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Spontaneous Irregular Motion of an Alcohol Droplet

By

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Abstract

A pentanol droplet on water moves spontaneously and the mode of this motion depends on the size of the droplet. A small droplet moves irregularly, a middle-sized droplet moves vectorially, and a large droplet splits into smaller droplets [1]. We analyzed the irregular motion of a droplet with a previously described model of spontaneous motion driven by the Marangoni effect.

§ 1. Introduction

A two-phase coexisting system, it is important to consider interfacial energy, which is proportional to the size of the interface. Interfacial energy is a component of free energy and depends on the temperature, the concentration of the surfactant, and so on. In general, interfacial tension decreases with an increase in temperature or an increase in the concentration of the surfactant. Under a nonuniform distribution of temperature or concentration of chemicals, an interfacial tension gradient appears and it. Instability of the interface due to the nonuniformity of interfacial tension is called the Marangoni effect [2].

Marangoni convection is a typical phenomenon that is driven by the Marangoni effect caused by a temperature gradient. It occurs when a liquid in contact with air in a thin container is heated from below. Thermocapillary convection, which is surface instability with a temperature gradient parallel to the surface, is also an example of the Marangoni effect [3, 4]. The tears of wine are a well-known phenomenon that driven by the Marangoni effect based on the nonuniformity of the concentration of a surfactant [5]. At the sidewall of a glass with wine, evaporation of alcohol makes a concentration gradient of alcohol and wine is pulled up by an interfacial tension gradient in a thin film of wine. As a result, droplets of wine appears at the thin film and the droplets fall down. An oil-water surface can also become instable due to nonuniformity of a surfactant. Nakache and co-workers reported that an oil-water surface with a surfactant oscillates spontaneously [6, 7].

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In a smaller system, interfacial effects are greater than volume effects such as gravity, and therefore it is easy to see the effect of interfacial energy in a small system. For example, the interface of a water droplet on the scale of millimeter becomes spherical in air [8]. In some systems, an object with a size on the order of millimeter moves spontaneously driven by the Marangoni effect. For example, a droplet with a silane coupling agent put on glass creates a difference in surface tension around the droplet itself, to exhibit spontaneous motion [9, 10]. Magome and co-workers found that a small oil droplet also runs spontaneously on glass in water with a surfactant [11, 12]. Another example of spontaneous motion driven by the Marangoni effect is the motion of a scraping of surfactant on water. The surfactant is distributed around the scraping, which makes the surface tension nonuniform, and the scraping begins to move spontaneously. The simplest example is the motion of a piece of paper with a soap scraping on water. The spontaneous motion of a scraping of camphor on water, which is a surface-active agent, is also well-known. Various types of spontaneous motion of a scraping of camphor have been reported by Nakata and co-workers [13–15]. It is interesting that some living organisms use the Marangoni effect and move on water like a scraping of camphor [16].

Although there have been many studies on spontaneous motion propelled by the Marangoni effect, details from the viewpoint of physics have not been clarified yet in many of such systems. We studied the spontaneous motion of an alcohol droplet on water from physical side of view. The mode of this motion depends on the size of the droplet. A small droplet moves irregularly, a middle-sized droplet exhibits vectorial motion, and a large droplet splits into smaller droplets. This dependence on the size of the droplet is caused by the instability of the shape of a droplet [1]. In this paper, we analyzed the irregular motion of a pentanol droplet. In addition, we exhibit that this irregular motion can be reproduced with a previously described model of spontaneous motion driven by the Marangoni effect [17–19].

§ 2. Experiments

Experiments were performed using the setup shown in Fig. 1. 100 ml of an aqueous solution of 2.3 vol% pentanol was poured into a petri dish with a diameter of 180 mm. The tip of a micro pipette was soaked in pentanol and then touched to the water surface, in order to create a small pentanol droplet. The droplet volume was approximately 10^{-2} μl. The motion of the droplet with this volume was irregular [1]. We assume that the volume of the droplet was proportional to the $3/2$th power of the cross-section. In order to visualize the motion of the droplet, oil-based ink (Pilot Corporation, Tokyo; INKSP-55-B) was dissolved in pentanol. We observed the motion of a droplet with a high-speed camera (RedLake MASD Inc., San Diego, CA; Motion Scope PCI). All experiments were performed at room temperature. In the analysis of movies of droplet motion, we determined the location of the droplet per $1/30$ second with Image J (http://rsb.info.nih.gov/ij/).

