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Precursors of impregnation

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Abstract. – The progression of a liquid inside a porous medium often involves two macroscopic fronts: a main one, at the bottom, which saturates the medium; and a much thinner one, ahead, which propagates using the fine structures of the porous material. We discuss here different characteristics of this precursor. We show in particular how it can move faster than the main front, although it follows confined paths. We also describe its dynamics, and compare our results with different experimental situations.

Diffuse fronts in impregnation experiments. – In many cases, the impregnation of a porous medium (such as paper, fabric, or powder) is well described by a diffusive-type law: the impregnated distance increases as the square root of time. This law also describes the progression of a liquid index in a capillary tube as long as gravity can be neglected, as shown in 1921 by Washburn [1]. Thus it has often been proposed to treat a porous medium as an array of parallel identical capillary tubes. But this very simple picture does not capture all the characteristics of the imbibition. For example, the front is generally not sharp (as it would be in an array of capillaries), but diffuse. This can be proved by measuring simultaneously the weight of the paper and the apparent position of the front (two very common types of measurement). We report in fig. 1 such an experiment, performed with a silicone oil (viscosity $\eta = 16\,\mathrm{mPa\,s}$, surface tension $\gamma = 20.6\,\mathrm{mN/m}$ and density $\rho = 950\,\mathrm{kg/m^3}$) impregnating a centimetric piece of paper (Whatman no. 4).

At the end of the experiment, the whole paper is impregnated (on the centimetric height h_0, to which there corresponds a mass m_0). In fig. 1, the height of the visible front and the mass are scaled by h_0 and m_0, respectively. Both laws are diffusive (and we can find in the literature many similar results obtained by either one or the other of these techniques), but the diffusion coefficients which can be deduced from the experiment are different: we find a larger value (by typically 30%) for the visible front than for the mass of the liquid. This difference can be interpreted by considering that liquid precursors are progressing ahead (they darken the porous material, and thus are detected by the eye), while the large pores of the material (which provide most of the mass, once saturated with the liquid) are filled more slowly.

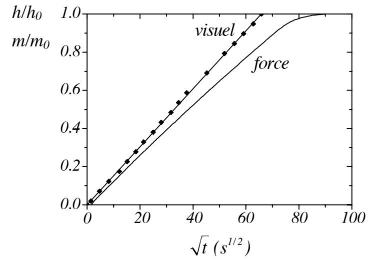

Fig. 1 – Comparison between the progression of the liquid front (full diamonds) and the increase of the mass (line), in a piece of paper put at $t = 0$ in contact with a wetting silicone oil. h_0 is the height of the sample, and m_0 the mass of the liquid once the paper is fully impregnated.

This suggests that the liquid front is wide, as shown by Williams for similar systems [2]. In Williams' experiment, a long strip of paper is brought in contact with a bath of oil and removed before the front reaches the end of the strip (thus, for $h < h_0$). The stripe is then cut up in small horizontal slices, which are weighed. Each mass is compared with the mass of a similar slice saturated with oil, which allows to reconstruct the filling rate of the porous along its length. Figure 2a shows the results of a similar experiment done with a paper in contact with a bath during 1700 s, 5500 s, 11700 s and a whole night, to which there correspond (apparently) impregnated lengths of 35 mm, 53 mm, 83 mm and complete saturation, respectively.

Close to the bath (z small), the paper is fully impregnated. Further, a diffuse front is observed, although a direct observation provides a very well-defined position h for the front. (In the case of an anisotropic porous medium, the front h is also observed to be rough in the direction perpendicular to the motion [3], which is not the case here.) The front width Δh increases throughout the liquid progression, and is found in fig. 2b to be linear in h, which shows that both the laws are diffusive in time.

