On the use of Zisman's function for the determination of the velocity of spontaneous capillary microflows

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ABSTRACT

Capillary-based microfluidic systems are increasingly used in the fields of biotechnology, medicine, thermics, energy and space. In such systems the energy source responsible for the flow is the surface energy of the walls.

Extending the Lucas-Washburn-Rideal (LWR) law, a general expression for the velocity and marching distance of an open capillary flow, valid for any channel geometry, has been reported in the literature. This expression stems from the balance between the capillary force and the wall friction.

In the case of non-polar liquids and some polar fluids, the introduction of the Zisman's relation between the cosine of the contact angle and the surface tension of the liquid brings a new perspective on the general expression of the capillary velocity. In this work, it is shown how the use of the Zisman's plot reduces the complexity of the prediction of a SCF and enables the determination of the maximum capillary velocity.

Keywords: Sponatneous capillary flow (SCF), Lucas-Washburn-Rideal (LWR) law, Zisman plot.

1.INTRODUCTION

The onset of spontaneous capillary flow in a microchannel and its dynamics depend on the geometry of the channel and on liquid-solid physical properties such as contact angle, surface tension and viscosity. This dependency was demonstrated first by Lucas, Washburn and Rideal for cylindrical channels [1-3] and later for open triangular channels by Rye, Yost and Romero [4-5], and Ouali et al. [6] for rectangular U-grooves, and Berthier et al. [7,8] for arbitrary channel shapes.

The universal relation for the velocity of capillary flows is [8,9]

$$V = \sqrt{\frac{h}{t} \frac{\gamma}{\mu} f(cos\theta)} \ , \qquad (1)$$

where V is the average flow velocity, t the time, h the channel characterisctic dimension (depth or radius), γ the liquid surface tension, μ the dynamic viscosity and f a non-dimensional geometrical factor which includes the contact angle θ. This expression—valid after a short establishment time—corresponds to a balance between the capillary force, which is constant for a uniform cross section channel, and the wall friction, which increases with the penetration distance. It reduces to the LWR law in the case of a cylinder.

Although there is no theoretical demonstration for the empirical Zisman law-which is approximately valid for for many substrates and many liquids [10,11]- the use of the Zisman plot considerably simplifies the approach to the understanding of the capillary flow. It has the advantage of eliminating the need of the determination of the contact angle. Hence it is shown that the function $f(cos\theta)$ can be simplified.

In particular, the approach using Zisman plot enables the determination of the maximum capillary velocity that can be reached in a microchannel of given geometry.

2.ZISMAN PLOT

Zisman [12] was the first to observe that, for a given wall material, the cosine of the contact angle is very often linked to the liquid surface energy by a linear function. Let us consider the Zisman's plot for PMMA [13] (figure 1). Five different liquids have been used. The data for DI water,

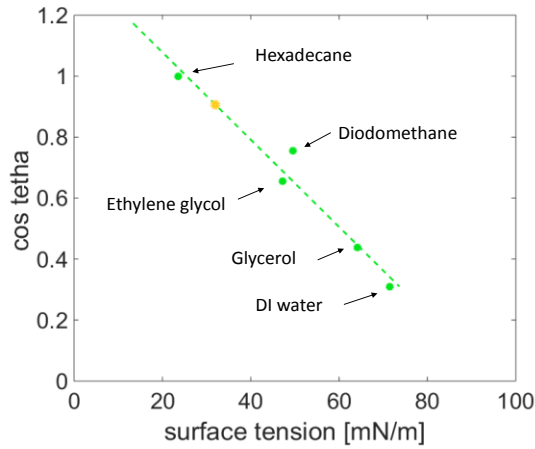glycerol, ethylene glycol, diiodomethane, and hexadecane are roughly aligned on the figure 1.

Fig.1. Zisman's plot for PMMA [13]. The surface tension of the liquid with air is plotted on the horizontal axis, and the cosine of the contact angle with the solid (here PMMA) is plotted along the vertical axis.

Many different Zisman's plots have been reported in the literature depending on the nature of the solid substrate. In figure 2, we have reported some Zisman's plots obtained for different solid surfaces, taken from the literature.
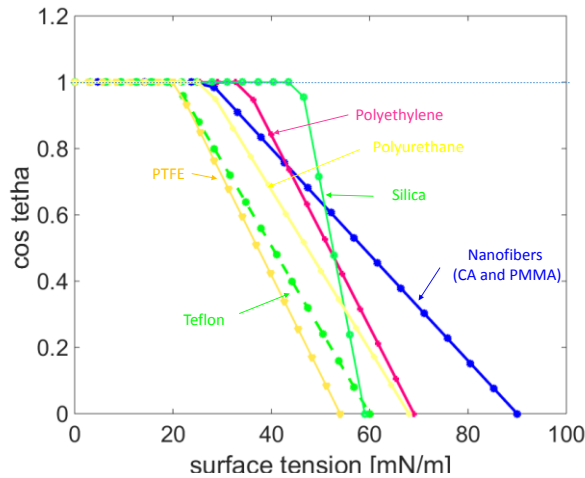

Fig.2. Zisman's plot for six solid substrates: Nanofibers (CA or PMMA) [13], polyethylene film [14], Teflon [15], silica [16], PTFE and polyurethane [17].

