A Camphor Grain Oscillates while Breaking Symmetry

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The self-motion of a camphor grain was investigated on a linear water route. The oscillatory motion along the water route was maintained for ca. 15 cycles. The driving force is discussed in relation to a rhythmic change in the surface tension, which depends on the surface concentration of the camphor layer. The essential features of the self-motion were reproduced by a numerical calculation in relation to the spatial distribution of the camphor layer at the air−water interface.

Introduction

Modeling of autonomous motors under isothermal conditions may help not only to understand biological and molecular motors but also to create a novel chemo-mechanical transducer that mimics living organisms. Such self-motion has been studied experimentally and theoretically.[1−28] For example, the self-motion of a liquid droplet (e.g., nitrobenzene,[6−9] mercury,[10] fluorocarbon,[11,12] and so on[21−28]) or a solid grain such as camphor[13−20] has been investigated as a simple experimental system. This spontaneous motion is generated as a result of Marangoni flow, which is induced by a chemical or thermal gradient acting on the droplet or the grain.[5−28] The manner of the motion depends on the anisotropic distribution of the surface-active substance absorbed on the droplet[6−10] or dissolved from the solid grain.[13−20]

We previously reported the self-motion of a camphor scraping at an air−water interface. The driving force of this motion is the difference in the surface tension around the camphor scraping (or camphor boat) because the camphor molecular layer diffused from the scraping decreases the surface tension at the air−water interface.[15−20] Various manners of self-motion (e.g., clockwise rotation, counterclockwise rotation, and uni-directional translation) and mode-switching between rotation and translation can be produced by changing the shape of the camphor grain.[15,16,19] In addition, the motion of scrapings of a camphor derivative, camphoric acid, changes characteristically depending on the pH of the aqueous phase.[17,18] Recently, we reported that a camphor scraping alternatively switches between rotational and translational motion by using a plastic cell which is consisted of two chambers connected by a linear route.[19] We also reported mode-selection for a camphor boat, which depended on whether the camphor scraping was attached to the boat and the shape of the cell.[20] These results suggest that the nature of the self-motion is sensitive to the outer environment, i.e., the boundary condition of the cell. However, the relationship between the distribution of the camphor molecular layer and the boundary condition of the water cell has not yet been clarified.

We observed the oscillatory motion of a spherical camphor grain in a linear water route while maintaining a heterogeneous distribution for the camphor layer. Such oscillatory motion can be reproduced by a theoretical simulation based on the reaction−diffusion equation together with the equation of motion.

Experimental Section

(+)-Camphor was obtained from Wako Chemicals (Kyoto, Japan). Water was first distilled and then purified with a Millipore Milli-Q filtering system (pH of the obtained water, 6.3). A camphor grain (diameter, ca. 2 mm) was dropped onto a water phase (1.0 mL) in a polystyrene cell (length, 30 mm; width, 4.5 mm; depth, 8 mm). The movement of the camphor grain was monitored with a digital video camera (SONY DCR-VX700) and recorded on videotape at 293 ± 1 K. The two-dimensional position of the camphor was measured using a digitizer with a minimum time resolution of 1/30 s.

Results

Figure 1 shows snapshots of the motion of the camphor grain in the water phase (top view) with a time interval of 1/6 s. The camphor grain showed oscillatory motion along the water route without colliding with the edge of the cell. This oscillatory motion (amplitude, 10 mm; frequency, 0.7 Hz) was maintained for ca. 12 s (or 10 cycles). After 10 cycles, the amplitude of oscillation decreased with time, and the camphor grain finally stayed in the center of the cell (no motion).

The solid and dotted lines in Figure 2 show the time variation of the camphor motion on the vertical axis and its velocity in Figure 1, respectively. The sustained oscillatory motion was maintained for 12 s after the camphor grain was dropped on the water surface. When the camphor grain moved around the center of the route, the velocity was almost constant. (Note existence of the constant velocity in Figure 2.) When the camphor grain moved around the edge of the cell, the waveform of the motion was sinusoidal. After 12 s (or 10 cycles), the amplitude decreased and the waveform of the oscillation became continuously sinusoidal at 12−20 s, i.e., the incidence of the constant velocity motion decreased. When a plastic cell with a short route (length, 7 mm; width, 4.5 mm; depth, 8 mm) was

