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Experimental verification of line tension by shape observation of micro-droplets on liquid substrate
液面上微小液滴の解析による線張力の実験的検証

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1. Introduction

In the recent technology development, getting more information about micro amount of liquids to manipulate is important. It is known that the state of surface influences more as the volume(scale) of liquids gets smaller. To obtain such the physical properties as surface-tension and interfacial-tension precisely is important. Furthermore, not only these two properties, there exists a possibility of factor, so called "line tension" , which influences on small amount of liquid as well although there are researches which point out that micron-scale liquid is due to the influence of optical error or the chemical non-uniformity of the solid substrate from theoretical and molecular simulation predictions as well and it is difficult to observed[1].

Regarding the line tension, it is considered as the work on the three-phase contact line, and that the origin of this force is surplus energy in three-phase contact line. When a liquid droplet is floating on an immiscible liquid surface, the static shape of droplets is determined by the surface tension of two liquids and the interfacial tension. This is well known as Neumann's triangle. The surface and interfacial tensions can be estimated from the profile of the droplet. Supposing if the line tension is acting, the interfacial profile changes and the line tension can be measured from the experimental shape.

In this study, we observed the droplet impinging to the immiscible liquid surface, and after the impingement as well. We analyzed the equilibrium shape of floating droplet with the surface/interfacial/line tensions of liquids.

2. Experiment

Figure 1 shows our experimental setup schematically, which is based on that in our previous paper[2]. We used the stroboscopic technique to observe high-speed phenomena of microdroplets.

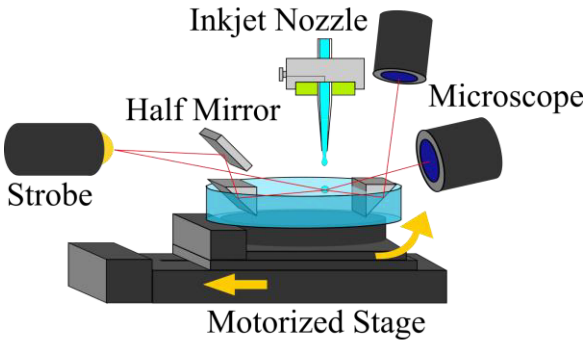

Fig. 1 Schematic view of experimental setup.

The device for droplet generation is an originally designed nozzle consisting of a glass capillary tube with the tip diameter of 30 μm sandwiched between two piezoelectric actuators.

A petri dish which was filled with the liquid to provide flat surface was set on the rotational stage. Observation system had two microscopes so that we could observe a floating droplet on the liquid from above and below the surface simultaneously. And two prisms were immersed in the bulk liquid to observe in liquid.

We observed the impinging process of a microdroplet to the immiscible liquid surface to estimate the time in which it took for the shape to stabilize. We used tetrabromoethane as the droplet and water as the bulk liquid. Surface tension σ and interfacial tension against the water γ are shown in **table 1**. Emitted droplets in the experiment had the diameters of ~30 μm and the velocity of approximately 2 m/s. Photos of droplets were shown in **Fig. 2**. From this figure, the droplet will reach the equilibrium state in 200 μs. The microdroplet needs over 100 ms to evaporate completely. In these fast time regions, which is less 1 ms, evaporation of the droplet can be negligible.

Table 1 Properties of the sample liquids.

Liquid	σ [mN/m]	γ [mN/m]
Water	71.8	
Tetrabromoethan	49.6	38.8

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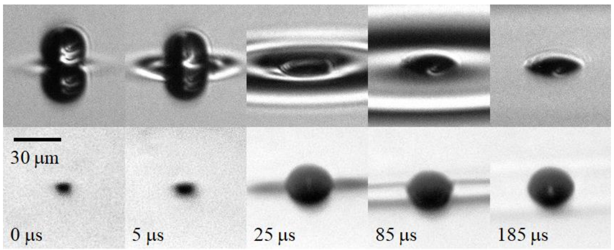

Fig. 2 Time sequence images of tetrabromoethane droplets impinging on water. The images in the top row show droplets above the surface, and the lower are below the surface including the reflected droplets by the surface, respectively.

