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Liquid trains in a tube

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Abstract. – Trains of juxtaposed drops in a tube are described and found to move spontaneously, in wetting conditions, because of their asymmetry. We focus on the coating properties of these devices, and show in particular that highly viscous species can be (self-) transported, thanks to the lubricating film left by the first drop. Different properties of these systems are finally displayed, which stress their versatility towards microfluidics applications.

Coating a solid with a liquid is a question of practical interest together with a classical field of interfacial hydrodynamics [1–8]. It is generally achieved by forcing a relative motion between a solid and a liquid: if a wetting liquid is displaced by a non-wetting fluid in a tube [3, 4], it leaves a film behind. The thickness h of this film results from a balance between viscosity η (which favours the film, because of the no-slip condition at the solid/liquid interface) and surface tension γ (since the film deposition implies a deformation of the free interface). The capillary number Ca compares viscous and capillary effects: $Ca = \eta V/\gamma$ (V denoting the velocity of deposition), and thus determines the film thickness h, as shown by Landau, Levich, Derjaguin and Bretherton [1–3]:

$$h = 1.34 r Ca^{2/3}\,, \tag{1}$$

where r is the tube radius. *Bretherton law* (eq. (1)) is obeyed if the film is thin enough to neglect geometric effects ($h < 0.1r$) [4] and thick enough to avoid the influence of long-range forces ($h > 100\,\text{nm}$) [7]. If the displacing fluid is of much higher viscosity than the coating one, eq. (1) remains valid, except for the coefficient which is multiplied by a factor $2^{2/3}$ (about 1.6), as shown by Schwartz *et al.* [5].

Film deposition can occur *spontaneously*, instead of being forced. Very generally, spontaneous motion in a tube is caused by an asymmetry between the advancing and the receding interfaces. In classical capillary rise, for example, the front is convex and the rear flat. Similarly, Weislogel designed a tube made with two materials of different wettability and showed that a drop spanning both sides of the boundary between these materials moves towards the most wettable side [9]. In the same spirit, Bain [10] and Ondarçuhu [11] designed *self-running drops*, made of a solvent containing species likely to react with the solid. These reactants

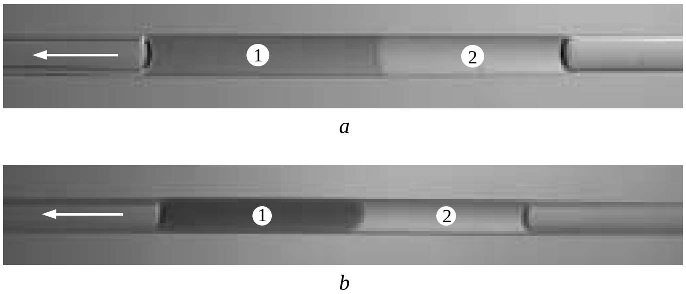

Fig. 1 – Bi-slugs made of a hydrophilic/hydrophobic couple of liquids in total wetting situation. In both cases, the tubes are millimetric and the arrow indicates the direction for the motion. In case 1 (a), the tube is hydrophilic and the intermediate meniscus is curved towards liquid 2. Here, the successive liquids are ethylene glycol (coloured with a dye) and a silicone oil juxtaposed in a glass tube. In case 2 (b), the tube is hydrophobic and the intermediate meniscus is reversed. The picture is obtained with a couple ethanol (coloured with a dye)/silicone oil in a transparent tube of polyethylene.

are chosen to be non-wetting for the solvent, so that as soon as they grafted on one side of the drop, the drop starts moving to avoid its trail. So, as it moves, the drop produces a dry coating of the solid, consisting in a monolayer of adsorbed molecules. This motion has been described by de Gennes [12], who also stressed that these drops are essentially *not* asymmetric: they need some slight perturbation to start moving such as occurs when they are brought into contact with the solid [13]. In an ideal isotropic situation, they would just generate autophobic barriers at their two extremities, and hence retract.