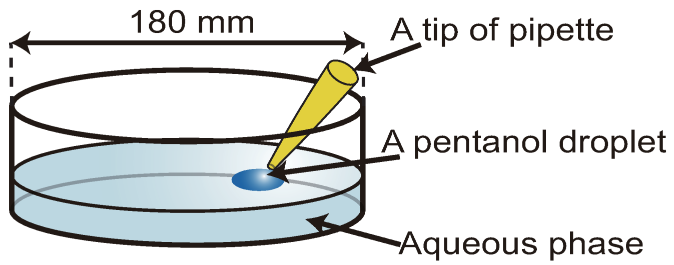

Figure 1. Schematic diagram of the experimental setup. The aqueous phase consisted of an aqueous solution of pentanol at a concentration of 2.35 vol% and the pentanol phase consisted of pentanol with oily ink to visualize the motion of the droplet.

Assuming that the location of a droplet at time t is $(x(t),\ y(t))$, the total moving distance of the droplet at t, $L_{td}(t)$, and the distance from the initial position during the time interval of t seconds, $L_{ee}(t)$, are,

$$L_{td}(t) = \sum_{k=0}^{\frac{t}{\Delta t}-1} \sqrt{(x((k+1)\Delta t) - x(k\,\Delta t))^2 + (y((k+1)\Delta t) - y(k\,\Delta t))^2}, \tag{2.1}$$

$$L_{ee}(t) = \left\langle \sqrt{(x(s+t) - x(s))^2 + (y(s+t) - y(s))^2} \right\rangle, \tag{2.2}$$

where Δt is the time interval between datas and $\langle\rangle$ means the average of the values with various s.

§ 3. Results

A pentanol droplet moved irregularly on the water surface soon after it was placed on the water (Fig. 2(a)). The time-dependence of $L_{td}(t)$ is shown in Fig. 2(b). $L_{td}(t)$ is proportional to $t^{1.0}$, which means the speed of the droplet was almost constant. The result with regard to $L_{ee}(t)$ is shown in Fig. 2(c). When t is small, $L_{ee}(t)$ is proportional to $t^{1.0}$. On the other hand, $L_{ee}(t)$ is proportional to $t^{0.5}$ at large t. Therefore, a droplet moves straight during a short time interval, but moves in a random walk overall.

§ 4. Discussion

The mechanism of spontaneous irregular motion in Fig. 2 is thought to be as follows. We can say from Fig. 2 that the shape of a droplet is almost circular. Pentanol diffuses from a droplet

