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Spontaneous dancing of a camphor scraping

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Spontaneous mode-switching was investigated for a camphor scraping at an air/water interface. The motion of a camphor scraping intermittently switched between revolution and translation. To clarify the nature of this spontaneous mode-switching, the surface tension at the air/water interface was measured and the diffusion of the camphor layer was visualized. The spatial heterogeneity of the camphor layer at the air/water interface may play an important role in this mode-switching.

Introduction

It is well known that heat engines, such as a gasoline engine, cannot violate the second law of thermodynamics. In addition, heat engines produce several environmental problems, *e.g.*, a greenhouse effect due to an increase in carbon dioxide. The Carnot cycle tells us that the coefficient of energy transduction should be less than $(T_h - T_l)/T_h$, where T_h and T_l are the absolute temperatures of the heat reservoirs at the high and low temperatures, respectively. Therefore, a large coefficient of energy transduction requires a high heat of combustion or a large energy source. On the other hand, biological motors work through the dissipation of chemical energy under almost isothermal conditions, *i.e.*, biological motors operate through some mechanism other than the Carnot cycle. Such motion is observed under non-equilibrium conditions, *e.g.*, chemical or thermal inhomogeneity.[1–13] Thus, the development of such a chemical engine, which works under isothermal conditions, is an important step in the creation of a novel chemical motor or artificial actuators which are capable of self-movement.[1,4,10–13]

More than a century ago, the self-motion of a small camphor scraping at an air/water interface was explained by Van der Mensbrugghe, and Rayleigh subsequently studied the retarding effect of contaminating oily substances on the self-motion of a camphor scraping.[14] However, it has not yet been clarified why the camphor scraping spontaneously continues to "dance". Recently, we reported that (1) the frequency of rotation depends on the temperature, surface tension, and chemical structure of the camphor derivatives, (2) the direction of rotation, either clockwise or counter-clockwise, is determined by asymmetry in the shape of the solid camphor scraping, and (3) the essential features of the motion of a camphor scraping could be reproduced by a computer simulation.[12,13] We believe that experiments on such motion imply the realization of chemo-mechanical energy transduction under isothermal conditions.

In this paper, we report that the motion of a camphor scraping intermittently switches between revolution and translation. To clarify the nature of this spontaneous mode-switching, the surface tension at the air/water interface was measured and the diffusion of the camphor layer was visualized. The spatial heterogeneity of the camphor layer at the air/water interface may play an important role in this mode-switching.

Experimental section

Camphor was obtained from Wako Chemicals (Kyoto, Japan). A camphor scraping was dropped onto pure water, which was first distilled and then purified with a Millipore Milli-Q filtering system (pH of the obtained water: 6.3), in a glass Petri dish (depth of the water phase: 5 mm).[13,14] The movement of camphor was monitored with a digital video camera (SONY, DCR-VX700) and recorded on video tape at 293 ± 1 K. The two-dimensional position of the camphor was measured using a digitizer. The minimum time resolution was 1/30 s. The surface tension at the air/water interface was measured by the standard Wilhelmy method.[15–17]

Results

Fig. 1 shows (a) a time trace of the orbital motion (revolution) and translational motion of a camphor scraping with a time interval of 1/30 s (top view) and (b) the time variation of the motion on the vertical axis of (a). In this experiment, a Petri dish with a larger surface area (150 cm²) for the water phase and a small camphor scraping (diameter: *ca.* 0.5 mm) were used to eliminate the experimental boundary condition, *i.e.*, the glass/water interface. The camphor scraping maintained revolution for several tens of minutes with intermittent translational motion, with an interval of *ca.* 1.5 s or *ca.* 5 cycles, as seen in Fig. 1.

Fig. 2 shows the camphor layer at the water surface with the addition of a fine plastic powder and mode-switching between revolution (a–c, h–j) and translation (f–g), where the black and white areas correspond to the camphor layer and the plastic powder layer. Here, 15 revolutions were observed between a and e, since we selected a larger scraping (diameter: *ca.* 1.0 mm) to obtain a larger change in the surface area of the camphor layer. The diameter of the camphor layer increased with the number of revolutions and reached *ca.* 30 mm.