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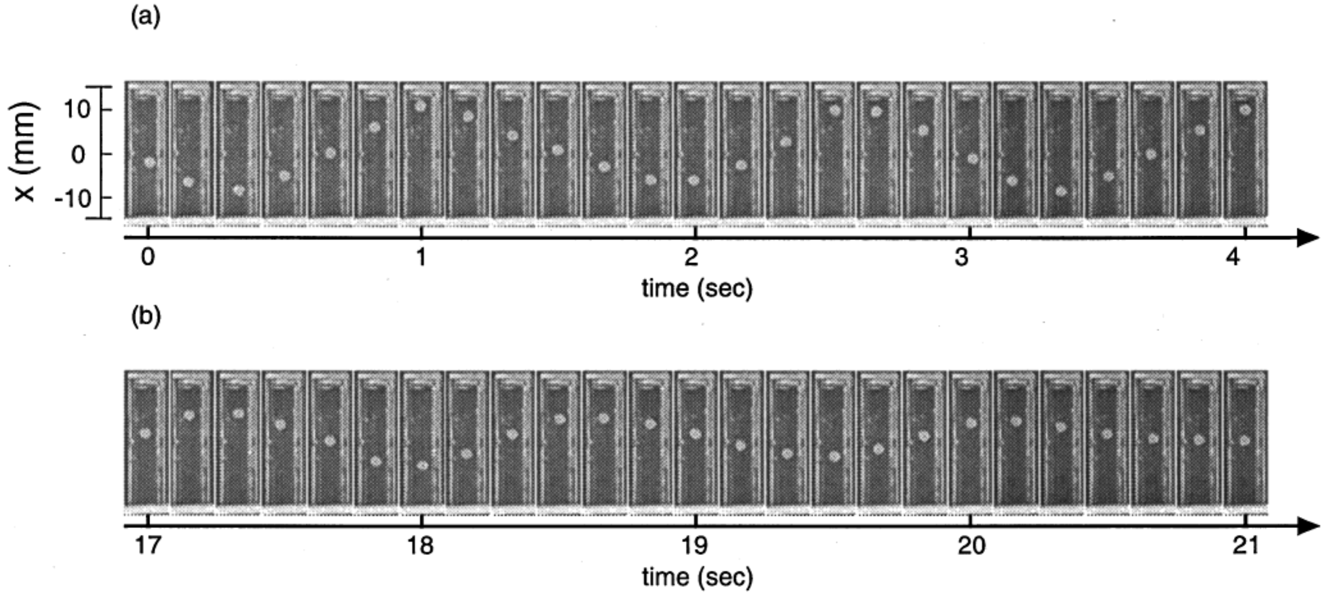

Figure 1. Snapshots of camphor motion with a time interval of 1/6 s in the aqueous phase (top view) at (a) $t = 0-4$ s and (b) $t = 17-21$ s after the camphor grain was dropped onto the air−water interface.

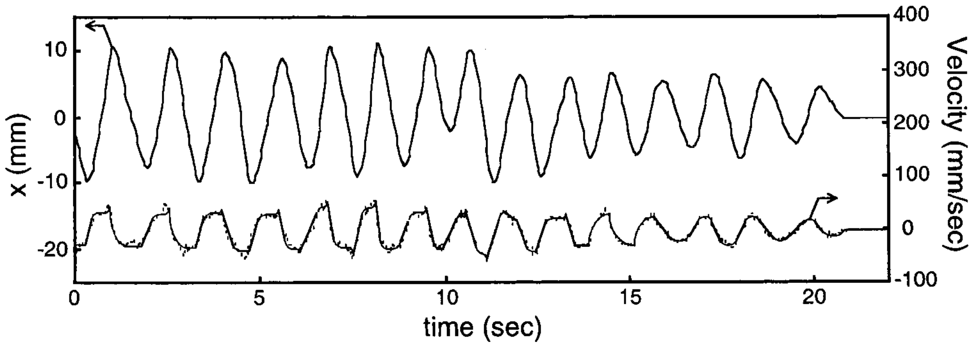

Figure 2. Time variation of the motion for a camphor grain. (Solid line) The vertical axis in Figure 2 corresponds to that in Figure 1. The broken line denotes the time variation of the velocity of the motion for the camphor scraping.

used for this experiment or when the temperature of the water phase was lower than 278 K, no motion was observed.[15]

