

Mode bifurcation on a self-propelled droplet driven by the Marangoni effect

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Abstract

In the thesis, self-propelled systems under non-equilibrium conditions are studied. Especially we focus on the regular motion of a droplet induced by interfacial instability and the mode bifurcation of motion.

When chemical concentration and/or temperature distribution at a fluid interface are inhomogeneous, the interface becomes unstable because the spatial gradient of interfacial tension is induced. This phenomenon is well known as Marangoni effect, and such agitated surface causes a flow called Marangoni convection. This convection and/or the interfacial tension gradient are expected to generate the motion of an object, such as an air bubble, a liquid droplet, or a solid particle. In such systems, choosing a suitable boundary condition, e.g., introducing internal or external asymmetry to the system, permits the object to undergo a regular motion with a specific mode according to the given asymmetry. Besides, the regular motion of a droplet can be caused in association with spontaneous symmetry breaking of the droplet shape. Here, in this thesis, experiments on self-propelled systems with a local energy source were carried out in order to investigate mode bifurcations between different types of regular motions.

First topic of this thesis is the self-propelled motion of a solid/liquid composite induced by the solutal Marangoni effect (Fig. 1(a)). When an oil droplet of oleic acid attached to a solid column of sodium oleate is placed on a water phase, a local gradient of surfactant concentration is generated by diffusion of oleate molecules, and hence the motion of the composite is induced. The composite exhibits a certain mode of regular motion, such as spinning, translational, or orbital motion, depending on the size of the solid. It is found that when the solid is much larger or smaller than the droplet, the spontaneous breaking of left-right symmetry occurs and results in rotational motion of the composite. This mode bifurcation is qualitatively reproduced by using ordinary differential equations by taking into account the scheme of spontaneous symmetry breaking.

Second topic is mode bifurcation of the laser-induced motion of a droplet, as shown schematically in Fig. 1(b). In the experiment, an oil droplet floating on a water surface is heated locally by irradiation of a laser. Under suitable laser power, the droplet is driven by the thermal Marangoni effect due to the local temperature gradient and exhibits regular periodic motion around the laser spot. As the laser power increases, the mode of the droplet motion bifurcates from rectilinear reciprocal motion to circular motion. The result shows that Marangoni flow inside the droplet becomes spontaneously asymmetric at high laser power, i.e., high energy flux rate. The essential aspects of this mode bifurcation can be described by a simplified mechanical model with the time-delayed function which reflects the effect of Marangoni convection.

Mode bifurcation in self-propelled systems is one of interesting phenomena in terms of non-equilibrium and non-linear physics. Overall, the mode of self-propelled motion under non-equilibrium conditions is highly dependent on the property of asymmetry in the field. In addition, above two experiments in this thesis indicate that the mode bifurcation is induced with an increase in the degree of asymmetry or non-equilibrium, i.e., the driving force, through the emergence of spontaneous symmetry breaking.

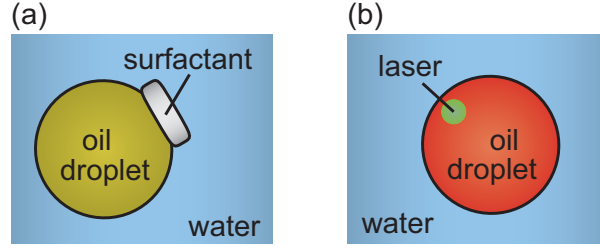


Figure 1: Schematic illustrations of experiments in this thesis. (a) A solid/liquid composite of a droplet and a solid soap is floated on water. (b) A droplet is locally irradiated by a laser.

Publication list

This thesis is based on the following original papers.

Published paper

- [1] “Spontaneous mode-selection in the self-propelled motion of a solid/liquid composite driven by interfacial instability”: Chapter 5
F. Takabatake, N. Magome, M. Ichikawa, and K. Yoshikawa, *J. Chem. Phys.* **134**, 114704 (2011).

Paper under submission

- [2] “Mode bifurcation of droplet motion under stationary laser irradiation”: Chapter 6
F. Takabatake, K. Yoshikawa, and M. Ichilawa.

Related papers

- [3] “Rotational motion of a droplet induced by interfacial tension”
K. H. Nagai, F. Takabatake, Y. Sumino, H. Kitahata, M. Ichikawa, and N. Yoshinaga, *Phys. Rev. E* **87**, 013009 (2013).
- [4] “Controlling negative and positive photothermal migration of centimeter-sized droplets”
M. Ichikawa, T. Iwaki, F. Takabatake, K. Miura, N. Magome, and K. Yoshikawa, *Phys. Rev. E* **88**, 012403 (2013).

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Part I

General introduction

Chapter 1

Introduction

1.1 Introduction

Thermal engines transfer chemical energy into mechanical energy through the generation of heat. Thus, the upper limit of thermal efficiency is limited by the difference between high and low temperatures in accordance with the second law of thermodynamics. In contrast, living organisms directly extract kinetic energy from chemical energy with high energy-conversion efficiency under isothermal conditions. Motor proteins and motile cells are typical examples of many such organisms which directly convert the chemical energy of chemical substances such as ATP into mechanical work without thermal cycle [5]. Even though the details of such spontaneous motion in living systems have been actively researched [6–8], our understanding of the underlying mechanism remains at a primitive stage. This is because of the complexity of actual living organisms consisting of a huge variety of elements; it is hard to investigate which elements play essential roles to generate motion. Therefore, there must be of scientific value to deal with non-biological self-propelled systems without complexity in order to gain an underlying mechanism for spontaneous motion.

Living phenomena arise under conditions in which the influx and the dissipation of free energy exist constantly, in contrast to an equilibrium state. Such systems involving energy flux, called non-equilibrium open systems, are far from equilibrium and cannot be described within the framework of equilibrium physics. In non-equilibrium open systems, spatio-temporally ordered structures, such as the oscillation of chemical concentrations and geometrical patterns, emerge spontaneously from uniform state. These structures, e.g., target or spiral patterns observed in reaction-diffusion systems of Belousov-Zhabotinsky reaction [10], are called dissipative structures [5, 9]. The regular pattern of convection cells (Bénard convection [11]) seen in thermal convection is also a famous example of dissipative structures. Such dissipative systems exhibit strong non-linearity, and thus various interesting phenomena, e.g., bifurcation and chaotic phenomena, can arise.

Self-propelled objects can be considered as energy-conversion systems in non-equilibrium open conditions. These systems are not only associated with the motion of living organisms but are also interesting from the standpoint of non-equilibrium physics. Indeed, self-propelled motions of liquid droplets, solid particles, and gels have been investigated both experimentally and theoretically from perspectives of non-linear science [12–18]. Among the phenomena of self-propelled motions, the self-agitation of a fluid interface induced by a spatial non-uniformity of interfacial tension is well known. This phenomenon is called the Marangoni effect [19] which is categorized into two traditional ones of thermal and solutal (chemical). The thermal Marangoni effect is caused by a temperature gradient, and the

solvent Marangoni effect by a chemical concentration gradient. The solvent effect is of particular relevance as it is regarded as a system which converts chemical energy directly into kinetic energy under isothermal conditions, as with living systems.

This work focuses on regular motions induced by the solvent and thermal Marangoni effects under non-equilibrium conditions. Self-propelled motion of a solid/liquid composite is caused by a local gradient of interfacial tension due to the diffusion of the surfactant from the solid soap, and mode bifurcation occurs with a change in the size of the solid. Alternatively, an oil droplet on water exhibits various regular motion when heated locally with a laser. As the laser power increases, droplet motion undergoes bifurcation through spontaneous symmetry breaking. Through the above mentioned investigations, we claim that the mode of self-propelled motion exhibits bifurcation depending on the degree of non-equilibrium or asymmetry.

1.2 Overview

In a series of our studies, including this thesis, we have investigated self-propelled motions driven by the Marangoni effect accompanied with mode bifurcations of motion. Generally, by introducing internal or external asymmetry to the system, it becomes possible to extract regular motion with a specific mode according to its asymmetry. In addition to such mode-selection, we reported experimentally that the mode of the self-propelled motion exhibits “spontaneous” bifurcation, even under boundary conditions with the same geometrical symmetry [1]. When a solid particle of surfactant is attached to an oil droplet floating on water, the resulting composite exhibits spontaneous motion where the direction of translational motion is uniquely determined because of its anterior-posterior asymmetry. Additionally, the torque arises in this system with a change in the size of the solid, i.e., the balance of head (solid) and body (droplet) of the composite. It has been shown that the essential features of the composite’s motion can be described by ordinary differential equations with a non-linear friction function. In other words, the paper used symmetry arguments for explaining experimental results. However, the mechanism of mode bifurcation is not yet clear in this model.

We therefore performed detailed theoretical analysis by calculating the flow field around the droplet [2]. In the paper, we considered a circular droplet with a supply source of surfactant molecules at the droplet interface. Surfactants diffusing from the source to the interface reduce interfacial tension, and thus inhomogeneity of tangential stress appears at the interface due to the surfactant concentration gradient. In response to this tangential stress, the motion of the droplet is induced through the generation of Marangoni flow around the droplet. As a result of calculating the flow field around the droplet using an advection-diffusion equation coupled with the Stokes equation, the droplet spontaneously rotates under the condition with high gradient of interfacial tension. Although quantitative comparison with experiment is quite difficult (several parameters such as the decomposition rate and the supply rate of surfactants are hard to measure experimentally), this theoretical model agreed well with an experiment in which the volume of the droplet was changed while the solid size was kept constant. Furthermore, it is expected that the droplet motion induced by local temperature gradients can be theoretically modelled in a similar way.

In order to verify whether the spontaneous mode bifurcation occurred in the thermal-induced motion of a droplet, we investigated the self-propelled motion of an oil droplet floating on an aqueous phase driven by local heating with a laser. First, we found that the attractive and repulsive motions of the droplet are induced; the droplet moves toward

the laser spot on an aqueous solution containing surfactant, while it moves away from the laser on pure water [3]. Through this study, it has become clear that the balance between temperature-dependence of interfacial tension at the air/water interface and that at the droplet interface is important in determining the direction of droplet motion. Shear stress due to the interfacial tension gradient at droplet interface tends to move the droplet toward the laser spot. On the other hand, the droplet is pulled away from the laser by the gradient force of interfacial tension at air/water interface.

Additionally it was found that, under the condition in which the attractive force is generated, the mode of the motion of a circular droplet bifurcates into qualitatively different types of regular motions [4]. The continuous motion of the droplet is induced by a spatially-fixed laser having a suitable laser power, and the mode bifurcation from rectilinear reciprocal motion to circular orbital motion is generated with an increase in the laser power. This mode bifurcation is discussed in terms of spontaneous symmetry breaking under a high gradient of temperature, and is reproduced with simple ordinary differential equations by incorporating a delay effect of the Marangoni convection and heated position.

The future research is to make a detailed theoretical approach on the laser-induced motion, such as flow field calculations using the Stokes equation by taking into account diffusion and advection of heat in a similar way to the case of chemically-induced motion [2]. Since we can experimentally measure temperature distribution around the droplet with an infrared camera, the quantitative comparison with experiment is expected to be done with more precision.

This thesis describes the details of ref. [1] and ref. [3] in part II and part III, respectively.

Chapter 2

Interface

2.1 Interfacial tension

An interface in chemistry or physics is defined as a boundary plane between different homogeneous phases such as a liquid, a solid, or a gas. In particular, an interface between a liquid and a gas or a solid and a gas is called a surface. The interface between two different fluids tends to be minimized through the deformation of fluids. Visible examples of this phenomenon are that a soap bubble in the air takes on a spherical shape and that water does not spill of a slightly overfilled glass as shown in Fig. 2.1(a). Such phenomena result from interfacial (or surface) tension, described this section.

Physical origin

Because the liquid is in a molecular aggregation state, molecules within the liquid attract each other by intermolecular interactions, such as van der Waals attraction. When a liquid makes contact with a gas like the air, while a molecule inside the bulk of the liquid is subject to interactions with neighboring molecules from all sides, a molecule on the surface interacts with other molecules of the liquid from only half of its side; the strength of the attracting force acting on it becomes lower than in the bulk (Fig. 2.1(b)). Thus the energy of the molecule becomes higher at the interface and it is desirable to decrease the number of molecules existing on the interface as much as possible in order to minimize the free energy. As a result, the pressure which attempts to minimize the surface area, i.e. the interfacial tension, is generated [20].

Since interfacial tension is connected to the energy loss at the interface, a stronger intermolecular interaction of constituent molecules results in a higher interfacial tension of the liquid. Interfacial tension also changes with temperature [21] because of temperature-dependent free energy.

