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Marangoni flow revisited

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ABSTRACT

A view of the Marangoni effect from the perspectives of all three possible interfaces as motion inducing agents is given. Arguments are made that it is required and sufficient that surface tension gradient at the substrate surface induce the flow while the liquid vapor surface tension gradient is unable to induce a flow on its own; that the flow is toward a lower interface potential at the wall liquid interface; and that this is an appropriate way of viewing the Marangoni effect is demonstrated with examples.

1. Introduction

The rise of wine along the walls of a glass cup (tears of wine) is a common example for Marangoni flow [1]. These types of flows exhibit fascinating scientific phenomena [2–5] with ramifications to variety of fields including microfluidic and integrated DNA analysis devices [6–8], extraction processes [9,10] and flow of sap in the xylem of high trees [11] just to name a few. The classic explanation for the tears of wine effect [12], as a Marangoni flow prototype [13], is given in many textbooks [13,14], and in one way or another is as follows: When the wine is placed in the cup it climbs along the walls to wet them much in the same manner capillary rise does. In the film of wine that covers the wall (see Fig. 1a), the evaporation that takes place is mainly of the alcohol (being more volatile). Hence, as the film reaches higher positions, z, on the wall, the concentration of the alcohol, c, becomes smaller and smaller, i.e. a gradient of concentrations, dc/dz, is created with lower alcohol concentration the higher the film is. Since the surface tension of water is much higher than that of alcohol, higher alcohol concentrations, c, correspond to lower surface tensions, γ [15]. Fig. 2 shows $d\gamma/dc$ (change of surface tension with alcohol concentration) versus c using data from Ref. [15]. In the tears of wine system, since the alcohol concentration decreases with height we can write:

$$dc/dz < 0. \tag{1}$$

Additionally $d\gamma/dc$ corresponds to a surface tension gradient, $d\gamma/dz$, via the chain rule:

$$d\gamma/dz = (d\gamma/dc) \cdot (dc/dz). \tag{2}$$

Thus, a gradient in the surface tension is created along the vertical direction with higher surface tension at higher regions. The classical explanation for the Marangoni effect is that the higher regions of the film, having higher surface tension, pull on the lower regions upward.

Unlike the concentration changes in the film, the alcohol concentration at the bulk below the film — see Fig. 1a — hardly decreases with time because the bulk's surface to volume ratio is much lower than that of the film. For the time scales associated with the Marangoni effect, the alcohol bulk concentration is approximately constant (in a quasi-steady state). Thus the bulk continuously replenishes the lower region of the film with almost constant low surface tension film (see Fig. 1 for the definition of the bulk and the film). The surface tension of the film is different at different heights ($\gamma(z_1) \neq \gamma(z_2)$), but at a specific height it approaches a constant value with time ($\gamma(z_1, t_1) \cong \gamma(z_1, t_2)$) once the system approaches the quasi-steady state. Thus at any time the higher regions of the film, having higher surface tension, pull on the lower regions upward (according to the classical explanation).

There are a few problems with this explanation, two of which we describe below. One problem is related to the fact that alcohol, being an amphiphilic molecule, stays preferentially at the surface and thus has a greater relative effect on the surface tension at *lower* concentrations, while the Marangoni effect is more prominent at *higher* concentrations. Thus we can see in Fig. 2 that the change of surface tension with alcohol concentration, $d\gamma/dc$, is more than 6 times greater for a ∼5% solution than it is for a 40% solution (and see also Refs. [15,16]). Since $d\gamma/dc$ is higher at lower values of c one would expect the Marangoni effect to be more pronounced at *lower* alcohol concentrations. Yet the opposite is true. A simple experiment shows that a for a 5% solution the Marangoni effect is not visible at all, while for the 40% solution it is very pronounced. In a careful experimental study, Fournier et al. [17] report that in their system the Marangoni effect was not visible for concentrations lower than 20%. On the other hand, their Fig. 4 shows the effect for 70% alcohol, where $d\gamma/dc$ is practically zero(!) — cf.

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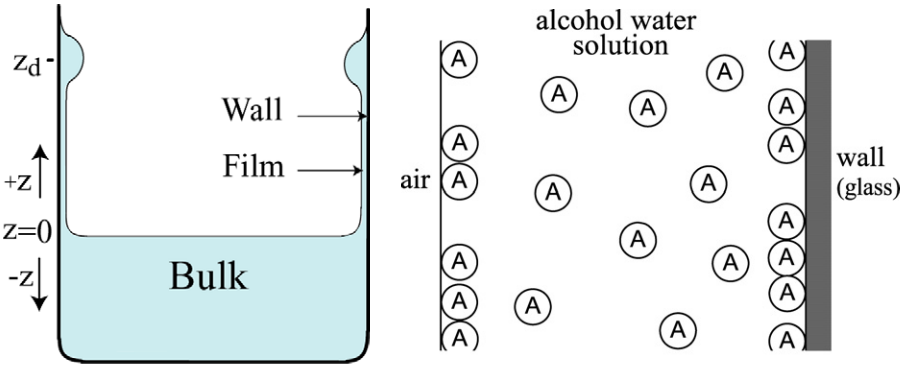

