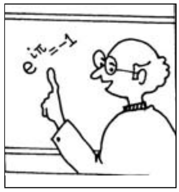

In this section of *Resonance*, we invite readers to pose questions likely to be raised in a classroom situation. We may suggest strategies for dealing with them, or invite responses, or both. "Classroom" is equally a forum for raising broader issues and sharing personal experiences and viewpoints on matters related to teaching and learning science.

The Inveterate Tinkerer
11. Marangoni Effect

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In this series of articles, the authors discuss various phenomena in fluid dynamics, which may be investigated via tabletop experiments using low-cost or home-made instruments. The eleventh article in this series demonstrates the Marangoni effect.

Procedure

The surface tension coefficient γ of a liquid is defined in terms of the increase in the Helmholtz free energy that accompanies an increase in the surface area of the liquid, at constant temperature and volume. The free energy at constant temperature and volume is minimised at thermodynamic equilibrium. Therefore, liquids in thermodynamic equilibrium adjust their shape to expose the smallest possible surface area. Further discussion of the concept of surface tension may be found in [1], and the reader may view the video cited in [2].

The *Marangoni effect* pertains to flows driven by surface tension gradients. Gradients of surface tension arise due to gradients in temperature or surfactant concentration on the interface between two fluids. A differential tangential (surface) stress (see [3] for a detailed theoretical discussion) causes motion of the liquids away from regions of low surface tension to regions of higher surface tension, and is retarded by viscous stresses. For nearly all liquids

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Marangoni effect, surface tension, surfactant.

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in thermodynamic equilibrium with their vapour, γ decreases with increase of temperature upto a critical temperature at which the distinction between the liquid and the vapour phase vanishes. For most common surfactants, γ is a monotonically decreasing function of the surfactant concentration until a critical concentration is achieved, beyond which it is a constant. Marangoni flows due to temperature gradients are characterized by the value of a dimensionless quantity called the Marangoni number (Ma), which is a ratio of surface tension force due to a temperature gradient and a viscous force:

$$Ma \equiv -\frac{d\gamma}{dT}\frac{L\Delta T}{\mu\kappa}.$$

Here L is a characteristic length scale across a temperature difference ΔT, μ is the dynamic viscosity, and κ is the thermal diffusivity.

A startling demonstration of the Marangoni effect may be shown by sprinkling finely ground pepper on a shallow layer of distilled water in a clean petri dish placed on a sheet of paper. If a drop of dilute aqueous soap solution (γ typically equals 25 mN/m at room temperature) is deposited at the centre of the water layer (γ equals 72 mN/m at room temperature) using a syringe needle, a gradient of surface tension is induced with the surface tension coefficient decreasing from the centre to the rim of the petri dish. The drop spreads radially outwards as a thin layer on the surface of water and the pepper powder acts as a tracer which is transported along to the rim. See the video: `youtube.com/watch?v=4dVHf7IVloI`

Another well-known demonstration of the Marangoni effect may be performed by cutting an arrow-shaped piece from a nitrile rubber glove and floating it on the surface of distilled water in a clean petri dish. If a small piece of camphor is deposited in the stern of the 'boat' using forceps, the boat is propelled forwards due to a locally reduced surface tension. The camphor dissolves in water causing differential tangential stresses at the fore and the aft of the boat. If small pieces of camphor are then sprinkled on the surface of the water, the boat stops moving and the pieces of camphor dart about vigorously in a random fashion due to nonuniform dissolution in water, see the video: youtube.com/watch?v=spDNbEaG_RM

1. Marangoni Flows Due to a Temperature Gradient

We poured a shallow layer of silicone oil (Loba Chemie, India) into a clean petri dish placed on a black paper, and sprinkled Fuller's Earth powder (Loba Chemie, India) on the surface. When a hot soldering iron is brought close to the surface, the increase of temperature near the tip of the iron reduces the surface tension coefficient of the oil. The consequent gradient in tangential stress causes the powder particles to move radially outwards near the tip, see the video: youtube.com/watch?v=z1lXpQlWAL4

Another demonstration of Marangoni flow may be carried out by pouring a shallow layer of liquid paraffin (CAS: 8012-95-1, Loba Chemie, India) into a clean petri dish placed on a black paper, and sprinkling lycopodium power on the surface. A small ice cube is dropped into the paraffin layer, which submerges just below the surface. The paraffin layer near the ice has higher surface tension due to lowered temperature, which pulls the surrounding lycopodium particles inwards. Note that the density of liquid paraffin is lower than that of ice, therefore the observed motion of lycopodium particles is primarily due to a temperature gradient at the surface, and not due to curvature of the meniscus alone, see the video: youtube.com/watch?v=mgxxoZKO0VQ

2. Tears of Wine

The shadow on the wall when an aqueous ethanol solution is swirled in a glass beaker, and illuminated exhibits 'tears of wine', which are essentially Marangoni flows.