The mathematical formulation of Zisman's plot for a given solid surface is obtained by a linear fit of the experimental points

$$\cos \theta = 1 - \left(\frac{\gamma - \gamma_{crit}}{\gamma_0 - \gamma_{crit}} \right) = \frac{\gamma_0 - \gamma}{\gamma_0 - \gamma_{crit}} \ , \qquad (2)$$

where γ_{crit} is the maximum value of the liquid surface tension where $\theta = 0$, and γ_0 the intersect of the Zisman's straight line with the horizontal axis ($\theta = 90°$). In order to take into account the domain below the critical surface tension, equation (2) can be rewritten as

$$\cos \theta = \min \left(1, \frac{\gamma_0 - \gamma}{\gamma_0 - \gamma_{crit}} \right) . \qquad (3)$$

3.CAPILLARY FORCE

Using (3), the capillary force (per unit length) at the triple line is

$$f_{cap} = \gamma \cos \theta = \gamma \min \left(1, \frac{\gamma_0 - \gamma}{\gamma_0 - \gamma_{crit}} \right) . \qquad (4)$$

The capillary force based on (4) is shown in figure 3 for the different substrates of figure 2.
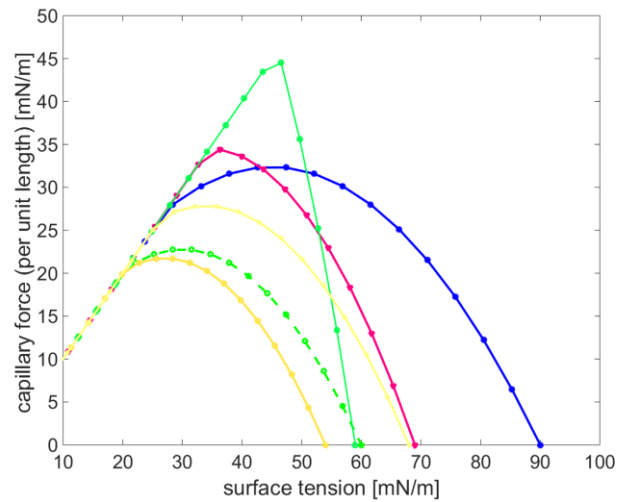

Fig.3. Capillary force (Z function) for the six different solid substrates. The surface tension of the liquid with air is plotted on the horizontal axis, and the capillary force per unit length is plotted along the vertical axis. Same colors as figure 2.

Figure 3 shows that, for a given substrate, there is a maximum for the capillary force, i.e. a liquid with a surface tension corresponding to the maximum of the capillary force.

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When γ_{crit} is relatively small, the maximum is reached for a surface tension of the liquid corresponding to a contact angle larger than zero ($\theta > 0$, and $\gamma > \gamma_{crit}$). Conversely, when γ_{crit} is large, the maximum corresponds to the liquid surface tension $\gamma = \gamma_{crit}$ (and $\theta = 0$).

In the following we note $Z(\gamma)$ the function at the right hand side of (4) which is the same as $f_{cap}(\gamma, \theta)$, but where the contact angle θ does not appear anymore.

$$Z(\gamma) = \gamma \min\left(1, \frac{\gamma_0 - \gamma}{\gamma_0 - \gamma_{crit}}\right). \tag{5}$$

4. CAPILLARY VELOCITY

The preceding relation (5) can be used to eliminate the contact angle θ in the expression (1) for velocity

$$V(t) = \sqrt{\frac{g(Z(\gamma))}{\mu}} \sqrt{\frac{h}{t}}, \tag{6}$$

where g is a function of the surface tension only. If the microchannel has a cylindrical shape, the Lucas-Washburn-Rideal law [1-3] yields

$$V = \sqrt{\frac{\gamma \cos\theta}{\mu} \frac{R}{t}} = \sqrt{\frac{Z(\gamma)}{\mu} \frac{R}{t}}, \tag{7}$$

where R is the cylinder radius. In such a case, the function $g(Z(\gamma))$ of equation (6) is simply $Z(\gamma)$. If we now consider a rectangular open U-groove, the expression for the velocity is [18]

$$V = \sqrt{\frac{h\gamma}{t} \frac{[(e+2)\cos\theta - e]}{12\mu\left(\frac{2}{e} + e\right)}} \tag{8}$$

where e is the aspect ratio of the channel ($e = w/h$). Using the function Z, equation (7) simplifies to

$$V = \sqrt{\frac{h}{t} \frac{[(e+2)Z - e\gamma]}{12\mu\left(\frac{2}{e} + e\right)}}. \tag{9}$$

And the travel distance is

$$z = \sqrt{\frac{h t[(e+2)Z - e\gamma]}{3\mu\left(\frac{2}{e} + e\right)}}. \tag{10}$$

In this case, the function $g(Z(\gamma))$ of equation (6) is

$$g(Z(\gamma)) = \frac{[(e+2)Z - e\gamma]}{12\left(\frac{2}{e} + e\right)}. \tag{11}$$

As expected, the contact angle θ does not appear in relations (6), (7), (9), and (10).