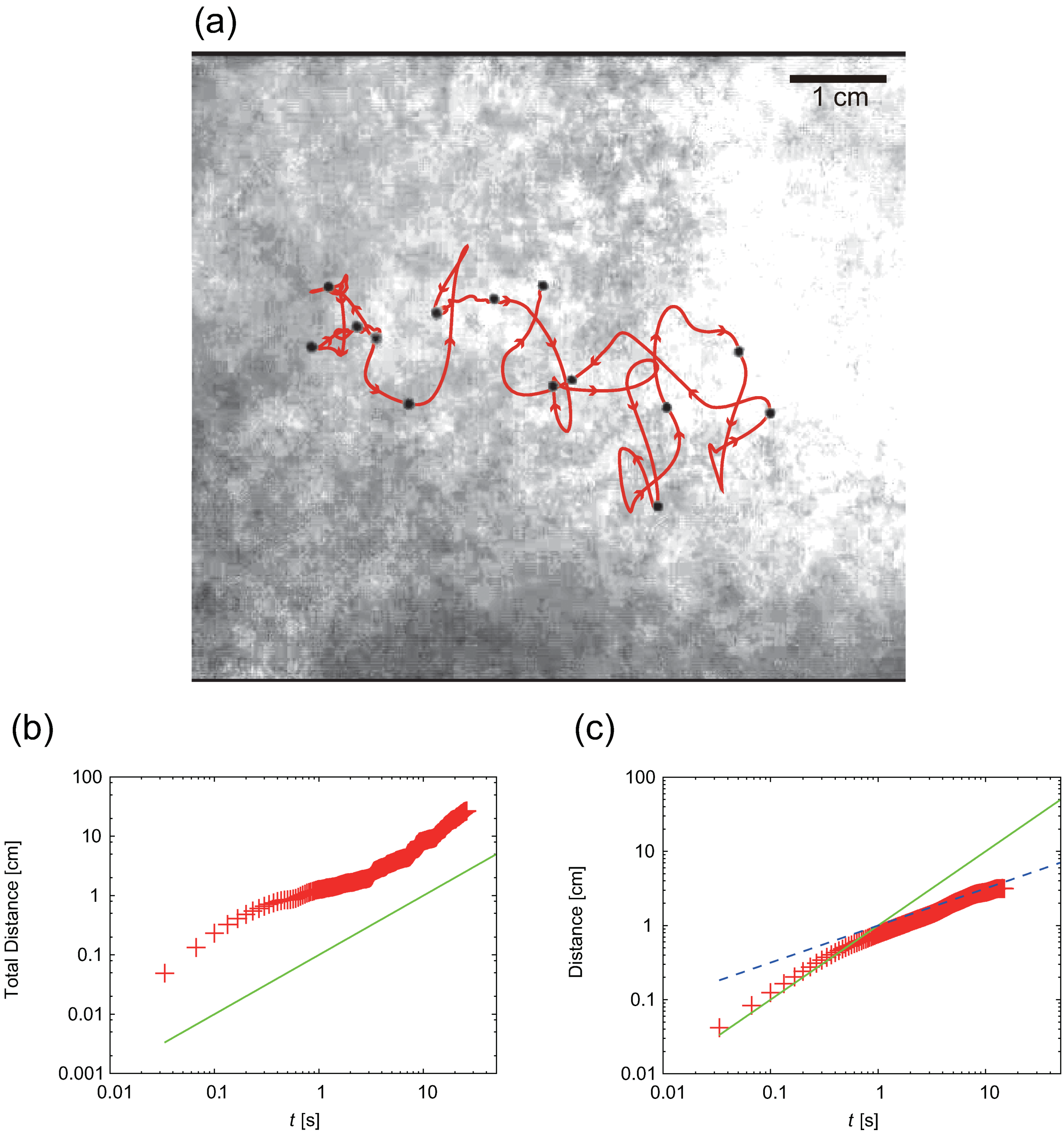

Figure 2. Motion of a pentanol droplet. The volume of a droplet was 2×10^{-2} μl. $t = 0$ is free choosen after the droplet is put on aqueous phase. (a) Trace of the irregular motion. Images of the droplet every 2 seconds are shown. The solid line indicates the trace of motion. (b) Time-dependence of L_{td}. The cross symbols show the experimental data. The solid line corresponds to $t^{1.0}$. (c) Time-dependence of $L_{ee}(t)$. The cross symbols show the experimental data. $t^{1.0}(t)$ is shown with a solid line and $t^{0.5}$ is shown with a broken line.