(a) (b)

Fig. 1. (a) Schematics of aqueous alcohol solution in a glass cap. For clarity, the film thickness is magnified out of proportion. (b) Enlargement of a section in the film region showing the alcohol molecules, circled 'A's, accumulate at the liquid–air and liquid–wall interfaces. Alcohol is depleted from the air interface and at higher locations (the system is constantly flowing) this decrease in concentration propagates to the wall interface. We schematically describe this by drawing at the lower air–liquid interface three circled 'A's together representing higher concentration, above it just two circled 'A's representing lower concentration and just one at the top representing an even lower concentration. At the wall–liquid interface we see the same feature (three–two–one), lagging at a somewhat higher height.

Fig. 2. More than that, Fournier et al. [17] showed that even at 100% alcohol, the humidity from the air suffices for a Marangoni effect to take place. Fig. 2 shows that the $d\gamma/dc$ close to 100% alcohol concentration is slightly positive (higher surface tension at more alcohol) which is *opposite* to the direction assumed by the classical explanation: the classical explanation cannot explain why the lower surface tension should pull on a higher surface tension (which is the case at these concentrations).

The second problem is general to any system so long as one considers the surface tension gradient at the heart of the explanation to be at the liquid–vapor interface as is the classical explanation. There are experimental evidences for a Marangoni flow at a liquid vapor interface where a bubble (say of air) is made to move either at zero gravity [18] or even on earth [19] against its buoyant direction due to surface tension gradient. Yet there are no reports of a Marangoni flow inducing liquid drop motion up in vapor or air against gravity [20] although the buoyant force is identical. Let alone a liquid film that, in addition to its own climbing against gravity, also needs to overcome the friction with the wall. Clearly the drops need a viscous medium to push against, and air or vapor is not viscous enough. To summarize this central problem we can consider the following types of Marangoni flow [21]:

(i) drops and bubbles surrounded by a liquid continuum;
(ii) sprays of drops in a gaseous continuum;
(iii) surface supported liquid films in a gaseous or liquid continuum.

There are examples for case (i) and (iii), but curiously for case (ii) the Marangoni flow has never been observed with any significance [21,22]. This suggests that the air is not dense enough to support a flow. We can exaggerate it further, and assume a liquid drop in vacuum. Clearly then the vacuum–liquid surface tension cannot induce a flow on its own, because there are no molecules in the vacuum against which the liquid can be pushed. Thus the classical explanation has a problem to explain the ability of the air–liquid interface to push the liquid without a support from any solid or viscous medium.

The first paper in this series deals with the related problem of two drops in which one seems to chase the other [23]. There we perform experimental study and again show that the solid interface is the flow inducing agent. Both papers show that the air–liquid interface alone cannot account for the Marangoni effect.

Below we consider the water/alcohol system as a "model system" in lieu of writing higher surface tension component and lower surface tension component, but the conclusions are true for any Marangoni flow. Even if we insist on the air–liquid interface as being the flow inducing agent, then to act as a pulling agent some relation to the wall is required because it is associated with two fluids one of which is vapor(!) (Fig. 1). For example the three phase contact line in drops is often associated with anchoring to the surface [14,24–29]. But even the force that moves the three phase contact line needs to be external. The air is not viscous enough to push the film up. However, if the solid–liquid interface is the flow inducing agent [2–5,30], then an additional anchoring point is not required. In any case, an explanation for the Marangoni effect needs to include the way the *wall* is associated with, or induces, the flow itself.

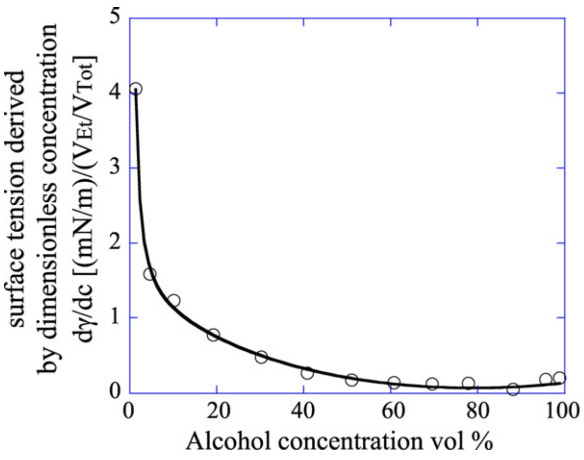

Fig. 2. The change of surface tension, $d\gamma/dc$, of aqueous ethanol solution as a function of ethanol fraction. The fraction, c, is $V_{\mathrm{Et}}/V_{\mathrm{Tot}}$ which stands for the ethanol volumetric fraction. The line is a guide to the eye; data is taken from [15,16].

