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Self-Synchronous Swinging Motion of a Pair of Autonomous Droplets

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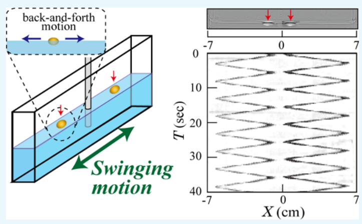
Supporting Information

ABSTRACT: Synchronized motion between two self-running oil droplets floating on an aqueous phase is reported. We describe the results of our observation on the interference between a pair of centimeter-sized nitrobenzene droplets undergoing back-and-forth motion on a waterway. The two droplets exhibit a swinging type of synchronization when a thin glass capillary is placed at the midpoint of the waterway with a narrow rectangle shape. Furthermore, 2:1 synchronized oscillation of the periodicities of this back-and-forth motion is generated when the capillary is shifted away from the center of the waterway. We discuss the mechanism of the emergence of synchronized swinging motion for the pair of droplets based on a simple mathematical model with nonlinear coupled differential equations.



INTRODUCTION

Living organisms maintain their lives through the dissipation of chemical energy under isothermal conditions. Through a long evolutionary process, organisms have developed a "technique" to generate macroscopic motion by diminishing the effects of large fluctuations, Brownian motion, inherent to individual molecular components with a length scale of nanometer, i.e., motor proteins. On the other hand, humans are adapting the approach by using rigid bodies to obtain macroscopic mechanical motion by suppressing fluctuation to achieve energy transduction. The realization of self-regulated macroscopic motion using chemical energy with a nonrigid body under mild conditions is a long-standing target of research and still remains an interesting subject. Recently, numerous studies have been undertaken to generate self-propelled motion on a macroscopic scale driven by thermodynamic nonequilibrium,[1−4] including chemical reactions,[5−9] transfer of a chemical substance,[10−29] temperature gradient,[30−33] photoirradiation,[34−38] external vibration,[39] stationary electrical potential,[40] and so on. These studies have revealed that various kinds of regular motions can be generated by the introduction of symmetry breakage in the experimental system in terms of either the shape of the objects or on the environmental boundary conditions.[1] In an experimental system with active droplets, fluctuation of the interface, or interfacial instability, due to the Marangoni effect has been proposed to cause specific macroscopic motions. It has been reported that irregular agitation induced by a chemical Marangoni effect can be transduced into characteristic repetitive up−down or rotational motion, simply by choosing appropriate boundary conditions.[10,26,41,42] For example, Sumino et al.[10] found that an oil droplet exhibits a rhythmic back-and-forth (reciprocating) motion under geometrical constraint with a narrow rectangle shape, whereas it undergoes random motion in an isotropic environment.

In the present study, we performed an experiment on the interference between a pair of active droplets undergoing back-and-forth the motion on a waterway with a narrow rectangle shape. The droplets exhibit a swinging type of synchronization when a glass capillary is placed at the midpoint of the waterway.

RESULTS AND DISCUSSION

Figure 1a shows the experimental system, where a pair of droplets of nitrobenzene (density: 1.2 g/cm^3) with the same volume (100 μL) are situated on an aqueous phase using a pipette. In our experiments, all of the chemicals were of analytical grade and purchased from Wako Pure Chemical Industries, Ltd. All of the experiments were carried out at room temperature (24 ± 2 °C). It has been found that heavy oil droplet, such as nitrobenzene and aniline, can float on aqueous solution by avoiding sinking to the bottom because of the supporting effect of the interfacial tension and tends to exhibit active self-propelled motion driven by Marangoni instability.[10,26,41,42] Before the investigation on the interference of the self-propelled motion of the couple of droplets, we have explored the effect of chemical compositions of the aqueous phase on the self-propelled motion; for example, we have explored the effect of chemical compositions of the aqueous phase on the self-propelled motion by adding various chemical species, such as sodium chloride, sucrose, quinine chloride, and acetic acid, at different concentrations. As the result, we found that the self-propelled motion of a nitrobenzene droplet becomes most vivid when submolar concentration of acetic acid is added to the aqueous solution. Thus, in the present study, we adapted acetic acid solution to observe the spontaneous motion of oil droplets and confirmed that a