Fig. 3a shows the time variation of the surface tension during the revolution of a camphor scraping on pure water. Here, the camphor scraping revolved (revolutional radius: *ca.* 10 mm) around the platinum wire (diameter: 0.5 mm) which was used to measure the surface tension, as indicated schematically in Fig. 3a. A small Petri dish with a diameter of 40 mm was used to obtain the revolutional mode around the platinum blade. The surface tension decreased rapidly when the camphor scraping was dropped on the water phase, and then slowly decreased with time. The surface pressure increased with the number of revolutions by *ca.* 5 mN m^{-1} for 5 cycles. Fig. 3b shows the dependence of the surface tension of the camphor layer on the distance from its center at the steady state. In this experiment, a camphor scraping (diameter: *ca.* 2 mm) was fixed on the platinum wire and then

(a)
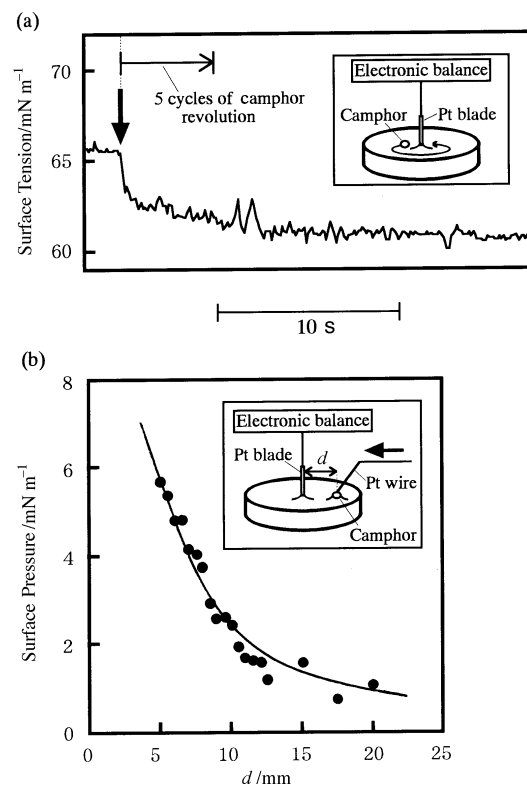

10 mm

(b)

2 s
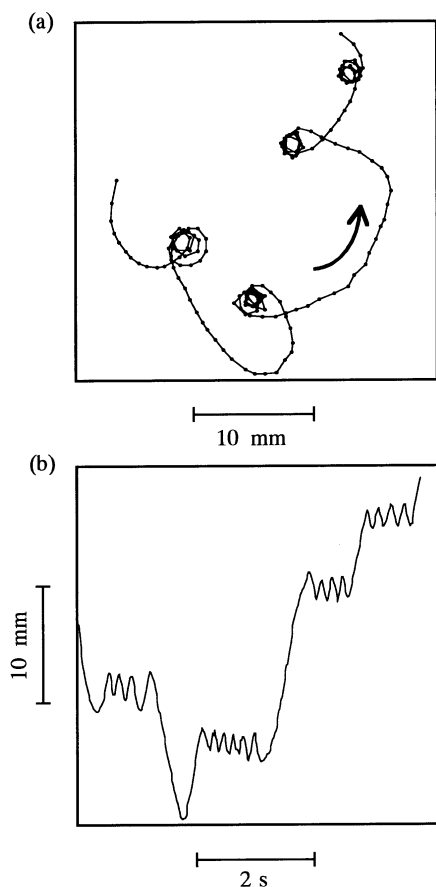
Fig. 1 (a) Time trace of the dancing of a camphor scraping on pure water with a time interval of 1/30 s (top view). (b) Time variation of the motion for a camphor scraping. The vertical axis for (a) corresponds to that for (b).

(a)

10 s

(b)

Fig. 3 (a) Time variation of the surface tension during the revolution of a camphor scraping on pure water. The camphor scraping was dropped on the water phase at the time indicated by the downward arrow. (b) Dependence of the surface pressure of the camphor layer on the distance from its center at the steady state.

attached to the water surface. The platinum wire with the camphor scraping was slowly moved on the water phase to measure the dependence of the surface tension on the distance. The surface pressure increased with a decrease in the distance between the camphor scraping and the platinum blade used to measure surface tension.

