Article

Spiral Thermal Waves Generated by Self-Propelled Camphor Boats

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Abstract: Spiral thermal surface waves arising from self-propulsion of the camphor-driven objects are reported. Spiral thermal waves were registered for dissolution and evaporation-guided self-propulsion. Soluto-capillarity is accompanied by thermo-capillarity under self-propulsion of camphor boats. The jump in the surface tension due to the soluto-capillarity is much larger than that due to the thermo-capillarity. The spiral patterns inherent for the surface thermal waves are imposed by the self-rotational motion of camphor grains. The observed thermal effect is related to the adsorption of camphor molecules at the water/vapor interface. The observed spirals are shaped as Archimedean ones.

Keywords: self-propulsion; camphor grain; thermal waves; soluto-capillarity; thermo-capillarity

1. Introduction

The fascinating phenomenon of spiral waves was registered within various experimental contexts, including the formation of spiral galaxies [1], rotating liquids [2–4] and insect populations [5]. The particular case of spiral waves is thermal waves, in which spirals are formed with 2D thermal fields, inherent for example for the Belousov–Zhabotinsky reaction [6–9]. Recall that the Belousov–Zhabotinsky reaction represents the reaction–diffusion system, including bromine and an acid and giving rise to a nonlinear chemical oscillator, acting far from thermodynamic equilibrium and giving rise to fascinating spatial patterns, the focus of recent extensive research [6–9]. We demonstrate spiral thermal waves emerging from the self-propulsion of camphor boats, floating on water. The phenomenon of self-propulsion attracted much attention of investigators during the past decade [10–15]. Self-propulsion was successfully exploited recently for micro-robotics applications as well as for the generation of electrical power [16–18]. One of the most studied self-propelled objects is the so called “camphor boat” studied first by Lord Rayleigh [19]. The motion of camphor boats is usually related to the soluto-capillary interfacial (Marangoni) flows [12,13,20–23]. Camphor decreases the surface tension of water, and the boat is driven by differences in the surface tension around it [20,21]. Obviously, motion becomes possible due to the breaking of symmetry of the surface tension field surrounding the camphor boat [20–25]. The breaking of symmetry may arise from the non-uniform dissolution of camphor. We demonstrate that thermal Marangoni flows accompanying the self-propulsion of camphor boats may be non-negligible and also contribute to the self-propulsion. Moreover, the self-propulsion of camphor boats gives rise to the spiral thermal fields, resembling those inherent for the Belousov–Zhabotinsky reaction [6–9].

2. Results

The experimental system is shown schematically in Figure 1a,b. Generally self-propulsion of the camphor-driven objects is possible under two scenarios, namely under evaporation and dissolution of
camphor \cite{19-21,25}. Both of the regimes were studied experimentally. When the self-propulsion was guided by dissolution of camphor, the grains were placed directly on the water surfaces, as shown in Figure 1a. A special rotator, depicted in Figure 1b, was designed for the study of the evaporation-guided self-propulsion. Camphor was placed in the polymer tubing, with a diameter of 1 mm.

![Figure 1a](image1.png)  

*Figure 1a*: Sketch of the experimental unit used for the study of spiral thermal waves arising from the self-propulsion of camphor grains. The self-propulsion is guided by the dissolution of camphor.

![Figure 1b](image2.png)  

*Figure 1b*: A sketch of the special rotator enabling the study of the evaporation–guided self-propulsion is depicted. The polymer disk prevented direct contact of camphor with water.

Thermal imaging of the water/vapor interface registered spiral thermal waves such as those depicted in Figure 2a–c and presented in the Supplementary Movie S1. Spiral waves were observed in the circular and rectangular vessels. Clockwise and counter-clockwise rotation of water was observed within the spiral thermal waves generated by camphor grains and rotors driven by the evaporation of camphor. Evaporation-induced rotation may be controlled by the shape of polymer tubing. It should be emphasized that the spiral thermal waves emerged from both the dissolution- and evaporation-guided self-propulsion (see Supplementary Movies S1 and S2). The maximal thermal contrast observed in the course of the motion of grain and rotation of the rotor was $\Delta T \approx 0.2$ K. Thus, the soluto-capillary Marangoni flows are accompanied in the reported experimental situation with the thermo-capillary ones. Recall that the co-occurrence of the soluto- and thermo-capillary flows takes place even for the famous phenomenon of “wine tears” \cite{26}. Let us estimate the contributions of thermo- and soluto-capillarity to the effect of self-propulsion. The total change in the surface tension $\Delta \gamma(T, c)$ is expressed as follows:

$$
\Delta \gamma(T, c) = \Delta \gamma_1 + \Delta \gamma_2 = \left(\frac{\partial \gamma}{\partial c}\right)_T \Delta c + \left(\frac{\partial \gamma}{\partial T}\right)_c \Delta T,
$$

