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The spontaneous motion of a slug of miscible liquids in a capillary tube

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1 Introduction

With the increasing demand of miniaturisation of medical devices and increased throughput, the concept of a lab-on-a-chip emerged and grew over the past 2 decades. In that context, the idea that liquid droplets could be used effectively as test tubes by confining within them analytes and reagents arose and *digital microfluidics* was born. The droplets can be transported in microchannels, reactions induced by mixing the reacting droplets, and with appropriate sensor the result of these reactions can be monitored and analysed. One of the drawback of such microfluidic systems is that they often require bulky pumping systems to circulate the fluids in the device. In the spirit of the work of Beebe and co-workers, [1,2], we explore in this paper whether the unique flow phenomena which occur at the small scale of microfluidic devices may be exploited to spontaneously actuate droplets confined in a microchannels. We will refer to such droplets as slug in the following. The driving force we propose to exploit is the gradient

of surface energy which arises when two droplets of different miscible liquids are placed side by side and led to coalesce in a capillary tube. One expects that if this surface tension gradient is large enough, it will be able to overcome viscous resistance and induce the motion of the slug down the tube. In principle, one expects this motion to be sustained until both fluids have fully mixed and hence surface energy has homogenized. The present authors have already demonstrated this actuation principle in an unconfined system, i.e. when the droplets are exposed to the surrounding atmosphere [3,4]. In this paper, we demonstrate that slugs can successfully be propelled in a capillary tube by mixing two different miscible liquids. We also propose a simple phenomenological model which explains some of the observed phenomena and expected scaling laws in terms of the key parameters of the problem such as the capillary diameter or the liquid properties. In the early 2000, Bico & Quéré studied the closely related problem of the self-propulsion of slugs of immiscible liquids [5,6]. In that case, the spontaneous motion is also observed but a thin layer of one of liquid phase remains attached to the wall of the capillary tube effectively creating a coating layer. The motion of the system in this case is sustained until the liquid from the slug which is transferred into the coated layer on the wall of the capillary tube is exhausted.

The paper is organized as follows, the next section describes briefly how the experiment was set-up and present illustrative results. The following section describes the mathematical model which describes the main flow characteristics. In the penultimate section, the experimental and numerical models are compared and scaling laws expected to govern the slug motion are presented. Finally, the paper closes with concluding remarks.

2 Experimental results

The experiments that were performed were elementary. A small plug of dyed distilled water was first drawn into the capillary tube by simply dipping it into a container of dyed distilled water. The liquid raised in the tube by capillary suction. The amount of liquid drawn into the tube can be controlled by the time it is immersed in the container (provided the final equilibrium height of liquid in the capillary tube has not been reached). The radius of the capillary tube which was used is 0.675 mm. The capillary tube was then placed horizontally on a white paper sheet for maximum imaging contrast close to a graduated ruler with the plug of dyed distilled water at one extremity of the tube. A plug of ethanol was then gently inserted using a micropipette at the extremity of the capillary tube where the water plug is present. Care was taken to transfer minimum momentum during this insertion. The experiment can be viewed on the video available as supplementary material or at <http://youtu.be/KVr2dtvvAGU>. A couple of still frame images can be seen in Figure 1.

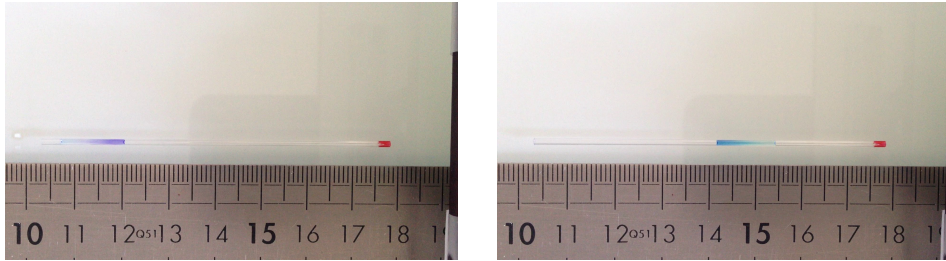


Figure 1 Slug evolution in the capillary tube. As time progresses, the slug moves from left to right

