

An Oil Droplet That Spontaneously Climbs up Stairs

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It has been reported that an oil droplet on a glass surface moves spontaneously in an oil-water system. This motion of an oil droplet can be understood as the spreading of a reactive droplet, which is induced by the interfacial tension gradient at the glass surface. In this paper, we focus on the spontaneous motion of an oil droplet climbing up stairs. We found that an oil droplet tends to move up the stairs rather than to step down. We describe some of the mechanisms of this unique behavior.

§1. Introduction

The motion induced by the soluto-capillary effect has attracted considerable interest since it was discovered in the mid-nineteenth century.¹⁾ One of the main interests of researchers who study the soluto-capillary effect is its nature as a chemo-mechanical energy transducer, which is different from conventional thermal engines. We have currently been studying a spontaneous motion at the interface of two immiscible phases, a so-called oil-water system, to better understand chemo-mechanical energy transduction in a real chemical system. A spontaneous fluctuation of interfacial tension has been reported, accompanied by motion at the interface in oil-water systems.²⁾⁻⁴⁾

Recently, we reported that the motion of droplet found in an oil-water system, iodine-containing nitrobenzene with cationic surfactant-containing water, can be understood as the motion of a reactive droplet⁵⁾⁻⁷⁾ by considering the effect of the glass surface.^{8),9)} Since a negative charge appears on a glass surface in natural pH, cationic surfactants are adsorbed onto the glass surface;¹⁰⁾ as a result, the glass surface becomes hydrophobic. On the other hand, iodine in an oil droplet reacts with the adsorbed cationic surfactants to make the glass surface bare and hydrophilic. Therefore, an interfacial tension gradient develops between the front and rear of an oil droplet, which drives the droplet through the Marangoni effect. Interestingly, in this oil-water system the motion of an oil droplet shows repetitive motion, which is usually prohibited in other reactive droplet systems. In fact, an oil droplet can show oscillatory or rotating motion on an appropriate glass substrate.⁸⁾

In our previous study, we found that motion at an oil-water interface could be controlled to be unidirectional motion by introducing an asymmetrical boundary condition.¹¹⁾ In the present study, we introduce an asymmetrical boundary condition to the shape of a glass substrate: a stair-like glass substrate. Unexpectedly, an oil droplet tended to climb up the stair-like substrate rather than to fall down. In this report we report the motion of an oil droplet climbing up stairs, and elucidate a

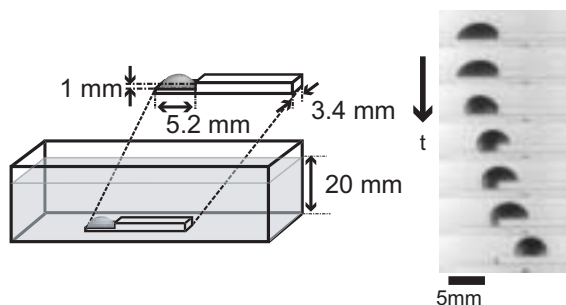


Fig. 1. (Left) Schematic illustration of the experimental setup. An oil droplet of 30–80 μl was put on a stair-like substrate. An oil droplet motion moving upward on a stair-like substrate. (Right) An oil droplet motion moving upward on a stair-like substrate. Time interval of each figure is 1/6 s. The amount of oil in the droplet was 80 μl . An oil droplet that stayed still retained an asymmetrical shape because of the shape of the stair-like substrate.

plausible mechanism for this motion of the self-moving droplet.

§2. Experiments

The aqueous phase was 1 mM Stearyl Trimethyl Ammonium Chloride (STAC) solution and the organic phase was a 5 mM iodine solution of nitrobenzene saturated with potassium iodide. STAC was prepared by recrystallization using acetone. For glass substrates, we used micro slide glass (Matsunami, Osaka; S9111). To make a stair-like substrate, slide glass was cut into rectangular plates 3.4 mm wide, and then stuck together with glass binder (Fig. 1). An oil droplet of 30–80 μl was placed on the substrate with a pipette. The motion of the oil droplet was recorded by a high-speed video camera (RedLake MASD Inc., San Diego, CA; Motion Scope PCI) at 60 frames per second. All measurements were carried out at room temperature ($20^\circ\text{C} \pm 3^\circ\text{C}$).

The center of mass (CM) of the droplet was taken from the center of pixels in a binary picture. The position was depicted with image-processing software (Image J (<http://rsb.info.nih.gov/ij/>)).

§3. Results

The motion of an oil droplet on a stair-like substrate is exemplified in Fig. 1. To show the effect of a stair-like boundary on oil-droplet motion, the result with a large droplet (80 μl) is shown. As we reported previously,⁸⁾ an oil droplet with a smaller volume (60 μl) climbs up stairs almost without stopping. In contrast, Fig. 1 shows that the oil droplet stayed for almost one second under the step of a stair and maintained its asymmetrical shape before it started moving again. Furthermore, the droplet started moving from the receding contact point, as shown in Fig. 1 (lower right). At the beginning of droplet motion, some of the droplet tries to go down the stair-like substrate (Fig. 2). An oil droplet with less-than-critical velocity (≈ 50 mm/s) does not go down the step and shows large deformation (middle panel in Fig. 2).