If the porous medium could be simplified in an array of similar tubes, the front would be sharp. We propose here to study what happens when considering the polydispersity of the pores, and restrict to the simple case of a porous medium constituted of two types of pores interconnected with each other. This minimal description should mimic different practical cases:

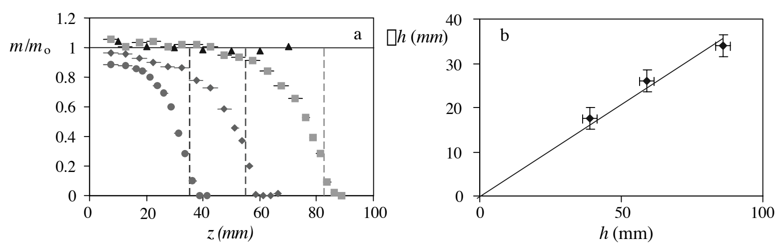

Fig. 2 – a) Mass of successive horizontal slices (height $\delta h = 3$ mm) along a long strip of paper in contact with a wetting liquid, as a function of the position z along the axis of progression of the liquid; m is normalised by m_0, the mass of this slice saturated by the liquid. The dashed lines indicate the apparent position of the liquid front, for each experiment. b) Extension of the front width as a function of its position, for the experiment reported in a).

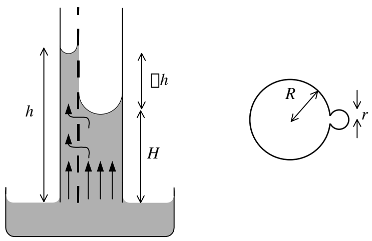

Fig. 3

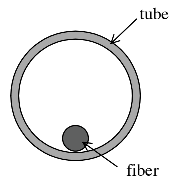

Fig. 4

Fig. 3 – Rise in interconnected tubes (side view and cross-section): the liquid rises faster in the smallest tube.

Fig. 4 – Cross-section of our experimental bidisperse model porous medium.

in a fabric, for example, both the intervals inside a yarn and between different yarns drive the liquid [4]; in rocks, it is often found that macro- and microfissures coexist and participate in the impregnation [5]; and even in very simple systems, such as assemblies of fibres or square tubes, the liquid progresses both at the centre of the tube, and also along the corners [6].

Impregnation of a bidisperse medium. – Our model is sketched in fig. 3: two interconnected tubes (radii R and r, $r < R$) are brought in contact with a bath of wetting liquid. The liquid invades the tubes, and we suppose that the height at time t is not the same in both tubes (difference Δh). We also suppose that the height of the rises in both tubes remains much smaller than the respective equilibrium height in these tubes, so that the effect of gravity can be neglected. Note finally a key point, which is the permanent interconnection between the tubes, as sketched in fig. 3: some porous media such as rocks should be better described by considering junctions of small and large tubes (so-called pore doublets) reconnecting further, which leads to quite different results [7].

If the tubes were not interconnected, the rise would be slower in the small one ($\Delta h < 0$), because of the higher friction (the diffusion coefficient in Washburn's law scales as the radius r of the tube). But here the situation is quite different: the viscous dissipation inside the small tubes is dramatically reduced, because the liquid there is pumped (thanks to a high Laplace depression) out of the large sections. We denote as h and $H = h - \Delta h$ the heights in the small and in the large tube, respectively. The flow rate can be neglected in the small tube. Because of the difference between the two radii ($r \ll R$), the viscous loss in the large tube can be written, according to Poiseuille law

$$\Delta P_1 = \frac{8\eta H}{R^2}\frac{\mathrm{d}H}{\mathrm{d}t}\,. \tag{1}$$

The liquid there is mainly driven by the Laplace pressure in the large tube ($2\gamma/R$, in absolute value), which leads to Washburn's equation

$$H = \left(\frac{R\gamma}{2\eta}\right)^{1/2} t^{1/2}. \tag{2}$$

In the precursor column of extension Δh and radius r, the liquid progresses with a mean velocity $\mathrm{d}h/\mathrm{d}t$ and the pressure loss due to viscous dissipation can thus be written

$$\Delta P_2 = \frac{8\eta \Delta h}{r^2}\frac{\mathrm{d}h}{\mathrm{d}t}\,. \tag{3}$$

The Laplace pressure which draws this precursor is the difference between the pressures in both tubes, and is (in absolute value)

$$\Delta P_2 = 2\gamma\left(\frac{1}{r} - \frac{1}{R}\right). \quad (4)$$

Putting together the previous equations, we can deduce the height of the precursor, and its variation as a function of time. In the limit $r \ll R$, it simply reads

$$\Delta h \approx \left(\frac{\gamma}{2\eta}\frac{r^2}{R}\right)^{1/2} t^{1/2}. \quad (5)$$