Definition of interfacial tension

When the surface area of the liquid is increased by dA , the required mechanical work δW is proportional to the number of molecules that newly come to the surface, i.e. the increased area dA ,

$$\delta W = \gamma \cdot dA. \quad (2.1)$$

Above coefficient γ corresponds to interfacial tension. Interfacial tension γ has dimensions of $[\text{mass} \cdot \text{time}^{-2}]$, thus interfacial tension is interpreted as force per unit length or energy

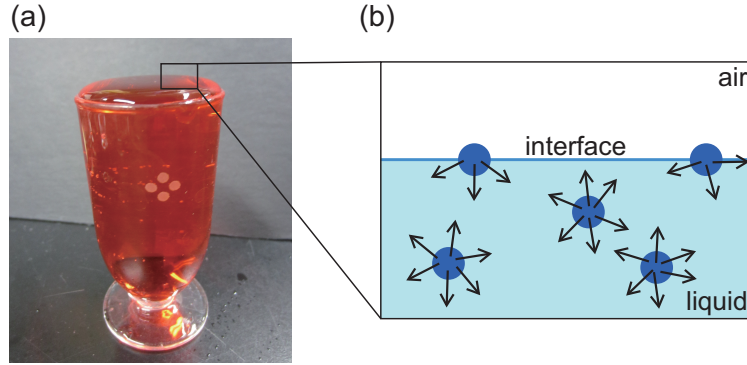


Figure 2.1: (a) Water (red-dyed) overflowing a glass does not overflow because of the interfacial tension between water and air. (b) Schematic illustration indicating the origin of interfacial tension. Molecules are in a higher energy state at the interface than in the bulk of the liquid.

per unit area. By considering interfacial tension as energy per unit surface area, it is defined as the increase of free energy F with increasing surface area A , as follows:

$$\gamma = \left[\frac{\partial F}{\partial A} \right]_{T,V,n} \quad (2.2)$$

where T , V , and n are temperature, the total volume, and the number of molecules, respectively [20].

Next, we shall regard interfacial tension as force. When soap solution forms a thin film on a square frame, one side of which is a movable bar, as depicted in Fig. 2.2, the soap film tends to decrease the surface area by moving this bar. Therefore, in order to maintain the shape of the film, pulling the bar with a force f is necessary. Because interfacial tension γ is considered as force acting on the unit length, the force needed to maintain the shape is described as

$$f = 2l\gamma. \quad (2.3)$$

Here, the coefficient 2 derives from the fact that there are two interfaces, i.e. the front and the back of the film.

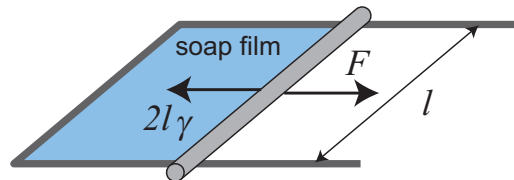


Figure 2.2: Schematic illustration of interfacial tension acting on the soap film: An example of the experiment in which it can be considered that interfacial tension is force per unit length.

2.2 Surfactant

Properties of surfactants

“Surfactants” tend to exist specifically at the interface and lower the interfacial tension between two phases. Surfactants are amphiphilic molecules, and usually consist of hydrophilic groups (heads) and hydrophobic groups (tails). Generally, the hydrophilic head has polarity, so it is soluble in polar solvents like water. On the other hand, the hydrophobic tail is a non-polar region composed of long fatty acid chains, and has a low affinity with polar solvents. According to the ionic characteristics of hydrophilic heads, surfactants are divided into ionic surfactants whose heads have net charge and non-ionic ones with heads that carry no electric charge; examples of surfactants are represented in Fig. 2.3.

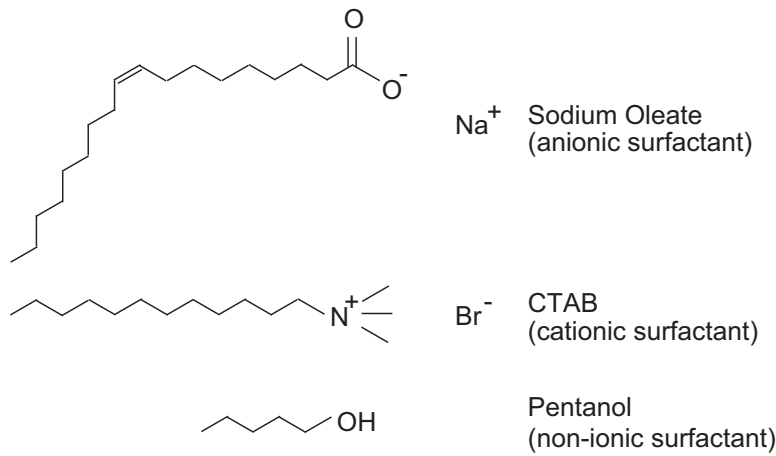


Figure 2.3: Examples of surfactants. Sodium oleate is an anionic surfactant, CTAB (Cetyltrimethylammonium bromide) is cationic, and pentanol is non-ionic. Pentanol is not strictly a surfactant but has an amphiphilic property.

If surfactant molecules separately exist in a polar solvent such as water, the hydrophilic heads are in a stable state while the hydrophobic tails are unstable. To dispel this instability, surfactant molecules tend to locate at the air/water or oil/water interface; the head groups will contact with the water and the tail groups will contact with the air or oil, resulting in the formation of a surfactant monolayer at the interface. Here surfactant molecules are considered to behave like an ideal gas at the interface, the area of which is A . Under the assumption that any dissolving of surfactants in the bulk liquids is negligible, total surface energy is described as

$$F = A(\gamma_0 + T\sigma(\log(\sigma a_0) - 1) + u_0\sigma), \quad (2.4)$$

where γ_0 is the interfacial tension of the bare interface, σ is surface concentration of surfactants, a_0 is a constant indicating the cross-sectional area of a single surfactant molecule, and u_0 represents the difference between the energy of a surfactant at the interface and the energy of a surfactant molecule existing in a solid of pure surfactant. In other words, the second term on the right side of the equation indicates ideal-gas-like entropy of surfactant molecules. Interfacial tension is given by the change in free energy with an increase in surface area, as in Eq. (2.2). By considering the number, N , of surfactant molecules at the

interface as constant and taking into account the relation $\sigma = N/A$, the interfacial tension in the presence of surfactants can be calculated as follows:

$$\gamma = \frac{\partial F}{\partial A} = \gamma_0 - T\sigma. \quad (2.5)$$

This equation indicates that the translational entropy of surfactant molecules increase with an increase in surface area, and thus the interfacial tension becomes lower by the presence of surfactants [22].

However, it must be noted that, because of the assumption of ideal-gas-like entropy, the above equation is correct only for cases in which the surface concentration of surfactants is sufficiently small. Generally, it is known that interfacial tension monotonically decreases with respect to the surfactant concentration in solution; the typical dependence of interfacial tension of surfactant concentration is shown in Fig. 2.4.

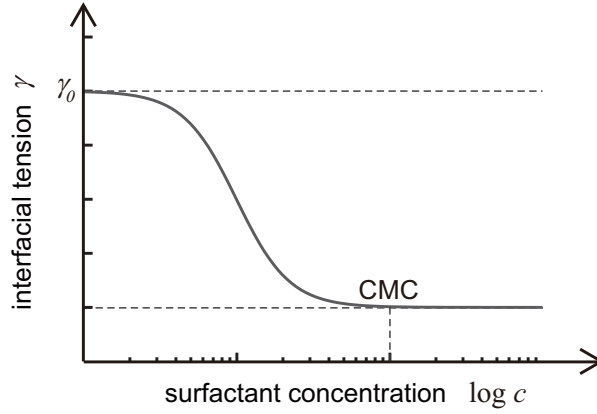


Figure 2.4: The typical change of interfacial tension with respect to surfactant concentration.

Aggregation of surfactant

As shown in Fig. 2.4, interfacial tension decreases in association with an increase in the concentration of surfactants in solution and becomes constant above the critical micelle concentration (CMC); surfactants form aggregation structures above the CMC. In a water phase, surfactant molecules form spherical structures called “micelle”, where the hydrophilic heads are outside of the volume in order to make contact with the surrounding water and the hydrophobic tails are inside, as schematically shown in Fig. 2.5(a). By forming such a structure, the hydrophobic tails can avoid contact with water. On the other hand, surfactants form a structure with the hydrophobic tails out, which is known as “reverse micelle”, in non-polar solvents such as oil (Fig. 2.5(b)). Alternatively, Fig. 2.5(c) shows a spherical-shell structure called a vesicle, composed of bilayer membrane of surfactant.

When surfactants are added to a two-phase system of liquids that are normally immiscible, such as water and oil, the two liquids become admixed with the surfactants forming (reverse) micelles, as shown in Figs. 2.5(d) and (e). This mixture of liquids is called emulsion, examples of which are milk, skin lotion, mayonnaise, and so on. Whether the surfactants form micelles (oil in water) or reverse micelles (water in oil) depends on the volume fraction of the liquids, temperature, and the geometric structure of the surfactants [23].

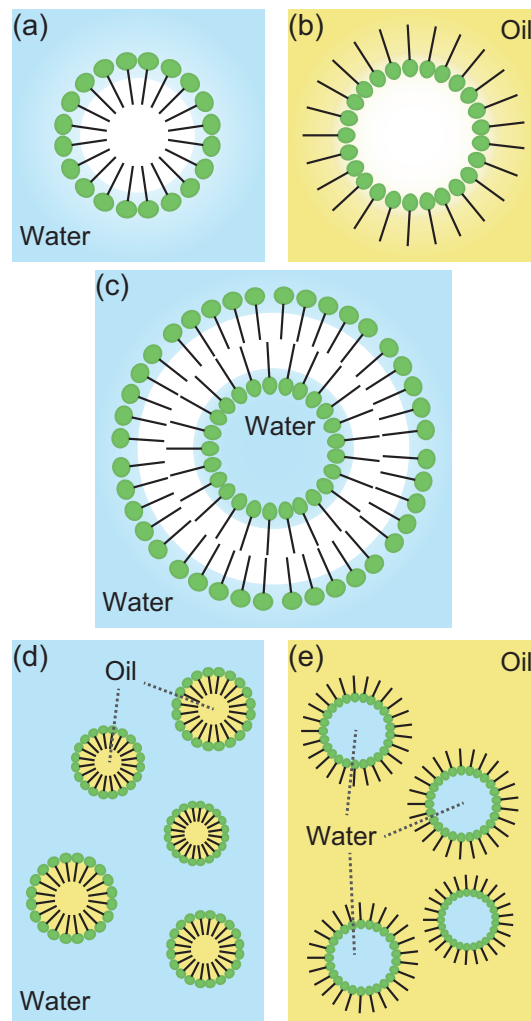


Figure 2.5: Schematic images of aggregation structures of surfactants in water and/or oil. Solid circles and lines indicate hydrophilic heads and hydrophobic tails, respectively. (a) Micelle in the water. (b) Inverse micelle in the oil. (c) Vesicle. (d) O/W (oil-in-water) emulsion. (e) W/O (water-in-oil) emulsion.

2.3 Interfacial instability

Marangoni effect

Interfacial tension depends on the concentration of surfactants, as described in the previous section, and also on temperature. Therefore, interfacial tension becomes spatially inhomogeneous under chemical or thermal non-equilibrium conditions, and tangential stress is generated on the interface. This Marangoni stress σ_M is described as the spatial gradient of the interfacial tension γ :

$$\sigma_M = \nabla \gamma. \quad (2.6)$$

Such inhomogeneity of interfacial tension is typically caused either by a temperature gradient or chemical concentration gradient at the interface; these phenomena are known as the thermal or solutal Marangoni effect, respectively. It is well known that Marangoni stress causes convection in bulk phases, as depicted in Fig. 2.6.

In the case of the thermal Marangoni effect, the system is characterized by the Marangoni number,

$$M = -\frac{d\gamma}{dT} \frac{L\Delta T}{\rho\nu\kappa}, \quad (2.7)$$

where γ is the interfacial tension, L is the characteristic length of system, ΔT is the temperature difference, ρ is the density of the liquid, ν is the kinetic viscosity, and κ is the thermal diffusivity [25]. The Marangoni number represents the proportion of interfacial tension forces to viscous forces, i.e., the strength of the thermal Marangoni flow. In the same way, the solutal Marangoni flow can be characterized by

$$M_c = -\frac{d\gamma}{dc} \frac{L\Delta c}{\rho\nu D}, \quad (2.8)$$

where c is the surfactant concentration and D is the diffusion coefficient.

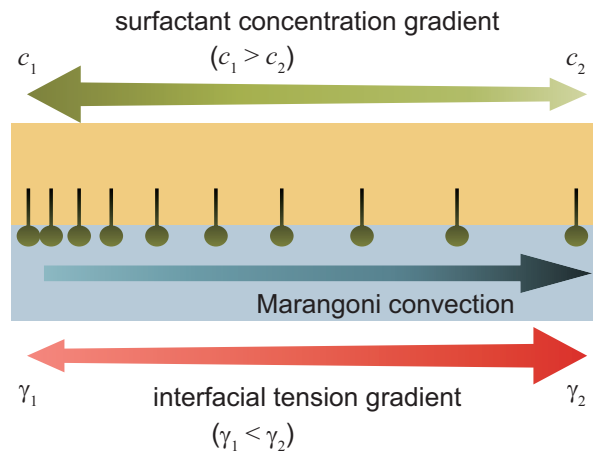


Figure 2.6: Schematic illustration of the solutal Marangoni effect. When the surfactant concentration at the interface becomes inhomogeneous, convection is generated by the tangential stress due to the interfacial tension gradient.

