Dynamics of a Camphoric Acid boat at the air-water interface

V. S. Akella,† D. K. Singh,† R. K. Singh,‡ S. Mandre,*,‡ and M. M. Bandi*,†

†*Collective Interactions Unit, OIST Graduate University, Okinawa, Japan 904-0495*
‡*School of Engineering, Brown University, 182 Hope Street, Providence, RI 02906, USA*

E-mail: shreyas_mandre@brown.edu; bandi@oist.jp

Abstract

TBD

1 Introduction

TBD

2 Experiment

The experiments were performed in a glass petri dish (25 cm in diameter) filled with de-ionized water to a height of 4 cm. A camphoric acid tablet (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 backlit illumination where the c-boat appears as a dark disk moving in a bright background. 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 3.6 cm away from the walls to exclude boundary effects. The 3.6 cm exclusion distance was empirically determined from the longest radial distance over which marangoni spreading of camphoric acid was prominent (see section results and discussion).

The shape and size of a chemical-laden tablet, e.g. a camphoric acid tablet, changes over the duration of the experiment as the substance undergoes dissolution or sublimation into the surrounding fluids. To decouple the shape from the chemical composition, the cboats were constructed by infusing camphoric acid in agarose gel tablets. Hot agarose solution (5% weight-to-volume) in de-ionized (DI) water (Milli-Q Integral Water Purification System with resistivity, $\rho = 18.2$ M$\Omega \cdot$cm at 25°C) was placed between two glass plates, set 1 mm apart with aluminum spacers, to obtain gel sheets of uniform thickness 1 mm, upon cooling. Gel tablets of 3 mm diameter were punched out from the sheet (using a 3 mm diameter 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.

The c-boat motion being governed by Marangoni force, surface tension difference between the ambient surface and CA entering the surface forms the primary parameter for this study. Since the c-boat holds a finite quantity of CA, its concentration monotonically decreases with time, thereby continually reducing the strength of the marangoni effect (see section results and discussion). Independent experiments modifying the ambient surface tension confirmed the role of surface tension difference as the primary parameter. 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) from known published tables.[1] Actual surface tension values were also independently confirmed with the pendant drop method on a tensiometer (OneAttension Theta tensiometer) at 25 °C.

A moving c-boat leaves camphoric acid in it's wake which can be qualitatively visualised via the distribution pattern of passive tracer particles decorating the surface. Hollow silica glass spheres (specific gravity 0.25 and 50 ± 10 μm diameter) sprinkled onto the air-water interface were used to follow the well defined comet-shaped particle-free region in the wake of a c-boat. The shape of this region provides a qualitative measure of the strength of marangoni force acting on the c-boat (see supplementary information).

3 Results and Discussion

When a c-boat is placed at the air-water interface, CA spreads radially and sets up axisymmetric interfacial tension gradients around the c-boat. Ambient fluctuations spontaneously break this symmetry and sharpen the gradients along a preferential direction; as a consequence a net force acts on the cboat and propels it. The boat's motion amplifies the asymmetry and maintains it, thereby permitting it's continued motion. Owing to constant dissolution of CA from the interface into the bulk fluid, the cboat motion continues until it exhausts all CA molecules. Whereas dissolution does globally reduce the surface tension of water, a single boat never contains sufficient CA (~ 7 mg) to achieve this; surface tension of CA saturated water (~ 8 g l^{-1}) is ~ 60 dy cm^{-1}. Over the course of an experiment, water replaces CA removed from the boat starting at the periphery and progressively proceeds radially inwards. Consequently, CA concentration at the cboat edge constantly decreases resulting in weaker interfacial tension gradients which decrease the boat speed as time progresses (figure **??**); this bears upon results to be discussed shortly. **If the 3 hour data to be plotted in fig2 does follow an exponential decay, we add a statement to the effect that, this behavior suggests that the instantaneous CA flux is proportional to CA concentration in the cboat at that instant.**

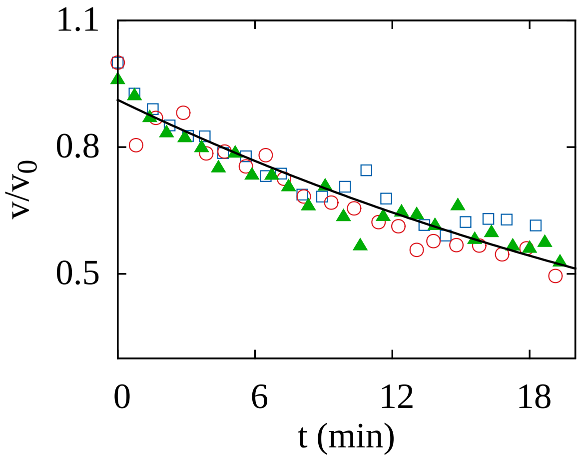

Figure 1: Normalized Cboat speed vs. time, fit to $e^{-\frac{t}{\tau}}$ where τ represents the life time of a cboat. Symbols correspond to different experimental trials.