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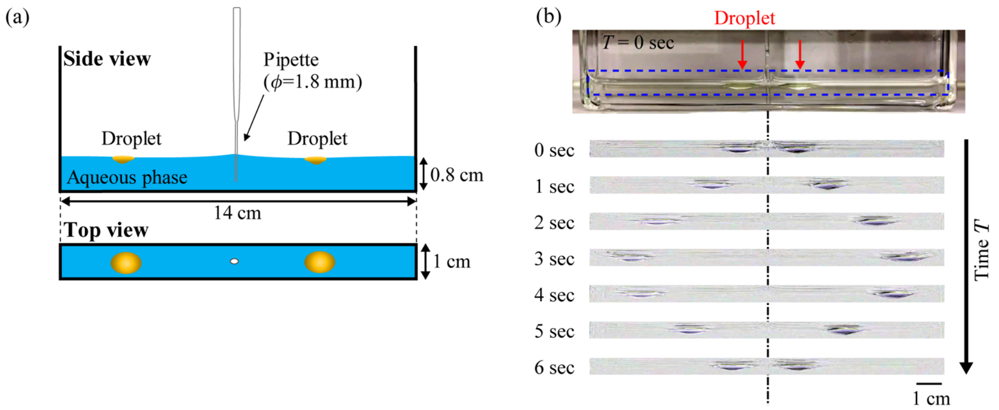

Figure 1. Pair of oil droplets exhibiting self-propelled motion on an aqueous phase in a narrow rectangular vessel. (a) Experimental setup: Two droplets of nitrobenzene (each 100 μL) were situated on an aqueous phase of 0.3 mol/L acetic acid. A pipette was inserted at the midpoint of the waterway. The droplets began to exhibit translational motion immediately after contact with the aqueous solution. (b) Upper image: Side view of the experimental setup. Lower image: Snapshots of the swinging droplets at 1 s intervals.

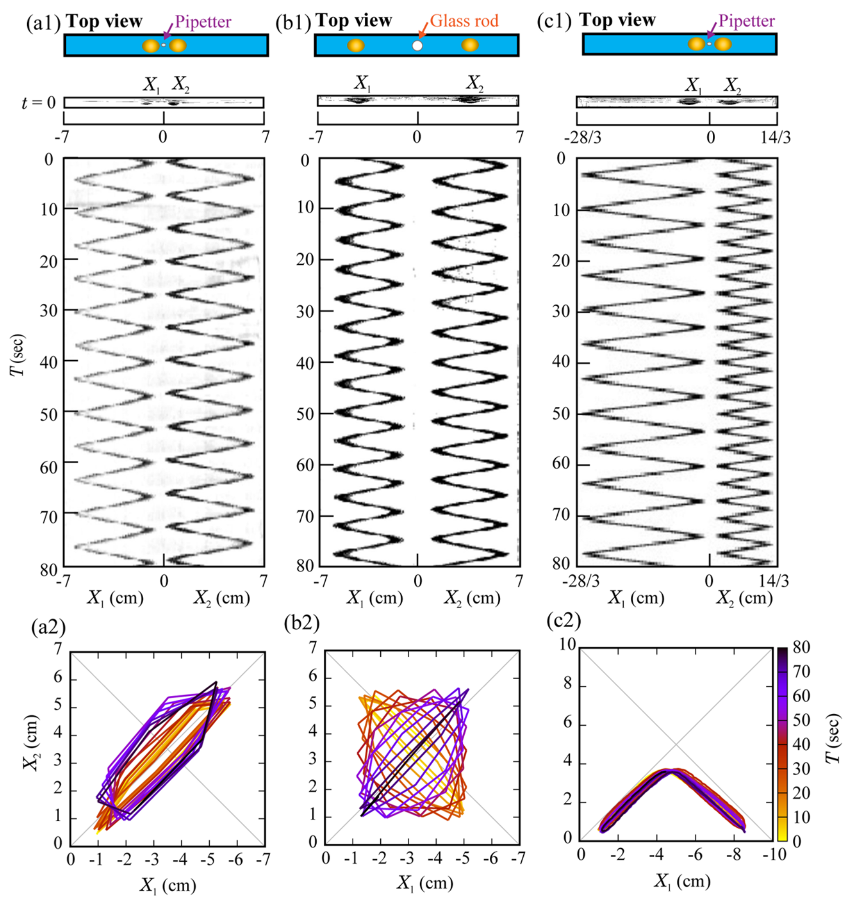

Figure 2. Analysis of the oscillatory motion of the two droplets. Upper part: spatiotemporal diagram based on the data regarding the movement of the droplets. (a1) Swinging motion with the 1:1 synchronization where a pipette with the diameter of 1.8 mm is inserted at the midpoint of the waterway. (b1) Out of synchronization under the same conditions as in (a1) except for the intervening object; a glass rod was positioned at the midpoint. (c1) 2:1 Synchronization when the narrow glass pipette was shifted toward the right. (a2−c2) Correlation diagrams between the motions of the left and right droplets, X_1 and X_2, respectively. For all of the experiments, the volume of the droplets was 100 μL and the aqueous phase was 0.3 mol/L acetic acid solution, using the waterway shown in Figure 1a.