Motion driven by interfacial instability

A famous example of phenomena related to the Marangoni effect is known as “tears of wine” [24, 26, 27], which is caused when the water-alcohol mixture is poured into a glass. In the thin film where the mixed liquid makes contact with the glass, the concentration of alcohol decreases by evaporation, and the interfacial tension increases in the film. The liquid moves upward in a thin film along the glass wall by the interfacial tension gradient. Then, the liquid is driven downwards by gravity as droplets, so that it appears to shed tears.

As represented by the “tears of wine” phenomenon, motions of a liquid can be induced by interfacial instability. A droplet on a chemically inhomogeneous solid surface is driven to the region of lower interfacial energy [28], as shown in Fig. 2.7. Under temperature gradients, a droplet lying on a solid surface can move in either directions of low or high interfacial energy, as a result of a balance between forces due to the gradient of interfacial energy and due to the interfacial tension gradient, i.e., the Marangoni effect [29].

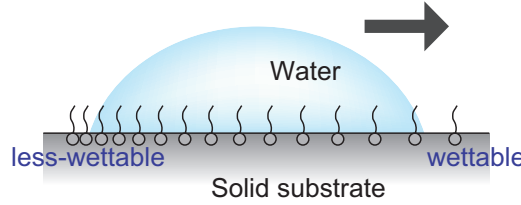


Figure 2.7: Motion of a water droplet on chemically inhomogeneous substrate. The droplet moves toward the more-wettable region.

Additionally, on a homogeneous solid substrate, self-propelled motion of a droplet can be caused by the spontaneous generation of local inhomogeneity most likely due to the chemical reactions [30, 31]. Similarly, a solid particle or a liquid droplet on a homogeneous liquid surface can exhibit self-motion by interfacial instability, e.g., motion of a camphor scrap [32] or an alcohol droplet [33] on a water surface. Such self-propelled motion is known to be triggered by microscopic fluctuations. For example, the beginning of the camphor’s motion is described as follows: Camphor molecules spread on the water surface and form a thin layer, resulting in a decrease in air/water interfacial tension around the camphor scrap. The surface tension around the scrap at rest is normally isotropic, and the scrap is kept in a rest state, as shown in Fig. 2.8(a). However, if the concentration distribution of camphor molecules becomes slightly anisotropic by fluctuations, the interfacial gradient around the scrap is generated and moves the scrap toward the high interfacial tension region (Fig. 2.8(b)). Once the scrap moves, anisotropic diffusion of the camphor molecules induces the gradient of interfacial tension, and the scrap is accelerated by the Marangoni effect, resulting in continuous motion with an almost constant velocity, as in Fig. 2.8(c).

Under large fluctuating conditions, the motion that occurred by such a mechanism is ballistic for a short time scale and is diffusive for a long time scale, much like Brownian motion [34]. This motion is called active Brownian motion and can be described by the following equation [35]:

$$\frac{d\mathbf{r}}{dt} = \mathbf{v} ; \quad \frac{d\mathbf{v}}{dt} = -\eta(\mathbf{v}) \mathbf{v} + \boldsymbol{\xi}(t), \quad (2.9)$$

where $\eta(\mathbf{v})$ is the non-linear friction coefficient, which is assumed to depend on velocity, such as $\eta(\mathbf{v}) = -\eta_1 + \eta_2 \mathbf{v}^2$. $\boldsymbol{\xi}(t)$ is a stochastic force indicating the fluctuation.

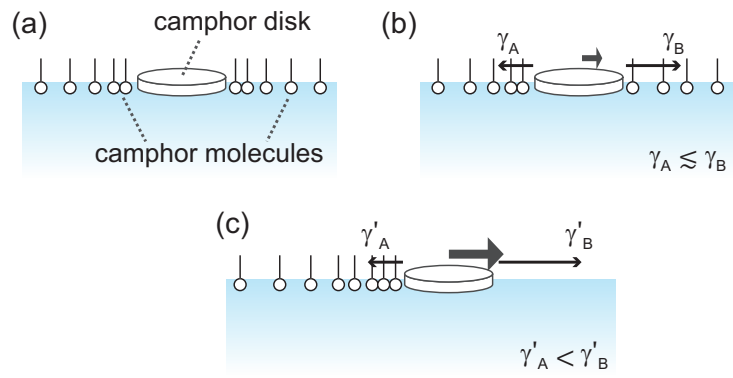


Figure 2.8: Schematic diagram of the mechanism of self-propelled motion of camphor scrap (disk), induced by microscopic fluctuation.

Chapter 3

Outline of the thesis

In this thesis, the mode bifurcation of self-propelled motion driven by interfacial instability, i.e., the Marangoni effect, is investigated. In chapter 2, basic knowledge about interfacial tension, which is important in understanding the Marangoni effect, and related phenomena were introduced.

Part II reports on the self-propelled motion of a solid/liquid composite induced by the chemical Marangoni effect, where an oil droplet attached to a solid soap is placed on a water phase. The mechanism of this motion is discussed in chapter 4, and the mode bifurcation is investigated in chapter 5. It is shown that the composite exhibits various characteristic motions, such as orbital motion and translational motion. The results indicate that the mode of this self-propelled motion switches with a change in the size of the solid column. The essential features of this mode bifurcation are discussed with a simple theoretical model, by considering nonlinear friction with proper symmetry.

The self-propelled motion of a mm-sized oil droplet floating on water, induced by a local temperature gradient generated by CW laser irradiation, is reported in part III. The circular droplet exhibits two types of regular periodic motion, reciprocal and circular, around the laser spot under suitable laser power. The bifurcation of droplet motion depending on the laser power is presented, and the essential aspects of mode bifurcation are discussed in terms of spontaneous symmetry breaking under temperature-induced interfacial instability, i.e., the thermal Marangoni effect.

Finally, in part IV, the summary of the contents in this thesis is presented and future problems are remarked upon.

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Part II

Motion induced by the solutal Marangoni effect

Chapter 4

Self-motion of a solid/liquid composite driven by interfacial instability

4.1 Introduction

It is well known that, when the distribution of surfactant concentration at an oil/water or an air/water interface deviates from equilibrium distribution by thermal fluctuations or something, the interface becomes unstable in association with spatial inhomogeneity of interfacial tension. This phenomenon called solutal Marangoni effect, as noted in chapter 2. Under such condition, the interface exhibits spontaneous mechanical agitation, which can cause macroscopic irregular motion of objects at the interface. Self-propelled motions of a liquid droplet and a solid particle induced by the solutal Marangoni effect have been attracting much interest [1–5].

Recently, it was found that such irregular motion can be transformed to a regular motion by introducing anisotropy into a physical or chemical boundary condition, or by introducing external potential [6–8]. In this chapter, we focus on the emergence of regular motion under spatially-isotropic outer boundary condition. It is found that a solid/liquid composite, which consists of an oil droplet and a solid soap, exhibits regular motion by breaking its internal anterior-posterior symmetry.

4.2 Materials and Methods

A solid/liquid composite consisting of an oil droplet and a solid soap was floated on the water phase as shown in Fig. 4.1(a). Water was purified with a MilliQ filtering system (Millipore corporation). The oil used for the droplet was oleic acid (Wako Pure Chemical Industries, Japan; 159-00246), and the volume was kept at 100 μl . The solid soap of sodium oleate (Nakarai Tesque, Kyoto; Code 257-02) was column-shaped with axial length of 3-4 mm, as shown in Fig. 4.1(b). Experiments were performed at room temperature.

The motion of the solid/liquid composite was captured by a digital video camera at 30 frames per second, and then analyzed with an image-processing software (ImageJ). Figure 4.1(c) represents snapshots of the moving composite.

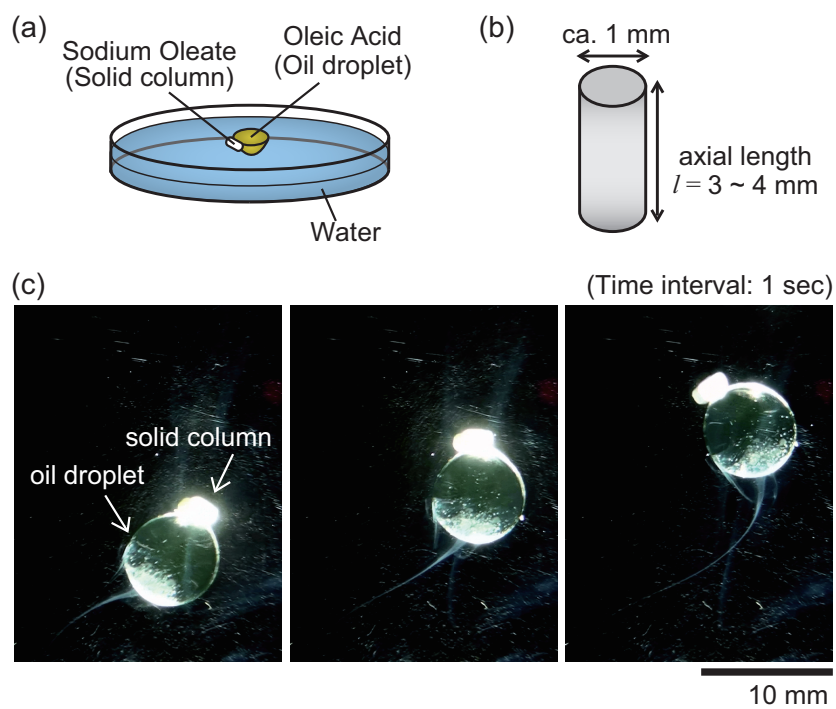


Figure 4.1: (a) Schematic illustration of overall experimental set-up. (b) Configuration of the solid column. (c) Snapshots of a self-propelled solid/liquid composite under dark-field optical observation. The solid column with the axial length of ca. 3 mm was used.

4.3 Experimental results

When a droplet of oleic acid or a solid scrap of sodium oleate is floated solely on water, no continuous motion is observed. On the other hand, when the solid soap comes into contact with the oil droplet, the composite of them exhibits continuous motion for more than several minutes. Figure 4.2 exemplifies the self-propelled motion of the composite on the water surface: snapshots of the composite and 20-sec trajectory of droplet-center are represented in (a), and time scales of the speed and the angular velocity of this motion are shown in (b). Here, the orientation of the composite is defined as the angle of the axis that combines the droplet-center and the solid-center, as shown in the top of Fig 4.3, and the angular velocity is the time subtraction of this angle. Those figures indicate that the composite exhibits translational motion accompanied by slight fluctuation in its orientation.

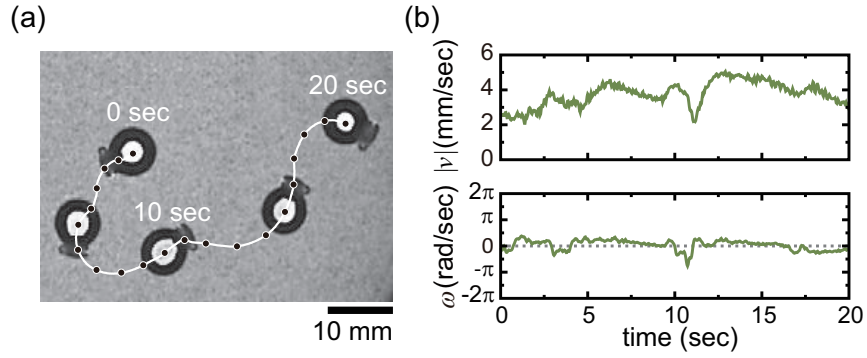


Figure 4.2: Characteristic motion of the solid/liquid composite. (a) The trajectory of the center of the droplet with shadowgraph image. (b) Time traces of the speed of translational motion (upper) and the angular velocity of spinning (lower). The angular velocity undergoes fluctuation around $\omega = 0$. The axial length of the solid column was ca. 4 mm.

Analytical results of the orientation of the composite and the direction of motion are represented in Fig. 4.3. Time traces of them shown in Fig. 4.3(a) indicate that the direction of motion changes following the change in the orientation of the composite. Besides, the probability of the angular difference between them shows a peak of $\alpha \simeq 0$, as shown in Fig. 4.3(b). Thus, the composite is considered to move by taking the solid column as the front side and achieve the regular translational motion.

