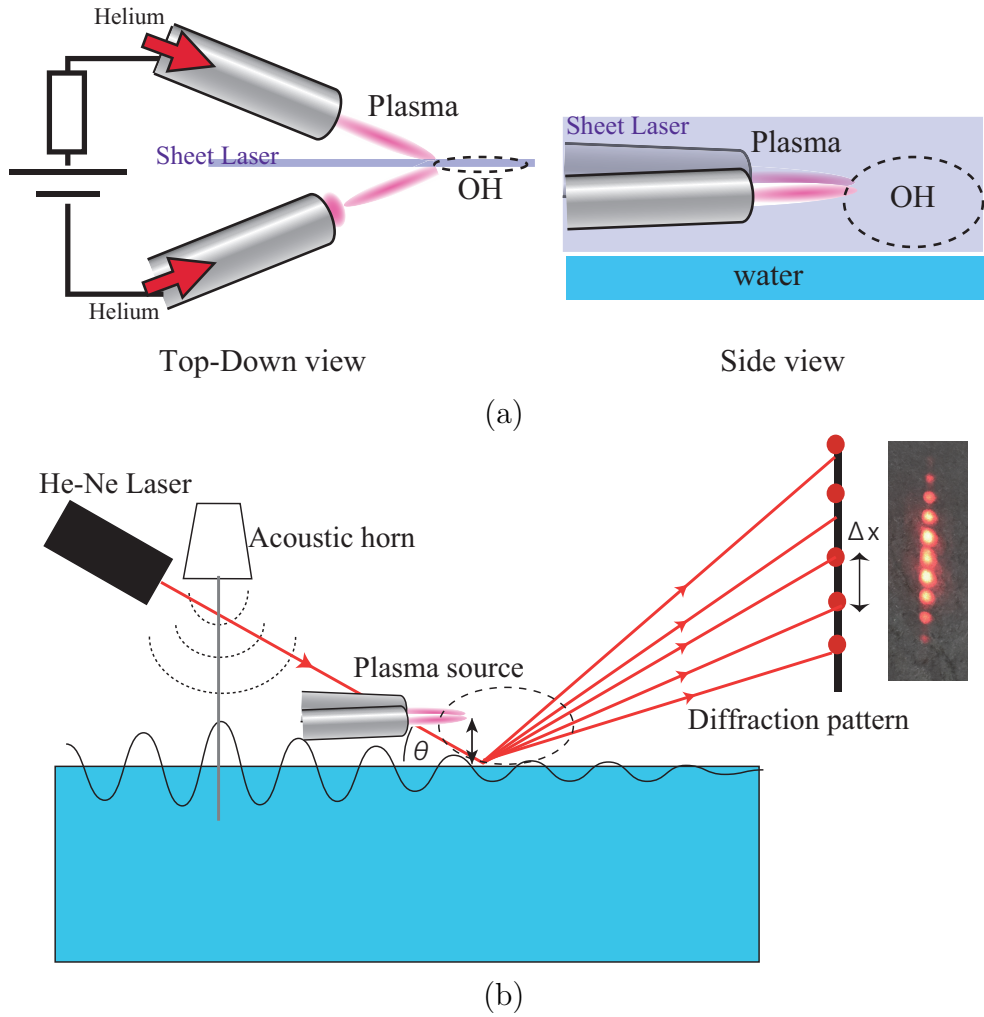


Figure 1. Experimental setup for measuring the surface tension of water interacting with the spatial afterglow of atmospheric-pressure plasma. (a) DC-driven atmospheric-pressure plasma source using intersecting helium flows. (b) System for measuring surface tension with help of acoustic capillary wave.

perturbation by the plasma on the water surface, we employed an atmospheric-pressure dc glow discharge with intersecting helium flows. The details of this plasma source have been reported in a previous paper [25]. Two metal tubes were installed at an acute angle, and the metal tubes were connected to a dc power supply via a register. The distance between the electrodes was 3.5 mm. Helium flowed at a rate of 500 sccm through the metal tube electrodes. In this discharge geometry, we observed a glow discharge with “v-shape” along the intersecting helium flows. The discharge current was 10-40 mA. We placed the v-shape discharge in parallel to the water surface at a vertical distance of 2-6 mm. Both the gas flow and the active plasma with the optical emission were not in contact with the water surface directly, and the water surface touched the outside regions of the active plasma and the downstream spatial afterglow. The water surface which faced onto the outside region of the spatial afterglow was irradiated with the He-Ne laser beam.