Here we consider trains of drops in a tube (or *multi-slug*), so that an asymmetry can be forced by construction. Let us start with a *bi-slug*, a juxtaposition of two liquid drops in a tube. Liquid 1 is taken hydrophilic and liquid 2 hydrophobic. If *both liquids wet the tube*, with the first one of higher surface tension ($\gamma_1 > \gamma_2$), the bi-slug spontaneously moves in the direction towards liquid 1 (incidentally, this behaviour was reported by Marangoni [14] for a system water/carbon disulfide, without any quantitative data). We first describe the driving force of this device, and then the dynamics, focusing on the coating properties of these systems.

If the solid is hydrophilic, liquid 1 wets better the solid than liquid 2 and the middle meniscus is curved towards 2. This *case* 1 is realised, for example, in a glass tube for the system ethylene glycol/silicone oil (fig. 1a), for which $\gamma_1 = 47.7\,\mathrm{mN/m}$, $\gamma_2 = 20.3\,\mathrm{mN/m}$ and $\gamma_{12} = 18.0\,\mathrm{mN/m}$, denoting γ_{12} the interfacial tension between both liquids. If the length is several centimeters, this bi-slug moves at a velocity of order 1 mm/s (for $r = 0.5\,\mathrm{mm}$). It leaves behind two concentric films: the film of liquid 1 was checked to have a thickness obeying eq. (1); the film of liquid 2, which is deposited on top of liquid 1, is much thinner.

The uncompensated capillary force acting on the bi-slug is written, per unit length of the contact line: $\Delta\gamma = \gamma_1 - \gamma_2 - \gamma_{12}$. Note that this driving force is the same for a dry tube and for a tube first prewetted by liquid 1, as shown in capillary rise experiments. By tilting the tube up to the angle α for which the motion stops ($\alpha = 16.5°$, for $r = 0.5\,\mathrm{mm}$ and a bi-slug ethylene glycol/silicone oil of $9 + 4.5\,\mathrm{mm}$, with respective densities 1.11 and 0.95), this force can be easily measured: we find $10.0 \pm 0.3\,\mathrm{mN/m}$, close to the expected value $9.4 \pm 0.5\,\mathrm{mN/m}$.

In *case* 2, the intermediate meniscus is turned inside out (curved towards 1). This situation is rarer, since it is achieved for hydrophobic solids wetted by *both* liquids. It is observed, for example, for the system ethanol/silicone oil in a tube of polyethylene (fig. 1b). Once again,

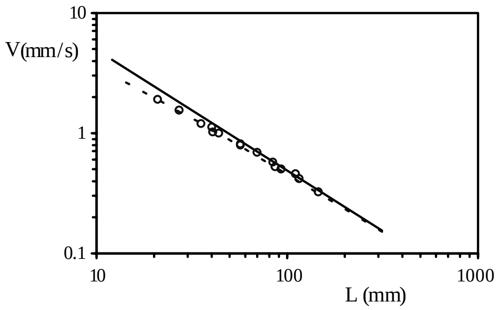

Fig. 2

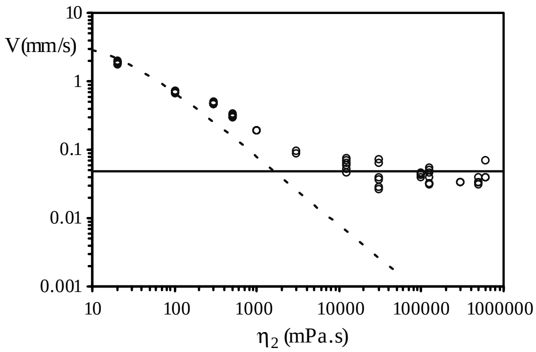

Fig. 3

Fig. 2 – Velocity of a bi-slug (ethylene glycol/silicone oil with matched viscosities, $\eta = 17\,\mathrm{mPa\,s}$) as a function of its length. The experiment is performed in a glass tube of radius $r = 0.34\,\mathrm{mm}$ prewetted with a film of ethylene glycol of thickness $4 \pm 1\,\mu\mathrm{m}$. The full line is eq. (2); the dashed one is derived from eq. (2) by considering a velocity-dependent correction in the driving force, due to the dynamic advancing angle θ ($\Delta\gamma = \gamma_1 \cos\theta - \gamma_2 - \gamma_{12}$, where θ is related to the velocity by Hoffman law: $\theta(V) \sim Ca^{1/3}$ with $Ca = \eta_1 V/\gamma_1$).