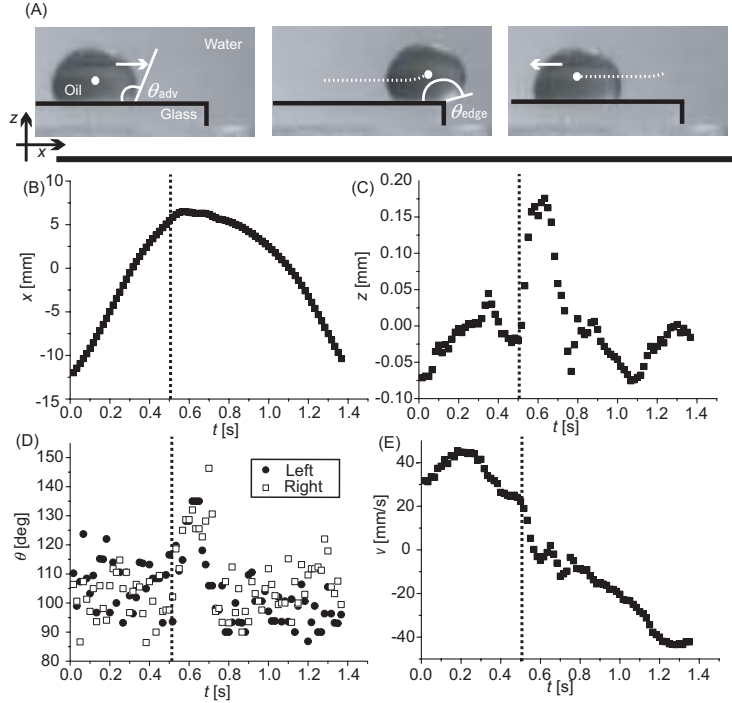


Fig. 2. (Upper) (A) The arrow indicates the direction of oil-droplet motion, and the point indicates the center of mass of the oil droplet, which is obtained from the pictures. The trace of motion is also shown as a dotted line in the second and third figures. The time interval for each picture is 0.1 s. (Lower) The measured data for the position of the apparent center of mass (B, C), and the left and the right contact angles (D). The velocity of the droplet is also shown (E). At the dotted line, an oil droplet reached the edge of the substrate.

§4. Discussion

It has become clear that an oil droplet tends to show unidirectional motion when climbing up stairs. This characteristic of the spontaneous motion of an oil droplet can be understood as a mechanical property of a reactive droplet with recovery of a glass surface.⁸⁾ The central problem to be solved is why motion up the stairs is preferred. There are two main mechanisms for achieving this regulation of motion; one prevents an oil droplet from falling down each step, and the other enables an oil droplet to climb each step.

One of the mechanisms that regulate the motion of an oil droplet is the effect of an edge of the glass substrate. In order to have a droplet move forward, advancing contact angle, θ_a , must satisfy $\theta_a \geq \theta_{adv}$. At the edge of substrate, in contrast, θ_a needs to satisfy $\theta_a \geq \theta_{edge}$ to have a droplet fall down from the edge, where $\theta_{edge} = 90^\circ + \theta_{adv}$. Thus, θ_a increases until it reaches θ_{edge} at the edge of the substrate. Here, accompanied by the increase in the advancing contact angle, the receding contact angle, θ_r , also increases to be the same as θ_a due to Laplace pressure. This increase in the contact angles causes the oil-droplet center of mass to rise (Fig. 2). Thus, the kinetic energy of the oil droplet is mainly stored temporally as

gravitational potential energy as in Fig. 2. The stored energy is then released to initiate the backward motion. Hence, the oil droplet changes its direction of motion at the edge of the substrate; i.e., the downward motion of an oil droplet is suppressed.

On the other hand, the mechanism to promote motion up a step can be explained by the asymmetrical shape of the oil droplet just before it climbs up. This asymmetrical shape restricts the initial motion of the oil droplet to be in the direction of the upper step. Please note that, in Fig. 1, the oil droplet at the lower step started its motion from the receding contact point on the lower step. Once the initial motion is determined, the direction is maintained because the motion of the oil droplet is driven continuously by the Marangoni effect. The direction of motion remains unchanged in the quasi-one-dimensional situation with continuous driving force, as has been indicated in our last study.⁸⁾ The detailed mechanism will be discussed in another paper.¹²⁾

§5. Conclusion

The spontaneous motion of an oil droplet is induced by the gradient of interfacial tension at a glass surface. This self-motion of an oil droplet is restricted by an asymmetrical boundary condition; i.e., a stair-like substrate. The stair-like substrate has two ways of limiting the motion of an oil droplet: restriction by the edge, which prevents the oil droplet from dropping down the stairs, and restriction related to the initial motion caused by the asymmetrical shape of the oil droplet just before it climbs up a step.

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