Measurement of liquid surface properties by laser-induced surface deformation spectroscopy

K. Sakai, D. Mizuno, and K. Takagi
Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
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We developed a technique of picking up the liquid surface in a noncontact manner by a cw-laser radiation. The momentum change of light at the laser transmission through the air-liquid interface appears as the radiation pressure, which deforms the liquid surface into the shape determined by the balance between the Laplace force of the curved surface and the radiation pressure. The displacement of the liquid surface is inversely proportional to the surface tension, which was measured by an optical probe. The dynamic response of the liquid surface deformation was theoretically derived under the periodical modulation of the radiation pressure. The experimentally observed spectra were in good agreement with the theory giving the dynamic properties of the liquid surface. The technique of the laser induced surface deformation has potential as a measurement tool of the surface dynamic properties, such as the time-dependent surface tension and surface viscoelasticity.

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I. INTRODUCTION

Recently, the laser trapping technique is making a great advance, in which the optical radiation pressure is applied to pick up very small particles. The focused laser beam holds and moves the particle with the precision of the optical wavelength [1]. The technique was proved useful as a noncontact method of manipulation and a tool of measuring micromechanical properties in materials. Several important studies on the effect of radiation pressure on the liquid surface were also proposed previously, in which the pulse lasers were employed as light sources [2–4]. The results show that the laser with sufficient power might introduce liquid surface deformation, of which the spatial and temporal profile might give information on the liquid surface properties.

In this paper, we introduce a method of picking up the liquid surface in a noncontact manner with the optical radiation pressure of the continuous wave (cw) laser. The laser beam incident to the liquid surface deforms the surface, since the momentum of the light is not conserved through the surface transmission and the discrepancy should be compensated by the Laplace force of the curved surface. We could expect several advantages with a cw laser over the conventional way of surface deformation with pulsed lasers. First, the spatial and temporal profile of the laser beam is quite stable, which is important for the quantitative measurement of the physical properties of the liquid surface. Second, the intensity of the cw laser can easily be modulated with adequate electro-optical devices. The harmonic modulation of the laser intensity would be useful to determine the dynamic surface properties by a spectroscopic method. In addition, the intensity of the laser used in this experiment is sufficiently low and we could neglect a harmful nonlinear effect. A virtual stable particle of surface curvature could also be generated on the liquid surface, which would be a useful tool to investigate the particle-particle interaction yielded through the surface curvature. In this study, we especially aimed to apply this technique to the measurement of the dynamic mechanical properties of the liquid surface. The dynamic response of the liquid surface under the periodical radiation pressure was calculated and compared to the experimental results obtained for pure and molecular-covered surfaces.

Up to now, one of the most useful methods of investigating the dynamic properties of liquid surfaces has been the capillary wave measurement. The spectroscopic study of the thermally excited surface tension wave (ripplon) is effective, especially in the high frequency region above 10 kHz [5–7]. The ripplon spectroscopy technique has, however, the experimental limit in the frequency range at around 10 MHz, where the sensitivity becomes poor due to the large damping of the ripplon: the ripplon is excited by the thermal energy, which is very weak and only $\sim k_B T$. It is also a disadvantage that the origin of the ripplon is the thermal fluctuation and that the phase of ripplons simultaneously propagating on the liquid surface is completely random. In other words, the ripplons are incoherent. If coherent surface vibration can be excited artificially in a high frequency range, it would make a great breakthrough to the time resolution of the surface measurement. The key technique required is the excitation of the rapid surface deformation without any mechanical touch, and the laser induced surface deformation would be very suitable for the purpose. The result of the study demonstrates the potential of the laser picking up this technique as an alternative measurement tool of the mechanical properties of liquid the surface.