4.4 Discussion

In contrast to the continuous motion of the composite exemplified in Fig. 4.2, when a droplet of oleic acid is put on a water surface in the absence of a solid soap, a self-propelled motion is not generated. Also, a solid scrap of sodium oleate exhibits a self-propelled motion for only 1-2 sec and then stopped soon. This short life-time self-propelled motion of the solid soap can be explained as follows. When a scrap is placed on the water surface, sodium oleate molecules dissolve in water phase and dissociate into sodium ions and oleate molecules (anionic surfactant molecules). Oleate molecules tend to spread out at the air/water interface because of its amphiphilic property. This kinetic process causes temporal instability at the interface near the scrap and drives the scrap of sodium oleate. In the case of a volatile surfactant scrap like camphor, surfactant molecules spread at the interface are released into

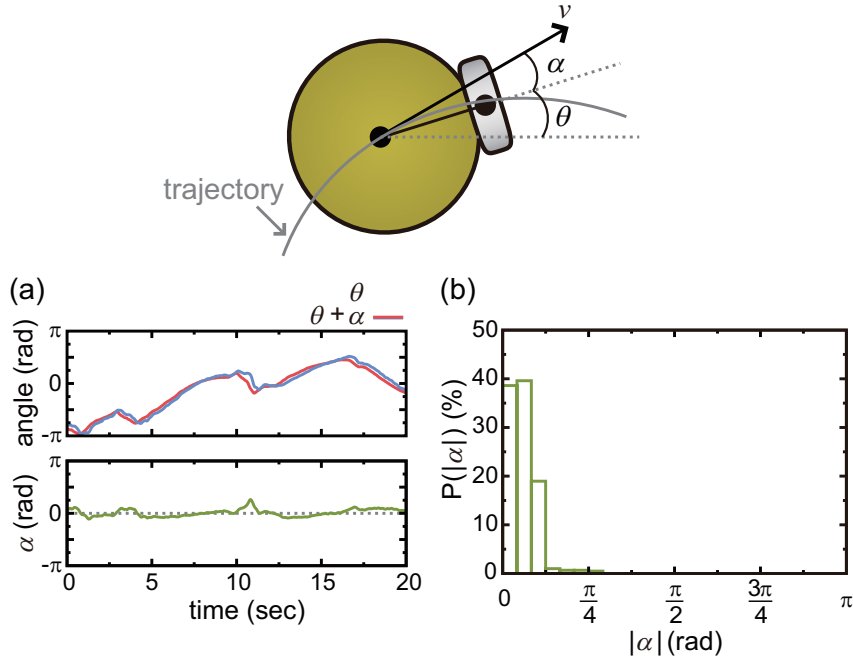


Figure 4.3: Comparison between the orientation of the composite and the direction of motion. The upper figure shows the definition of θ and α ; the orientation of the composite, θ , is the angle of the axis combining the center of the droplet and the solid column. The difference between θ and the direction of motion is α . (a) Top: Time traces of θ and the direction of motion $\theta + \alpha$. Bottom: Time traces of the angular difference α . (b) Histogram of the absolute value of α , and its peak is $\alpha \simeq 0$.

the air within a shorter time scale. Thus the inhomogeneity of the surfactant concentration at the interface is maintained, and motion of the scrap persists for a long time [9,10]. On the other hand, in the case of sodium oleate which is involatile and water-soluble, the interface is covered with a surfactant monolayer and reaches an equilibrium state after 1-2 sec; surfactant concentration around the scrap becomes homogeneous, which results in the termination of self-propelled motion.

Next, let us discuss the cause of the self-propelled motion of a solid/liquid composite, in terms of surface instability. The oil/water interfacial tension near the solid column is lowered because surfactant molecules dissolved from the solid exist at the interface. On the other hand, the interfacial tension far from the solid remains in a natural state. Thus, it is expected that a spatial gradient of oil/water interfacial tension is generated around the composite, where the tension near the solid is low and that far from the solid is relatively high.

For the self-propelled motion of solid particles induced by interfacial tension gradient, it is known that particles generally move from the area of low interfacial tension toward the area of high interfacial tension. However, in this experiment, the composite moves toward the region of low interfacial tension by taking the solid column as the forward side. The mechanism of this motion can be described as follows.

Tangential stress (Marangoni stress) around the oil/water interface is generated because of the gradient of the interfacial tension as mentioned in chapter 2. In response to this stress, shear flow called Marangoni convection is induced around the composite, as depicted Fig. 4.4. Thus, it is highly probable that the driving force, which propels the droplet toward the low interfacial tension region, is caused by the momentum transfer through the generation of shear flow [11,12].

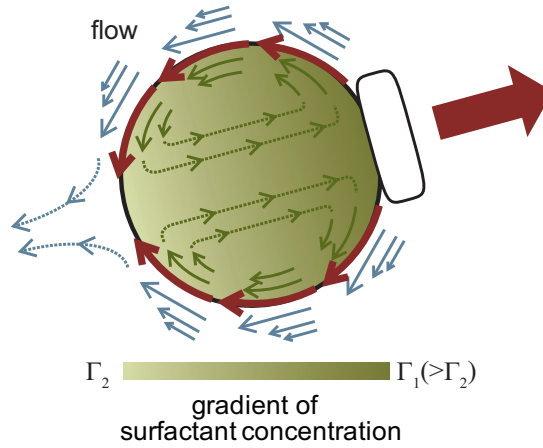


Figure 4.4: Schematic diagram of the mechanism of the self-propelled motion induced by solital Marangoni effect. The gradient of oil/water interfacial tension is generated by the gradient of surfactant concentration, and thus Marangoni convection around the composite is caused. Accompanied by the generation of convection, the composite gains the driving force.

By investigating the moving composite, it is observed that the milky stream occurs on the rear side opposite to the solid column as exemplified in Fig. 4.1. This fact indicates that the surfactant molecules (oleate molecules) at the oil/water interface tend to escape to the

bulk aqueous solution, forming aggregates such as micelles and O/W emulsions. Due to the balance between the supply of surfactants from the solid column and such escape into the bulk solution, the spatial gradient of the surfactant concentration or the interfacial tension is considered to be maintained. Thus, the self-propelled motion of the composite continues over a relatively long time that extends to several minute, through such dissipative process.

4.5 Conclusion

It is experimentally found that a solid/liquid composite floating on water exhibits regular self-propelled motion induced by Marangoni instability. By attaching a solid soap to an oil droplet, anterior-posterior asymmetry of the surfactant-concentration field around the composite can be introduced. The direction of translational motion is confined to move by taking the solid as the front side because of the asymmetric field. The results show that the motion of the composite is not induced by the simple interfacial tension gradient, but driven through the generation of Marangoni convection due to interfacial tension gradient.

In this chapter, the size of the solid column was approximately fixed, and the experiment and the analysis were done focusing only on relation between the direction of the composite and that of the motion. We will report the mode bifurcation of motion with a change in the size of solid column, in next chapter.

Chapter 5

Mode bifurcation of the self-propelled motion of a solid/liquid composite

5.1 Introduction

The self-propelled motion of liquid droplets, solid particles, and gels under non-equilibrium conditions has been actively studied [3,13]. Recently, it is reported that an asymmetrically-shaped solid particle or droplet can exhibit regular motion with a specific mode [9,14], where the mode is highly dependent on the asymmetric characteristic of the object shape; a boomerang-shaped particle exhibits ballistic motion, and a comma-shaped one exhibits rotational motion. In this chapter, the mode bifurcation with a change in the degree of asymmetry is investigated by use of the solid/liquid composite introduced in chapter 4. We controlled the degree of asymmetry by changing the size of the solid column and investigated the modes of self-propelled motion under various conditions.

As reported in chapter 4, the direction of translational motion is restricted due to anterior-posterior asymmetry of the composite. Additionally, the composite exhibits rotational motion through spontaneous left-right symmetry breaking. It is found that the mode bifurcation of motion is generated by changing the relative size of the solid column with respect to that of the droplet. The essential features of above mode bifurcation are reproduced by using ordinary equations by taking account of the spontaneous symmetry breaking on geometry of the composite and on driving torque acting on it.

5.2 Materials and Methods

A droplet of oleic acid and a solid column of sodium oleate were floated on water in the same way as the experiment in chapter 4. The volume of the oil droplet was 100 μl , and a solid column with a desired axial length, from 1 to 5 mm, was used. The motion of the solid/liquid composite with variously-sized solid was captured by a digital video camera at 30 frames per second at room temperature, and then analyzed by ImageJ.

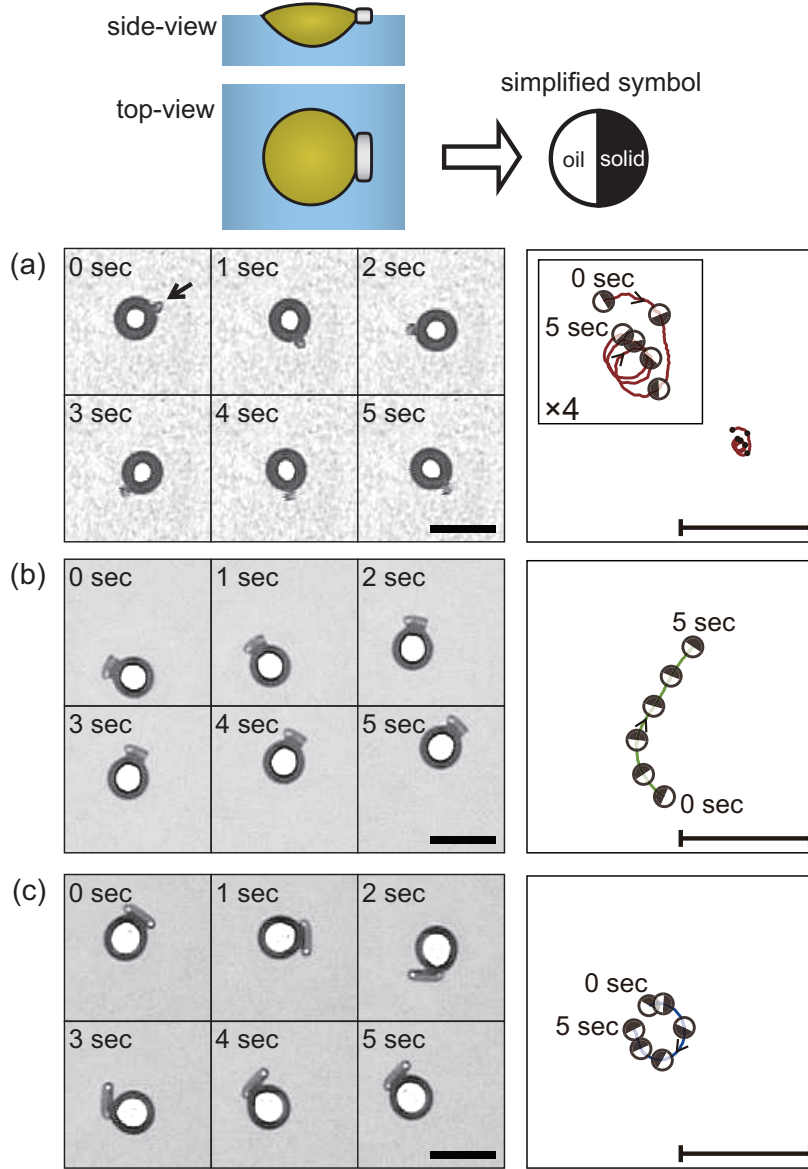


Figure 5.1: Typical examples of the self-propelled motion of a composite depending on the axial length of the solid column, where the volume of the droplet was kept at $100 \mu\text{l}$. The upper panels show schematic images of the solid/liquid composite together with the corresponding simplified symbol. (a, b, c) Left: Shadow-graph images of the composite, where the circular object is the oil droplet (time interval: 1 second, scale bar: 10 mm). The arrows in the images indicate the position of the solid column. Right: Trajectory of the droplet-center over 5 seconds and the orientation of the composite every 1 second (scale bar: 10 mm). (a) The axial length of the solid column, $l \approx 1$ mm. The composite exhibits spinning motion with the solid column rotating around the periphery of the droplet. (b) $l \approx 3$ mm. Translational motion is observed accompanied by slow rotation. (c) $l \approx 5$ mm. Orbital motion is generated together with spinning motion around its centroid with the same periodicity.

5.3 Experimental results

Figure 5.1 exemplifies the characteristic modes of self-propelled motion with a change in the size of the solid column: the left figures are shadow-graph images of the composite, and the right graphs show trajectory of the center of the droplet over 5 seconds. When the axial length of the solid column is about 1 mm, the composite exhibits spinning motion as shown in Fig. 5.1(a). When the axial length is about 3 mm, translational motion accompanied by relatively slow rotation is occurred, as shown in Fig. 5.1(b). When the axial length is about 5 mm, shown in Fig. 5.1(c), the composite exhibits orbital motion together with spinning motion around its centroid, where the period of orbital motion is equals to that of spinning motion. That is, the mode of self-propelled motion of the composite changes from spinning motion to translational motion and then orbital motion, with an increase in the axial length of the solid column.