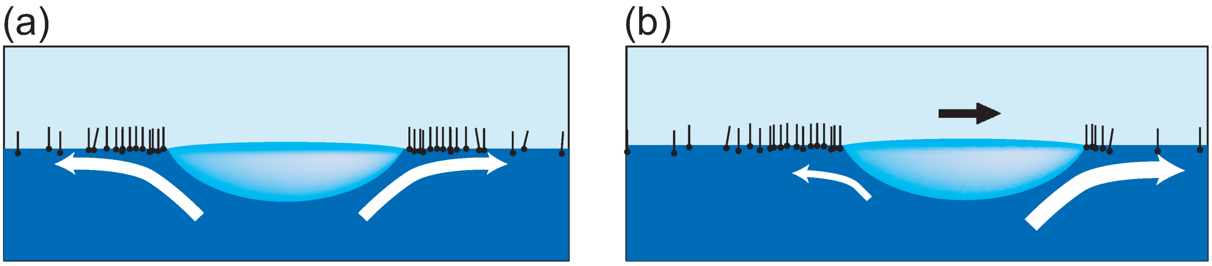

Figure 3. Schematic diagram of the distribution of pentanol molecules on a water surface. The white arrows represent flow due to the Marangoni effect. The droplet moves in the direction of the black arrow. (a) When the droplet stops, the pentanol distribution is symmetric. (b) Once the droplet moves, the gradient of the pentanol concentration in the front increases, and the droplet continues to move.

on water, therfore its distribution around a motionless droplet is isotropic. Since pentanol on water evaporates and dissolves in water, the pentanol concentration is lower at the location farther from the droplet. Although water flows due to the Marangoni effect, convection is isotropic and the droplet does not move. Once the droplet is slightly advanced due to fluctuation, the gradient of the pentanol concentration in the front of the droplet becomes greater than that in the rear. The convection in the front also becomes stronger than that in the rear because of the negative dependence between the interfacial tension and the pentanol concentration. Since the front experiences a stronger pull due to convection, the droplet continues to move. If the direction of the motion changes, the distribution of pentanol changes, too. Therefore, the direction of motion is neutrally stable (Fig. 3).

We now consider the irregular motion of a droplet with the model discussed by Nagayama [17], which describes the spontaneous motion of a disk of surfactant on water. Since the droplet in Fig. 2(a) remains circular, we use this model and consider a droplet as a disk. In this model, surfactant is supplied from the disk and diffuses on the water surface, and then evaporates and dissolves in water. The disk is driven by the interfacial tension around it. Random forces caused by a fluctuation of interfacial tension are applied to the disk.

The equation of motion for a droplet is,

$$m\frac{\mathrm{d}^2\boldsymbol{x}_\mathrm{p}}{\mathrm{d}t^2} = -\mu\frac{\mathrm{d}\boldsymbol{x}_\mathrm{p}}{\mathrm{d}t} + \boldsymbol{F}_\mathrm{T}(\boldsymbol{x}_\mathrm{p}(t), c(\boldsymbol{x}, t); r) + \boldsymbol{\xi}(t), \tag{4.1}$$

where $\boldsymbol{x}_\mathrm{p}$ is the position of the center of gravity of the droplet, m is the mass of the droplet, μ is the constant surface viscosity, $\boldsymbol{\xi}(t)$ is random force, $\boldsymbol{F}_\mathrm{T}$ is the force caused by interfacial tension around the droplet, and r is the radius of a droplet. We consider that $\boldsymbol{\xi}(t)$ is a white Gaussian random force, i.e. $\left\langle \xi_\alpha(t)\xi_\beta(s)\right\rangle = \sigma^2\delta_{\alpha\beta}(t-s)$. Since pentanol diffuses on water, evaporates, and dissolves into water,

$$\frac{\partial c}{\partial t} = D\nabla^2 c - k\,c + G(\boldsymbol{x}, \boldsymbol{x}_\mathrm{p}(t); r), \tag{4.2}$$

$$G(\boldsymbol{x}, \boldsymbol{x}_\mathbf{p}(t); r) = \begin{cases} b\,c_0 \; |\boldsymbol{x}_\mathrm{p}(t) - \boldsymbol{x}| < r \\ \;0 \;\; |\boldsymbol{x}_\mathrm{p}(t) - \boldsymbol{x}| > r \end{cases}, \tag{4.3}$$

where $c(\boldsymbol{x}, t)$ is the concentration of pentanol on water, D is the diffusion constant of pentanol, $k\,c$ means evaporating and dissolving, and $b\,c_0$ is the supply of pentanol from a droplet. Considering that interfacial tension is a decreasing function of $c(\boldsymbol{x}, t)$ and that $\boldsymbol{F}_\mathrm{T}$ is the resultant of interfacial tension,