regular back-and-forth reciprocating motion is generated in a reproducible manner. To observe the interference between the droplets undergoing back-and-forth motion, we placed a glass capillary (ϕ = 1.8 mm for the part dipped into the waterway) at the middle of the waterway, as depicted in Figure 1a. In the absence of a glass capillary on the waterway, the droplets tend to merge together to form a single droplet through the collision. With a capillary, the twin droplets remain each other on the left and right chambers without fusion and exhibit a back-and-forth motion. Figure 1b shows images of the droplets taken at 1 s intervals, revealing that the droplets exhibit a swinging-type synchronization.

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Figure 2 shows the spatiotemporal diagrams for the droplet motion. As shown in Figure 2a1, the droplets undergo 1:1 swinging-type synchronization, where a narrow pipette (ϕ = 1.8 mm) was put at the middle of the waterway in the experiments as depicted in Figure 1. When the intervening narrow pipette was replaced by a thick glass rod (ϕ = 5.0 mm), the droplets exhibit unsynchronized motion. It is noted that replacement of the interference barrier of the narrow pipette by the glass rod with a wider diameter causes the coupling strength between the self-moving droplets to be weaker. The difference in the interference mode of coupled motion can be depicted as a phase diagram, as shown in Figure 2a2,c2. For a 1:1 synchronized motion, the trajectory shows a regular loop along a straight line with a slope of unity (Figure 2a2). Figure 2c1 shows the spatiotemporal diagram when the intervening pipette was positioned on the right-hand side of the waterway, revealing the appearance of a 2:1 synchronization of the back-and-forth motion. Recently, we have reported the up−down self-propelled motion for a floating oil droplet by prohibiting translational motion using a thin glass rod.[43] It was found that a pair of neighboring droplets undergo an in-phase synchronization. Such an experimental trend was argued in terms of the Marangoni effect under gravitational instability for a heavy oil droplet. The mode of the synchronization of the swinging-type motion in the present study is regarded to correspond to the in-phase synchronization of the up−down motion of the two droplets.

To clarify the mechanism that underlies the synchronized motion of the two droplets, we performed a numerical study based on a simple theoretical model. We adopted a model for self-propelled directional motion on a quasi-one-dimensional waterway, as in a previous study[10]

$$m\frac{d^2x}{dt^2} = \eta\left(1 - \alpha\left(\frac{dx}{dt}\right)^2\right)\frac{dx}{dt} + [\text{mutual interaction}] + [\text{boundary effect}] \quad (1)$$

where m denotes the mass of the droplet, η is the viscosity of water, and α is the ratio between the driving force and viscous damping. In our modeling, we omitted the noise term used in the previous study[10] to abstract the essential quality of the self-propelled motion through simplification of the differential equation. Equation 1 implies that the self-propelled motion is a phenomenon generated under thermodynamically open conditions, i.e., competition between the driving force and viscous damping.

Next, we consider the motion of the droplets on the left-hand and right-hand sides of the waterway by using dimensionless positional variables, x_1 and x_2, corresponding to the left and right droplets, respectively

$$\frac{d^2x_1}{dt^2} = \mu_1\left(1 - \alpha\left(\frac{dx_1}{dt}\right)^2\right)\frac{dx_1}{dt} + \frac{\gamma}{(x_2 - x_1)^2} - \frac{\partial U}{\partial x_1}$$
$$\frac{d^2x_2}{dt^2} = \mu_2\left(1 - \alpha\left(\frac{dx_2}{dt}\right)^2\right)\frac{dx_2}{dt} - \frac{\gamma}{(x_2 - x_1)^2} - \frac{\partial U}{\partial x_2} \quad (2)$$

where μ_1 and μ_2 are the parameters that determine the period of back-and-forth motion, and they are set to ca. 0.35. The value of α is set to 0.26. The variables of x_1 and x_2 are defined as negative and positive, respectively. Thus, the differential equations on x_1 and x_2 in eq 2 are symmetric with respect to each other. The second term on the right-hand side of eq 2 represents the interaction between the two droplets. Here, we simply assumed that the interaction between two droplets is inversely proportional to the square of the distance between them;[42] thus, the interaction is effective only when the distance between them is short and tends to induce an in-phase motion. The last term of eq 2 represents the boundary effect, or potential energy of the vessel wall and barrier of the inserted capillary or rod. We chose these values to reproduce the stable translational motion of the droplets.