Discussion

The self-motion of a camphor scraping on a water phase with a significantly large surface area can be explained by the following mechanism.[13,15] (I) The camphor layer diffuses from the scraping and the surface tension around the scraping decreases. (II) Due to the anisotropic shape of the scraping, the camphor layer is heterogeneously distributed around the scraping, and therefore the surface tension around the scraping is not uniform. (III) The camphor scraping moves to another place with a higher surface tension (or a lower concentration of the camphor layer) around the scraping to reduce the spatial gradient of the surface tension, i.e., the rotation and translation of motion depend on the shape of the camphor scraping.[13−20] When a water bath with a significantly large surface area (e.g., 150 cm^2) was used for this experiment, either clockwise or counterclockwise rotation was observed depending on the shape of the camphor scraping.[15,16] On the other hand, no rotation was observed in the present cell. Since the diffusion and sublimation of the camphor layer are inhibited in the horizontal direction on the water route because of its restricted surface area, the driving force for rotation cannot develop. When either the plastic route was shorter than 7 mm or the temperature of the water phase was lower than 278 K, no motion was observed: a concentration gradient for camphor did not develop because the camphor layer was accumulated around the cell due to the relatively low rate of sublimation, and it was difficult to achieve a surface tension gradient as the driving force.[15] Thus, the camphor grain is sensitive to the boundary of the cell rather than the shape of the grain, and the diffusion of the camphor layer is allowed only to the direction along the water route.

We now introduce a two-dimensional mathematical model for camphor motion to clarify the self-motion of the camphor scraping in the cell, which is constructed by referring to the above mechanisms I−III. First, we assume that the camphor grain is a material particle because of its sufficiently small volume. The motion of the camphor grain can be then described by the following classical Newtonian equation:[15,18]

$$\rho \ddot{\mathbf{x}}_c(t) = \nabla \gamma(u(\mathbf{x}_c(t),t)) - \mu \dot{\mathbf{x}}_c(t) \tag{1}$$

where $\mathbf{x}_c(t) = (x_c(t), y_c(t))$ denotes the center of mass of the camphor grain, $u(\mathbf{x},t)$ is the concentration of the diffused camphor layer, ρ is the surface density of the camphor scraping, and μ is the surface viscosity constant. On the basis of our experimental results,[19,29−31] the surface tension γ may be expressed as a function of $u(\mathbf{x},t)$, as follows:

$$\gamma(u(\mathbf{x},t)) = \frac{\gamma_0}{cu(\mathbf{x},t) + 1} \tag{2}$$

where γ_0 is the surface tension of water and c is constant.

Second, we consider the equation for the surface concentration of the camphor layer. The concentration of the camphor layer diffused from the grain without a change in mass is decreased by sublimation into the bulk air phase and by dissolution to the air−water interface. Therefore, the model equation for the concentration of the camphor layer $u(\boldsymbol{x},t)$ is deduced by the reaction−diffusion equation, as follows:[19]

$$\frac{\partial \boldsymbol{u}}{\partial t} = D\Delta u - ku + F(\boldsymbol{x}_c(t);r_0),\ \boldsymbol{x} \in \Omega,\ t > 0 \qquad (3)$$

where D is the diffusion coefficient of the camphor layer diffused to the air−water interface, k is the sum of the rates of sublimation (k_1) and dissolution (k_2) of the camphor layer at the air−water interface ($k = k_1 + k_2$), r_0 is the radius of the camphor grain, and Ω is the surface area of the water bath. The function F, which is related to the diffusion of the camphor layer from the camphor grain to the air−water interface, is expressed by eq 4:

$$F(\boldsymbol{x}_c(t);r_0) = \begin{cases} bS_0, & |\boldsymbol{x}_c(t) - \boldsymbol{x}| \le r_0, \\ 0, & |\boldsymbol{x}_c(t) - \boldsymbol{x}| > r_0, \end{cases} \qquad (4)$$

where S_0 is the constant amount to be supplied by the camphor grain, and b is the rate of diffusion of the camphor layer from the camphor scraping. Here, we assume that the decrease in the mass of the camphor grain by diffusion of the camphor layer is negligible (the mass of the grain is constant).

To reproduce spontaneous oscillation in the narrow cell, we consider the one-dimensional initial and boundary value problems for eqs 1−4:

$$\begin{cases} \dfrac{\partial u}{\partial t} = D\dfrac{\partial^2 u}{\partial x^2} - ku + F(x_c(t);\ r_0),\ 0 < x < L,\ t > 0 \\ \rho \ddot{x}_c(t) = \dfrac{\partial}{\partial x}\dfrac{\gamma_0}{cu(x_c,t) + 1} - \mu \dot{x}_c(t),\ t > 0 \end{cases} \qquad (5)$$

and

$$F(x_c(t);r_0) = \begin{cases} bS_0, & |x_c(t) - x| \le r_0 \\ 0, & |x_c(t) - x| > r_0 \end{cases} \qquad (6)$$

with the initial conditions

$$\begin{cases} u(x,0) - u_0(x), & 0 \le x \le L, \\ x(0) = x_0, & \dot{x}(0) = x_1, \end{cases} \qquad (7)$$

and nonflux boundary conditions

$$\frac{\partial}{\partial x}u(0,t) = \frac{\partial}{\partial x}u(L,t) = 0,\ t > 0 \qquad (8)$$