Discussion

The camphor scraping intermittently switched between the revolutional and translational modes at the air/water interface. When the camphor scraping switched from revolution to translation, the camphor layer observed before switching was maintained for several seconds. The surface tension decreased with the duration of the revolution of the camphor scraping.

We can discuss the mechanism of the spontaneous switching of the camphor scraping based on these results, as indicated in Fig. 4. A camphor scraping dissolves into the outer environment by forming a thin layer at the interface around the scraping, since hydrophobic camphor molecules have weak surface activity (Fig. 3). The manner of revolution is determined by the shape of the camphor scraping. Therefore, continuous revolutional motion may be due to maintenance of the camphor shape and of the floating state of the camphor scraping at the air/water interface. The surface density of the camphor layer may increase with an increase in the number of
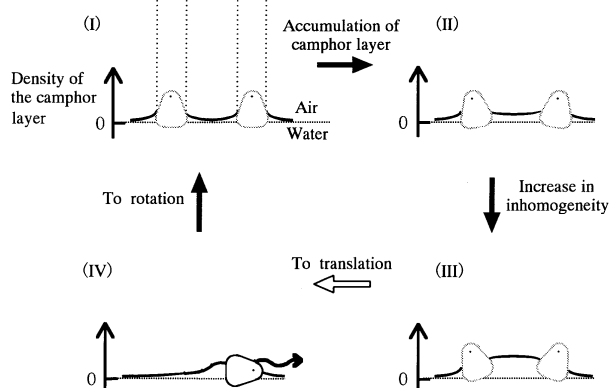
(a)　　(b)　　(c)　　(d)　　(e)

(f)　　(g)　　(h)　　(i)　　(j)

50 mm
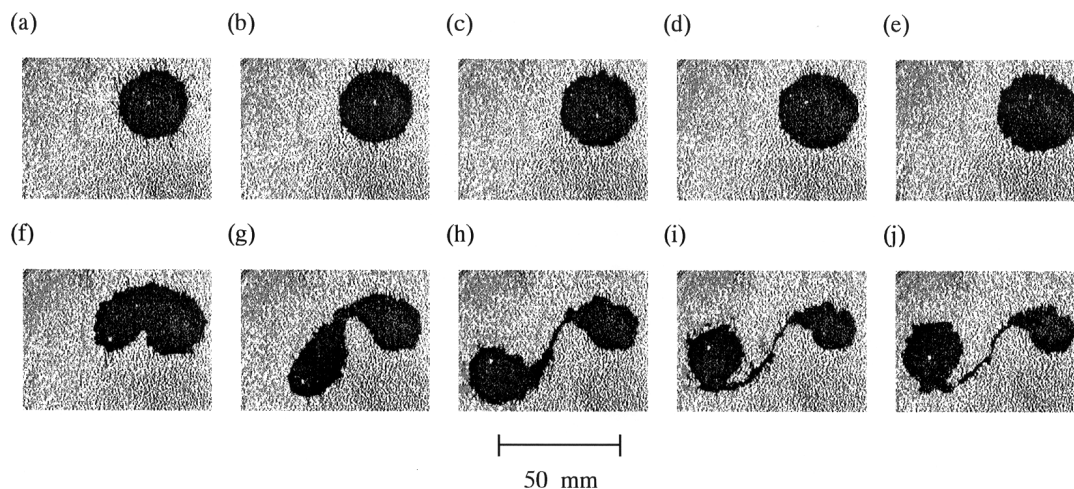
Fig. 2 Snapshots of the switching between revolution (a–e and h–j) and translation (f–g) of a camphor scraping with time intervals of 2 s (a–c) and 1 s (c–j) (top view).

