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Dynamics of a camphoric acid boat at the air–water interface

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ABSTRACT

We report experiments on an agarose gel tablet loaded with camphoric acid (c-boat) spontaneously set into motion by surface tension gradients on the water surface. We observe three distinct modes of c-boat motion: harmonic mode where the c-boat speed oscillates sinusoidally in time, a steady mode where the c-boat maintains constant speed, and an intermittent mode where the c-boat maintains near-zero speed between sudden jumps in speed. Whereas all three modes have been separately reported before in different systems, controlled release of Camphoric Acid (CA) from the agarose gel matrix allowed the observation of all the three modes in the same system. These three modes are a result of a competition between the driving (surface tension gradients) and drag forces acting on the c-boat. Moreover we suggest that there exist two time scales corresponding to spreading of CA and boat motion and the mismatch of these two time scales give rise to the three modes in boat motion. We reproduced all the modes of motion by varying the air–water interfacial tension using Sodium Dodecyl Sulfate (SDS).

1. Introduction

The self-motion is an essential part of biological life. In the animal kingdom, usually the chemical energy is converted into mechanical energy by various mechanisms. However, in the inanimate world, electrical or magnetic energy is converted into mechanical energy to drive the motion. In both the animate and inanimate worlds, a common mechanism for the self-motion is *via* the imbalance of surface tension known as *Marangoni propulsion*. These forces can be classified as solutal or thermal when a solute or temperature, respectively, modifies the surface tension. Tears-of-wine [1,2] is a classical example of solutal (or agent induced) Marangoni effect. Thermal Marangoni effects [3] are a commonly encountered phenomenon in welding industry.

The scientific interest in the motion of objects governed by the surface tension gradients started in 1686 with the first reported observations by Heyde [4]. Later, Alessandro Volta [5], Giovanni Battista Venturi [6], Biot [7] and Lord Rayleigh [8], among others, studied the motion of objects on the surface of water. However, Van der Mensbrugghe [9] first explained that the motion is due to the modification of surface tension of water by the object. For a historical introduction up until 1869 please see Charles Tomlinson's excellent review [10]. Since then many researchers have been studying motion of objects driven by the surface tension gradients. These studies are at Reynolds numbers spanning over 4–5 orders of magnitude ($\sim 10^{-3}$–10^2). Few examples are: motion of liquid droplets on a solid surface with surface energy gradient [11], motion of ethanol driven gel tablets on the air–water interface [12], propulsion of Belousov–Zhabotinsky drops in fluorinated oil [13], motion of camphor boats at the air–water interface [14], motion of solid/liquid composites on water [15]. Recently, Nagayama et al. [16] developed a simple mathematical model for self-propulsion driven by surface tension gradients. These systems continue to attract much attention due to the simplicity and robustness in preparation. Despite the rich history, the self-propelled particles/drops continue to remain relevant in modern times, be it in statistical mechanics within the context of active matter [17], hydrodynamic context of viscous Marangoni propulsion [18], biological context of chemo-mechanical transduction [19], autonomous motion and self-assembly [20], and reconfigurable actuators in soft matter physics [21], among others. More recently, Liang Hu et al. [22] successfully mimicked the motion of an amoeba-like motion by altering the surface properties of the liquid metal alloy.

In this article, we present an experimental study of the self-motion of agarose gel tablets loaded with camphoric acid (CA) at the air–water interface, henceforth referred to as c-boats. We identify three distinct modes of motion, namely a harmonic mode

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where the c-boat speed undergoes time-varying sinusoidal oscillations, a steady mode of constant c-boat motion, and an intermittent mode where the c-boat remains at rest between sudden jumps in speed and position at nearly regular time intervals. Whereas all three modes have been separately reported in the published record [23–25,12] in a variety of systems, we show these seemingly different self-propulsive modes arise from a common description. The camphoric acid boat system had been extensively studied by Nakata et al. [26,27] however control release of camphoric acid from the agarose gel matrix enabled us to observe all the three modes of oscillation in the same system. Through metered dosage of Sodium Dodecyl Sulfate (SDS) to control the air–water surface tension, we experimentally trace the origin of self-propulsive mode selection to CA–water surface tension difference.

2. Experimental methods

We constructed the camphoric acid boats (c-boats) by infusing camphoric acid in agarose gel tablets similar in spirit to the procedure of Soh et al. [28], thus keeping tablet structurally intact for the entire duration of the experiment. An important consequence of structural intactness is that the shape effects on drag are constant during the course of an experiment. Hot agarose solution (5% weight-to-volume) in de-ionized (DI) water (Milli-Q Integral Water Purification System with resistivity, $\rho = 18.2$ MΩ·cm at 25 °C) was placed between two clean glass plates, set 10^{-3} m apart with aluminum spacers, to obtain gel sheets of uniform 10^{-3} m thickness, upon cooling. Gel tablets of 3×10^{-3} m diameter were punched out from the sheet (Biopunch, Ted Pella Inc.). These gel tablets were introduced in a saturated solution of camphoric acid (CA) (Wako Pure Chemical Industries, Ltd., Cat. No. 036-01002) in methanol and left for 2 hours for CA to diffuse into the gel tablets. Prior to experiments, gel tablets were rinsed in DI water to precipitate CA in the gel matrix.