As coalescence occurs, the slug is seen to move down the capillary tube in the absence of any apparent applied force. The motion is, as expected, in the direction of the liquid of higher surface tension, i.e. the dyed water in this case, and therefore away from the extremity of the capillary tube. The motion is sustained until both liquid have fully mixed. Therefore, it is expected that the slug velocity will be maximum early on and decay towards zero as time progresses. This is confirmed by Figure 2 which shows the velocity of the slug as a function of time. The maximum velocity observed is on the order of 2 to 3 cm/s. The intensity of the blue dye (most clearly seen on the video) is also a good indicator of the mixing rate of the two liquids.

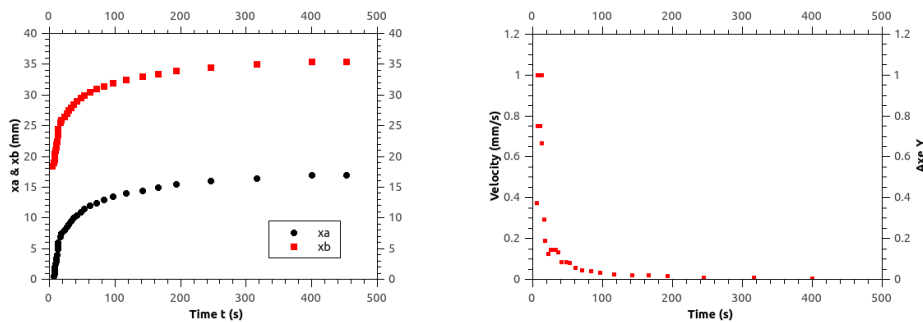


Figure 2 Position of the edges of the slug as a function of time (left-hand figure) and velocity of the slug as a function of time (right-hand figure)

3 Phenomenological model

With the above phenomena observed, there remains to explain the main flow features through a basic fluid mechanics analysis which is adapted from the work of Bico & Quéré [6]. The basis of this analysis is Newton second law applied to the slug shown in Figure 3. In this sketch, the slug moves from left to right with a velocity $V(t)$, D_1 indicates the volume initially occupied by ethanol and D_2 that initially occupied by the water. Referring to Figure 3, the forces which apply on the liquid slug are:

1. A net surface tension force which applies on the perimeter of the capillary tube of radius R , $2\pi R(\gamma_r \cos(\theta_a) - \gamma_l \cos(\theta_r))$, where γ_r, γ_l are the surface tension on the right-hand and left-hand sides of the slugs and θ_a, θ_r are the advancing and receding contact angles, respectively.

2. A viscous force which results from the shear stress developed at the wall of the capillary tube. This force can be expressed as $8V(\mu_w l_w + \mu_e l_e)\pi$ where μ_w, μ_e are the dynamic viscosities of pure water and pure ethanol and l_w, l_e are the initial length of the water and ethanol slugs.
3. A net viscous dissipation term at the moving contact which has been shown in [7] to be equal to $2\pi R \left(\frac{3\mu_e V \Gamma}{\theta_r} + \frac{3\mu_w V \Gamma}{\theta_a} \right)$. This dissipation force is evaluated by calculating the viscous stress in a wedge which moves with the velocity of the advancing or receding contact line. Balancing the non-compensated capillary force with the viscous force close to the contact line leads to $\theta_d = \left(\frac{6\Gamma \mu V}{\gamma} \right)^{\frac{1}{3}}$ where θ_d is the dynamic contact angle (either advancing or receding) and Γ involves the natural logarithm of the macroscopic and molecular length scales. It is thought have a value close to 15 [6] which is the value adopted in the following.