II. DYNAMIC RESPONSE OF SURFACE UNDER PERIODICAL RADIATION PRESSURE

The momentum carried by the propagating light is expressed as I/c, where I is the light intensity and c is the light velocity in the medium. The momentum is not necessarily conserved when the light transmits through the interface separating the two media with optically different properties. The discontinuity of the momentum appears as the radiation pressure applied to the interface. When the light is normally incident from the medium with the index of refraction n_1 to the other medium with n_2, the radiation pressure is given by the following equation of the momentum conservation:

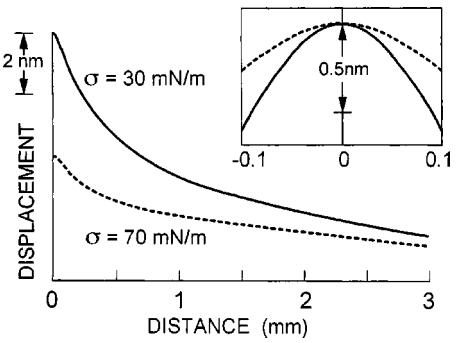

FIG. 1. The expected surface deformation of the liquid surface under the laser radiation with the power of 300 mW and beam diameter of 100 μm. The inset shows the surface shape expanded around the center of the Gaussian laser beam.

$$n_1\frac{i_0(\mathbf{r})}{c}=(1-R)n_2\frac{i_0(\mathbf{r})}{c}-Rn_1\frac{i_0(\mathbf{r})}{c}-p(\mathbf{r}). \tag{1}$$

Here, $\mathbf{r}$ represents the position on the surface, $p(\mathbf{r})$ is the local radiation pressure, $i_0(\mathbf{r})$ is the energy density of light per unit interface area, and R is the energy reflectivity of the light given by $R=(n_1-n_2)^2/(n_1+n_2)^2$. In case the light penetrates the interface from the optically sparse medium to the dense one, the radiation pressure works to pick up the interface to the opposite direction to the light propagation. This effect is also understood as the electro-striction phenomenon: the optically dense material with higher dielectricity is attracted by the electric field of light. As shown later, the spot size of the pump laser is much larger than the optical wavelength and the expected surface deformation. In this case, we can neglect the lateral component of the radiation pressure just near the liquid surface.

As for the gas-liquid or liquid-liquid interface, the radiation pressure is compensated by the gravity and the Laplace force, the normal component of the interfacial tension applied to the curved interface. The light incidence thus causes the deformation of the interface. Here, we consider that the continuous light is normally incident to the air-liquid interface at $z=0$ from the air to the liquid filling the half space of $z<0$. The surface displacement $\xi(\mathbf{r})$ under the light radiation is given by the following equation:

$$-\sigma\Delta\xi(\mathbf{r})+\rho g\xi(\mathbf{r})=p(\mathbf{r}). \tag{2}$$

Here, σ is the surface tension and g is the gravity constant. When the continuous laser beam with the Gaussian profile with width w and the power I_0 is incident to the liquid surface, the displacement is described by the following balance equation in the cylindrical coordinate:

$$-\sigma\left(\frac{\partial^2\xi}{\partial r^2}+\frac{1}{r}\frac{\partial\xi}{\partial r}\right)+\rho g\xi=\frac{I_0}{\pi cw^2}(n-1-nR-R)e^{-r^2/w^2}, \tag{3}$$

where $\mathbf{r}$ is taken from the center of the Gaussian beam. Figure 1 shows the expected surface deformation of pure water and ethanol calculated by Eq. (3) with $I_0=300$ mW and $w=100\,\mu$m. The density and surface tension are $\rho=998\,\mathrm{kg/m^3}$ and $\sigma=72.75$ mN/m for water, and $\rho=785\,\mathrm{kg/m^3}$ and $\sigma=22.27$ mN/m for ethanol at a temperature of 20 °C. Though the absolute displacement is as small as 2 nm for water, the surface deformation can be sensitively measured by means of the optical method. The principle of detection is briefly given in the following: The deformed liquid surface works as an optical lens. The effect of the gravity can be neglected under the condition that the beam diameter is small and $\sigma/w^2\gg\rho g$ holds. The curvature at the center of the deformation directly gives the focal length of the lens as [8]

$$f=\frac{\sigma\pi cw^2}{I_0(n-1-nR-R)(n-1)}, \tag{4}$$

which is about 4 m at the above conditions. Measurement of the focal length with an appropriate optical system yields the surface curvature and thus the surface tension in a noncontact manner. We used another laser beam to detect the curvature of the deformed surface. A weak probe laser goes through the deformed surface and the beam profile changes after transmitting the surface. The focal length of the surface is obtained by observing the change in the beam diameter of the probe laser at the far field.