Here, we give the following matching condition to exist the solution for eqs 5−8:

$$u(\cdot,t) \in C^1(0,L) \qquad (9)$$

In our numerical simulation based on eqs 5−9, we fix the parameters as follows: $D = 1.0$, $\mu = 0.17$, $r_0 = 0.2$, $\rho = 1.0$, $\gamma_0 = 2.0$, $b = 1.0$, and $c = 0.5$. Parameters L and k are controllable because they can be experimentally changed.

Figure 3 shows the phase diagram in the L-k plane for the numerical simulation based on eqs 5−9. Oscillatory motion was not observed for a route shorter than 5.0 due to an insufficient driving force with the small surface area. Figure 3 suggests that the oscillatory motion is generated within a certain region of k.

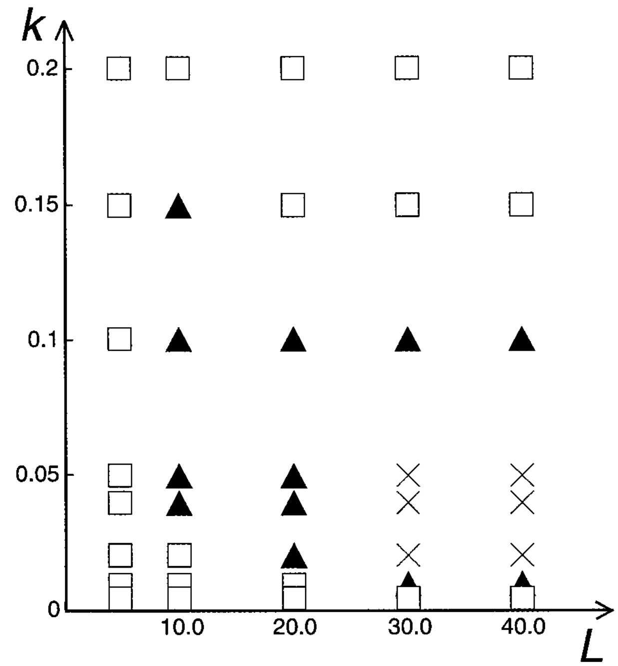

Figure 3. Phase diagram in the L-k plane for a numerical simulation based on eqs 5−7. The symbols □, ▲, and × are the states for the stationary solution, the oscillatory solution, and collision with the boundary, respectively.

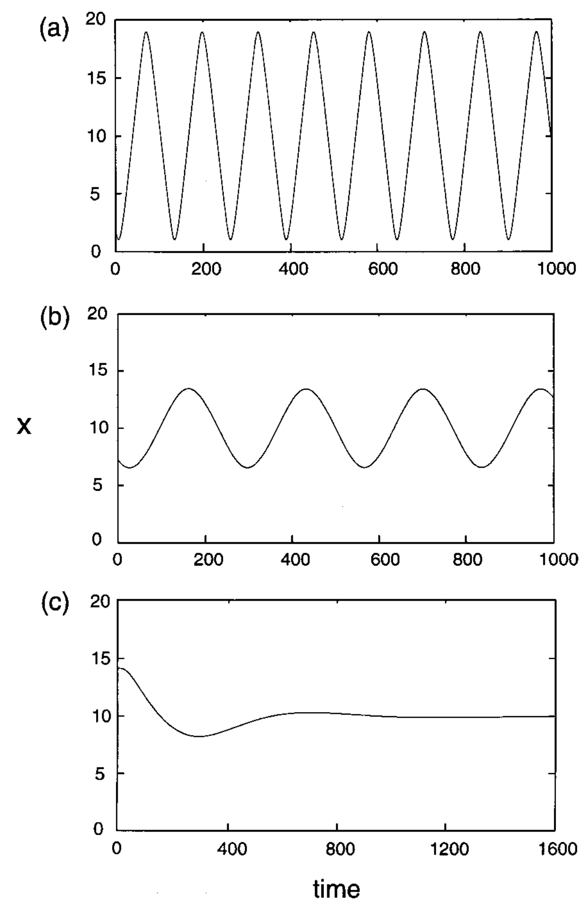

Figure 4. Computer simulation of the temporal change in camphor motion at $L = 20.0$ based on eqs 5−8. (a) $k = 0.1$, (b) $k = 0.01$, and (c) $k = 0.005$.