$$U = \begin{cases} k(x - a)^2, & 0 \le |x| \le a \\ 0, & a < |x| \le b \\ k(x - b)^2, & b < |x| \end{cases} \quad (3)$$

The potential energy U is schematically depicted in Figure 3a2−c2, where we consider the repulsive effect due to the meniscus near the glass wall and inserted pipette/rod. We adopted the parameters for the boundary effect, k = 80, a = 0.25, b = 6.75, to roughly reproduce the geometry of the meniscus around the hydrophilic glass wall. Figure 3a1,b1 shows the results of the numerical simulation when the waterway is divided at the midpoint. To check for the appearance of the synchronized state, μ_1 and μ_2 are set to be somewhat different: μ_1 = 0.36, μ_2 = 0.32. Figure 3a1 shows a 1:1 synchronization, corresponding to the experiment in

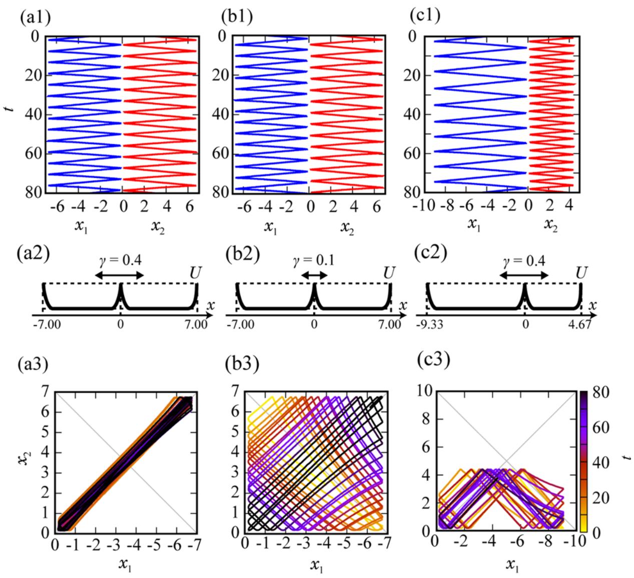

Figure 3. Numerical simulation of the motion of a pair of droplets calculated with eq 2; the values of the parameters are given in the text. (a1) 1:1 Synchronization when the strength of the interaction parameter is γ = 0.4 at the middle of the waterway. (b1) Out of synchronization when the strength of interaction is smaller γ = 0.1. (c1) 2:1 Synchronization when the intervening barrier is shifted to give a 2:1 ratio for the respective lengths of the waterway under conditions similar to those in (a2). The result of numerical simulation for t = [0,100], where the time step is 0.01. (a2−c2) The profiles of the potential function U, where x_1,x_2 = 0 corresponds to the position of the glass pipette or rod, and the edges on the left and right correspond to the position of the walls of the vessel. Around the vicinity of the boundary, we considered the effect of the meniscus as explained in the text. (a3−c3) Correlation diagram of between the left and right droplets denoted as x_1 and x_2, respectively.

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Figure 2a1, with the interaction parameter γ = 0.4. On the other hand, Figure 3b1 shows the unsynchronized state, where the interaction parameter is smaller γ = 0.1. Figure 3c1 shows the appearance of 2:1 synchronization, where the waterway is divided 2:1, suggesting a reproduction of the experimental trend in Figure 3c2. Except for the placement of the barrier, the parameters for 2:1 synchronization are the same as those for 1:1 synchronization. In our simple model equations, the important spatial variables were not included such as size and morphology of the droplets and the width and depth of the waterways. It is noted that, through such very simple mathematical modeling, the essential features on the behavior of a pair of the self-propelled droplets have been well reproduced.

In summary, we have clarified that the synchronized swinging motion of a pair of droplets is generated in a spontaneous manner. When we vary the relative length of the waterway as a control parameter, the mode of synchronization changes from 1:1 to 2:1. It may be interesting to extend the experiments to produce other types of synchronized motion, such as mode coupling with more than two droplets and the interaction of different-sized droplets. These studies are expected to contribute to the development of a system that exhibits self-organized motion working driven by chemical nonequilibrium under isothermal condition.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01533.

- Additional experimental results to clarify the recovery of synchronization, when the droplets undergo 1:1 swinging-type synchronization (Figure S1) (PDF)
- Real-time observation on the 1:1 swinging-type synchronization (Video S1) (AVI)
- Real-time observation on the unsynchronized motion (Video S2) (AVI)
- Real-time observation on the 2:1 swinging-type synchronization (Video S3) (AVI)
- Real-time observation on the recurrence of 1:1 synchronization against the effect of a disturbance (Video S4) (AVI)

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Notes

The authors declare no competing financial interest.

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