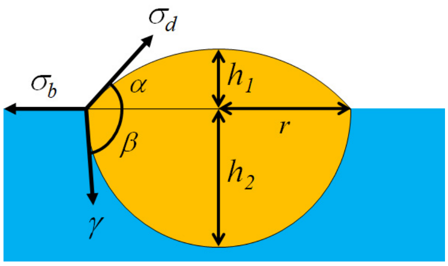

Fig. 3 Typical side view of a floating microdroplet.

3. Result and discussion

The whole shape of the droplet on the liquid surface is united two spherical caps, as shown in **Fig. 3**, where r, h_1 and h_2 are radius of contact line circle, height of the spherical cap in the air, height of the spherical cap in the liquid, respectively, and α, β represent the angles against the bulk liquid surface. The surface tension of the droplet, the surface tension of the bulk liquid and the interfacial tension between the droplet and the bulk liquid are σ_d, σ_b and γ, respectively. These parameters were obtained by image analysis of microscopic photos of the droplet. In this work, the gravitational effect can be negligible because the droplet is much smaller than the capillary length ~2 mm and could be regarded as parts of a perfect sphere.

The equilibrium shape of the droplet on the liquid surface can be derived by minimizing the surface energy. The line tension τ is surplus energy on the three-phase contact line. Thus, under the condition of constant of volume, the following two equations are obtained.

$$\sigma_d \cos\alpha + \gamma\cos\beta - \left(\sigma_b - \frac{\tau}{r}\right) = 0 \qquad (1)$$

$$\sigma_d \sin\alpha - \gamma\sin\beta = 0 \qquad (2)$$

Equation (1) and (2) represent horizontal and vertical force balance at the contact line, respectively.

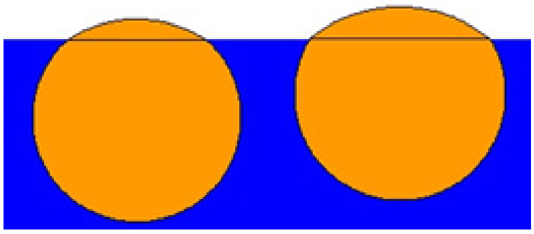

Fig. 4 Interfacial profiles of tetrabromoethane droplets on water surface at the equilibrium state. (Left) Experimental shape (Right) Neumann's triangle prediction without line tension.

Without considering line tension, τ become zero in eq. (1)

Figure 4 shows the interfacial profiles of the droplets on the liquid surface. From the figure, Neumann's triangle cannot represent droplets profiles accurately. Here, experimental angle α, β, the surface tensions σ_d and σ_b are substituted for the equations, then we obtained $\gamma = 37$ [mN/m] and $\tau / r = 48$ [mN/m]. The literature value of the interfacial tension is 38.8 mN/m, which is almost the same with our experiment. In this case, the radius r of the experiment was 8.5 µm and we got $\tau = 410$ [nN]. The line tension was the order of 10^{-7} N in our experiments. By the molecular simulations, Law et. al.[3] predicted line tension was the order of 10^{-10} N. The reason for the difference may be that the experimental line tension does not act on the contact `line' but on the contact `region', in which sufficient molecules of two kinds of liquids and air will interact with each other.

4. Conclusion

We observed the droplets impinging and floating on the liquid surface from above and below the surface simultaneously. The equilibrium shape of the microdroplet was different from that predicted from Neumann's triangle only with the surface and interfacial tensions. Considering the line tension, we succeeded in measuring the interfacial tension. We revealed the line tension worked on micron-scale liquid.

References

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3. B. M. Law and et al, Progress in Surface Science 92 1 (2017)