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# Rough wetting

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**Abstract.** – If a rough surface is put in contact with a wetting liquid, the roughness may be spontaneously invaded depending on the surface pattern and the wetting properties of the liquid. Here, we study the conditions for observing such an imbibition and present practical achievements where the wetting properties of the surface can be predicted and tuned by the design of a solid texture. The contact angle of a drop on such a surface (where solid and liquid coexist) is discussed. Finally, the dynamics of the liquid film is found to obey a diffusive-type law, as in the case of porous wicking.

*Introduction.* – The wetting behavior of an ideal flat solid is fixed by its chemical composition (Young's relation). But real solids are rough, which affects their wettability (or non-wettability) [1–3]. For example, if hydrophobicity and roughness are cleverly combined, a water drop deposited on such a surface can remain nearly spherical [4–7]. This can be understood by the fact that the liquid is only in contact with the upper part of the relief: the roughness is mainly filled with air, which leads to super-hydrophobicity [6, 7]. This letter deals with the opposite situation where the surface is rather hydrophilic. We first point out a possible invasion of the roughness, when a textured surface is put in contact with a liquid reservoir. The conditions of this imbibition are described as a function of the geometric parameters of the surface design. Then, we study the apparent contact angle of a drop deposited on a textured surface, and finally characterize the dynamics of invasion.

*Critical contact angle of imbibition.* – Figure 1 shows a rough surface put in contact with a liquid reservoir, with a film propagating inside the texture. The Young relation is locally valid and for partial wetting the top of the roughness remains dry. We call $\phi_S$ the solid fraction remaining dry, and $r$ the solid roughness (ratio of the actual solid area over its projected one).

If the imbibition front rises by a small quantity $dz$, the interfacial energies change with a quantity $dE$ (written per unit width of the sample) given by

$$dE = (\gamma_{SL} - \gamma_{SV})(r - \phi_S)dz + \gamma(1 - \phi_S)dz, \quad (1)$$

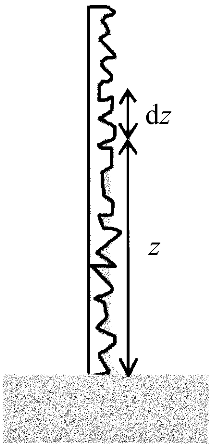


Fig. 1

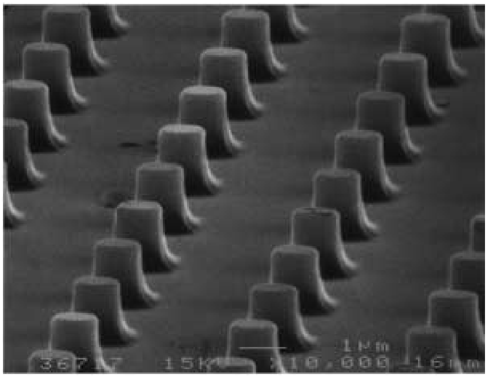

Fig. 2

Fig. 1 – Rough surface in contact with a reservoir. A small displacement d$z$ of the imbibition front of height $z$ is considered.

Fig. 2 – Microstructured surface with regular micronic spikes used for the experiment. Surface parameters can accurately be estimated from the picture. We get $r = 1.3$ and $\phi_S = 5\%$.

where $\gamma_{SL}$, $\gamma_{SV}$ and $\gamma$ are, respectively, the solid/liquid, solid/vapor and liquid/vapor interfacial tensions. The first term in eq. (1) is related to the replacement of a dry solid by a wet one. It is proportional to the wetted area, *i.e.* to the factor $(r - \phi_S)$. The second term is less usual in impregnation processes: it is related to the creation of a liquid/vapor interface associated with the film propagation. Note that gravity was ignored in (1), which corresponds to textures of small size (much smaller than the capillary length) and small heights. The gravity-limited case is treated in the appendix.

The liquid should rise if d$E$ is negative. Introducing Young's law ($\gamma \cos\theta = \gamma_{SV} - \gamma_{SL}$) gives, as a condition for imbibition,

$$\theta < \theta_c \quad \text{with } \cos\theta_c = \frac{1 - \phi_S}{r - \phi_S}, \tag{2}$$

where $\theta$ is the equilibrium contact angle of the liquid on an ideal flat surface of the same chemical composition.