The panels on the left in Fig. 5.2 show time traces of the angular velocity of spinning motion ω and the speed of translational motion $|\mathbf{v}|$ over 30 seconds. Histograms of the angular velocity ω over 60 seconds are shown in the panels on the right. When $l \simeq 1$ mm, the direction of spinning motion spontaneously switches in a stochastic manner, as shown in Fig. 5.2(a). The probability of the angular velocity shows a pair of symmetric peaks in addition to the lower peak of $\omega \simeq 0$. The symmetric peaks which deviate from $\omega = 0$ reflect the emergence of spinning motion and the fluctuation of the direction of spinning. When the solid column becomes larger, $l \simeq 3$ mm, a broad peak appears at around $\omega \simeq 0$, as shown in Fig. 5.2(b). This distribution indicates that the composite exhibits mostly translational motion accompanied by fluctuation of its orientation. When the solid size is around 5 mm, as shown in Fig. 5.2(c-1, c-2), the peak of the distribution deviates from $\omega = 0$, which corresponds to the occurrence the orbital motion which is exemplified in Fig. 5.1(c). In Fig. 5.2(c-1), the generation of the right-handed and left-handed rotation is exemplified. Either mode with the right-left symmetry breaking is encountered, as shown in Fig. 5.2(c-2), during the observation on the similar experimental condition. Thus, the mode bifurcation of this self-propelled motion depending on the axial length l of the solid column is represented by the characteristics or symmetry of the probability distribution with ω .

Summarizing the results of experiment, a phase diagram of the mode of self-propelled motion as a function of the axial length l of the solid column is given in Fig. 5.3. As indicated by the tilted broken lines, there exists finite width of coexistence region between spin and translation and between translation and orbital motion, suggesting the bistability on the system characteristics.

5.4 Mechanical modeling and discussions

As discussed in chapter 4, the gradient of the interfacial tension induces Marangoni convection around the solid/liquid composite and exerts the driving force on the composite by the momentum transfer through the generation of shear flow parallel to the oil/water interface. Here, to grasp the essence on the mode bifurcation of self-propelled motion, we would like to adopt a simple mechanical model; the translational motion of the composite is driven by the apparent driving force $\mathbf{F}$, of which the magnitude $|\mathbf{F}|$ is time-independent and the orientation is time-dependence associated with spinning motion. Under such framework of the modeling, translational motion of the composite is expressed as follows:

$$\frac{d\mathbf{r}}{dt} = \mathbf{v} ; m \frac{d\mathbf{v}}{dt} = -\eta_v \mathbf{v} + \mathbf{F}, \quad (5.1)$$

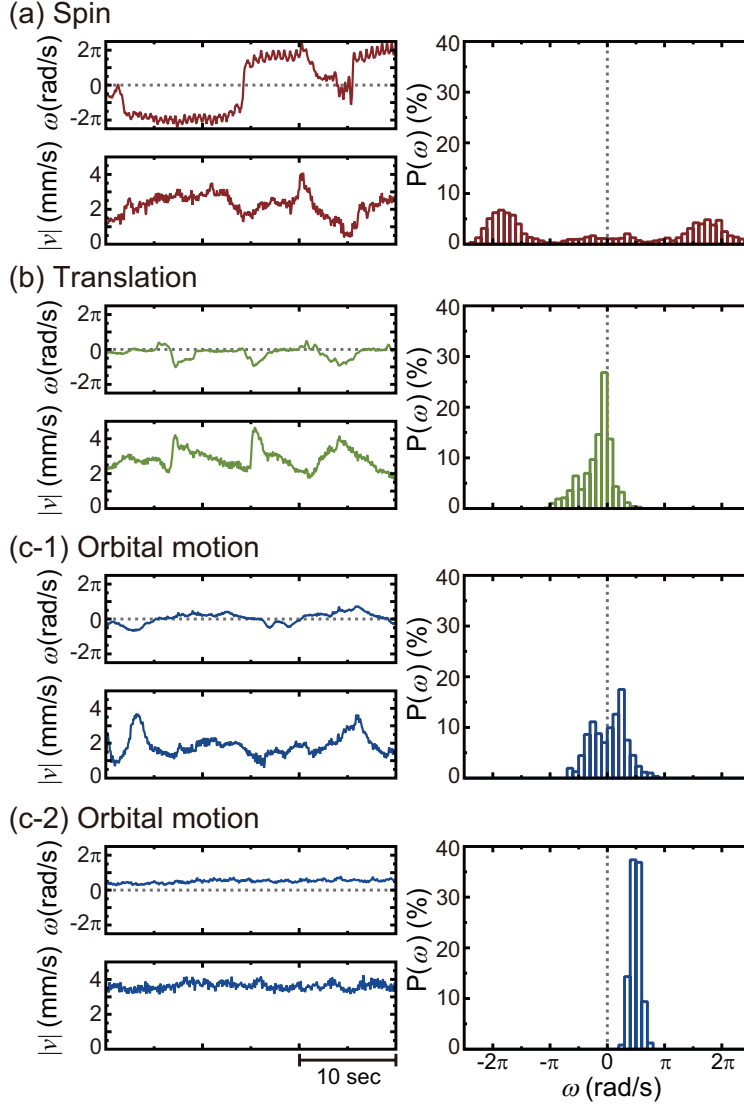


Figure 5.2: Experimental characteristics of self-propelled motion of the composite. (a), (b), and (c-1) are the same observations as in Figs. 5.1(a), 5.1(b), and 5.1(c), respectively. Left: Time traces of the angular velocity ω and the speed $|v|$ of motion. Right: Histograms of the angular velocity ω over 60 seconds. (a) The axial length of the solid column, $l \simeq 1$ mm. (b) $l \simeq 3$ mm. (c-1, c-2) $l \simeq 5$ mm. Different time-stage is given to indicate the characteristics of bimodality on the orbital motion. The direction of rotation switches to right and left in (c-1), while the direction is unchanged in (c-2).

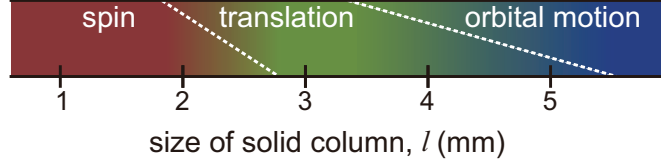


Figure 5.3: Phase diagram of self-propelled motion, showing the dependence of the motional modes on the axial length of the solid column. The tilted broken lines indicate coexistence regions, in which two modes can be occurred.

$$\text{with } \mathbf{F} = \begin{pmatrix} F_x \\ F_y \end{pmatrix} = \begin{pmatrix} F \cos \theta \\ F \sin \theta \end{pmatrix}, \quad F = |\mathbf{F}|, \quad (5.2)$$

where m is the mass of the composite, $\mathbf{r}$ is the displacement of the center of mass, $\mathbf{v}$ is the velocity of translational motion, $\eta_v > 0$ is the friction coefficient, and $\mathbf{F}$ is the driving force due to the above-mentioned Marangoni effect. In Eq. (5.2), θ indicates the angle of the axis that combines the centers of mass of the oil droplet and that of solid column, as shown schematically in Fig. 5.4.

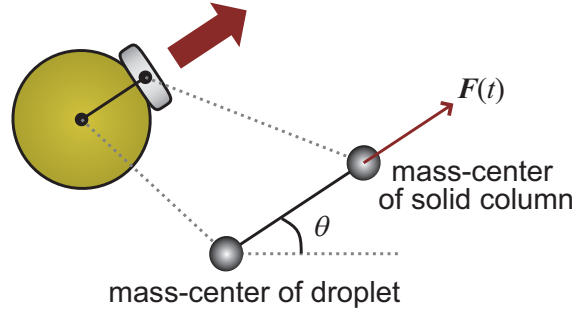


Figure 5.4: Frame format of the model. The orientation of the composite, θ , is defined as the angle of the axis which combines the droplet-center and the solid-center. The driving force $\mathbf{F}$, whose orientation is parallel to that of the composite θ , is considered to act on the composite.

As for the rotational motion, we adopt a term of non-linear friction as

$$\frac{d\theta}{dt} = \omega; \quad I \frac{d\omega}{dt} = -\eta_\omega(\omega) \omega + \xi_\omega(t), \quad (5.3)$$

where ω is the angular velocity and I is the moment of inertia. $\eta_\omega(\omega)$ represents the friction function that includes the contribution from driving torque in addition to the usual positive friction. ξ_ω is the noise term indicating the random fluctuation due to interfacial and fluidic instability. To interpret the essential features of mode bifurcation, we simply adopt a symmetry requirement: $\eta_\omega(\omega) = \eta_\omega(-\omega)$. As shown in the picture of Fig. 5.1, together with the experimental data of Fig. 5.2, the composite tends to induce rotational motion, accompanying by the spontaneous symmetry breaking. In order to take into account such self-driving force on the rotational motion, we adopt negative rotational “friction”, $-\eta_2 \omega^2 < 0$. So as to prevent the diverge of the rotation due to the negative friction, we also add the quartic term of $\eta_3 \omega^4 > 0$. Thus, the friction function $\eta_\omega(\omega)$, including not only

frictional torque but also the driving torque due to Marangoni instability [3] together with geometrical asymmetry of the composite, can be described as

$$\eta_\omega(\omega) = \eta_1 - \eta_2\omega^2 + \eta_3\omega^4, \quad (5.4)$$

where η_1 , η_2 and η_3 are positive coefficients.

By non-dimensionalizing procedure, the equations describing the motion of the composite is transformed into the following equations:

$$\frac{d\tilde{x}}{d\tilde{t}} = \tilde{v}_x; \quad \frac{d\tilde{v}_x}{d\tilde{t}} = -\tilde{v}_x + \tilde{F} \cos \theta, \quad (5.5)$$

$$\frac{d\tilde{y}}{d\tilde{t}} = \tilde{v}_y; \quad \frac{d\tilde{v}_y}{d\tilde{t}} = -\tilde{v}_y + \tilde{F} \sin \theta, \quad (5.6)$$

$$\frac{d\theta}{d\tilde{t}} = \tilde{\omega}; \quad \frac{d\tilde{\omega}}{d\tilde{t}} = -\tilde{\eta}_\omega \tilde{\omega} + \tilde{\xi}_\omega, \quad (5.7)$$

where $t = (m/\eta_v) \tilde{t}$ and $\mathbf{r} = \sqrt{I/m} \tilde{\mathbf{r}}$. $\tilde{t}$, $\tilde{x}$, $\tilde{y}$, $\tilde{v}_x$, $\tilde{v}_y$, and $\tilde{\omega}$, are dimensionless variables. The dimensionless friction function in Eq. (5.7), $\tilde{\eta}_\omega$, is

$$\tilde{\eta}_\omega(\tilde{\omega}) = \tilde{\eta}_1 - \tilde{\eta}_2 \tilde{\omega}^2 + \tilde{\eta}_3 \tilde{\omega}^4 = \tilde{\eta}_1 (1 - \alpha \tilde{\omega}^2 + \beta \tilde{\omega}^4), \quad (5.8)$$

where $\alpha = \tilde{\eta}_2/\tilde{\eta}_1$ and $\beta = \tilde{\eta}_3/\tilde{\eta}_1$. According to Eq. (5.8), the friction function $\tilde{\eta}_\omega$ becomes negative within a certain range of angular velocity ω if $\alpha^2/\beta > 4$, which implies that the active driving force is generated. Additionally, it is noted that the fixed points of the Eq. (5.7) at $\tilde{\omega}^* \neq 0$ become more stable than a stable fixed point at $\tilde{\omega}^* = 0$ when $\alpha^2/\beta > 16/3$, indicating the rotational motion becomes dominant. Figure 5.5 exemplifies the numerical results based on Eqs. (5.5)-(5.8). In numerical calculations, $\tilde{\xi}_\omega$ is simply taken as the white Gaussian noise whose dispersion is s :

$$\langle \tilde{\xi}_\omega(\tilde{t}) \rangle = 0; \quad \langle \tilde{\xi}_\omega(\tilde{t}) \tilde{\xi}_\omega(\tilde{t}') \rangle = s\delta(\tilde{t} - \tilde{t}'). \quad (5.9)$$

Numerical calculation was performed by the 4-th order Runge-Kutta method with a time increment of $\Delta\tilde{t} = 0.05$.

It is to be noted that the essential aspects of the experimental results as shown in Fig. 5.2 are reproduced by choosing appropriate parameters. In these simulations, to gain insight on the mechanism of the mode bifurcation, we examine the effect of two parameters, α and s , while others are fixed to be constants; $\tilde{\eta}_1 = 1.0$, $\beta = 1.0$, and $\tilde{F} = 0.1$.