2. Discussion: Alternative explanation for the Marangoni effect

2.1. Abandoning surface tension analogy to force

The classical explanation views surface tension as force. On its face there should be no problem: surface energy [31], E/A, namely energy, E, per unit area, A, equals the surface tension, namely force, F, per unit length, L (cf. Fig. 3 showing a liquid film on a frame with a movable wire; in the figure $F/L = E/A$ where $A = LX$).

The above well known feature of surface tension surprises some beginners because force is the derivative of energy with the dis-

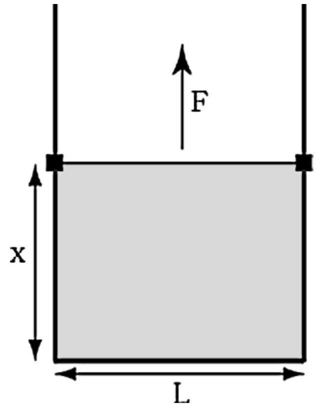

Fig. 3. A film stretched on a frame with a movable wire.

tance [32] and thus the energy would equal the force only if it changes exponentially with the distance, which is not the case here. Indeed, the energy does not equal the force here but the energy *per unit area* equals the force *per unit length*. In general also $F/L \neq E/A$, however these two physical quantities equal in the specific case where the surface energy is constant with the position X, in which case the energy simplifies to $E = FX$ instead of the general $E = \int F\,dX$ (like gravitation force $m \cdot g$ and the gravitational potential energy $E = \int F\,dz = mgz$). Yet, in the Marangoni flow the surface tension is not constant with the distance and therefore the force/length interpretation of the surface energy is not appropriate here. The energy per area, as we shall see, is a more appropriate approach in this case.

2.2. Viewing surface tension as energy or potential

Experimentally, the fact that drops accumulate on top of a thin film shows that this place of drop accumulation is a potential sink for the liquid. We also know that the potential sink should be on the surface of the wall (of the cup), i.e. at the liquid solid interface, because we already concluded that any holding of the liquid must be on a viscous or solid medium. Leading to the potential sink should be a gradient in the liquid–solid interfacial energy. The total energy in the system is the sum of the gravitational energy ($E = mgz$) and the interfacial energy as written in Eq. (3). Here, in line with the classical explanation, we neglect the kinetic energy and the heat energy due to evaporation which have a small contribution once a steady state is reached. Another similarity to the classical explanation is that the gradient is induced by the evaporation process and is constant with time (once steady state is reached) but not with position.

$$E_{\text{total}} = E_{\text{interface}} + E_{\text{gravity}}. \tag{3}$$

Since the gravitational energy is linear with the height (mgz), a minimum in the total energy can only be achieved if the interfacial energy decreases with the height with a slope that is smaller than $-mg$ at a low height, and greater than $-mg$ at higher heights. Mathematically, if the interfacial energy is a continuous function then for $z > 0$, cf. Fig. 1,

$$d(E_{\text{surface}})/dz < 0 \tag{4}$$

and

$$d^2(E_{\text{surface}})/dz^2 > 0. \tag{5}$$

An example for such energy profile is given in Fig. 4.

Experimentally we also know that the change in interfacial potential is associated with a reduction in alcohol concentration with the height. We deduce then that the adsorption of alcohol on the solid surface tends to *increase* the interfacial energy. This may sound surprising because usually surface adsorption tends to decrease surface tension. However, while this is the case for surfactants at the *liquid–air* interface, it is not the case for surfactants at the *liquid–glass* interface and other polar or charged solid surfaces [33,34]. In the case of polar solid surfaces in contact with polar liquids like water, surfactants (e.g. alcohol [35–38]) tend to *increase* the interfacial energy [33,34,39–43] (i.e. hydrophobize the surface) and the *total energy* is minimized due to the reduction in the energy at the *bulk* of the surfactant solution. Be the details of surface hydrophobization as they may, the increase in the surface energy with alcohol concentration is the only way to account for the experimental observation of the Marangoni effect. The Marangoni effect is therefore *a migration of aqueous solution along a solid (or viscous) medium from a high to low solid–liquid interfacial potential* [44]. The solid liquid interfacial energy is a "potential ladder" for the solution to climb on. This also explains why water vapor suffice to cause a Marangoni effect for a glass with 100% alcohol [17]: the water, even if a small amount, is "repelled" [45] from the hydrophobic surface that the adsorbed alcohol creates.