This technique of inducing surface deformation by laser can also be applied for the generation of capillary waves. The radiation pressure is proportional to the light intensity and, therefore, the surface vibration can be excited by applying the amplitude modulation to the laser intensity. By monitoring the surface vibration, we can determine the dynamic properties of the surface, such as time-dependent surface tension or surface viscoelasticity. Here, we calculate the dynamic response of the surface under the periodical modulation of the laser radiation pressure. When the light is focused onto a circular spot, the surface wave generated is in the cylindrical mode. The response function is obtained by solving the hydrodynamic equation under the boundary condition of the radiation pressure applied by the light. First, the freely oscillating mode of the cylindrical surface wave with the cylindrical wave number m is given as

$$\begin{aligned} v_r&=AJ_1(mr)e^{mz}e^{i\omega^* t},\\ v_z&=AJ_0(mr)e^{mz}e^{i\omega^* t}, \end{aligned} \tag{5}$$

and

$$p_h=-\frac{\rho}{m}\omega AJ_0(mr)e^{mz}e^{i\omega^* t}.$$

Here, A is the amplitude of the surface oscillation, v_r and v_z are the velocity of the substrate liquid in the radial and vertical direction, respectively; p_h is the change in the pressure, J_0 and J_1 are the zeroth and first order Bessel functions; and ω^* is the complex angular frequency expressed by the frequency ω and the temporal damping constant of the surface wave Γ as $\omega^*=\omega+i\Gamma$. The dispersion relation is given by [9]

$$\omega^* = (\rho/\sigma)^{1/2} m^{3/2} + 2i(\eta/\rho)m^2, \tag{6}$$

where η is the viscosity of the liquid. The forced vibration of the liquid surface under the periodical radiation pressure at the angular frequency ω is expressed by the integrating of the cylindrical surface waves over the cylindrical wave number m. The velocity v_z is then written as

$$\nu_z(r,t) = \int_0^\infty A(m) J_0(mr) e^{mz} e^{i\omega t} dm. \tag{7}$$

Here, $A(m)$ represents the amplitude of the cylindrical surface wave with the cylindrical wave number m. The boundary condition is that the Laplace force of the curved surface and the hydrodynamic pressure caused by the fluid flow should compensate the radiation pressure due to the laser incidence. It is then given by

$$\sigma\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right) v_z = -\frac{\partial}{\partial t}\left(-\frac{i\rho\omega}{m} v_z + P_0 e^{-r^2/w^2} e^{i\omega t}\right), \tag{8}$$

where P_0 is the radiation pressure at the center of the beam and is determined through Eq. (1). Here, we neglect the viscous term to determine the eigenfrequency of the surface vibration with mode m, since the viscous term does not give the important effect on the eigenfrequency in the low frequency region of $\omega \ll \sigma/w\eta \sim 10^6\ \mathrm{s}^{-1}$ [9,10]. The effect of the viscosity is taken into account later in Eq. (12) by introducing the complex eigenfrequency of Eq. (6) as the first order approximation of the strict solution [11]. By substituting Eq. (7) into Eq. (8), we obtain the equation determining $A(m)$ as

$$\int_0^\infty \left(\frac{\sigma}{i\omega} m^2 + \frac{i\rho\omega}{m}\right) A(m) J_0(mr) dm = P_0 e^{-r^2/w^2}. \tag{9}$$

Then $A(m)$ is, in turn, obtained by the inverse transformation of Eq. (9) as

$$A(m) = \frac{i m^2 \omega w^2 P_0}{2(\sigma m^3 - \rho\omega^2)} e^{-m^2 w^2/4}. \tag{10}$$

The surface displacement $\xi(r,t)$ is then calculated as

$$\xi(r,t) = \int_0^\infty \frac{m^2 w^2 P_0}{2(\sigma m^3 - \rho\omega^2)} e^{-m^2 w^2/4} J_0(mr) e^{i\omega t} dm. \tag{11}$$

If the probe laser beam to detect the surface deformation is neatly focused to a spot size with a diameter smaller than the exciting laser beam, the signal is proportional to the curvature at the center of the surface deformation and the frequency spectrum is given by