With decreasing marangoni force strength in time, the c-boat exhibits three distinct modes of motion over 1-10 s timescales. Figure **??** also shows time traces of c-boat speed at specific intervals corresponding to these three modes. At early times and high surface tension difference, the c-boat speed exhibits harmonic oscillations about the mean (see fig. **??**b). This mean speed and oscillation amplitude continuously decrease with time **Sathish to confirm, else remove** and transition to the second distinct mode where the c-boat moves with steady speed (see fig. **??**c). The third distinct mode of relaxation oscillations emerges at long times and low surface tension differences where c-boat motion occurs in periodic bursts interspersed with durations where no c-boat motion occurs (see fig. **??**d).

We analysed the amplitude and frequency dependence of the c-boat speed oscillations with time to characterise the behavior within, and the transition between, the individual modes of motion. The amplitude, defined as the difference between the maximum and minimum

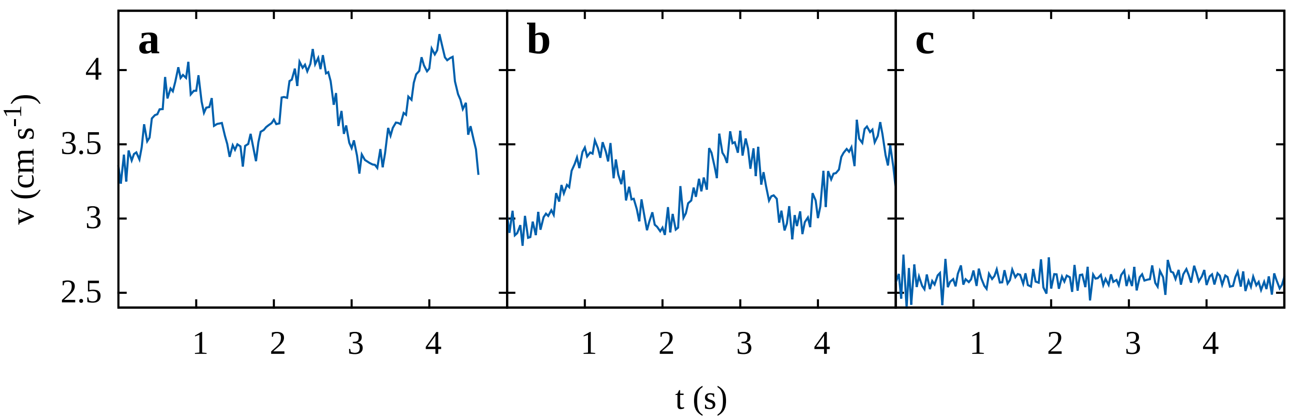

Figure 2: **(a)** at ~ 4 min, **(b)** at ~ 7 min, **(c)** at ~ 16 min

speed within an oscillation, is plotted in fig. **??**a as a function of time, and the corresponding oscillation frequency is shown in fig. **??**b. The oscillation amplitude in the harmonic regime continuously decreases with time. The instance when the amplitude becomes zero marks the transition to steady motion **(Sathish, approx. and exactly what time?)**. Under the regime of steady motion, the amplitude of oscillations is zero, and the frequency is undefined. At a later time **(Sathish, approx. and exactly what time?)**, the amplitude and the frequency jump to finite values, as the behavior of the cboat transitions to that of relaxation oscillations. The frequency of oscillation after this transition is finite, and continuously decreases with time, whereas the amplitude increases (does it? ... confirm). Knowing that the Marangoni force strength monotonically decreases with time, the observation that the transitions between the different modes occur at finite times indicates that they occur at a critical value of Marangoni force strength.

The continuity of the Marangoni force strength with time can be confirmed via visualization of the comet trail left behind the cboat. In particular, the comet trail provides a visualization of the asymmetry in the CA distribution around the cboat. The shape and size of the comet trail is, therefore, indicative of the nature of underlying dynamics, and any abrupt changes would be made visible by the comet trail. Direct visualization of the comet trail for the three modes of cboat motion is shown in fig. **??**e-g. The reducing size of the comet trail implies a decrease in the strength of the net Marangoni force propelling the cboat. **What the hell do we see in the comet trail dynamics?**

To further verify that the Marangoni force strength is indeed the parameter governing these transitions, we independently change the ambient surface tension. By introducing different amounts of SDS in the petri dish, the surface tension was reduced from 72 dy/cm (pure water) down to 59 dy/cm. The motion of freshly prepared cboats was observed a fixed duration (XX mins) after beginning the experiment, to control for the effects of CA depletion. The cboat in the presence of SDS exhibited the three modes of motion in the same order as the ambient surface tension is continuously decreased. As the time traces of cboat speed in figure 4 show, the cboat motion shows harmonic oscillations for ambient surface tension value of 72 dy/cm, steady motion for XX dy/cm, and relaxation oscillations for 65 dy/cm. The comet tail structure also shows features similar to the those observed when the transitions were a result of CA depletion from the cboat. While introduction of SDS may change the Marangoni forces on the interface, our observations suggest that the qualitative behavior of the cboat motion is preserved under these dynamics.