(1)
where $\Delta \gamma_1 = \left( \frac{\partial \gamma}{\partial c} \right)_T \Delta c$ represents the contribution of soluto-capillarity, whereas $\Delta \gamma_2 = \left( \frac{\partial \gamma}{\partial T} \right)_c \Delta T$ is the term due to the thermo-capillarity. The value of the $\Delta \gamma_1$ was established in Ref. [27] experimentally as $|\Delta \gamma_1| \approx 1.1 \times 10^{-3} \frac{J}{m^2}$. Assuming for the temperature gradient of the surface tension $\left| \left( \frac{\partial \gamma}{\partial T} \right)_c \right| \approx 17.7 \times 10^{-5} \frac{J}{K \cdot m^2}$ (see Ref. [28]) and $\Delta T \approx 0.2K$, we estimate $|\Delta \gamma_2| \approx 3.5 \times 10^{-5} \frac{J}{m^2}$. Thus, we conclude that the interrelation $|\Delta \gamma_1| \gg |\Delta \gamma_2|$ takes place and the motion of camphor boats is mainly due to the soluto-capillarity. However, the thermal effect may be of primary importance for the understanding of the self-propulsion, when the strong exponential dependency of water viscosity is considered [28]. Thus, thermal waves play an essential role in the breaking of the symmetry, resulting in the motion of the camphor boat [23].

![Figure 2](image-url)

**Figure 2.** (a) The sequence of thermal images representing spiral thermal surface waves, generated under the dissolution-guided self-propulsion of camphor grains. Thermographic images were taken in the course of motion of the camphor grain. Brighter pixels correspond to the higher temperatures. (b) The sequence of thermal images representing spiral thermal waves in the stationary regime, generated under the evaporation-guided self-propulsion of the rotor, shown in Figure 1b. Degrees illustrate the rotation of the polymer tubing filled with camphor. Thermographic images were taken in the course of the rotation. Brighter pixels correspond to the higher temperatures. (c) Thermal images illustrating the stationary regime of rotation of the camphor sample are shown. Degrees illustrate the rotation of the camphor grain. The spiral thermal surface wave is clearly seen.
3. Discussion

The thermal spirals evolved towards the walls of vessels during ca 0.5–1 s and afterwards remained stable (in other words, stationary, see for example Figure 2b,c) during ca 10 s. The radial temporal displacement of the labeled water particle, located at the water/vapor surface, is shown in Figure 3 (for the details, see Section 4). It is recognized from Figure 3, that at the initial stage of propagation, taking place ca 0.4 s, the radial displacement of the marker occurs with the constant velocity \( v = \frac{dr}{dt} = \text{const} \approx 7.5 \times 10^{-4} \text{ cm/s} \). This means that, at this stage, the spiral is an Archimedean one, described in the polar coordinates \( (r, \theta) \) by the equation:

\[
 r(t) = \frac{\pi}{\omega} \theta(t) + c = \frac{\lambda}{2\pi} \theta(t) + c; \quad \omega = \text{const}; \quad c = \text{const},
\]

where \( \lambda \) is the wavelength of the Archimedean spiral and \( c \) denotes the initial radial location of the camphor grain. Actually, \( \omega = 10.8 \pm 0.5 \text{ rad/s} \) and \( \lambda \approx \frac{2\pi}{\omega} \approx 4.4 \pm 0.2 \text{ cm} \) were registered. It should be emphasized that the angular frequency \( \omega \) coincides with the frequency of self-rotation of the camphor grain.

![Figure 3. The temporal dependence of the radial displacement of the marker taken in the course of the spiral wave propagation is depicted.](image)

It was demonstrated that the eventual Archimedean geometry of the spiral appearing under the Belousov–Zhabotinsky reactions may be independent of their chemical kinetic basis and arises from the symmetry considerations [29]. It was demonstrated in the seminal paper by Alan Turing that formation of spiral patterns in initially homogeneous reaction–diffusion systems, such as Belousov–Zhabotinsky reactions, becomes possible due to the spontaneous breaking of symmetry [30]. Contrastingly, in our experiments, the spiral geometry is imposed by the self-rotational motion of the camphor grain. This conclusion is supported by the fact that the angular frequency \( \omega \) appearing in Equation (2) coincides with that of the self-rotation of the camphor grain.

We are far from an exhaustive, quantitative explanation of the observed spiral, thermal waves. However, qualitative arguments will be useful for understanding of the phenomenon. What is the physico-chemical source of the observed thermal waves? One of these sources is enthalpy of the chemical reaction of dissolution of camphor by water. However, thermal waves were observed in the situation when the disc-like rotator, shown in Figure 1b, blocked the dissolution of camphor in water. Thus, it is plausible to relate the formation of the thermal waves to formation of the adsorbed layer of camphor molecules surrounding the self-propelled object. The suggested mechanism implies transport of the camphor molecules from the vapor phase to the water/vapor interface, followed by the heat release. The spatially-temporal periodic nature of formation of this layer was discussed in Ref. [31]. The enthalpy of periodic adsorption, in turn, (consider that adsorption is always exothermic)
may give rise to the reported thermal waves. The role of the adsorption of the volatile elements (which is camphor in our case) in the evolution of Marangoni flows was discussed in Ref. [32]. It is reasonable to relate the formation of steady spiral thermal patterns observed under the velocities of the self-propulsion $v \approx 2.0 \text{ cm s}^{-1}$, which are much smaller than the threshold one $v_{\text{min}} = 4 \sqrt{4g\gamma/\rho} \approx 23 \text{ cm s}^{-1}$ (where $\rho$ is the water density), necessary for formation of steady capillary–gravity waves under straight uniform self-propulsion [34–37]. This effect was explained in Ref. [34], in which it was demonstrated that no velocity threshold exists for the steady spiral wave patterns, appearing under the circular motion of the self-propelled bodies, explored in our experiments.