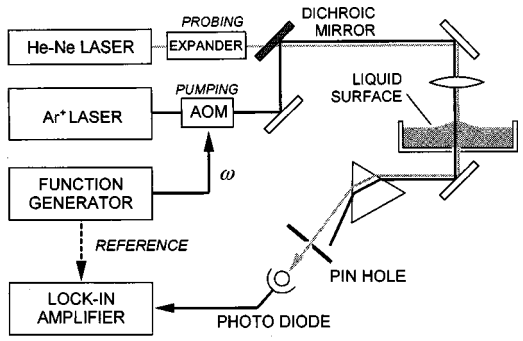

FIG. 2. Block diagram of the experimental setup.

$$S(\omega) \propto \int_0^\infty \frac{m^4 e^{-m^2 w^2/4}}{\rho(\omega^2 - \omega^{*2})} dm. \tag{12}$$

Here, we replaced the real eigenfrequency $\omega_0 (= (\sigma/\rho)^{1/2} m^{3/2})$ by the complex frequency ω^* in order to take the effect of energy dissipation due to the viscous flow of the fluid into consideration. The response function thus becomes the complex value and shows the delay in phase from the oscillation of the pump laser intensity.

III. EXPERIMENT

As described in the previous section, we can artificially introduce the liquid surface deformation by irradiating the surface by an appropriate laser beam. Noncontact measurement of the surface properties is possible with an optical probe to observe the caused surface deformation. In addition, the dynamic response of the surface under the temporally modulated laser radiation would provide us with the information on the dynamic process in the liquid surface, such as the molecular sorption relaxation and the phase transition of the Langmuir films. In this section, we describe the measurement system of the laser induced surface deformation.

The experimental setup is schematically shown in Fig. 2. The light source for excitation is an Ar^+ laser with the maximum output power 500 mW and the wavelength 514.5 nm. The pump laser beam is focused onto the liquid surface by a lens, and has an ideal Gaussian profile in the focal plane. The width is determined by diffraction limit as $w \sim \lambda f/\pi d$, where f is the focal length of the lens, λ the wavelength of the laser in air, and d is the initial diameter of the laser beam. The spot size of the laser at the surface can be controlled by changing the focusing lens. The high frequency limit of the excited capillary waves would be determined by the optical diffraction limit, and $w < 1\ \mu$m is actually available with the aid of a microscope objective, the corresponding frequency being in the megahertz region.

The surface deformation is detected by a probing He-Ne laser with the output power of 10 mW. The probe laser beam is expanded about ten times larger than the pump laser and then superimposed on the pump laser by a dichroic mirror. The pump and probe lights are focused onto the surface by the same lens. The probe laser with a larger beam width is focused within a smaller spot than that of the pump laser on the surface. Therefore the approximation used to derive Eq.

(12) safely holds. The transmitting probe light is separated off by optical dispersion of a prism and the intensity near the center is detected with a pinhole.

The deformation of the liquid surface works as a lens and the beam diameter of the probe laser in the plane of the pinhole depends on the lens power. When the surface displacement is small, the intensity at the beam center is inversely proportional to the beam diameter. The light is fed to a photodiode and the signal is analyzed by a lock-in amplifier to which the reference is given by the modulation signal of the pump-laser beam. The intensity of the laser beam is sinusoidally modulated by an acousto-optic modulator. Sweeping the modulation frequency, we can observe the frequency spectrum of the response function of the liquid surface. The static and absolute value of the surface displacement is obtained at the modulation frequency lower than $\omega \sim(\sigma/\rho)^{1/2}w^{-3/2}$: in the present case, $\omega \ll 10^4\,\mathrm{s}^{-1}$.

Here, we have to pay attention to the effect of the laser induced heating. The temperature increase due to the optical absorption might cause the fluid convection and deforms the surface. The temperature modulation by the chopped laser light is, however, dominated by the thermal diffusion process and limited in the frequency range lower than $\omega_T < (\Lambda/C_p)w^{-2}$, where Λ and C_p are the thermal conductivity and the specific heat of the substrate liquid. The cutoff frequency $\omega_T/2\pi$ is calculated to less than 10 Hz in the present case, which is sufficiently lower than that observed in the experiment. Actually, as shown later, the observed spectrum is well fitted by the theory of Eq. (12) showing that the thermal effect can be neglected in the present experiment. The effect should be taken into account, however, when the diameter of the focused laser beam is small and the cutoff frequency crosses over the measurement frequency.