Criterion (2) (logically) appears as intermediate between wetting and wicking criteria. For a flat surface ($r \to 1$), the surface is wetted if the contact angle reaches 0 ($\theta_c = 0$), while a porous medium ($r \to \infty$) is invaded for liquids having a contact angle smaller than $\pi/2$ ($\theta_c = \pi/2$). More generally, since we have $r > 1$ and $\phi_S < 1$, eq. (2) always defines a critical contact angle intermediate between 0 and $\pi/2$. Thus, the ability of a textured surface to drive a liquid can be tuned by its surface design. For a given surface composition and liquid (*i.e.*, fixing $\theta$), the nature of the texture (which determines $r$ and $\phi_S$) decides if condition (2) is satisfied, or not. In a general case (disordered surfaces), the parameters $r$ and $\phi_S$ are deeply intricate (and $\phi_S$ may depend on $\theta$). However, the use of micropatterned surfaces allows to decouple these two parameters, and even to treat them as independent, which is now discussed using such a model surface.

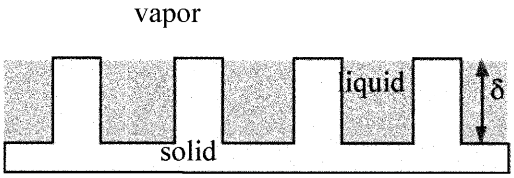


Fig. 3

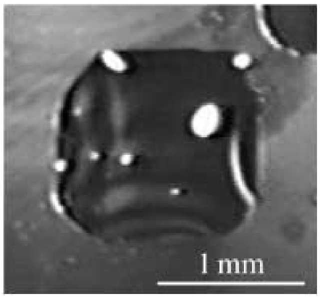


Fig. 4

Fig. 3 – Pinning of the contact lines on the corners of the crenellations which ensures a constant value for the surface fraction $\phi_S$.

Fig. 4 – Metastable square drop of ethyl malonate ($\theta = 32°$) on the structured surface. The contact line follows the directions of the rows.

*Surfaces with a controlled design.* – Figure 2 shows a surface achieved by Marzolin by casting a sol-gel silicate on a silicon wafer [8]. It consists in spikes (typical size one micron) which are regularly spaced. We used this model surface to test a possible invasion of the texture by various liquids.

For having a partial wetting with oils, octadecyl trichlorosilanes were grafted on the sample. A planar silicon wafer where the same molecules were grafted was used as a reference surface, allowing us to measure the advancing contact angle $\theta$. The measurements were done optically with an accuracy of 5° and the contact angle hysteresis on these surfaces was found to be small ($< 10°$).

Then, experiments similar to the one sketched in fig. 1 were realized with different liquids (*i.e.* various contact angles). The sample was partially immersed in a reservoir of liquid, and the existence of an invasion (or not) was monitored, together with the dynamics of the rise. The film was easily detected thanks to the darkening it induced on the sample. Our major result is the observation of an invading film climbing up to the top of the sample (typically one centimeter) for liquids having a small contact angle. A threshold in contact angle was indeed observed, above which the invasion was not observed. The value of this threshold was found to be between 30° and 35°.

The surface roughness $r$ is easy to estimate from SEM (scanning electronic microscopy) images and is $r = 1.30$ ($\pm 0.05$). The solid fraction $\phi_S$ on such a surface should be independent of the contact angle $\theta$, because of the possibility for the contact lines to pin on the corners of the crenellations (fig. 3) [9]. If the angle is larger than 0, the top of the spikes remains dry; in the same time, an angle smaller than $\pi/2$ makes favorable the filling of the texture by the liquid. In such conditions, the parameter $\phi_S$ is just the ratio of the area of the top of the spikes over the total area of the sample, which is 5% here [10]. Then, relation (2) predicts a value of $\theta_c$ equal to 40°.