Considering relation (6) for different liquids, the function

$$H(\gamma, \mu) = \frac{g(Z(\gamma))}{\mu}, \tag{12}$$

can be viewed as a coefficient that characterizes the velocity of the capillary flow. This coefficient decreases continuously with increasing viscosities, and—for a given viscosity—has a maximum for a certain value of γ, depending on the shape of the channel and the nature of the solid walls (figure 4).
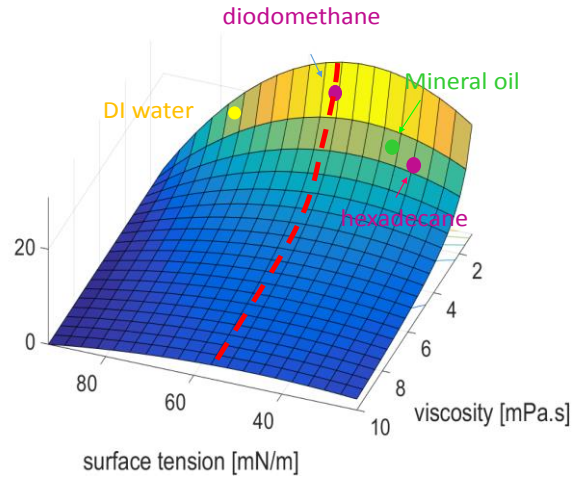

Fig.4. Capillary velocity coefficient $H(\mu, \gamma)$ for the six different solid substrates (only four can be seen, glycerol and ethylene glycol have viscoities outside the range of the picture). The red dotted lines correspond to the locus of the maxima.

5. NUMERICAL RESULTS

In a rectangular U-groove milled in a PMMA plate, of width 1 mm and depth 1.6 mm, the marching distances as functions of time—based on relation (9)—are plotted in figure 5 for

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the 5 liquids which physical properties are indicated in the table 1 below [2].

Physical property	Water	Hexadecane	Glycerol	Diiodomethane	Ethylene glycol
γ [mN/m]	71.5	23.5	64.1	49.6	47.2
μ [mPa.s]	1	3	1410	2.8	16.9
Contact angle	72	0	64	41	49

Table 1. Physicochemical properties of some fluids, from [11].

One sees in figure 5 the importance of viscosity for capillary velocity: the two most viscous liquids (glycerol and ethylene glycol) shows very slow penetration in the channel.
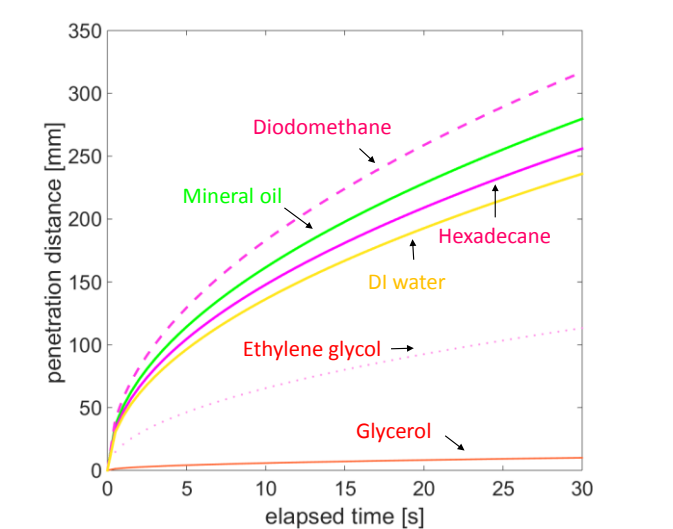

Fig.5. Marching distance vs. time in the U-groove: the liquid viscosity has a major effect, the two slowest liquids are the two most viscous.

CONCLUSION

The dynamics of capillary flows depends on many parameters such as channel geometry, liquid viscosity, liquid surface tension, and contact angle. The use of Zisman's plot can be interesting to predict the dynamics of the capillary flow without having to know the contact angle. A function—called here the *Z* function—has been derived based on the Zisman's approach showing that the capillary velocity can be determined by only two physical parameters, i.e. the liquid surface tension and the liquid viscosity.

Of course, a Zisman's characterization of the surface must be performed in the first place. But as soon as this characterization is done, the determination of the capillary velocity (and travel distance) is straightforward since surface tension and viscosity of most liquids are reported in the literature.

Finally this approach produces immediately the maximum velocity that can be reached in a channel of given shape.

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