Fig. 1a shows a schematic of the experimental setup. All experiments were performed in a glass petri dish (0.25 m in diameter) filled with de-ionized water to a height of 0.04 m. A c-boat was gently introduced at the air–water interface and its self-motion was recorded with a Nikon D800E camera at 30 frames per second. The petri dish was placed atop a uniform back-lit LED illumination source operating with direct current to avoid alternating current flicker interference in image processing. The c-boat appears as a dark disk moving against a bright background in the current imaging technique as shown in Fig. 1b. The experimental images were post-processed with image analysis algorithms written in-house to obtain the c-boat position and velocity as a function of time. The c-boat position and velocity information employed in the analysis was confined to a region 0.036 m away from the walls to exclude boundary effects. The portion of c-boat trajectory (red in Fig. 1b) lying outside the dashed white circle in Fig. 1b at a distance of 0.036 m from petri dish wall were excluded from the analysis. This 0.036 m exclusion distance was empirically determined from the longest radial distance over which Marangoni spreading of camphoric acid was prominent. Only blue sections of the c-boat trajectory within the inner circle bounded by white dashed line in Fig. 1b were used in all the analysis to follow. As mentioned earlier, a c-boat is driven by the surface tension gradients and to independently verify the role of surface tension on the three modes of c-boat motion, we varied the surface tension of the ambient interface by introducing metered dosage of Sodium Dodecyl Sulfate (SDS) (Wako Pure Chemical Industries, Ltd., Cat. No. 196-08675) following published tables [29]. Actual surface tension values were also independently confirmed with the pendant drop method on a tensiometer (OneAttension Theta tensiometer) at 25 °C.

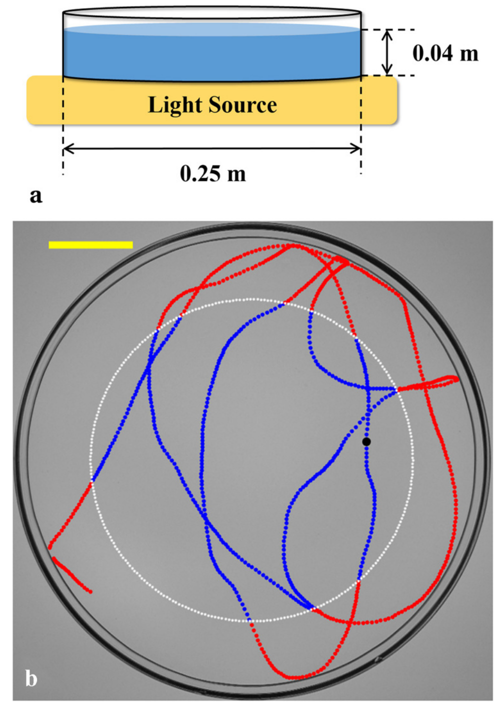

Fig. 1. (a) Experimental setup (side view): Glass petri dish (0.25 m diameter) filled with deionized water to 0.04 m height was placed on a light tablet. A camera recorded c-boat self-motion from above yielding images as shown in (b) where the c-boat appears as a dark disk in gray background. Only trajectories (blue) in a 0.178 m diameter circular region within the dashed white circle were analyzed and the rest (red) discarded to exclude boundary effects from petri dish wall. Scale bar = 0.03 m. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

3. Results & discussion

Camphoric acid is a white crystalline organic compound and mildly soluble in water. When dissolved to the solubility limit ($\sim 8 \times 10^{-3}$ kg·l^{-1}), the surface tension of CA + Water solution is $\sim$60 mN·m^{-1}. Soon after placing a c-boat on surface of water, there exists a thin annular region, immediately next to the boundary of the c-boat, where CA is adsorbed/dissolved and beyond the region the concentration of CA is zero. The surface tension is low in the annular region and is equal to the ambient surface tension ($\gamma = 72 \times 10^{-3}$ N·m^{-1}) outside. This results in sharp gradient/shock in surface tension which relaxes by spreading CA onto the surface (see movie *S1.avi* in supplementary info). This relaxation process gives rise to a time scale τ_1, which will be discussed later. However, the spreading cannot continue indefinitely due to the dissolution of CA in water. On a side note, the CA spread radius scales with time as $t^{1/2}$ (Fig. 2b). This is an experimentally well established [30] scaling for volatile oils spreading on water surface. Therefore, one can conclude that the scaling is identical when either evaporation/dissolution or both result in loss of material from the surface.

In the steady state, CA radially spreads to a finite distance R beyond which CA concentration is nearly zero and axially symmetric CA concentration gradients (and hence surface tension gradients) are set up around the c-boat. By virtue of the symmetric surface tension gradients there is *no* driving force on the boat but steady state Marangoni flows are generated in the underlying fluid. Ambient fluctuations spontaneously break this symmetry and sharpen the gradients along a preferential direction; as a consequence a net force acts on the c-boat and propels it (see *S2.avi* in the supplementary info). The c-boat motion enhances the asymmetry and the boat accelerates until (1) c-boat escapes to a CA free region