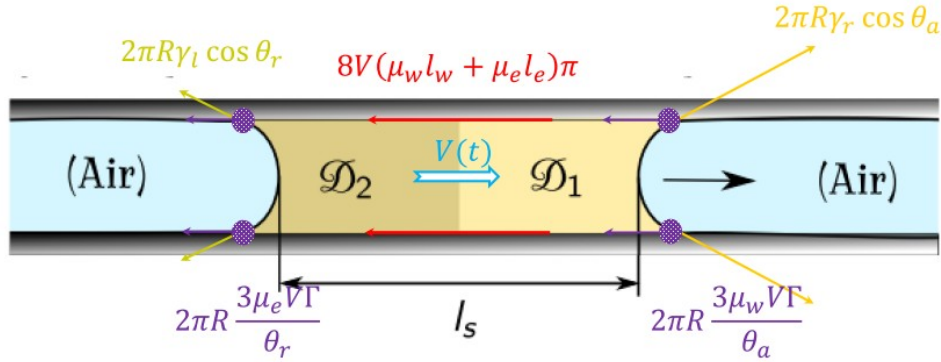


Figure 1 Sketch of the slug and the corresponding force balance

Hence, from Newton's second law, we can deduce

$$m \frac{dV}{dt} = 2\pi R (\gamma_r \cos(\theta_a) - \gamma_l \cos(\theta_r)) - 8V(\mu_w l_w + \mu_e l_e)\pi - 2\pi R \left(\frac{3\mu_e V \Gamma}{\theta_r} + \frac{3\mu_w V \Gamma}{\theta_a} \right) \quad (1)$$

The surface tensions γ_r, γ_l are functions of the mixture composition. The surface tension of pure ethanol γ_e is 0.022 Pa.m and that of pure water γ_w is 0.71 Pa.m. For water-ethanol mixtures, the corresponding surface tension has been measured in [8] and is well described by the following correlation:

$$\frac{\gamma_w - \gamma(c)}{\gamma_w - \gamma_e} = \frac{1 + a(1-c)}{1 - b(1-c)} c \quad (2)$$

where $(a,b)=(0.917,0.956)$ are constants and c is the concentration of ethanol in the mixture. To proceed further, we need a model which described the concentration of ethanol in the moving slug. Two mechanisms are responsible for the mixing of ethanol

and water. The first one is molecular diffusion. The coefficient of diffusion for liquid ethanol in liquid water is $D = 1.6 \times 10^{-9} \text{ m}^2/\text{s}$ [9]. An additional transport mechanism which is responsible for the mixing of ethanol and water is convection. It was shown by Taylor in the 1950s [10] that in a reference frame which moves with the slug, mixing can be represented by an effective diffusion coefficient D_{eff} which is the sum of the molecular diffusion D and Taylor dispersion such that

$$D_{eff} = D + \frac{R^2 V^2}{48D} \quad (3)$$

Accordingly, in a reference frame which moves with the slug, the concentration of ethanol must satisfy the following equation:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D_{eff} \frac{\partial c}{\partial x} \right) \quad (4)$$

subject to the following initial and boundary conditions

$$c(x, t=0) = 1 - H(x - l_1); \quad \left. \frac{\partial c}{\partial x} \right|_{x=0} = \left. \frac{\partial c}{\partial x} \right|_{x=L} = 0 \quad (5)$$

where H is the Heaviside function and L the total length of the slug. The zero slope boundary condition is justified by the fact that we expect no ethanol flux at either end of the slug. There exists an analytical solution to the above diffusion problem with the following form:

$$c(x, t) = \frac{l_1}{L} + \sum_{n=1}^{\infty} \frac{2}{n\pi} \sin\left(\frac{n\pi l_1}{L}\right) \cos\left(\frac{n\pi x}{L}\right) \exp\left(-D_{eff} \left(\frac{n\pi}{L}\right)^2 t\right) \quad (6)$$

Figure 4 illustrate the ethanol concentration variation and the corresponding variation in surface tension for a hypothetical value of the diffusion constant $D_{eff} = 3 \times 10^{-6} \text{ m}^2/\text{s}$ and $L=1.8 \text{ cm}$, $l_1=1 \text{ mm}$. These parameter values are representative of actual values reported in the next section.