This value is close to the observed one—but we consider as significant the small difference between both. Criterion (2) is thermodynamic, and metastable states can also be achieved because there are activation barriers to jump for the contact line. This is related to the disconnected nature of the texture: if we easily understand how a wetting liquid can invade a continuous groove in a solid [11], it is less obvious to figure out how the contact line pinned on a row of spikes can "know" that there is another row ahead. (Thus, hysteresis can occur:

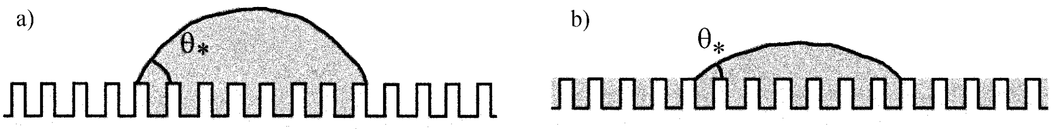


Fig. 5 – a) Wenzel regime: the surface is dry ahead the contact line. b) Film regime: the roughness is filled with a liquid film. The drop lies on a solid/liquid composite surface.

it is not the same thing to force a film inside a textured solid and leave it evolve, and to let it spontaneously invade the textures.) In our case, the progression of a film could be ensured by the presence of menisci around each spike and conditioned by the fact that each meniscus can reach the spike ahead from it. If we simplify the meniscus in a one-dimensional prism, the minimum contact angle $\theta_{\mathrm{min}}$ ensuring a sufficient extension is simply given by $\tan\theta_{\mathrm{min}} = \delta/d$, with $d$ the distance between two spikes and $\delta$ their height. For our sample ($\delta = 1.2\,\mu$m and $d = 2.5\,\mu$m), $\theta_{\mathrm{min}}$ is equal to 27°, slightly lower than $\theta_{\mathrm{c}}$, as observed experimentally. If a drop is deposited in a metastable situation ($\theta_{\mathrm{min}} < \theta < \theta_{\mathrm{c}}$), the liquid contact line follows the spikes rows and adopts a square shape as illustrated in fig. 4. This result reminds beautiful experiments from Lenormand on capillary imbibition of two-dimensional porous networks [12].

A symmetric situation occurs when one tries to mop up a liquid drop deposited on the surface: dewetting is expected if the Young contact angle is higher than the critical value ($\theta_{\mathrm{c}} = 40°$ in case). A much higher value was experimentally observed: after the drop has been sucked up, a film remains trapped if $\theta$ is lower than 60°. As it recedes, the imbibition front has to dewet spike rows. On such rows, both the solid roughness and the surface fraction are *locally* higher than their mean value: we measure for a row $r = 2.0$ and $\phi_{\mathrm{S}} = 20\%$, which gives from eq. (2) $\theta_{\mathrm{c}} = 63°$, in much better agreement with our measurements.

*Effective contact angle.* – A related question is the contact angle adopted by a small drop deposited on a rough surface. Two regimes are expected depending on whether the roughness is flooded or not (figs. 5a) and b)).

1) If the Young contact angle $\theta$ exceeds the critical angle $\theta_{\mathrm{c}}$, the rough surface is dry ahead the contact line (fig. 5a)). This situation has been described by Wenzel [1] and leads to a magnification of the cosine of the contact angle:

$$\cos\theta^* = r\cos\theta, \tag{3}$$

where $\theta^*$ is the effective contact angle on the rough surface.

2) When the Young angle is smaller than $\theta_{\mathrm{c}}$, the roughness is impregnated (then, part of the liquid is sucked, which can generally be neglected because of the small size of the texture) (fig. 5b)). Thus, the drop stands on a surface composed with solid and liquid. Considering a small variation d$x$ of the position of the contact line leads to a variation of surface energy $\mathrm{d}E = (\gamma_{\mathrm{SL}} - \gamma_{\mathrm{SV}})\phi_{\mathrm{S}}\,\mathrm{d}x - \gamma(1-\phi_{\mathrm{S}})\mathrm{d}x + \gamma\cos\theta^*\mathrm{d}x$. The latter quantity is zero at equilibrium, which leads to (using Young's relation)

$$\cos\theta^* = 1 - \phi_{\mathrm{S}}(1-\cos\theta). \tag{4}$$

This expression shows that the effect of a film is indeed to improve the wetting ($\theta^* < \theta$), but that it is not possible to induce a wetting transition by texturing a solid: complete wetting of the rough surface ($\theta^* = 0$) is only achieved when $\theta = 0$. The crossover between the two regimes is continuous (eqs. (3) and (4) are equivalent for $\theta = \theta_{\mathrm{c}}$), which is a difference with