Top view

Revolution of a camphor scraping

Side view

(I)

Density of
the camphor
layer

0

Air
Water

Accumulation of
camphor layer

(II)

0

To rotation

Increase in
inhomogeneity

(IV)

To translation

(III)

0

0

Fig. 4 Schematic diagram of the mechanism of spontaneous switching between revolution (States I, II, and III) and translation (State IV). Mode-switching occurred by repeated cycling through States I, II, III, and IV.

revolutions, and therefore the degree of inhomogeneity of the surface density will increase (State II). Such an inhomogeneous camphor layer may induce a change in the floating state of the camphor scraping, as seen in State III, *i.e.*, the centroid and the contact interface with the water phase will change. Consequently, revolution will change to translation (State IV), and revolution will then be regenerated by shifting to another air/water interface with a smaller camphor layer or a pure air/water interface (State I). Thus, mode-switching will continue by cycling through States I–IV.

The critical value of the degree of inhomogeneity for mode-switching may be 5–8 cycles of revolution in the experiment in Fig. 1, since the interval of mode-switching is almost regular, as seen in Fig. 1b. The number of revolutions and the period for switching changed depending on the size and shape of the camphor scraping. In general, the number of revolutions and the period for switching increased with the size of the camphor scraping,[12] *e.g.* the number of revolutions and the period for switching were *ca.* 15 cycles and *ca.* 6 s with the camphor scraping (diameter: *ca.* 1 mm) in Fig. 2. A light scraping may be affected by the instability of the camphor layer. Appreciable mode-switching was not observed for rotation around its centroid since rotation was unlikely to have had an influence on the instability of the camphor layer due to settling of the centroid of the camphor scraping at the air/water interface.

Regarding the increase in the surface pressure with the number of revolutions, the density of the camphor layer will increase with the number of revolutions (Fig. 3a). The higher gradient of the surface pressure for d smaller than 10 mm suggests the existence of either inhomogeneity of the camphor layer or instability of the floating state of the camphor scraping around it (Fig. 3b). An increase in the accumulation or instability of the camphor layer was observed as an increase in the diameter of the camphor layer with the number of revolutions (Fig. 2a–e). Due to the accumulation of the camphor layer, the camphor layer exists on the same interface for a few seconds even if revolution switches to translation (Fig. 2f–i). In contrast, the camphor layer in translation is immediately diminished within a second by the dissociation and sublimation of camphor molecules (Fig. 2d—h).[12] The fact that the

manner of revolution (*i.e.*, the radius and frequency of revolution) after translation is similar to that before translation suggests a return to the original and stable floating state of the camphor scraping at a pure air/water interface. Thus, translational motion may be associated with rotational motion since the interfacial morphology of the scraping in contact with the aqueous phase may be varied even with the same scraping when it is tilted at the air/water interface.

In addition to the effect of the gradient in the surface tension, a solutocapillary effect (or soluto-Marangoni effect), which involves surface convection from low to high surface tension, should also be considered as an important factor in camphor motion.[18–20] The effect of surface convection, due to the gradient of the surface tension, is induced by the absence of slip between the peripheral edge of the particle lying in the interface and the interfacial liquid, and bulk motion will be induced by the absence of slip between the surface of the particle at the air/water interface and the liquid below it. Actually, we noticed the convective motion of fluid induced by the capillary effect in our experiment. A larger convective motion was observed when camphor motion switched from rotation to translation.

Conclusion

The spontaneous mode-switching observed here may be induced by a change in the floating state of the camphor scraping, which is related to its centroid and the shape of the contact surface with the air/water interface. The intermittence of this mode-switching is observed when the spatio-temporal heterogeneity of the camphor layer, which increases with revolution, exceeds a threshold value. According to the Curie–Prigogine theorem, vector processes cannot couple with scalar variables, such as an ideal chemical reaction, in a "linear" system under isotropic conditions.[21–23] This implies that chemo-mechanical coupling becomes possible with a violation of either the linear or isotropic conditions.[10] Thus, it may be natural to expect that effective chemo-mechanical coupling can be realized in the absence of both linear and isotropic conditions. We believe that the spatio-temporal heterogeneity in the chemical potential generates various motions with self-assembly, such as macroscopic vectorial motion and mode-switching which are highly sensitive to the outer environment, and may be useful for realizing artificial motors which mimic motor organs or organelles in living organisms under "nonlinear" and isothermal conditions.

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