Thus, Δh is found to be positive (the liquid indeed progresses faster in the little tube), and diffusive in time. Using eq. (2) in the same limit of contrasted radii, we find that the relative gradation of the liquid front only depends on the tubes geometry:

$$\frac{\Delta h}{h} \approx \frac{r}{R}\,. \quad (6)$$

This behaviour qualitatively agrees with the different data reported in figs. 1, 2 for real porous media. This suggests that data in fig. 1 can be understood by considering that the darkened zone corresponds to the filling of small precursor spaces, while the weight measurement mainly implies the filling of large "tubes". Thus, modelling a real porous medium by a bidisperse network of tubes is a simple way for understanding behaviours which cannot be captured by Washburn's law.

Of course, our results hold only if both fronts progress. At larger heights, the front in the large tube reaches its equilibrium height H_0, which is classically given by a balance between Laplace and hydrostatic pressures ($H_0 = 2\kappa^{-2}/R$ for a wetting liquid, denoting as κ^{-1} the millimetric capillary length). The liquid keeps progressing inside the small tube, but the viscous dissipation associated with this flow is dominated by the friction along the length Δh (for $\Delta h > \kappa^{-2}r^4/R^5$), which yields a simple Washburn's law in a tube of radius r ($\Delta h^2 = r\gamma t/2\eta$). Thus, the progression in the small tube becomes much slower (the diffusion coefficient is reduced by a factor r/R) than before, when the progression in these tubes was enhanced by the filling of larger tubes below (eq. (5)).

Examples. – As an example, we achieved model bidisperse capillary tubes by introducing a small fiber (radius of 170 μm) in a larger tube (radius of 600 μm), as sketched in fig. 4. The interstice between the fiber and the tube inner wall is likely to play the role of a small tube.

In a first series of experiment, we introduced a slug of liquid (silicone oil, of viscosity $\eta = 16\,\mathrm{mPa\,s}$ and surface tension $\gamma = 20.6\,\mathrm{mN/m}$) at one end of such a horizontal tube, so that the liquid only progresses along the interstice. We denote as $h_1(t)$ the position of the liquid index in this case. In a second experiment, we brought the whole horizontal system in contact with a reservoir of liquid, so that a liquid front could progress both in the tube and along the interstice, with the respective positions $H_2(t)$ and $h_2(t)$. The results are reported in fig. 5.

In each case, the square of the position of the menisci is plotted as a function of time, and all the data follow a diffusive-type law ($h^2 = \mathrm{d}t$). In the experiment with two fronts (h_2 and H_2), the liquid indeed progresses faster in the smallest "tube", and this progression is itself much faster than when the same film is emitted from a fixed slug at the end of the tube (position h_1). Denoting the respective diffusion coefficients as d_2, D_2 and d_1, and using eqs. (2) and (5), we expect that d_2 scales as $R + 2r$, D_2 as R and d_1 as r. Thus, these coefficients are not independent, and we should have

$$d_2 \approx D_2 + 2d_1. \quad (7)$$

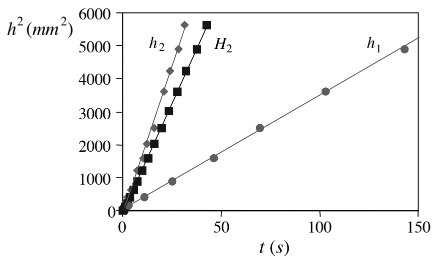

Fig. 5

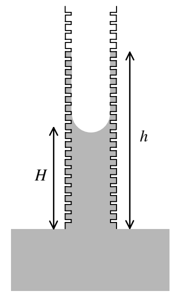

Fig. 6

Fig. 5 – Progression of menisci in a horizontal tube such as sketched in fig. 4. If a slug is first introduced in the tube, the liquid only progresses along the fiber (h_1). If the tube is brought in contact with a reservoir of wetting liquid, a meniscus moves in the tube (H_2) and ahead of it, liquid creeps along the fiber (h_2), much faster than in case 1.

Fig. 6 – Double front in a porous capillary tube.