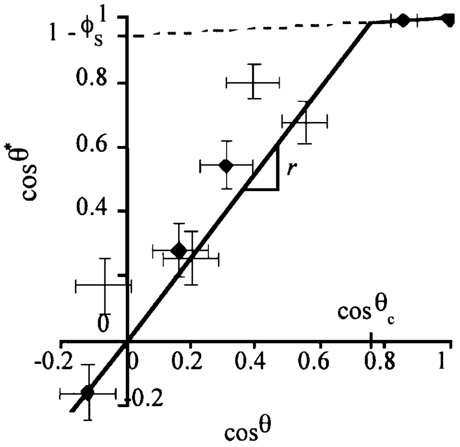


Fig. 6

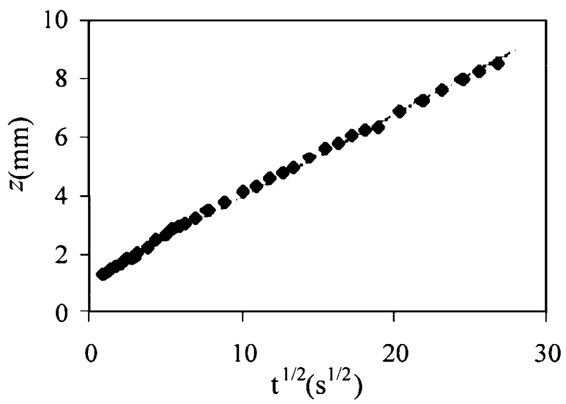


Fig. 7

Fig. 6 – Cosine of the contact angle $\theta^*$ measured on the textured surface as a function of the angle $\theta$ on the reference surface. The empty and full symbols correspond to static receding and advancing angles, respectively, and the full lines to eqs. (3) and (4).

Fig. 7 – Rise experiment realized with a silicon oil ($\gamma = 20.6\,\text{mN/m}$, $\theta = 0$, $\eta = 16\,\text{mPa s}$). The front height is plotted *vs.* the square root of the time. The dotted line is eq. (5) with $\beta = 4.1$.

the hydrophobic case, where the contact angle is observed to jump as soon as air is trapped below the drop [2, 6, 13].

Drops of various liquids were deposited on both the reference and the textured surfaces. The cosine of the observed contact angle $\theta^*$ on the rough surface is displayed in fig. 6 as a function of the cosine of the angle $\theta$ on the reference surface. The lines corresponding to eqs. (3) and (4) have been drawn without any adjustable parameter and show a fair agreement with experimental data.

The range of the imbibition regime in fig. 6 is rather small because of the sample microstructure and it would be worth realizing other designs with various values of $r$ and $\phi_S$. But it is indeed observed in this regime that the contact angle remains non-zero, in a domain of angle $\theta$ where Wenzel's law would have predicted a wetting transition ($\theta^* = 0$). Note finally that the Wenzel law seems to remain valid when $\theta$ is slightly higher than 90° (the drop weight is probably sufficient to overcome a weak pinning of the contact line on the corner of crenellations).

*Dynamics of imbibition.* – The time evolution of the imbibition front is a major issue in practical applications. It reminds capillary rise in porous materials, which is generally described by the classical Washburn law [14]: a constant capillary pressure balances a Darcy viscous dissipation, which leads to a diffusion law for the imbibition.

Here, the driving capillary pressure $\Delta P_{\rm L}$ derives from the relation $\mathrm{d}E = -\Delta P_{\rm L}\,\mathrm{d}V$, where $\mathrm{d}E$ is the energy variation induced by a small rise $\mathrm{d}z$ of the front line (eq. (1)) and $\mathrm{d}V$ the associated variation of liquid volume. For crenellated surfaces, $\mathrm{d}V$ (written per unit length) is a simple function of $\phi_{\rm S}$ and $\delta$, the depth of the roughness: $\mathrm{d}V = (1-\phi_{\rm S})\delta\,\mathrm{d}z$. Thus, we find: $\Delta P_{\rm L} = \gamma/\delta(\cos\theta - \cos\theta_{\rm c})/\cos\theta_{\rm c}$. The viscous force per unit area in the liquid film can be estimated from a classical Poiseuille law for a liquid flowing on a plane. It writes: $\Delta P_{\rm V} = 3\eta V z/\delta^2$, noting $\eta$ the liquid viscosity and $V$ its mean velocity ($V = \mathrm{d}z/\mathrm{d}t$). The presence of the spikes should not alter the scaling laws in this force, but increase it by a numerical factor that we call $\beta$.