The sample cell is made of glass and the pump and probe laser beams penetrate through the liquid surface and also the bottom of the cell without making harmful stray light. The sample liquid is sufficiently deeper than the wavelength of the expected surface waves.

IV. RESULTS AND DISCUSSION

(i) *Static measurement of surface tension.* The present technique of the laser induced surface deformation (LISD) was applied to the noncontact measurement of the static surface tension. The LISD signal depends also on the refractive index of the liquid and, therefore, the sample whose surface tension is controlled without any change in the optical properties is preferable as the standard material to examine the instrumental performance of the system. We therefore prepared a monomolecular film of myristic acid expanded on water surface as the sample. The surface tension can be controlled by changing the surface density of the adsorbed molecules of myristic acid through expansion or compression of the surface area. Langmuir films are known to possess surface viscoelasticity, which might affect the wave propagation. At low modulation frequencies below 100 Hz, however, the absolute displacement is almost determined only by the surface tension, and the surface wave propagation is insensitive to the surface viscoelasticity.

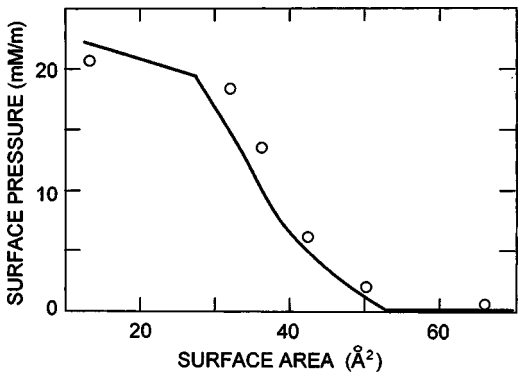

FIG. 3. The π-A isotherm of the myristic acid monolayer measured by laser induced surface deformation technique (open circles) and the Wilhelmy method (solid line).

Figure 3 shows the relation between the surface pressure and the surface area allowed for one molecule of myristic acid. The surface tension was obtained as the inverse of the signal amplitude in a relative measurement with respect to the value on bare water surface, $\sigma = 72.75$ mN/m at 20 °C. The modulation frequency of the pump laser was 60 Hz. The solid line is the result obtained by the Wilhelmy plate method for the same sample. The results of these two measurements agree well, showing the validity of the LISD technique for measuring the surface tension.

(ii) *Laser induced surface wave spectroscopy*. The dynamic response of the surface deformation was obtained by sweeping the modulation frequency of the pump laser. Figure 4 shows the frequency spectrum of the surface deformation obtained for the surface of pure water. The solid curves show the behavior of the response function theoretically calculated from Eq. (12) with the actually measured beam width of $w = 80\,\mu$m. The spectra of the real and imaginary parts have characteristic shapes. A remarkable feature is that the real part crosses zero at the characteristic frequency ω_c. This behavior is attributed to the resonant excitation of the surface wave. The Gaussian profile of the laser radiation pressure can be decomposed to a series of Bessel functions with a finite distribution of m. The characteristic frequency accurately gives the surface tension through the numerical calcu-

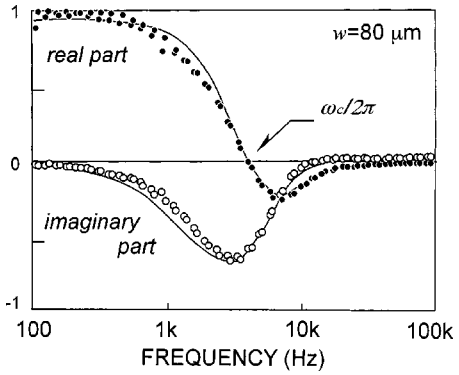

FIG. 4. Typical example of the LISD spectrum obtained for the water surface. The solid lines show the result of a theoretical calculation of Eq. (12).