A comparison between Figs. 5.5 (a) and (b) reveals the mode bifurcation from rotational motion to translational motion, corresponding the experiments in (a) and (b) of Fig. 5.1. The larger value of α^2/β in (a) with respect to (b) in Fig. 5.5 is regarded as to represent a higher possibility of symmetry breaking between clockwise and anticlockwise spinning motions under irregular fluctuation due to the interfacial instability. This matches with the experimental trend that small solid column tends to rotate faster. The larger value of s in the (c-1) represents approximately a high possibility that the composite is subject to larger motional fluctuation due to the instability or external perturbations. This large fluctuation causes the flip-flop fluctuation of the direction of the orbital motion. When the size of the solid column deviate largely from the similar magnitude to that of the droplet, rotational motion of the composite shows bistability of clockwise and anticlockwise as in the experiments. Therefore, large enough unbalance between the sizes of the solid and the liquid in the composite, as in (a) and (c), corresponds to the state with large α^2/β , and the balanced condition as (b) is described as the effect of small α^2/β .

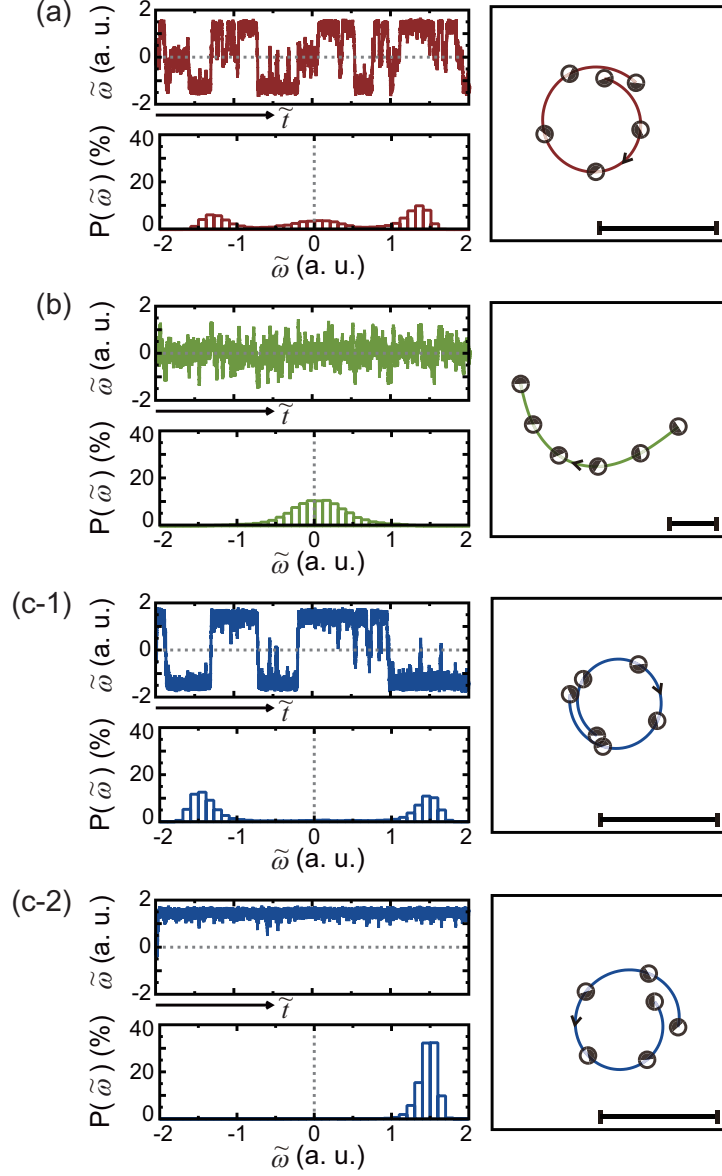


Figure 5.5: Numerical results based on Eqs. (5.5) - (5.8). Left: Time traces of the angular velocity $\tilde{\omega}$ and histograms of $\tilde{\omega}$ ($0 \leq \tilde{t} \leq 1000$). Right: Trajectories of the centroid of the composite for a short period ($400 \leq \tilde{t} \leq 405$). The scale bars represent the same length on the four trajectories. (a) $\alpha = 2.4, s = 0.3$. (b) $\alpha = 1.8, s = 0.3$. (c-1) $\alpha = 2.7, s = 0.5$. (c-2) $\alpha = 2.7, s = 0.3$. The other fixed parameters are $\tilde{\eta}_1 = 1.0, \beta = 1.0, \tilde{F} = 0.1$. The initial state is given by $\tilde{x}(0) = \tilde{y}(0) = 0, \tilde{v}_x(0) = \tilde{v}_y(0) = 0, \theta(0) = 0$, and $\tilde{\omega}(0) = 0$.

5.5 Conclusion

We have experimentally demonstrated the appearance of mode bifurcation in the self-propelled motion of a solid/liquid composite. The driving force is the interfacial instability caused by non-uniformity in the surfactant concentration or by spontaneous symmetry breaking the geometric configuration on the composite. Mode bifurcation among spinning, translational motion, and orbital motion is caused with a change in the size of the solid column. The essential features of the experimental observation have been reproduced by adopting a simple mechanical model with ordinary differential equations, by taking into account the scheme of spontaneous symmetry breaking.

In the mechanical modeling in this study, we consider the driving force induced by the Marangoni effect as a constant for the sake of simplicity. Indeed, the driving force acting on the composite can be simulated with the Stokes equation by considering the gradient of oil/water interfacial tension [11], which was recently investigated in our further study [15].

Since almost all self-moving organelles and cells exhibit a head-tail asymmetry, our simple experimental and numerical models may give deeper insight into mode switching in living systems.

Appendix

Mode bifurcation with a change in the volume of droplet

In chapter 5, it is showed that self-propelled motion of a solid/liquid composite undergoes bifurcations with a change in the axial length of the solid. In this section, the change in the mode of self-propelled motion was investigated when not only the solid size but also the volume of the droplet was changed.

Figure 5.6 shows histograms of the angular velocity ω depending on the volume of the oil droplet, where the axial length of the solid is about 3 mm. When the volume is less than $150 \mu\text{l}$, the probability of ω shows a peak at around $\omega \simeq 0$, indicating that the composite exhibits translational motion. When the volume is $200 \mu\text{l}$, the composite sometimes exhibits rotational motion in addition to translational motion, where the probability of ω shows a distribution with a pair of symmetric small peaks of $\omega \neq 0$ and larger peak around zero. As shown in Figs. 5.6(c) and (d), a single peak deviating from $\omega = 0$ appears in the distribution, which corresponds to the generation of steady rotational motion when the volume is between 250 and $300 \mu\text{l}$.

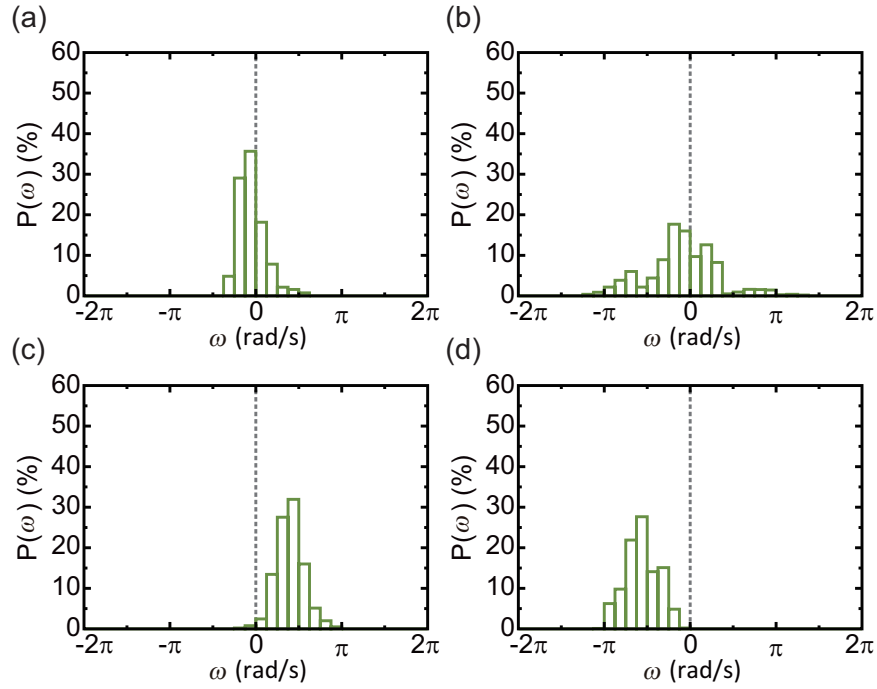


Figure 5.6: Histograms of the angular velocity ω over 60 seconds. The axial length of the solid column was kept at about 3 mm. The volume of the oil droplet was (a) 150, (b) 200, (c) 250, and (d) $300 \mu\text{l}$.

As a result of performing experiments by changing both the axial length of the solid column and the volume of the droplet, the phase diagram of the mode of motion is as Fig. 5.7. This diagram indicates that the composite exhibits translational motion when the axial length of the solid is similar in size to the radius of the droplet, while the composite shows rotational motion (spinning or orbital motion) when the sizes of the solid and the droplet are widely different. What it comes down to is that the mode bifurcation of the

motion of a solid/liquid composite occurs depending on the relative size of the solid column (head) to the size of the droplet (body).

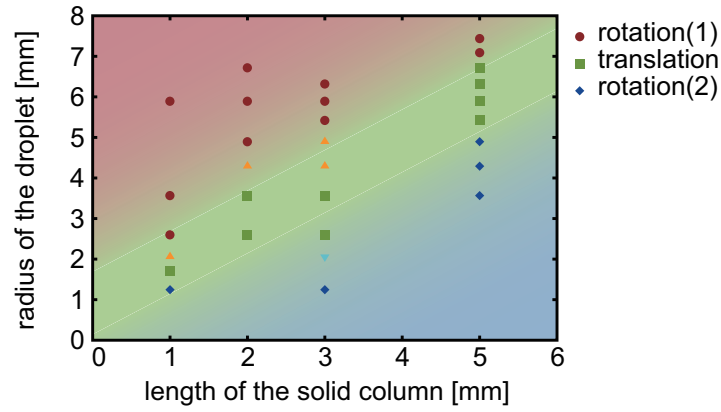


Figure 5.7: Phase diagram of the mode of self-propelled motion, which shows the dependence on the relative size of the solid column to that of the droplet. Triangular marks indicate coexistence state.

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Part III

Motion induced by the thermal Marangoni effect

Chapter 6

Mode bifurcation of droplet motion under stationary laser irradiation

6.1 Introduction

According to the second principle of thermodynamics, all macroscopic regular motion ceases and is transformed into thermal energy, i.e., random Brownian motion, with time. On the other hand, living organisms exhibit regular motion under thermodynamically dissipative conditions. Thus, there is currently considerable interest in clarifying the physics that underlie the regular motion in dissipative systems.

Through recent studies on self-propelled motions, it is becoming clearer that irregular motion can be converted to regular motion through the selection of suitable experimental conditions, e.g., through the introduction of internal or external asymmetry to the system [1]. For example, the direction of translational motion can be determined by the introduction of anterior-posterior asymmetry to a chemical property or physical structure of an object [2–4], and rotational motion can be caused for an object with a rotationally asymmetric shape [5,6]. Furthermore, the emergence of regular motion in self-propelled particles through spontaneous symmetry breaking has attracted increasing interest, not only with regard to physics but also biology [7]. However, most studies have adopted a strategy of inducing mode-selection by changing some geometric property in the experimental set-up, and little is known about the mode-selection of regular motion for a geometrically symmetric object.

Here, we focus on the instability of a liquid/liquid interface, or the Marangoni effect [8], to cause macroscopic motion under stationary dissipative conditions [9–12]. It is well known that random macroscopic agitation is generated by the Marangoni effect induced by a thermal or chemical inhomogeneity at the interface. This agitation causes macroscopic liquid flow known as Marangoni convection. Interestingly, it has been reported that a droplet or bubble can exhibit macroscopic motion propelled by Marangoni convection [13–16].

In this chapter, we investigated the motion of a mm-sized droplet driven by thermal Marangoni convection induced by local heating with a spatially-fixed laser. The results showed that, with a change in the heating power, or in the degree of non-equilibricity, the mode of the self-motion of a circular droplet bifurcates into qualitatively different types of regular motion through spontaneous symmetry breaking.

6.2 Materials and Methods

A droplet of oleic acid floating on the surface of an aqueous solution was irradiated with converged laser light with a width of ca. 1-2 mm, as shown in Fig. 6.1. Experiments were performed at room temperature (ca. 23 °C). The oleic acid (analytical grade, 159-00246) was purchased from Wako Pure Chemical Industries. The wavelength of the laser (Genesis MX 532-5000, Coherent) was 532 nm. Water was purified with a MilliQ filtering system (Millipore) and contained 0.1-wt% red dye (consisting of 85% dextrin and 15% new coccine, Kyoritsu Foods Co. Inc.) to enhance the absorbance of green light. The motion of the droplet was captured at 30 frames per second by a digital video camera (HDR-CX700, SONY) with a x6 magnifying lens, and then analyzed by image-processing software (ImageJ).