$$\boldsymbol{F}_\mathrm{T} = \int_{|\boldsymbol{x}_\mathrm{p}(t) - \boldsymbol{x}| = r} \gamma_\perp \, dl, \tag{4.4}$$

$$\gamma_\perp = \frac{\gamma_0}{ac(\boldsymbol{x}, t) + 1} \frac{\boldsymbol{x}_\mathrm{p}(t) - \boldsymbol{x}}{|\boldsymbol{x}_\mathrm{p}(t) - \boldsymbol{x}|}, \tag{4.5}$$

where $\gamma_\perp$ is the component of interfacial tension normal to the boundary between water and the droplet.

We normalize the Eqs. (4.1)-(4.5) by using the following dimensionless variables and parameters,

$$bt \to t, \quad \sqrt{\frac{b}{D}}\boldsymbol{x} \to \boldsymbol{x}, \quad \frac{\mu}{bm} \to \mu, \quad \frac{1}{b^2 m}\sqrt{\frac{b}{D}}\boldsymbol{\xi}(t) \to \boldsymbol{\xi}(t),$$
$$\frac{1}{b^2 m}\sqrt{\frac{b}{D}}\sigma \to \sigma, \quad \frac{c}{c_0} \to c, \quad \frac{k}{b} \to k, \quad \frac{1}{b^2 m}\gamma_0 \to \gamma_0, \quad \text{and } \mathrm{ac}_0 \to \mathrm{a} \quad .$$

The following dimensionless equations are derived with these variables and parameters,

$$\frac{\mathrm{d}^2 \boldsymbol{x}_\mathrm{p}}{\mathrm{d}t^2} = -\mu \frac{\mathrm{d}\boldsymbol{x}_\mathrm{p}}{\mathrm{d}t} + \boldsymbol{F}_\mathrm{T} + \boldsymbol{\xi}(t) \quad , \tag{4.6}$$

$$\frac{\partial c}{\partial t} = \nabla^2 c - kc + G(\boldsymbol{x}, \boldsymbol{x}_\mathrm{p}(t); r) \quad , \tag{4.7}$$

$$G(\boldsymbol{x}, \boldsymbol{x}_\mathbf{p}; r) = \begin{cases} 1 \; |\boldsymbol{x}_\mathrm{p}(t) - \boldsymbol{x}| < r \\ 0 \; |\boldsymbol{x}_\mathrm{p}(t) - \boldsymbol{x}| > r \end{cases} \quad , \tag{4.8}$$

$$\boldsymbol{F}_\mathrm{T} = \int_{|\boldsymbol{x}_\mathrm{p}(t) - \boldsymbol{x}| = r} \frac{\gamma_0}{ac(\boldsymbol{x}, t) + 1} \frac{\boldsymbol{x}_\mathrm{p}(t) - \boldsymbol{x}}{|\boldsymbol{x}_\mathrm{p}(t) - \boldsymbol{x}|} dl \quad . \tag{4.9}$$

Figure 4 shows the results when $r = 2.5,\ \mu = 1,\ k = 0.05,\ \gamma_0 = 0.6,\ a = 0.5$, and $\sigma = 4$. In this model, the index of $L_\mathrm{td}(t)$ is $t^{1.0}$. In addition, the index of L_ee is 1.0 at small t and 0.5 at large t. This result was analytically derived in a similar model [18].