Let us estimate the dimensionless numbers, governing the evolving of spiral thermal waves, which are the Reynolds (Re) and Prandtl (Pr) numbers:

$$Re = \frac{\rho v L}{\eta}; Pr = \frac{c_p \eta}{\kappa},$$

where $\eta$, $c_p$, and $\kappa$ are viscosity, specific heat and thermal conductivity of water at the conditions of the experiment, respectively, $v$ and $L$ are the characteristic velocity and dimension correspondingly [12,13]. Assuming $\rho = 10^3 \text{ kg m}^{-3}; \eta \approx 9 \times 10^{-4} \text{ Pa s}; c_p \approx 4.2 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}; \kappa \approx 0.6 \text{ W m}^{-1} \text{ K}^{-1}; L \approx 10^{-3} - 10^{-2} \text{ m}$ and $v \approx 10^{-2} - 10^{-1} \text{ m s}^{-1}$, we estimate $Re \approx 10^1 - 10^2$ and $Pr \approx 6.3$. This means that the propagation of spiral waves occurs within the laminar regime; however, both momentum and heat dissipate through the fluid at the about the same rate under the evolving of the spiral thermal waves. The last consideration makes the exact quantitative analysis of the phenomenon extremely challenging.

4. Materials and Methods

Vessels of various shapes were used for the study of the self-propulsion: Petri dishes (Corning Crystal Polystyrene) with the diameters of 140 mm and 85 mm, square polystyrene vessels with dimensions of $210 \times 210 \text{ mm}$ and $110 \times 180 \text{ mm}$. The de-ionized water, used as supporting liquid, was purified by a synergy UV water purification system from Millipore SAS (Molsheim, France) and its specific resistivity was $\hat{\rho} = 18.2 \text{ M\Omega cm}$ at $25^\circ\text{C}$. The vessels were filled with de-ionized water; the height of the supporting liquid $h_l$ was $7 \pm 1 \text{ mm}$. Camphor grains with dimensions of $(4 \pm 1) \times (4 \pm 1) \times (6 \pm 2) \text{ mm}$ were prepared from Camphor (96%), supplied by Sigma-Aldrich (St. Louis, MO, USA). The temperature of water varied within the range of $25$–$35^\circ\text{C}$. All the experiments were performed under atmospheric pressure.

The self-propelled motion of camphor grains and propagation of spiral thermal waves was visualized with the Therm-App TAS19AQ-1000-HZ thermal camera. The resolution was: $384 \times 288$ pixels ($\approx 110.000$ pixels); the LWIR (longwave infrared) measurements were carried out at the wavelength of $7.5$–$14 \mu\text{m}$, the accuracy of the thermal camera was: NEDT (noise equivalent differential temperature) $< 0.07^\circ\text{C}$, and the frame rate was $26$ frames/s.

Quantitative treatment of the thermal movies was carried out as follows: a straight line was built along the camphor boat, and the location of crests of thermal waves located on this straight line were fixed. The location of the first crest of the thermal wave was called the “marker”, which was used for the calculation of the radial velocity $v$ appearing in Equation (2).

5. Conclusions

To conclude, we report the fascinating phenomenon of propagation of spiral thermal waves emerging from the motion of camphor-driven floating self-propelled objects. The soluto-capillarity mainly guides the self-propulsion. Thermo-capillarity, in turn, gives rise to propagation of the spiral
Archimedean thermal waves, resembling those observed under Belousov–Zhabotinsky reaction [6–9]. It is reasonable to suggest that the spiral geometry of the observed thermal waves is imposed by the self-rotational motion of the camphor grain, and this is in contrast to the spiral patterns inherent for reaction–diffusion systems, in which spiral patterns emerge under the spontaneous breaking of the symmetry of the system [30]. We relate the observed thermal effect to the adsorption of camphor molecules at the water/vapor interface [31,32]. It seems reasonable to assume that spiral thermal surface waves reflect the quasi-periodic distribution of camphor at the water/vapor interface [31]. The reported effect is important for understanding of the self-propulsion of floating bodies, exploited recently for micro-robotics and micro-fluidics applications and also for the ecologically friendly generation of electrical energy [16–18,38,39].

Supplementary Materials: The following are available online at http://www.mdpi.com/2410-3896/5/3/51/s1, Supplementary Movie S1: Spiral thermal waves arising from the self-propulsion of camphor grain; Supplementary Movie S2: Spiral thermal waves arising from the self-propulsion of camphor filled rotator.

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Abbreviations

| Abbreviation | Definition                      |
|--------------|---------------------------------|
| 2D           | two-dimensional                 |
| ca           | Circa (approximately)          |
| Re           | Reynolds number                 |
| Pr           | Prandtl number                  |

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