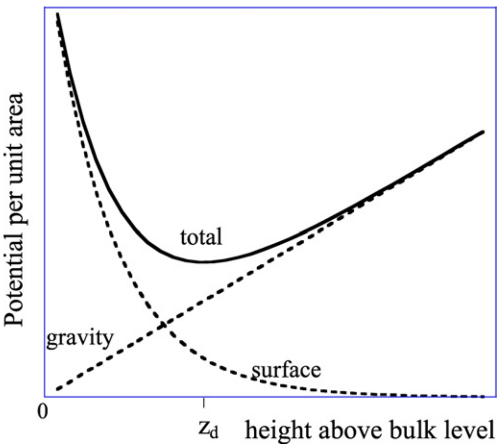

Fig. 4. A qualitative representation of the total potential that corresponds to a Marangoni system such as that of Fig. 1a: of a glass vertical surface in equilibrium with alcohol water solution. The total potential is the sum of the surface and gravitational potentials for $z > 0$.

Thus we have three distinct regions along the surface.

(I) In the bulk (see Fig. 1a) the glass surface is covered with the densest alcohol monolayer in the system which makes it the most hydrophobic surface in the system. The alcohol surface density, and hence surface potential, are constant with the height in this region as formulated in Eq. (6).

$$dE_{\text{surface}}/dz \cong 0 \quad \text{for } z < 0 \text{ in Fig. 1a}. \tag{6}$$

(II) Then in the film above it ($z > 0$ in Fig. 1a), the surface is less hydrophobic and gradually becomes even less hydrophobic with the height due to the faster evaporation rate of alcohol compared to water. At lower regions of the film ($0 < z < z_d$) there is a flow upward which is induced by the surface potential gradient whose absolute value is greater than the gravitational potential gradient:

$$dE_{\text{surface}}/dz + mg < 0 \quad \text{for } 0 < z < z_d \text{ in Fig. 1a}. \tag{7}$$

(III) We know that the reason for surface energy gradient is the evaporation of alcohol from the solution. As the height increases there should be less and less alcohol available for evaporation. Correspondingly the surface potential should reach asymptotically a constant value (i.e. $dE_{\text{surface}}/dz \cong 0$) when the alcohol concentration becomes very small (at high enough heights) (cf. Fig. 4). When this happens, the gravitational potential dominates over the surface potential. So for $z > z_d$ we get

$$dE_{\text{surface}}/dz + mg > 0 \quad \text{for } z > z_d \text{ in Fig. 1a} \tag{8}$$

and at the center of mass of the drop, $z = z_d$ we get

$$dE_{\text{surface}}/dz + mg = 0 \quad \text{for } z = z_d \text{ in Fig. 1a.} \tag{9}$$

Hence from the estimation of the weights of drops at different heights, the surface potential gradient can be evaluated. To generalize, we write that the total potential is the sum of the gravitational and the surface potentials (Eq. (3)) as sketched qualitatively in Fig. 4.

It has been known for some time that the no slip condition does not hold for a Marangoni flow [21], and here we show that the solid surface actually induces the flow. It is interesting to note that recent leading Marangoni effect studies indeed consider either a solid or a viscous phase of the interface to explain the effect (see for example [2–5,30]). This paper shows that it is the rule rather than the exception.

3. Summary

In summary, we prove that the air–liquid interface cannot induce Marangoni flow for the classical case of "tears of wine" since the surface tension gradient required for the process is opposite to what one should expect: the flow is non-existent at small alcohol concentrations where it is expected to be maximal according to surface tension gradient argumentations, and it does exist at the highest alcohol concentrations where it is not expected to occur at all according to surface tension gradient argumentations.

We then show conceptually that the air–liquid interface cannot induce Marangoni flow generally since the air is not viscous enough to support the liquid. Further, since the surface tension is varying in this problem, it is easier to treat the problem in terms of surface energies rather than tensions. We then explain the Marangoni effect as a flow that is induced at the solid–liquid interface by a surface potential gradient. The gradient is formed by the alcohol (exemplifying a volatile surface active component) that adsorbs on the liquid solid interface. At the bottom of the climbing film, the alcohol concentration is the highest and the surface is the most hydrophobic (highest interfacial energy). The surface becomes less and less hydrophobic as the height increases since there is less and less alcohol to hydrophobize the glass wall. The aqueous solution is moving along the solid–liquid interface to a place of lower interfacial energy, and concentrates at the place where the gradient of the interfacial energy equals the gravitational one: mg. The liquid will keep accumulating there until it will be so heavy that it will start flowing down.

Acknowledgments

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[44] By "solid–liquid" interface we refer to an interface between the moving liquid and another viscous medium (be it a solid or another liquid, but not vapor).
[45] "Repelled" is not accurate terminology. Rather, the water molecules are attracted by the hydrophilic regions more than by the hydrophobic regions, but in both cases the molecular interaction is attractive here.