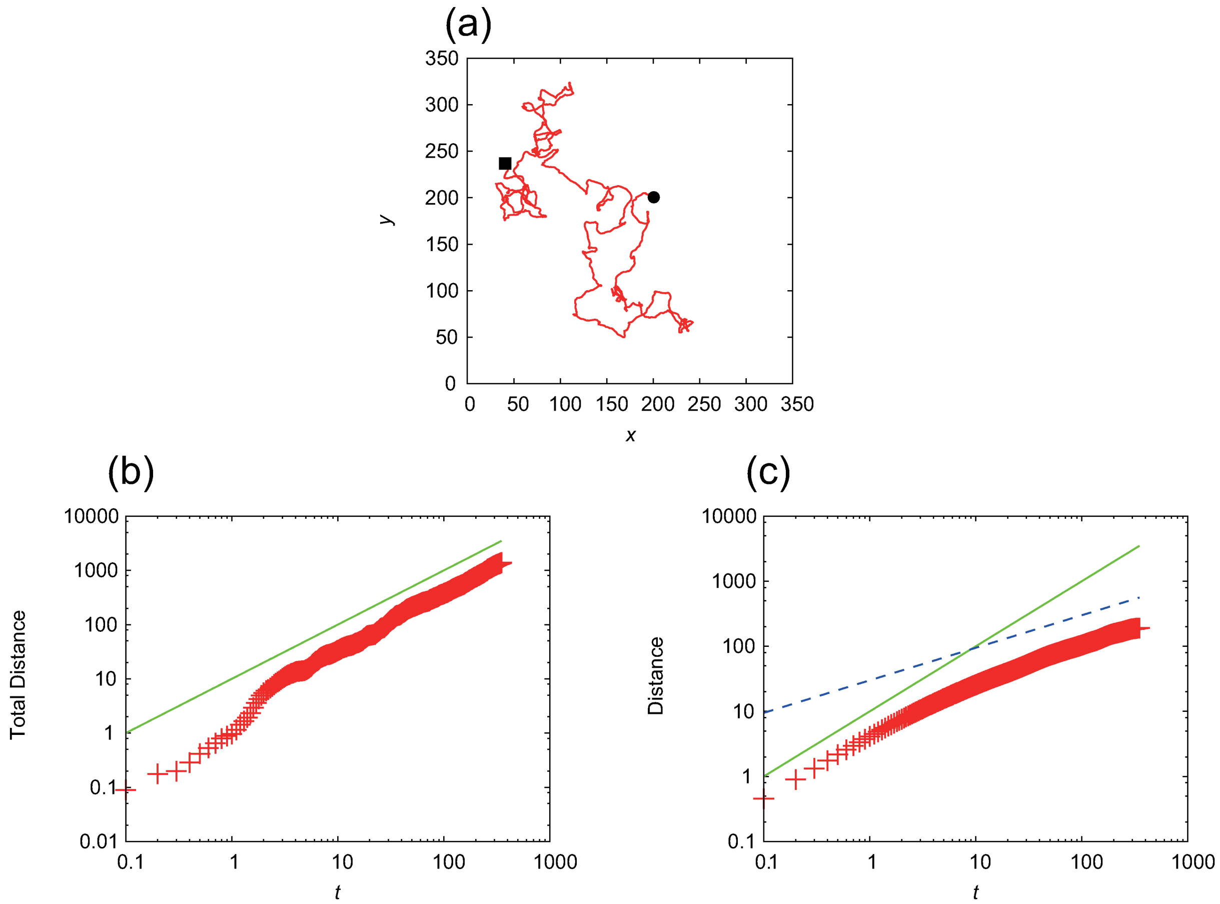

Figure 4. Computer simulation of the model for spontaneous motion of a pentanol droplet. (a) Trace of the center of gravity of the droplet. The initial posiotion is denoted with • and the final position is denoted with ■. (b) Time-dependence of $L_{\mathrm{td}}(t)$. The solid line represents $t^{1.0}$. (c) Time-dependence of $L_{\mathrm{ee}}(t)$. The solid line and the broken line represent $t^{1.0}$ and $t^{0.5}$, respectively.

§ 5. Conclusion

A pentanol droplet floating on water exhibits spontaneous motion. When the droplet is small (around 0.01 μl at room temperature with 2.35 vol% pentanol aqueous solution), this motion is irregular. A droplet moves with almost constant speed. The distance from the initial position is proportional to $t^{1.0}$ at small t, and proportional to $t^{0.5}$ at large t. Therefore, while the motion of a droplet is straight during a short time period, it shows a random walk overall. This time-dependence of motion can be reproduced with a model for spontaneous motion driven by interfacial tension which considers a droplet as a disk of surfactant.

§ 6. Acknowledgement

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