However, we varied ξ by modifying the air-water interfacial tension using SDS. Figure **??** shows the speed traces of a cboat at different intervals of time when the air-water interfacial tension is lowered to 65 $\mathrm{dy} \cdot \mathrm{cm}^{-1}$. We observe that, the average speed of the cboat at different intervals decreases and the period of the oscillations increases. Another subtle observation is the distance travelled by the cboat, area under the speed vs. time curves, between oscillations is approximately equals to the distance, R out to which CA molecules are spread by the Marangoni flow and beyond R, CA concentration is zero due to dissolution. During the course of experiment R constantly decreases due to dissolution of CA in water.

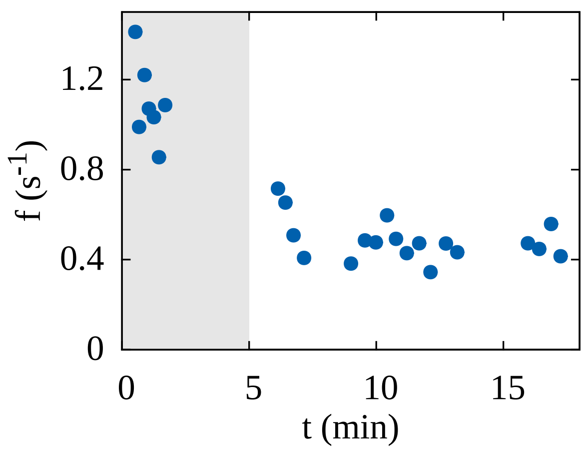

Figure 3: Frequency of oscillation vs. time. Grayed out area is the transient phase during which excess CA present on the surface of the cboat.

4 Summary

TBD

Acknowledgement VSA, DKS, and MMB were supported by the Collective Interactions Unit at the Okinawa Institute of Science and Technology. MMB acknowledges L. Mahadevan for introducing the camphor boat system and subsequent scientific discussions, and D. Vu Anh for help with preliminary experiments. VSA would like to thank Pinaki Chakraborty for discussions. The authors acknowledge Kenneth J. Meacham III for help with experiments.

References

(1) Mysels, K. J. *Langmuir* **1986**, *2*, 423–428.

(2) Dussaud, A. D.; Troian, S. M. *Physics of Fluids* **1998**, *10*, 23–38.

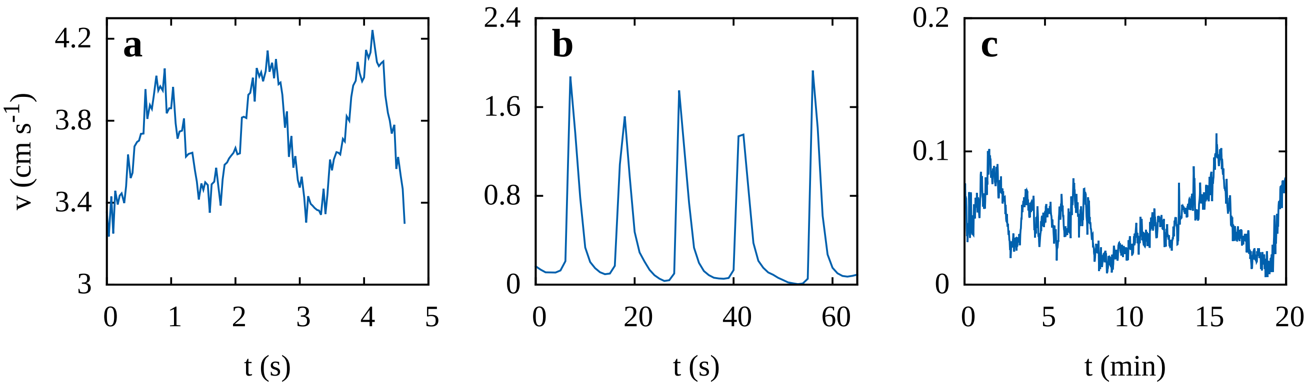

Figure 4: **(a)** at $\sigma = 72$ dy cm^{-1}, **(b)** at $\sigma = 65$ dy cm^{-1}, **(c)** at $\sigma = 59$ dy cm^{-1}