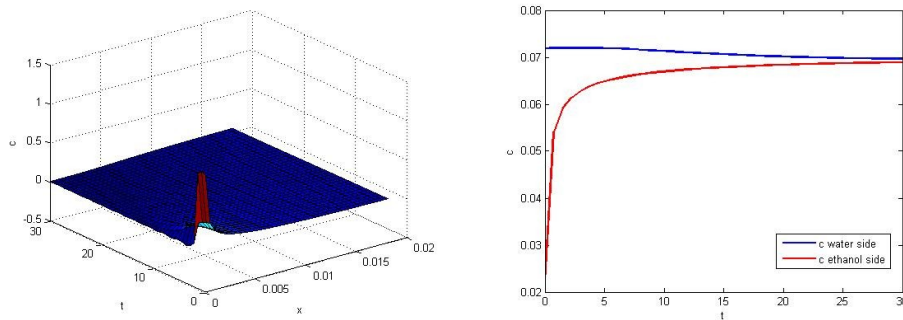


Figure 4 Variation of ethanol concentration as a function of space and time (left-hand figure); Corresponding variation of surface tension at the water and ethanol sides (right-hand figure)

The Ordinary Differential Equation, eq. (1), resulting from the mathematical model is easily solved in MATLAB using the *ode45* routine.

4 Results and scaling laws

In order to assess the validity of the model developed above, we calculate the velocity predicted using eq. (1) for the experimental run shown in the video provided as supplementary material or at <http://youtu.be/KVr2dtvvAGU> and compare with the actual measured velocity. The slug length L is 1.8 cm, the initial ethanol slug length l_i is 1 mm, the capillary tube radius is 0.675 mm, the viscosity of pure water is 1×10^{-3} Pa.s and that of ethanol 1.261×10^{-3} Pa.s. The results are summarized on Figure 5 which confirm that the model is able to predict reasonably well the magnitude and trend of the velocity variation.

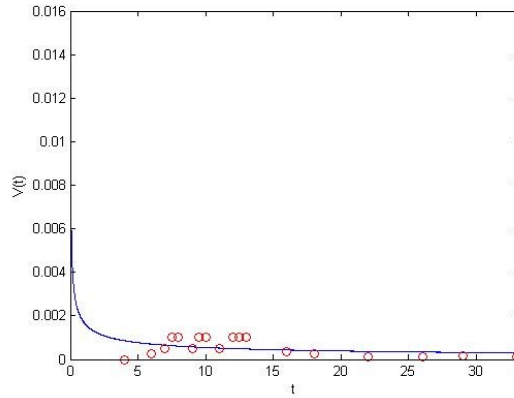


Figure 5 Comparison of the velocity predicted by the model (in m/s) and that measure experimentally

Unfortunately, we could not capture experimentally the early time dynamic to truly validate the model at early times. Nonetheless, a number of things can be stated for sure: the model correctly predicts a peak initial velocity which decays as time proceeds as observed in experiments. Taylor dispersion plays a key role in the mixing mechanism. Molecular diffusion alone cannot possibly account for the velocity decay rate. Numerical experiments with the molecular diffusion alone shows that the decay rate would be much slower.

With increased confidence that the proposed model is relevant to describe the slug dynamics, we next concentrate on trying to deduce scaling laws which govern the total distance travelled by the slug. We expect the travelled distance L_t to scale like the product of the maximum velocity, V_{max} , with the time required for ethanol and water to fully mix (T_d) since motion will cease beyond that time. We expect the time required for mixing to be:

$$T_d : \frac{L^2}{D_{eff}} = \frac{L^2}{D \left(1 + \frac{R^2 V_{max}^2}{48 D^2} \right)} \quad (7)$$