To measure the OH radical density in the gas phase, we used laser-induced fluorescence (LIF) imaging spectroscopy [23–25]. The discharge space was illuminated with a tunable laser beam at a wavelength of 261.5 nm. The laser beam excited OH radicals from the ground state [$X^2\Pi(v'' = 0)$] to an electronic excited state [$A^2\Sigma^+(v' = 2)$]. The image of the fluorescences by the transitions from $A^2\Sigma^+(v' = 2)$ to $X^2\Pi(v'' = 2)$, from $A^2\Sigma^+(v' = 1)$ to $X^2\Pi(v'' = 1)$, and from $A^2\Sigma^+(v' = 0)$ to $X^2\Pi(v'' = 0)$ were captured using a charge-coupled device camera with a gated image intensifier. The $A^2\Sigma^+(v' = 0)$ and $A^2\Sigma^+(v' = 1)$ states were produced by the vibrational energy transfer from $A^2\Sigma^+(v' = 2)$. The temporal variation of the LIF image was obtained by changing the delay time between the termination of the discharge and the oscillation of the tunable laser pulse. Note that we have to pay considerable attention to the influences of the collisional quenching and the rotational temperature to obtain the spatial distribution of the OH radical density [23]. However, in this experiment, we did not take care the collisional quenching and the rotational temperature. Hence the image of LIF obtained in this experiment gave us the rough representation of the distribution of the OH radical density.

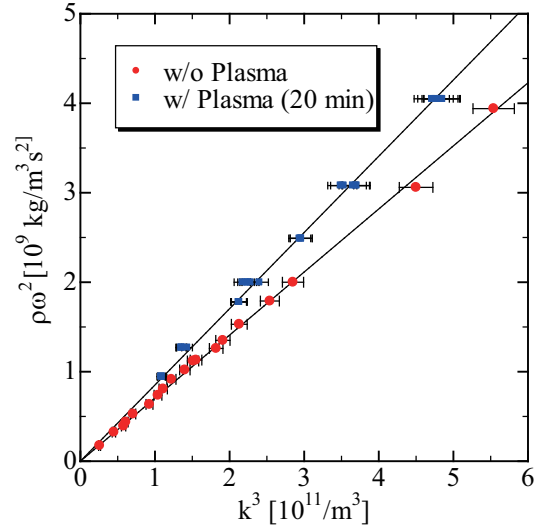


Figure 2. Dispersion relations of capillary waves. The surface tensions derived from the slopes of the proportional relationships are 73 ± 2 and 82 ± 4 mN/m in the absence and presence of the plasma, respectively.

3. Results

We examined the dispersion relation of the capillary wave both in the presence and the absence of the plasma. The discharge current for producing the plasma was 20 mA. As shown in Fig. 2, the dispersion relations observed on the untreated water and the water irradiated with the plasma for 20 minutes agreed with Eq. (1), indicating that the ideal capillary waves were excited in the present experimental apparatus. The surface tensions were evaluated from the slopes of the proportional relationships shown in Fig. 2.

The surface tension of the untreated water was 73 ± 2 mN/m, which agreed well with the known value. As can be understood from the figure, the surface tension was enhanced to 82 ± 4 mN/m by the irradiation of the effluent of the atmospheric-pressure plasma.

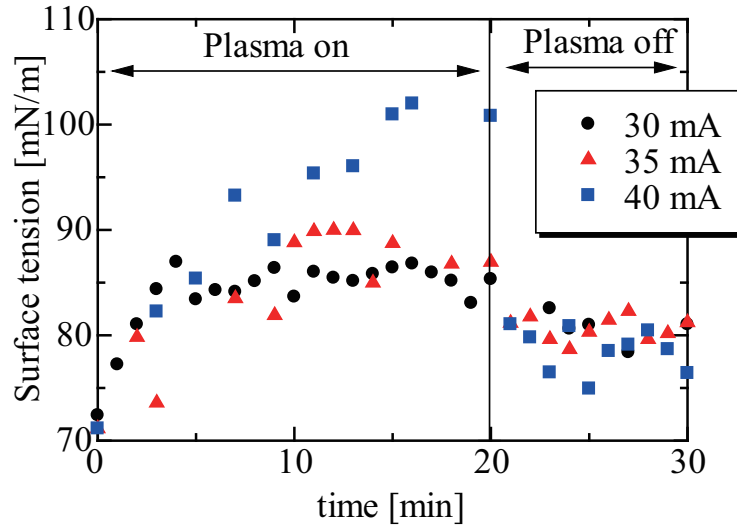


Figure 3. Temporal change in surface tension of water irradiated with spatial afterglow of atmospheric-pressure plasma. The plasma was generated between 0 and 20 min.