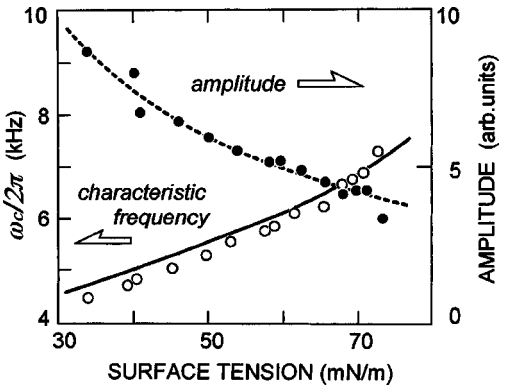

FIG. 5. The low frequency limit of the amplitude and the characteristic frequency of the LISD spectrum obtained for the surface of the SDS solution plotted against the surface tension. The solid and dashed lines show the theoretical prediction.

lation of Eq. (12), while it is approximately given by $\omega_c \sim(\sigma/\rho)^{1/2}w^{-3/2}$. By changing the width of the laser beam, we can obtain the dependence of the characteristic frequency [12]. The dynamic behavior of the surface can then be studied as is performed in the ripplon spectroscopy [7,12–14]. In addition, the amplitude of the signal, $|S(\omega)|$, decreases with frequency showing that the dynamic surface deformation cannot follow the rapid modulation of the radiation pressure above the characteristic frequency. The characteristic frequency is about 6 kHz in the present case of $w=80\,\mu$m, as is actually shown in the spectra. The imaginary part shows a minimum around the cutoff frequency, indicating that the laser power effectively transfers to the surface wave energy.

As described above, the characteristic frequency of the spectrum and the amplitude of the surface displacement independently give the surface tension of the liquid. We applied the measurement system for the surface of surfactant solutions. We prepared aqueous solutions of the sodium dodecyl sulfate (SDS) with various concentrations below the critical micellar concentration of 6.0×10^{-3} mol/l. The surface tension of the solution sensitively depends on the concentration in this region, while the optical property is almost constant since the surfactant concentration is very low. Figure 5 shows the characteristic frequency and the signal amplitude obtained as a function of the surface tension of solutions measured by the Wilhelmy plate method. The width of the laser beam at the surface is $w=80\,\mu$m. The signal amplitude decreases with the surface tension. According to Eqs. (1) and (2), the amplitude of the surface deformation is inversely proportional to the surface tension and the dashed line shows this behavior. The result agrees well with the theory, again showing the validity of the system as the static measurement of the surface tension, as shown previously for the case of insoluble monomolecular films.

The characteristic frequency indicated by the open circles in the figure increases with surface tension. The solid line shows the theoretical curve obtained through the calculation of Eq. (12) for each value of the surface tension. The theoretical curve fairly reproduces the behavior of the experimental results, except for the systematic discrepancy appearing in the low surface tension region where the surface layer of the surfactant molecules becomes dense. The result indicates that the resonant surface vibration is slower than expected. A possible reason of this discrepancy might be due to the effect of the surface viscoelasticity. The molecular layer formed on the liquid surface is known to possess two-dimensional viscoelastic properties, which might affect the surface wave propagation [6,8]. In fact, the ripplon spectroscopy on the surface of the SDS solution showed that the phase velocity of the ripplon decreases by several percent at the present concentrations [9]. In addition, the surface viscoelasticity is known to modulate the apparent damping constant of the surface wave and change the LISD spectrum. More detailed study would be required to examine the effect of the surface viscoelasticity on the LISD spectrum.

In conclusion, we successfully introduced a deformation of the liquid surface in a noncontact manner by using the laser radiation pressure. The technique was applied for the characterization of mechanical properties of the liquid surface. In this study, we used the laser beam with the Gaussian intensity profile, which generates the cylindrical surface wave. Another effective mode of the surface wave is the plane wave, which can be exited by the line focus of the laser beam with a cylindrical lens. The theoretical analysis of the plane wave is much simpler than the cylindrical wave. A somewhat more sophisticated way of surface wave generation is the optical fringe method in which two laser beams cross at the surface. We have already started the preliminary experiment and obtained the result, which will soon be reported.

The LISD method is also useful as the technique of introducing surface curvature. Microparticles floating on the liquid surface are known to interact with each other through the surface curvature induced by themselves. The LISD technique might generate a virtual particle of the surface curvature and the above interaction could be directly measured with this artificial curvature of the liquid surface.

ACKNOWLEDGMENT

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