To visualize advective flow, we performed an experiment with a droplet that contained polystyrene particles with a diameter of $100\ \mu\text{m} \pm 1.5\ \mu\text{m}$ (4310A, Thermo Scientific). A flow field analysis was performed with the PIV plugin for ImageJ.

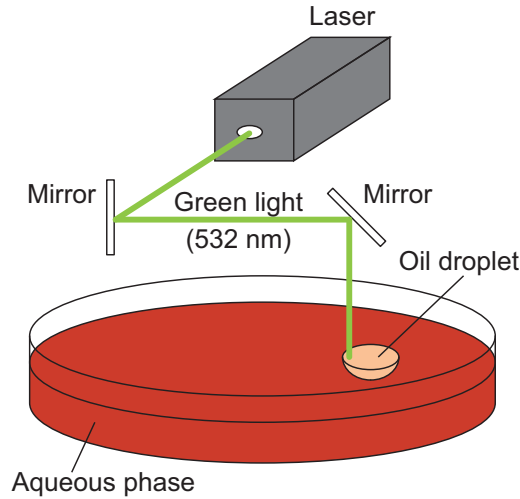


Figure 6.1: Schematic illustration of the experimental set-up. An oil droplet floating on a water phase was irradiated by a laser.

6.3 Experimental Results

Figures 6.2(b) and (c) show the motion of a 20- μl droplet under stationary laser irradiation. As the laser power is increased to 0.10 W, the droplet begins to exhibit slight random motion, as shown by the trajectory of the center of the droplet in Fig. 6.2(b)top; the droplet is initially pulled to the center of the laser irradiation and then undergoes fluctuation. The next bifurcation from random motion to rectilinear reciprocal motion, as shown in the middle of Fig. 6.2(b), occurs at around 0.25 W. Above ca. 0.60 W, circular motion, as shown in the bottom of Fig. 6.2(b), occurs as the result of bifurcation from rectilinear reciprocal motion. We confirmed that these regular motions, reciprocal and circular, continue for more than several tens of minutes; for this amount of time before stopping, the heating effect for the whole droplet and the evaporation of the solvent should be negligible. Figure 6.2(c) shows spatio-temporal plots for the distance L from the origin to the droplet interface,

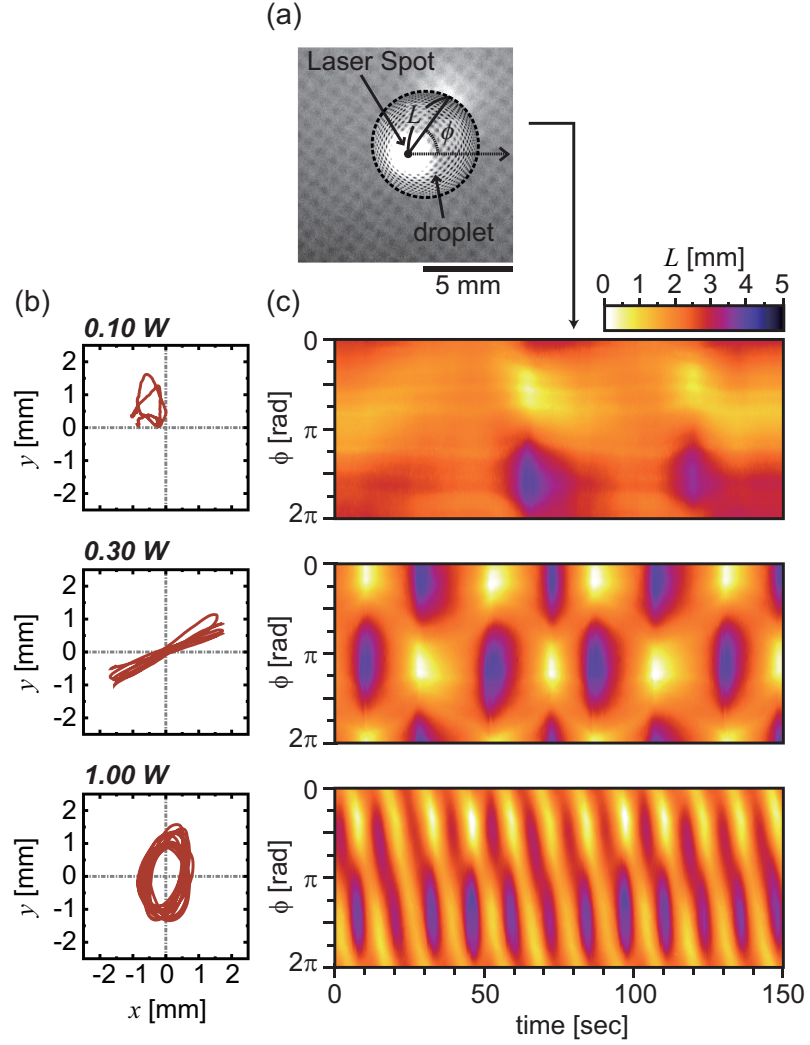


Figure 6.2: Droplet motion driven by stationary laser irradiation. The volume of the oil droplet was $20 \mu\text{l}$. The laser power, in the order from the top, was 0.10, 0.30, and 1.00 W. (a) Snapshot of the droplet irradiated by the laser. The definitions of L and ϕ are also shown. (b) Trajectories of the droplet's center. (b-2) Spatio-temporal diagrams for L , where L is the distance from the laser spot to the boundary of the droplet, and ϕ is the angle from a certain fixed horizontal axis.

as depicted in Fig. 6.2(a), and reveals bifurcation from random motion through reciprocal motion to circular motion. As shown in the top of Fig. 6.2(c), at 0.10 W the droplet exhibits intermittent behavior between the resting state and the fluctuating state. At both 0.30 and 1.00 W, the droplet exhibits stable time-periodic motion.

In these experiments, due to technical conditions with the use of a multimode laser beam, the radius of the laser focus increased gradually from 1.0 mm (0.30 W) to 2.1 mm (1.00 W), accompanied by a slight spatial shift of the center of the laser spot from the initial position to less than 0.2 mm at 0.30 W and 0.5 mm at 1.00 W. Basically, both the shift and the fluctuation of the laser spot fell within the size of the laser spot. Thus, the magnitude of both reciprocal motion and circular motion were considered to be sufficiently larger than the size and shift of the laser spot. The origin of each graph in Fig. 6.2(b) is the effective center of the laser spot, i.e., the center of the trajectories for 0.30 W and 1.00 W.

The characteristics of droplet motion, as represented by the translational speed and the direction of motion, are indicated in Fig. 6.3. As the laser power is increased, the speed of the motion, $|\mathbf{v}|$, tends to increase, as shown in Fig. 6.3(a). This result implies that the energy influx rate into droplet motion increases proportionally with the laser power or laser heating. Figure 6.3(b) shows time-series data for the orientation of the velocity vector, θ_v . When the laser power is 0.30 W, θ_v remains constant in a short time-scale and periodically changes by 180 degrees. On the other hand, under a laser power of 1.00 W, θ_v changes continuously with time. These behaviors correspond to rectilinear reciprocal motion and circular motion, respectively.

Figure 6.4 shows flow fields inside the droplet, obtained from an analysis of the motion of polystyrene particles. In this experiment, 5 μl oleic acid containing particles was added to a 20- μl oleic acid droplet, and the droplet was then irradiated with a green laser. When the laser power is around 0.40 W, symmetrical twin-roll convection is generated inside the droplet, as shown in Fig. 6.4(a). In contrast, the flow field inside the droplet becomes asymmetric under a higher laser power of about 1.50 W (Fig. 6.4(b)). Thus, the presence of symmetry breaking in convection is considered to be directly related to the occurrence of the mode bifurcation from rectilinear motion to circular motion.

6.4 Discussions

We have experimentally shown that laser-induced droplet motion is accompanied by specific mode bifurcation. The observed motion is clearly due to the spatial instability of interfacial tension, i.e., the thermal Marangoni effect [16, 17]. Under local heating with a laser, a temperature gradient emerges around the laser spot, which causes a gradient of interfacial tension at the oil/water boundary. This spatial gradient of the interfacial tension induces shear flow at the interface, called Marangoni convection. When the laser spot is directed inside the droplet, Marangoni flow forms twin vortices inside the droplet, similar to the motion of a swimmer performing the breaststroke (Fig. 6.4). Viscous drag force at the interface under this flow condition ordinarily propels the droplet toward the laser spot [17].

We now discuss the mechanism of the mode bifurcation under the assumption that the droplet maintains a hemi-spherical shape during motion for simplicity. We adopt the following simple equations which describe the motion of the center of mass:

$$\frac{d\mathbf{r}}{dt} = \mathbf{v} ; m \frac{d\mathbf{v}}{dt} = \mathbf{f}^{\text{dr}} - \mathbf{f}^{\text{res}}, \quad (6.1)$$

where $\mathbf{f}^{\text{dr}}$ is the driving force resulting from Marangoni convection, which was observed in

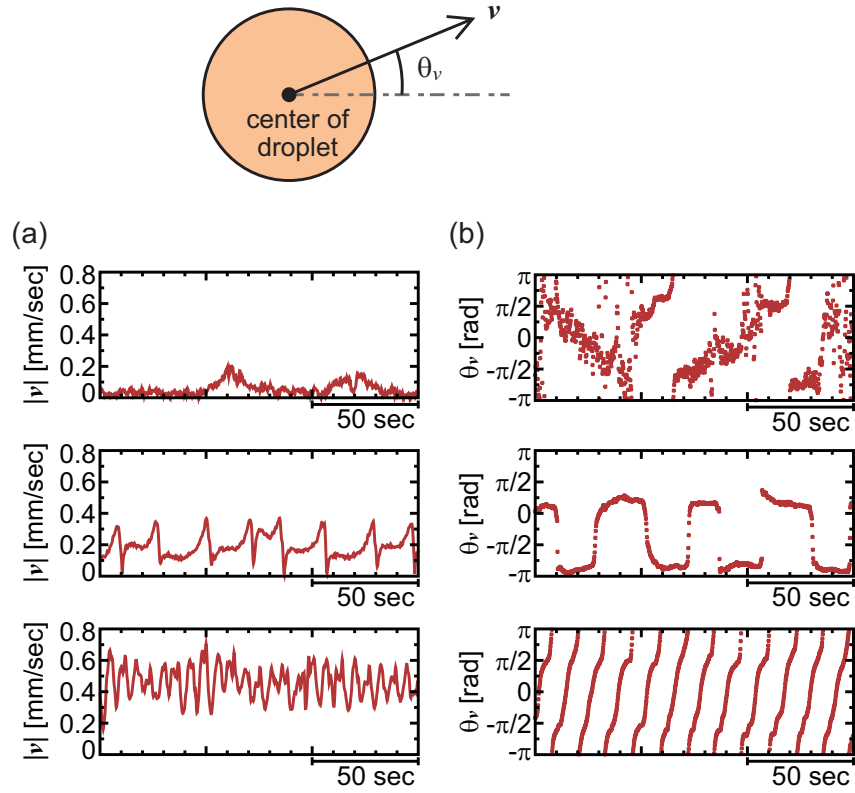


Figure 6.3: Characteristic features of each mode, i.e., random, reciprocal, and circular motion, as in Fig. 6.2. Top panel shows a schematic image of the definition of $|\mathbf{v}|$ and θ_v . (a) Time traces of the speed of motion, $|\mathbf{v}|$. (b) The orientation θ_v of the velocity vector $\mathbf{v}$. Laser power is (top) 0.10 W, (middle) 0.30 W, and (bottom) 1.00 W.