Figure 3 shows the time evolutions of the surface tension after the ignition of the discharge, when the discharge currents were 30, 35, and 40 mA. The error in the surface tension shown in Fig.3 was estimated to be $\pm 5\%$. The distance between the water surface and the spatial afterglow of the plasma was 5.5 mm. At all the discharge currents, the surface tension increased gradually after the plasma ignition, as shown in Fig. 3. When the discharge current was 40 mA, the surface tension reached 100 mN/m at 20 min after the ignition of the discharge. At the termination of the discharge, the surface tension decreased to 85 mN/m suddenly, and after that, we observed the gradual decrease in the surface tension. However, it did not return to the initial value. We observed a constant surface tension of approximately 80 mN/m at a very long time (days) after the termination of the discharge.

We verified the increase in the surface tension by observing the flow on the water surface. As shown in Fig. 4, we used a glass plate with a rim, and it was filled with water. We floated glass beads to visualize the flow on the water surface. The plasma source shown in Fig. 1 was placed at the top of the photograph. The movie version of Fig. 4 is provided as a supplementary file. When the plasma was not ignited, the flow of water toward the bottom of the photograph was caused by the gas flow, as shown in Fig. 4(a). When the plasma was ignited, we observed the additional flow, which had the direction toward the irradiation point of the plasma, along the rim of the glass plate, as shown in Fig. 4(b). It is widely known that a gradient of the surface tension drives the flow in fluid, which is called the Marangoni effect. The direction of the flow induced by the Marangoni effect is from the region with a lower surface tension to the region

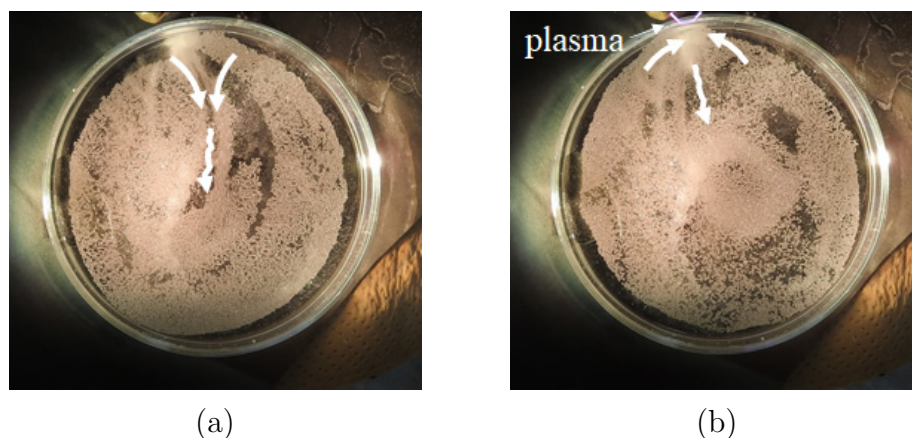


Figure 4. Flow on water surface visualized by floating glass beads in (a) presence and (b) absence of plasma. This is an upper view of a petri dish with glass beads on water. Plasma is located at the top of the picture. The white arrows indicate the direction of the flow. The movie versions of the figures are uploaded as a supplementary file.

with a higher surface tension. Therefore, the experimental result shown in Fig. 4 also indicates the localized increase in the surface tension on the water surface irradiated with the effluent of the plasma.

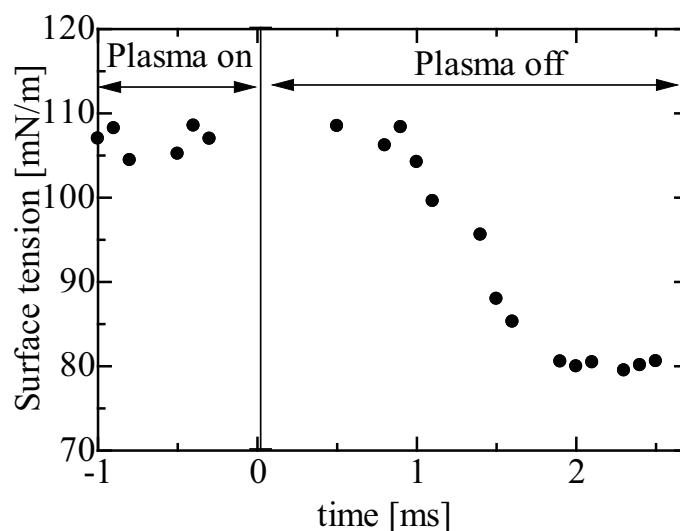


Figure 5. Transient change in surface tension of water after termination of plasma irradiation