Aqueous ethanol solution (20% by volume) was swirled in a glass beaker, and illuminated using the torch of a cellphone in a darkened room. The shadow on the wall exhibits 'tears of wine' [4], which are essentially Marangoni flows. Upon swirling the alcohol solution, a thin film coats the wall of the beaker. Alcohol concentration is reduced due to evaporation in the thin film, relative to the bulk. The surface tension coefficient of the solution decreases with increase of alcohol concentration, hence its mag-

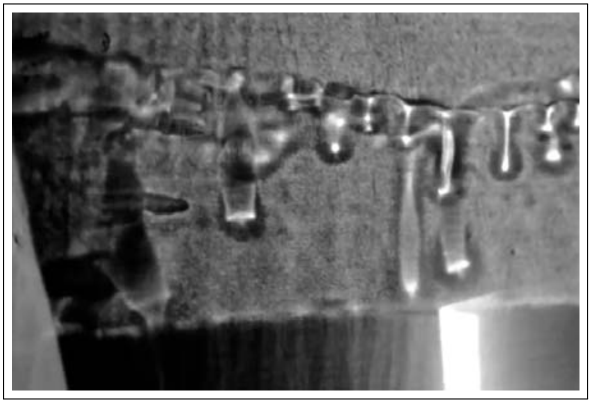


Figure 1. The 'tears of wine' phenomenon as seen in a shadowgraph.

nitude is higher in the thin film, which drives Marangoni flows upwards from the bulk. The upward flowing liquid accumulates in a band at the top, eventually flowing down after thickening to a point where it becomes gravitationally unstable, appearing as 'tears of wine'. See *Figure* 1 and the video: `youtube.com/watch?v=VU_ymXxzKIM`

3. Marangoni Bursting of Oil-isopropanol Droplet in Water

A mixture of oleic acid and isopropanol with a few drops of black Camlin ink was prepared. The ink forms a suspension of fine black particles. When a drop of this mixture falls on a shallow layer of water in a clean petri dish placed on a light box (Artograph LightPad), remarkably beautiful patterns are observed (see *Figure* 2) as the isopropanol layer spreads radially outwards and evaporates on the surface of the water transporting along the ink particles. See the video taken with a high-speed camera (Phantom M110) and macro lens: `youtube.com/watch?v=eIMGqOhWxaQ`

4. Marangoni Bursting of Water-isopropanol Droplet in Oil

A mixture of isopropanol in water (70% by volume) with methylene blue was prepared. A few drops of this liquid were poured using an ink dropper on the surface of a shallow layer of sunflower oil in a clean petri dish placed on white paper. The drop

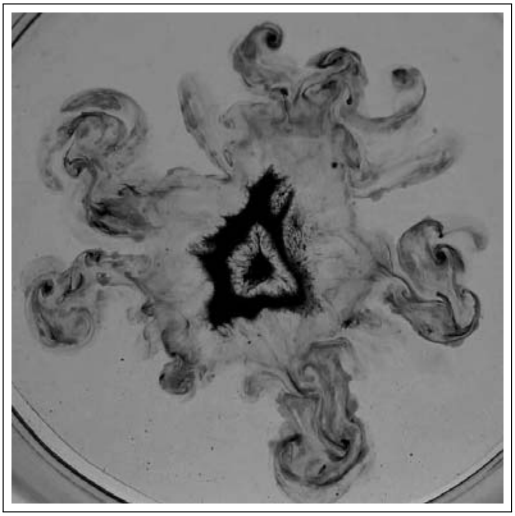


Figure 2. Pattern formed by a drop of isopropanol-oleic acid mixture (with dye) spreading on a pool of water.

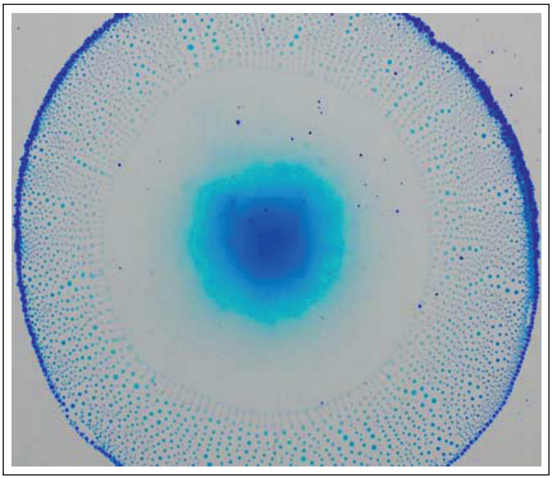


Figure 3. Pattern formed by drops of aqueous isopropanol (with dye) spreading on a pool of sunflower oil.

spreads radially and spontaneously fragments into a myriad of minute droplets (see *Figure* 3) as the alcohol evaporates. See [5] for a detailed theoretical discussion and the video:
`youtube.com/watch?v=58DaAntkvwQ`

5. Benard–Marangoni Instability

The Benard–Marangoni instability concerns a thin, horizontal layer of uniform thickness of a homogeneous, incompressible, New-