Experimentally, we find $D_2 = 137\,\mathrm{mm}^2/\mathrm{s}$ and $d_1 = 34\,\mathrm{mm}^2/\mathrm{s}$, which yields for $D_2 + 2d_1$ a value 15% larger than the measured slope $d_2 = 177\,\mathrm{mm}^2/\mathrm{s}$. This agreement is quite satisfactory, because our system is slightly more complicated than the model: the bidispersity is obtained with a fiber instead of a second tube, which should introduce a numerical coefficient for the equivalent tube. In addition, the limit $r \ll R$ is not fully satisfied in our experiment.

More generally, a porous medium may be modelized as an assembly of tubes with a textured (or rough) inner surface (fig. 6). It is reported in the literature that mesoscopic films can progress in such textures [8–10], so that the surface roughness acts as a small tube connected with the main one.

Let us consider an inner surface decorated with posts as sketched in fig. 6. The texture is defined by its roughness α (ratio of the actual solid area over its projected one), its proportion ϕ_S (surface area of the tops over the total surface area) and the depth δ of each post. The energy variation $\mathrm{d}E$ associated with a progression $\mathrm{d}z$ of a film inside the texture is $\mathrm{d}E = -\gamma \cos\theta(\alpha - \phi_\mathrm{S})\,\mathrm{d}z + \gamma(1 - \phi_\mathrm{S})\,\mathrm{d}z$, denoting as θ the contact angle. (The first term is the interfacial energy gained by filling the inside of the texture, while the second one expresses the interfacial cost of the liquid/vapor interface created as the film moves.) The film progresses if $\mathrm{d}E$ is negative, *i.e.* if the contact angle is smaller than a quantity θ_c, given by $\cos\theta_\mathrm{c} = (1 - \phi_\mathrm{S})/(\alpha - \phi_\mathrm{S})$ [10]. The pressure ΔP_3 driving the film is derived from the relation $\mathrm{d}E = -\Delta P_3(1 - \phi_\mathrm{S})\delta\,\mathrm{d}z$, which yields for a wetting liquid ($\theta = 0$)

$$\Delta P_3 = \frac{\gamma}{\delta}\frac{\alpha - 1}{1 - \phi_\mathrm{S}}\,. \tag{8}$$

In a textured tube, a film can escape from a meniscus (as pictured in fig. 6) if ΔP_3 is larger than $2\gamma/R$, *i.e.* if we have $2(1 - \phi_\mathrm{S})\delta < (\alpha - 1)R$ —a condition which should be fulfilled generally, if the surface is rough enough. Then, the film forms a precursor ahead of the main front, and equations derived in the second section should describe its diffusion. On a scaling point of view, the texture is equivalent to a small tube, provided we take as an equivalent radius r the quantity $\delta(1 - \phi_\mathrm{S})/(\alpha - 1)$ (from eq. (8)). The progression of this film should also modify the contact angle of the main meniscus, which is in contact with a solid filled with liquid [10]. Thus, in this (quite general) situation, the contact angle deduced from the application of Washburn's law would be different from the Young contact angle θ.

Conclusion. – Very usually, the impregnation of a porous material brought in contact with a wetting bath is monitored indifferently by watching the liquid front or by weighing the material. We have shown that both methods lead to a diffusive-type law, but with a different diffusion coefficient: the optical front rises faster than the mass front. This behaviour was interpreted by considering that at least two categories of channels (narrow and large ones) are interconnected in the porous material: then, two distinct fronts diffuse, the precursor being the front in the smallest pores which pump the liquid inside the larger ones. This discussion stresses how delicate it can be to use Washburn's law to characterise the wetting of a porous medium, since this law indeed predicts a diffusive-type kinetics (and thus seems to agree with a weight experiment, or an optical one, when done separately), but ignores the polydispersity of the channels, and thus the possibility for a gradation of the front to take place. In addition, the presence of a precursor may modify the apparent contact angle of the main front, and thus (there again) lead to erroneous conclusions if using Washburn's law for a contact angle measurement. Conversely, these precursors might be used practically as indicators of the arrival of a main front, or for generating in a controlled way gradients of matter in a porous medium.

For liquids which totally wet the material, the gradation of the fronts should be still more complex, since microscopic wetting films also propagate, ahead from the fronts [11]. These films can play an important role since they fix the driving force of the menisci, which progress on them. They can also connect together different pockets of liquid in a disordered porous medium, and control the transport properties. But they should not alter our conclusions, because of their microscopic thickness —which makes them invisible and of negligible mass.

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