The time constant of the sudden decrease in the surface tension at the termination of the plasma was examined by using a high-speed camera for capturing the image of the laser diffraction pattern. Figure 5 shows the transient change in the surface tension after the termination of the discharge. The distance between the water surface and the spatial afterglow of the plasma was 5.5 mm, and the discharge current was 40 mA. As shown in the figure, the surface tension remains constant for approximately 0.5 ms after the termination of the discharge, and after that, we observed the decrease in the

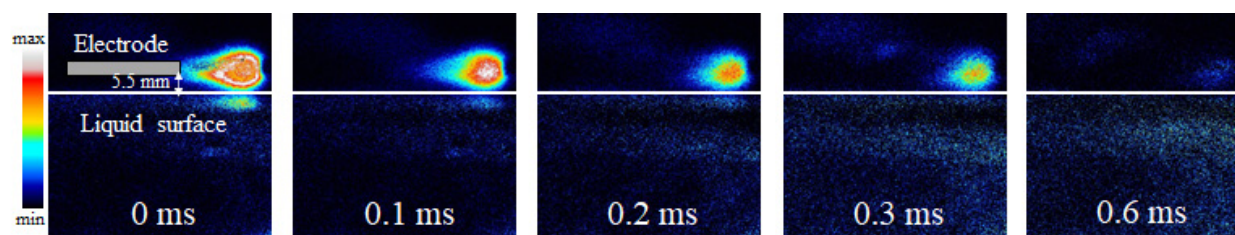


Figure 6. LIF images of OH radicals observed at various delay times after termination of discharge.

surface tension. Figure 6 shows the LIF images of OH radicals in the spatial afterglow at various delay times after the termination of the discharge. The OH radicals in the active plasma region were not detected since the dye laser beam passed through only the spatial afterglow region. As shown in the figure, we observed the decay of the OH radical density. The time constant for the decrease in the OH density is roughly 0.5 ms, which agrees with the delay time when the surface tension started the temporal decrease.

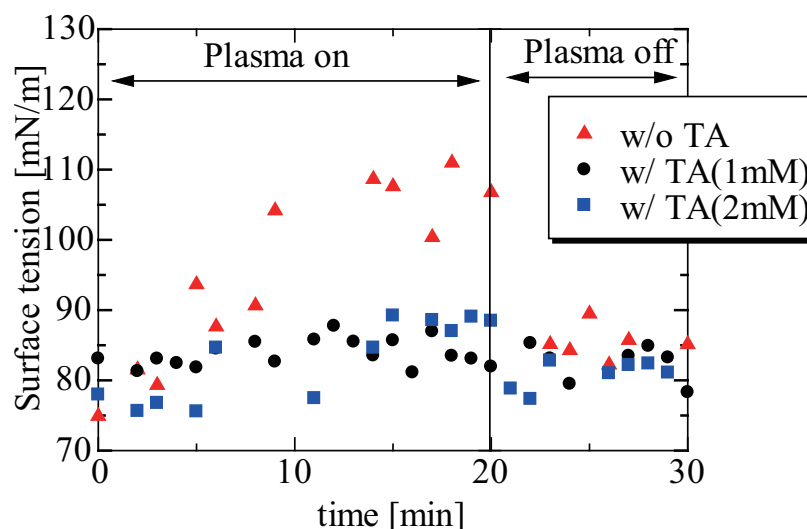


Figure 7. Temporal change in surface tension of pure NaOH solution and NaOH solutions with the admixture of terephthalic acid with concentrations of 1 and 2 mM.

Figure 7 shows the temporal change in the surface tension of a NaOH solution with the admixture of terephthalic acid (TA). TA is widely used for trapping OH radicals and for measuring the amount of OH radicals in liquids interacting with plasmas [8–10]. As shown in Fig. 7, the temporal variation of the surface tension of the pure NaOH solution was similar to those shown in Fig. 3. In contrast, when TA was admixed into the NaOH solution at concentrations of 1 and 2 mM, we did not observe the increase in the surface tension even if the solution surface was irradiated with the effluent of the plasma. This result suggests that the increase in the surface tension by the irradiation of the effluent of the plasma is closely related to liquid-phase OH radicals.