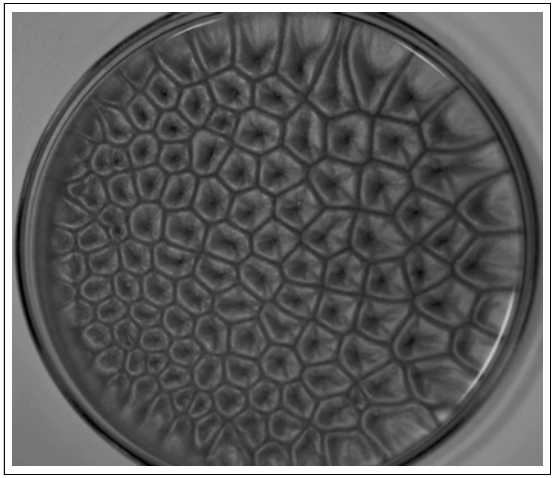


Figure 4. Benard–Marangoni instability with silicone oil and metallic paint.

For sustained Marangoni convection, the induced motion at the surface must be stabilised by viscous drag and thermal diffusion.

tonian liquid heated from below at an isothermal solid boundary and an adiabatic free surface above in contact with air at a temperature lower than the solid boundary. In [6], it has been shown that this system is linearly unstable for Marangoni numbers exceeding 80. Temperature non-uniformities at the surface induce surface tension gradients which are destabilising, with buoyancy playing a negligible role for thin fluid layers. For sustained Marangoni convection, the induced motion at the surface (which is cellular in nature) must be stabilised by viscous drag and thermal diffusion.

A shallow layer of silicone oil mixed with metallic powder (Camlin Fabrica silver paint) was poured into a clean glass petri dish and heated using a hot plate to 175 ^{o}C. We observe the slow appearance of near hexagonal cells (see *Figure* 4) on the surface. The motion of metallic particles indicates that the fluid rises in the centres of the hexagonal cells and descends at their edges. The size of the hexagonal cells is of the same order of magnitude as the thickness of the layer. On stirring the mixture with a glass rod, the cells reappear suggesting (nonlinear) stability of the cellular pattern to an external perturbation at a fixed temperature, see the video: `youtube.com/watch?v=v2vMXmuC818`

Figure 5. Filamentary structures formed by drops of liquid Duco cement spreading on a pool of water.

6. Suggestions for Further Work

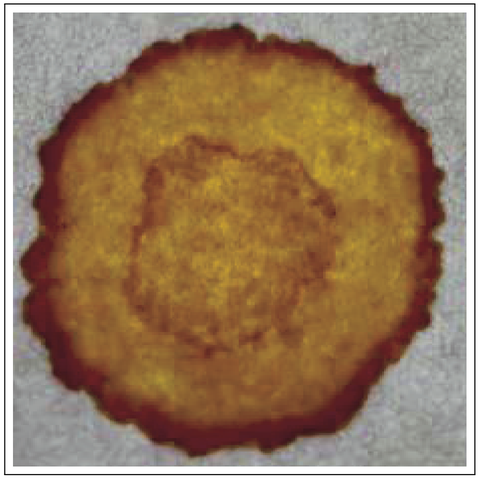
Experiment 1: Marangoni Effect with Duco Cement

Duco cement (ITW Devcon, United States) is a household cement composed of nitrocellulose, camphor, acetic acid, and volatile components such as acetone and isopropanol. When a drop of cement is squeezed onto a shallow layer of water in a clean petri dish placed on a black paper, it forms unusual ribbon-like filaments (see *Figure* 5). Volatile components of the mixture which evaporate cause a reduction in temperature, increasing the local surface tension coefficient near the filaments, which move about in a complex rotary fashion. The author is not aware of any theoretical discussion of the shapes of the observed spiral structures. See the video: `youtube.com/watch?v=l1-tIKCKCu8`

Experiment 2: Coffee-ring Effect

It is a common observation that coffee spilt on cloth/paper leaves behind a ring-shaped deposit on the surface upon evaporation of the liquid (see *Figure* 6). The coffee grounds stick to the surface, while evaporation which is most pronounced near the edges, increases the surface tension near the perimeter, causing a differential tangential stress. The induced radial flow causes formation of a ring-shaped deposit (see [7] for a detailed discussion).

Figure 6. Ring-like stain left by a coffee drop on filter paper.



Concentrated coffee solution was dropped onto filter paper using a pipette and its motion filmed using a DSLR camera (Nikon D3200) with macro lens for a duration of 20 minutes. The video was processed to extract every 25th frame, which were recombined into a time-lapse video. The resulting spread of the coffee stain may be seen in the video: `youtube.com/watch?v=k38LBbpXLXI`

Experiment 3: Vapor Bubbles on a Heated Submerged Wire

The translational motion of vapor bubbles on a heated nichrome wire (diameter = 0.26 mm) submerged in silicone oil in a glass tank, may be shown to occur due to thermal Marangoni stresses [8]. The nichrome wire was heated by connecting to a DC power supply via a current of ≈ 3 A, with appropriate safety precautions to avoid electrocution. See the video taken with a high-speed camera and macro lens: `youtube.com/watch?v=OqWpSFBdBBw`

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