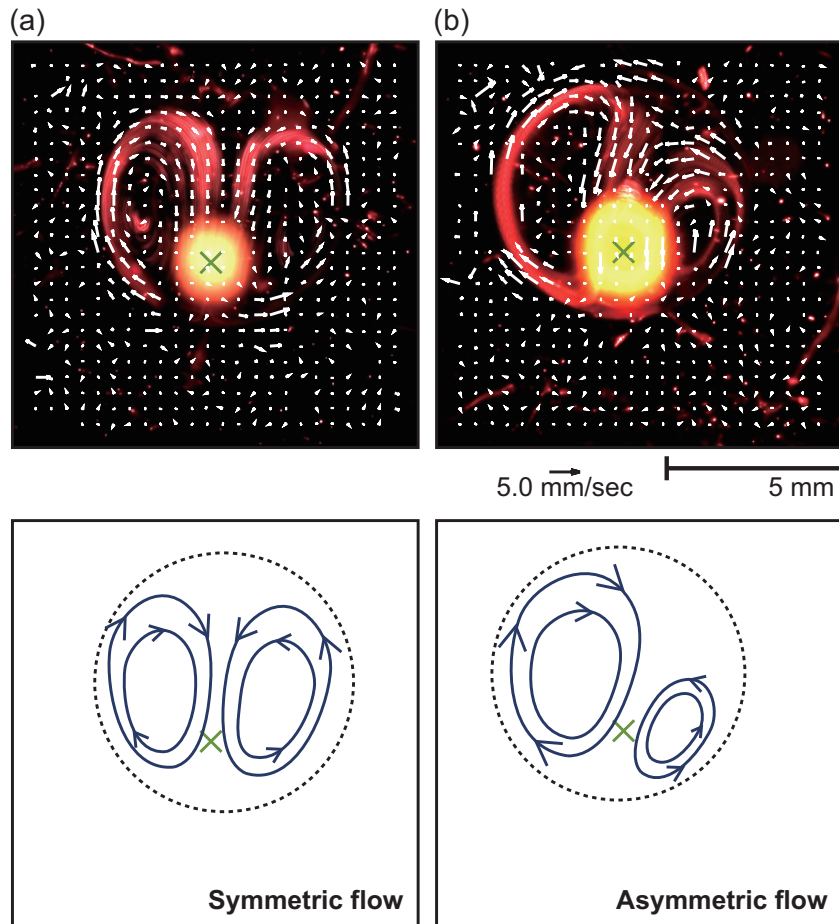


Figure 6.4: Flow fields inside the droplet under laser irradiation. The upper photos are exposed for 1 sec. The volume of the droplet was $25 \mu\text{l}$. The lower figures show schematic illustrations of convection inside the droplet. Cross marks indicate the centers of laser irradiation. (a) Laser power was 0.40 W, and the droplet exhibited rectilinear motion. (b) Laser power was 1.50 W, and circular motion occurred.

the experiment, and $\mathbf{f}^{\text{res}}$ is the resistive force acting on the droplet. The spatial temperature distribution generated by a laser can be given as $a' \exp(-r^2/(2c^2))$ in polar coordinates with the origin at the center of the laser spot. Since the driving force is approximated to be proportional to the spatial gradient of the temperature [13, 15], the net force acting on the droplet without historical efforts mentioned later can be roughly described as follows, when the droplet remains in a fixed position:

$$\mathbf{f}_0^{\text{dr}} \simeq b \frac{d}{d\mathbf{r}} \left(a' \exp \left(-\frac{r^2}{2c^2} \right) \right) = -a\mathbf{r} \exp \left(-\frac{r^2}{2c^2} \right). \quad (6.2)$$

Here, we have to consider that the history should remain in both the temperature distribution and the convection inside the moving droplet. Thus, we simply apply the following self-decaying time kinetic equation of the driving force:

$$\frac{d\mathbf{f}^{\text{dr}}}{dt} = -\frac{1}{\tau} \left(\mathbf{f}^{\text{dr}} - \mathbf{f}_0^{\text{dr}}(\mathbf{r}) \right). \quad (6.3)$$

For the resistive force, which includes friction at the interface, the effective resistance in the angular direction is considered to be greater than that in the radial direction due to the effect of convection with a symmetrical roll structure. Therefore, the resistive force can be expressed as $\mathbf{f}^{\text{res}} = \gamma_r v_r \mathbf{e}_r + \gamma_\phi v_\phi \mathbf{e}_\phi$ ($0 < \gamma_r < \gamma_\phi$), where $\mathbf{e}_r$ and $\mathbf{e}_\phi$ are unit vectors in the radial (r) direction and angular (ϕ) direction, respectively.

When the units of length, time, and mass are set to c , τ and m respectively, non-dimensionalized equations become:

$$\frac{d\mathbf{R}}{dT} = \mathbf{V}, \quad (6.4)$$

$$\frac{d\mathbf{V}}{dT} = \mathbf{F}^{\text{dr}} - (\Gamma_R V_R \mathbf{e}_R + \Gamma_\Phi V_\Phi \mathbf{e}_\Phi), \quad (6.5)$$

$$\frac{d\mathbf{F}^{\text{dr}}}{dT} = - \left(\mathbf{F}^{\text{dr}} + A\mathbf{R} \exp \left(-\frac{R^2}{2} \right) \right). \quad (6.6)$$

Here, capital letters in the equations indicate dimensionless quantities. Figure 6.5 shows the numerical results with the above Eqs. (6.4)-(6.6) calculated by employing the 4th-order Runge-Kutta method with a time increment of $\Delta T = 10^{-3}$ for 5×10^6 steps. Resistance coefficients are fixed as $\Gamma_R = 0.030$ and $\Gamma_\Phi = 0.035$, and the parameter of the temperature distribution A is changed. Slight perturbations are given in the initial conditions, $(X(0), Y(0)) = (0.3, 0.4)$, $(V_X(0), V_Y(0)) = (0.001, 0.0)$. The trajectories of the final state (last 10^5 steps) for $A = 0.010, 0.050$, and 0.080 are shown in Fig. 6.5(a). The motion changes from the rest state to linear reciprocal motion and circular motion with an increase in A , corresponding to the heating rate.

Figure 6.5(b) represents the change in the translational kinetic energy per unit mass of the droplet's center-of-mass motion in the numerical simulation: the blue solid line indicates the average of the total translational energy $|\mathbf{V}|^2/2$, while the red dashed line and green dotted line indicate the radial component $\dot{R}^2/2$ and the angular component $(R\dot{\Phi})^2/2$, respectively. In the numerical simulation, as in Fig. 6.5(b), the total translational kinetic energy increases with an increase in the value of A . When A is smaller than 0.050 , the radial component of this kinetic energy is larger than the angular component; straight motion

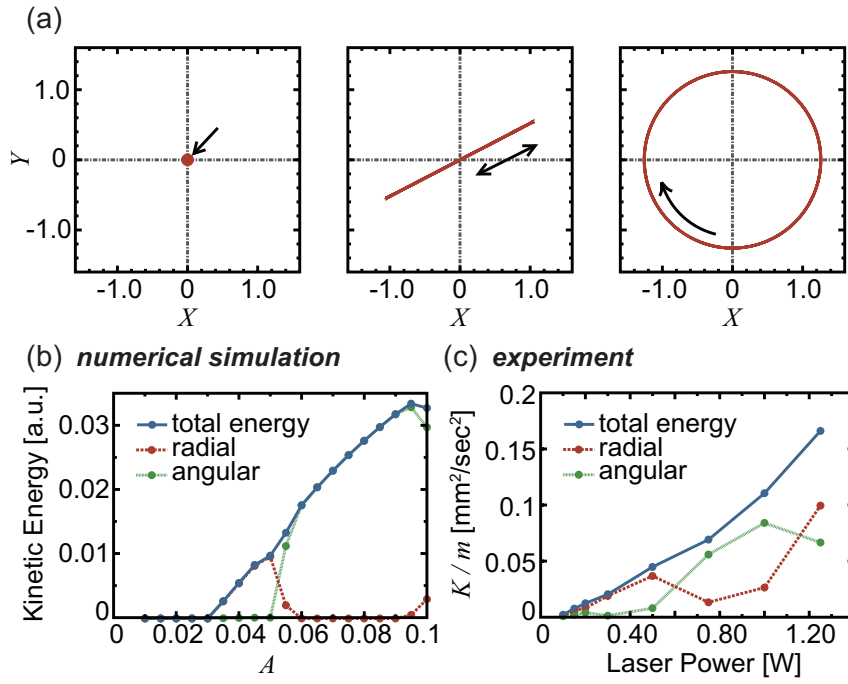


Figure 6.5: (a) Numerical result based on Eqs. (6.4)-(6.6): trajectories of the center of the droplet. From the left, $A = 0.010$, 0.050 , and 0.080 , respectively. (b) Graph shows the variation in translational kinetic energy per unit mass against the parameter A in the numerical simulation. (c) Experimental result regarding the variation in kinetic energy per unit mass with respect to the laser power.

is dominant in this region. With an increase in A , the angular component increases and exceeds the radial component at around 0.055. Thus, circular motion becomes dominant above $A = 0.055$. In the experiment, the translational kinetic energy shows similar behavior (Fig. 6.2). The value of the angular component eclipses that of the radial component at around 0.60 - 0.70 mW, and the droplet begins to exhibit circular motion.

As mentioned above, the essential aspects of the experimental observation were reproduced in the numerical model by considering that the value of A in the model corresponds to the laser power in the experiment. Thus, the essence of the finite time behavior observed in the experiment can be captured by the simple time-delayed function without a detailed numerical analysis of Marangoni instability. To gain further insight into the mechanism of motion, it would be necessary to take into account the spatial extension of the droplet and the detailed flow field inside the droplet by adapting Stokes equations, where the equations may or may not be reduced to the same role as the delayed function. If they are not the same, the present system may be multilevel with respect to different bifurcation mechanisms.

6.5 Conclusion

We experimentally demonstrated that when an oil droplet floating on water is locally heated by laser irradiation, the circular droplet exhibits various regular periodic motions around the spatially-fixed laser spot. With an increase in the laser power, i.e., the magnitude of the temperature gradient, mode bifurcation from rectilinear reciprocal motion into circular motion is generated. Such mode bifurcation is interpreted in terms of spontaneous symmetry breaking depending on the energy influx rate. The essential features of this mode bifurcation are qualitatively reproduced by simple mechanical model, by taking into account the effect of Marangoni convection.

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Part IV

General conclusion

Chapter 7

Conclusion

7.1 Conclusion

In this thesis, the mode bifurcation of self-propelled motion induced by Marangoni instability is reported.

When an oil droplet of oleic acid attached to a solid column of sodium oleate is floated on a water phase, the composite exhibits various modes of self-propelled motion, such as spinning, translational, and orbital motion. The motion of the composite is caused by a local concentration gradient of surfactants due to the diffusion of oleate molecules from the solid. Thus, the direction of translational motion is determined by asymmetry property of the composite, where the composite moves with the solid column forward (chapter 4). The results show that the composite assumes a certain mode of self-propelled motion depending on the relative size of the solid with respect to that of the droplet. If the solid column is much larger or much smaller than the droplet, rotational motion of the composite occurs through spontaneous breaking of left-right symmetry. It becomes clear that this mode-selection is characterized as sub-critical bifurcation from the analysis of experimental data, and the essence of this mode-selection can be reproduced by ordinary differential equations by considering non-linear rotational friction (chapter 5). This result indicates that the mode of self-propelled motion is determined not only by the property of asymmetry, e.g., rotational asymmetry or anterior-posterior asymmetry, but also by the degree of asymmetry.

In chapter 6, the self-propelled motion of an oil droplet, which is locally heated by a CW laser, is investigated. It is found that the motion of the droplet is induced through the generation of thermal Marangoni convection, and undergoes a bifurcation from rectilinear reciprocal motion to circular motion with an increase in the laser power. This mode bifurcation is qualitatively described by simple coupled differential equations, by taking into account the effect of Marangoni convection. From the experimental and the numerical results, it is confirmed that circular motion of the rotationally-symmetric droplet is caused according to spontaneous symmetry breaking with an increase in the magnitude of driving force.

From these two topics, it is suggested that the mode bifurcation of self-propelled motion under a local gradient of interfacial tension is induced by a change in the degree of non-equilibrium, through the spontaneous symmetry breaking. The discussions in this thesis may provide further insights into the mechanism to generate various modes of regular motion in living systems.

7.2 Future problems

As a progression of the study, we took a theoretical approach to the mechanism of self-propelled motion of an oil droplet which has a source of surfactant supply at oil/water boundary. In this study, flow field around the droplet was calculated using an advection-diffusion equation coupled with the Stokes equation, and it was found that the droplet can spontaneously rotates when its radius is an appropriate size. There are still small problems remaining in comparing experimental and theoretical results quantitatively, because the theoretical model neglects the size of the solid and contains parameters difficult to measure in the experiment. However, this theoretical result was in good agreement with the result of experiment in which the size of the droplet was changed, with the solid size being fixed [1].

Similar theoretical discussions might be applicable to the case of laser-induced motion of the droplet, which is introduced in chapter 6. In the thermal system, temperature distribution is permitted to be visualized with an infrared camera, and thus the distribution of interfacial tension can be estimated. Therefore, it is expected that the quantitative comparison between experimental result and theoretical one is done with more precision than chemical systems. In addition, by increasing or decreasing the laser power continuously, features of the mode bifurcation can be investigated in detail, e.g., whether the bifurcation is subcritical or supercritical. Such studies will expand an understanding of the mechanism of mode bifurcation.

In this thesis, we focus only on the motion of a circular shaped droplet without deformation. As we look at the behavior of living cells, many of them move with changing their shape [2–4]. The spontaneous deformation of the liquid droplet and the self-propelled motion coupled with deformation recently attract much interest also from a standpoint of physics [5, 6]. In the study of self-propelled motion of a droplet under local irradiation by a laser, we found that the droplet can undergo spontaneous deformation at high laser power, by using other kinds of oil as a droplet [7]. It might be beneficial to investigate experimentally droplet motions occurring in association with deformation, in order to gain a further understanding of the relation between motion and deformation.

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