Fig. 3 – Bi-slug velocity as a function of the viscosity of the second drop. The lengths of both drops are fixed and are, respectively, $L_1 = 15 \pm 2\,\mathrm{mm}$ and $L_2 = 16.0 \pm 0.5\,\mathrm{mm}$. The experiments are performed in a glass tube of radius $r = 0.51\,\mathrm{mm}$ prewetted with a film of ethylene glycol of thickness $4 \pm 1\,\mu\mathrm{m}$. The first drop is made of ethylene glycol and the viscosity of the second one is varied using series of silicone oils. The dashed line indicates what would be a Poiseuille motion taking into account the viscosities and lengths of both drops; for $\eta_2 \gg \eta_1$, it is eq. (2) with $L = L_2$ and $\eta = \eta_2$. The full line is eq. (3), using for h the Bretherton law (eq. (1)) numerically modified by Schwartz (as explained in the text).

the system spontaneously moves but it leaves behind a *single* film of liquid 2, of thickness given again by eq. (1). Since the middle meniscus now drives the motion, the driving force is $\Delta\gamma = \gamma_1 - \gamma_2 + \gamma_{12}$. We have checked this value by direct measurement of the force. Note finally that in a partial wetting situation, a bi-slug does not move: using Young's equation, which relates the different contact angles to the different surface tensions, it can be shown that the capillary forces compensate exactly. All these arguments can be generalized to a multi-slug.

We have studied the dynamics of these trains in prewetted tubes, in order to avoid complications due to dissipation close to the contact line(s) [15]. Then, at low Reynolds number, the interfacial driving force is just balanced by the viscous force, which produces a steady motion. If the liquids have the same viscosity, the classical Poiseuille law provides the viscous force: per unit volume, it is $8\pi\eta V/r^2$, with η the dynamic viscosity. Introducing the slug length L, its volume $\pi r^2 L (L \gg r)$ and the perimeter of each contact line ($2\pi r$), the slug velocity can be written:

$$V = \frac{\Delta\gamma}{4\eta}\frac{r}{L}\,. \tag{2}$$

Experiments performed with various liquids (more viscous than water) indeed showed that the motion is steady. In fig. 2, we displayed the velocity of a bi-slug (ethylene glycol/silicone oil, $\eta = 17\,\mathrm{mPa\,s}$) as a function of its length L, in a glass tube prewetted by a $4 \pm 1\,\mu\mathrm{m}$-film of liquid 1. Equation (2) is the straight line of slope -1 and describes quite well the motion of long bi-slugs. For short slugs, the velocity is smaller than that predicted by eq. (2) because of the dissipation in the front meniscus, which causes the advancing angle $\theta(V)$ to be larger than $0°$ (its static value). For most wetting liquids, $\theta(V)$ obeys a simple power law at small capillary number [16]: $\theta(V) = \beta Ca^{1/3}$ ($Ca = \eta_1 V/\gamma_1$), where the coefficient β is larger for a dry tube than for a prewetted one [17]. In this situation, γ_1 must be replaced by $\gamma_1 \cos\theta$ in the driving force $\Delta\gamma$. This leads to an implicit equation for V, which is solved in fig. 2 (dashed line), in fair agreement with the data. Note finally that all these results remain qualitatively unchanged in a dry tube: the bi-slug still moves, but at about half the velocity, because of the stronger dissipation in the front meniscus (a similar behaviour is observed in classical capillary rise).