4. Discussion

An image of water surface is relevant to the change in the surface tension is shown in Fig. 8. In general, molecules in a bulk liquid are subject to intermolecular forces from other molecules from all directions and have low free energy. In other words, molecules in a bulk liquid are at a balanced state. On the other hand, molecules on the gas-liquid interface are acted upon by internal molecules but not by gas molecules, so molecules on the surface have higher free energy than internal molecules. In other words, they are at an imbalanced state. The difference between the energy states of molecules inside and at the interface results in the surface tension. For example, the surface tension becomes lower by adding a surfactant, since the surfactant lines up at the interface and it reduces the difference in the intermolecular forces. The present experimental results clearly show the increase in the surface tension by the irradiation of the effluent of the plasma, indicating the fact that the energy state of molecules at the plasma-water interface becomes more imbalanced.

Possible effects of the plasma irradiation on the surface tension are the heat transfer and the orientation of molecules induced by the sheath electric field. However, it is known that both the increase in the liquid temperature and the orientation of molecules result in the decrease in the surface tension [26, 27]. Figures. 5, 6, and 7, suggest the contribution of liquid-phase OH radicals to the increase in the surface tension. In particular, the rapid decrease in the surface tension from 110 to 80 mN/m within 2 ms after the termination of the discharge, which is shown in Fig. 5, is possibly due to the disappearance of OH radicals. It is noted here that the time resolution of the present measurement is determined by the frequency of the acoustic capillary wave. Since the frequency of the acoustic capillary wave was 400 Hz, the temporal change in the surface tension shown in Fig. 5 is probably lengthened by the limited temporal resolution. On the other hand, the slow increase (for 20 min) in the surface tension after the ignition of the plasma and the gradual decrease (for 5 min) in the surface tension after the termination of the discharge, both are shown in Fig. 3, cannot be explained by the direct effect of OH radicals, since liquid-phase OH radical is a short-lived species. Furthermore, the surface tension did not return to its original value even after a very long time (days). These slow phenomena suggest the contribution of long-lived chemicals to the increase in the surface tension. A typical stable molecule that is produced in the experimental condition is H_2O_2 , which has a surface tension of 80.4 mN/m at a temperature of 20 °C if the concentration is 100% [28]. However, considering the dilution by the diffusion and the flow, it is impossible to explain the surface tension observed in the slow phenomena only by the production of H_2O_2 . At the moment, we cannot suppose other chemicals which have a more significant influence on the surface tension than H_2O_2 .

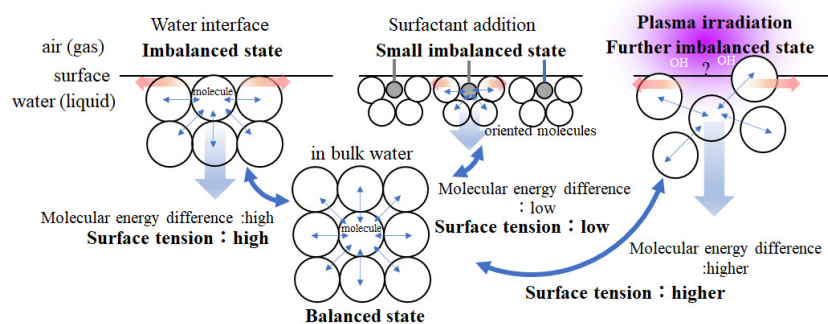


Figure 8. Image of water surface in relevant to change in surface tension.

5. Conclusions

In this study, we measured the surface tension of a plasma-water interface using a method based on the dispersion relation of the acoustic capillary wave. The experimental result shows the increase in the surface tension by the plasma irradiation. The increase in the surface tension means the increase in the free energy at the water surface. We have suggested that short-lived OH radicals and some long-lived chemicals contribute to the increase in the surface tension, but the experimental results cannot be explained completely only by the effects of OH radicals and H_2O_2 . Further investigations such as a molecular dynamics simulation of the plasma-water interface are necessary to obtain the realistic image of the water surface which has the enhanced surface tension observed experimentally.

Acknowledgment

This work was supported by JSPS KAKENHI Grant Numbers 20H00135.

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