If we assume that the maximum velocity is given by balancing the net surface tension driving force (the first force in the list of forces on the slug reported above) with the bulk viscous dissipation (the second force in that list), we obtain that

$$V_{\max} : \frac{R\Delta(\gamma \cos(\theta))}{4\mu L} \quad (8)$$

Combining eqs (7) and (8) and assuming that Taylor dispersion dominates over molecular diffusion leads to the following scaling law

$$\frac{L_t}{L} : \frac{LD}{R^2 V_{\max}} \quad (9)$$

Accordingly, the slug travelled distance should increase linearly with the slug length, the diffusion coefficient but should decrease with the square of the capillary radius. This scaling law is tested numerically by systematically varying L , D , and R from the base case described previously and computing the travelled distance using the mathematical model. Note that the total length of the slug is varied but the initial ethanol concentration is kept the same, i.e. l_i/L is constant. The results, shown in Figure 6, confirm that the travelled distance varies linearly with the slug length, the diffusion coefficient, and the inverse of the capillary radius squared.

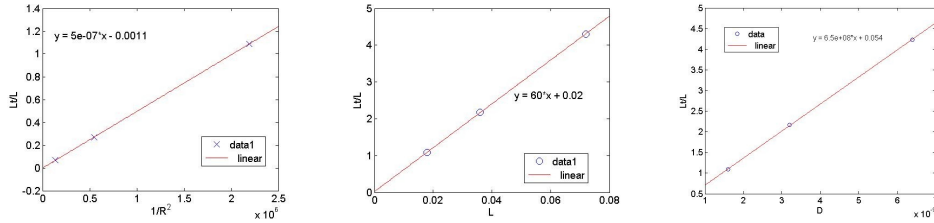


Figure 6 Effect of R , L , and D on the slug travelled distance. The symbols indicate the results from the simulations and the full lines linear fits.

The fact that the scaling law above applies allows us to make an additional inference. Namely, V_{\max} in eq. (9) cannot possibly be a function of L , D , and R . If it were, a different exponent would be observed in the scaling law (eq. (9)). This implies that the maximum velocity is not dictated by an initial balance between the driving capillary pressure and the viscous dissipation in the bulk (terms 1 and 2 in the list of forces on the slug). If it were, the maximum velocity would be given by eq. (8) which is a function of L and R hence invalidating the scaling law. The only other possibility is that the maximum velocity is dictated by a balance between the driving capillary pressure and the viscous dissipation at the contact line (terms 1 and 3 in the list of forces on the slug). In other words, in the early stages, the model suggests that most of the energy dissipated by viscous stresses occurs in a region close to the contact lines instead of in the bulk of the slug.

5 Concluding remarks

In this paper, we have demonstrated that the surface energy imbalance which arises at the extremities of a slug of miscible liquids is able to induce the spontaneous motion of the slug confined in a capillary tube. To demonstrate this phenomena, we considered a system of water and ethanol. The slug clearly moved in the direction of the initial water

slug which would have the highest surface tension. The motion is sustained for a while but the velocity of the systems gradually decreases. This is attributed to the mixing of the two liquids which results in the balance of surface energy on either side. Besides demonstrating the feasibility of this actuation mechanism, we have also proposed a simple model which appears able to capture the main features of the slug motion. This model is based on Newton's second law and predict the initial peak velocity followed by a gradual decay. Forces which are accounted for include net surface tension force, viscous dissipation at the wall in the slug bulk and net viscous dissipation in the contact line region. Our result confirm the importance in Taylor dispersion in the mixing of the two phases. The Taylor dispersion which effectively represents mixing by convection increases by several orders of magnitude the mixing rate and hence shortens the traveling time of the slug since motion ceases when the slug is fully mixed. Using simple scaling argument, we were also able to show that the slug travelled distance is expected to increase linearly with the slug length, the diffusion coefficient, and the inverse of the capillary radius squared. Furthermore, this result suggests that main mechanism for energy dissipation is viscous stresses at the slug contact lines (advancing or receding).

Acknowledgements

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