We now consider the second liquid much more viscous than the first ($\eta_2 \gg \eta_1$), in case 1. Experimentally (fig. 3), it is observed that the bi-slug moves at a velocity much higher (up to 10^3 faster) than predicted in eq. (2) with $\eta = \eta_2$ (the latter behaviour corresponds to the straight part of the dashed line, in fig. 2). We interpret this remarkable mobility as due to the film left behind by the first drop, which lubricates for the second one. Then, most of the dissipation takes place in the film, of thickness $h \ll r$. The viscous drop slips on the film, where it generates a Couette flow. The viscous force (per unit volume) is then $\eta_1 V/h^2$, and acts in the film volume $2\pi r h L_2$. Balancing this force with the driving capillary force yields the bi-slug velocity

$$V = \frac{\Delta\gamma}{\eta_1}\frac{h}{L_2}\,. \tag{3}$$

Equation (3) is an implicit equation for the velocity V, because h also depends on V. In the case of a drop pushed by a fluid of small viscosity, h is given at small capillary number by Bretherton law (eq. (1)). But we stressed that in the opposite limit we are interested in ($\eta_2 \gg \eta_1$), this law remains valid, except for the coefficient which is larger [5]. Then, the thickness is given by $h = 2.14 r(\eta_1 V/\gamma_{12})^{2/3}$, so that V is *independent* of η_2 in eq. (3), which becomes $V = 9.62\ (\Delta\gamma/\eta_1)(\Delta\gamma/\gamma_{12})^2(r/L_2)^3$.

This latter equation is drawn in fig. 3, where it can be observed that a bi-slug has indeed the ability for entraining very viscous species at a respectable speed. The data were obtained with bi-slugs ethylene glycol/silicone oil, keeping the drop lengths constant but varying the viscosity of the oil over a wide range: the ratio η_2/η_1 passes from 1 to $4 \cdot 10^4$, while keeping γ_2 and γ_{12} nearly constant. The velocity of the bi-slug is plotted *versus* the viscosity of the oil η_2. The velocity decreases and eventually becomes independent of η_2, at very large η_2. The decreasing line is eq. (2) (taking into account both drop lengths and liquid viscosities), while the constant line is eq. (3), as mentioned above. Note finally that the thickness of the second film deposited on top of the first one raises an interesting question. By measuring the shortening of the second drop, we observed experimentally that this film is much thinner ($< 1\,\mu$m) than the first one, and more so if the oil is viscous. Of course, this is also due to the lubricating action of the first drop: the second film is deposited on a liquid on which it slips, which makes it much thinner. A quantitative theory remains to be made, on this question.

In the context of microfluidics, where micromanipulation of drops often requires the use of external fields (thermal gradients, electric fields, or even gravity), the system we described offers an interesting alternative, mostly because of its simplicity and versatility. It realizes both self-transport and self-coating in a confined medium, and these properties can possibly be finely tuned as follows.

1. A bi-slug produces either a *double* or a *single* coating of the tube, depending on the case (1 or 2), so that coating properties can be varied according to the application. Case 1 was found to be the most interesting, because it provides a lubrication of the tube allowing the

transport of a very viscous species. A double film is deposited, which can be used for mixing at low Reynolds number or realizing chemical reactions close to a solid interface. Case 1 can also be used in capillary rise experiments with highly viscous fluids: placing a small drop of liquid 1 in front greatly speeds up the first steps of the rise.

2. Transport (and coating) can be targeted by adjusting the length of the first drop: since it empties as the train moves, the motion stops when all the drop has turned into a film. This position can be determined from the coating laws. In case 2, the same result can be achieved by adjusting the size of the second drop. A targetted transport can also be realized using miscible liquids (for example, pure water/soapy water), which defines a *case* 3 (no intermediate meniscus). Then, the driving force $\Delta\gamma$ reduces to $\gamma_1 - \gamma_2$ and the mixing time determines the final position of the drop.

3. The motion of a bi-slug can possibly be reversed by constructing an adapted tri-slug: in the example we mainly developed, juxtaposing a drop of a light silicone oil to liquid 1 (ethylene glycol), makes the train move back, because of the small surface tension of this oil. Tri-slugs can also be used for encapsulating viscous or toxic species.

4. We restricted our examples to viscous trains which generate slow motions. For practical applications, it would be interesting to reach higher speeds. This can be easily realized using liquids of lower viscosity: the speed of a centimeter bi-slugs water/ether in a glass tube is found to be of the order of 1 m/s, about 10^3 higher than the speed reported in this paper.

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