Figure 4 shows the time-variation of oscillatory motion (state ▲) with (a) a constant velocity and (b) a sinusoidal waveform, and (c) no motion (state □) (see Figure 3) depending

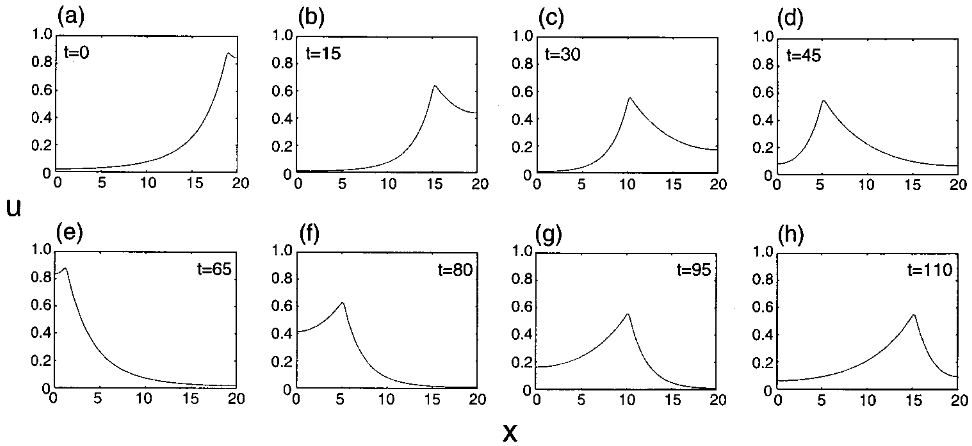

Figure 5. Computer simulation of the concentration of the camphor layer with a time interval of $t = 15$ based on eqs 5−9. x at the maximum concentration is the position of the camphor grain, x_c. The parameters are the same as those in Figure 4a.

on k. The experimental results in Figures 1 and 2 can be described by the following temporal profiles (i−iii). (i) sustained oscillation with a constant velocity, (ii) the waveform changes to be sinusoidal and its amplitude decreases with time, and (iii) the camphor grain is stopped at the center of the cell. Existence of the constant velocity is due to $\rho\ddot{\mathbf{x}}_c(t)$ reaches 0 in eq 1. In the actual experiments, the camphor grain or camphor boat indicated the uniform motion when the surface area of water phase was significantly large.[15,20] Figure 4 suggests that the continuous changes in states i, ii, and iii correspond to those in a, b, and c, respectively. Thus, k decreases with time because the dissociation or sublimation of camphor molecules leads to a saturated concentration on the water phase or at the air phase around the air−water interface.

Figure 5 shows the time variation of the accumulated camphor layer, $u(\mathbf{x},t)$. For example, when $\mathbf{x}_c(t)$ is close to one of the edges of the cell, $u(\mathbf{x}, t)$ increases around the edge of the cell at $k = 0.1$ and $L = 20$. The gradient of the concentration of the camphor layer decreases: the particle can no longer move in the same direction and therefore oscillates while reversing the direction of its self-motion. If the particle is placed at the center of the one-dimensional cell, ideally no motion should be observed. Thus, the particle can begin oscillation only if the system has an asymmetric initial condition, and the particle maintains its oscillation while spontaneously breaking the homogeneous distribution of the camphor layer.

Conclusion

A camphor grain maintains oscillatory motion while spontaneously breaking the homogeneous distribution of the camphor layer along the water route. To clarify the mechanism of this oscillatory motion, a theoretical simulation based on the reaction−diffusion equation reproduced such camphor motion, and the surface concentration of the camphor layer was then calculated using the equation. We succeeded at reproducing the spontaneous motion of a camphor grain by using a numerical simulation.

According to the Curie-Prigogine theorem, a vector process cannot couple with scalar variables, such as an ideal chemical reaction, in an isotropic system under a steady state. This implies that a vectorial flow can be induced when the reaction field is "anisotropic", such as in the present experimental system, and also as seen in the artificial and biological heterogeneous membranes.[32−34] As an application of these results, we may be able to create various types of spontaneous switching by making cells and camphor grains of various shapes. We believe that the present study may be useful for realizing artificial motors or chemo-mechanical transducers, which mimic motor organs or organelles in living organisms under nonlinear and isothermal conditions.

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