If hydrostatic pressure is negligible (which is the case at the beginning of the imbibition), balancing the capillary pressure with the viscous force leads to a diffusion law

$$z = \left( \frac{2}{3\beta} \frac{\cos\theta - \cos\theta_c}{\cos\theta_c} \frac{\gamma\delta}{\eta} t \right)^{1/2} . \tag{5}$$

Gravity would soften the flow rate and finally provide an equilibrium height (of metric scale) described in appendix.

Rise experiments were recorded with a video camera. The front line is slightly distorted by defects on the sample but the data are reproducible and the rise rate does not depend on the surface orientation. An experiment made with a silicone oil ($\gamma = 20.6\,\mathrm{mN/m}$, $\theta = 0°$, $\eta = 16\,\mathrm{cP}$) is diplayed in fig. 7.

The rise height $z$ is plotted *vs.* the square root of time. A diffusive-type law is indeed observed, as expected. The zero ordinate corresponds to the millimetric extension of the macroscopic meniscus. The slope of the straight line allows us to estimate the coefficient $\beta$ for our surface: $\beta = 4.1$, which was confirmed with other wetting liquids. The validity of eq. (5) was finally checked in a partial wetting situation (for $\theta < \theta_c$). The imbibition was still found to be diffusive but the rise slown down because of the reduction in the driving force due to the non-zero value of $\theta$. The contact angles deduced from a fit with eq. (5) were found to be close (less than 5°) to the ones measured optically on the reference surface.

*Conclusion.* – We have described and illustrated with a model surface the different regimes of wetting of a rough surface exposed to a liquid. A two-dimensional imbibition of the roughness is observed if the Young contact angle of the liquid (obtained on an ideal smooth surface of same composition) is below a critical value $\theta_c$, which depends on two independent geometrical parameters: the *surface roughness* $r$ (ratio of the actual surface over the projected one) and the *solid fraction* $\phi_S$ (surface fraction corresponding to the top of the relief). The dynamics of imbibition film follows a diffusive-type law, as classically observed in wicking of a three-dimensional porous medium.

Thus, surface roughness modifies the contact angle when a drop is deposited on the surface. Beyond $\theta_c$, the liquid explores the whole relief and the cosine of the liquid contact angle is magnified by the surface roughness (Wenzel regime). Below $\theta_c$ (imbibition regime), the drop lays on a composite solid/liquid surface which leads to a large reduction of the contact angle. Building other micropatterned surfaces should be helpful for generalization of this approach to more complex structures. It should help to control the wetting and imbibition properties of a surface by tuning its design.

* * *

We thank S. Herminghaus for sending to us the very similar results he obtained for the criterion of impregnation in a texture (eq. (2)). We also thank C. Marzolin for putting at our disposal his model surfaces.

## Appendix

*The law of capillary rise for a textured surface.* – Hydrostatic pressure limits the rise in fig. 1. Balancing gravity with the capillary pressure $\Delta P_L$ leads to the equilibrium height $h = \gamma/\rho g\delta(\cos\theta - \cos\theta_c)/\cos\theta_c$, with $\rho$ the liquid density. Thus, heights of some meters are expected for micrometric patterns, which justify that we neglect gravity for centimetric rises as presented in the section *Dynamics of imbibition*.

Imbibition might be followed by weighing the sample while the liquid is rising. Two forces are then detected: a capillary suction $f_c$ by the macroscopic meniscus and the weight $f_w$ of the liquid exploring the rough structure. The capillary force (per unit length of the contact line) writes $f_c = \gamma \cos\theta^*$. The weight of liquid at the height $z$ is easily evaluated for crenellated structures (also per unit length): $f_w = (1 - \phi_S) z\delta\rho g$. Once the equilibrium height is reached ($z = h$), the global force $f$ measured is given by $f = r\gamma\cos\theta$, which surprisingly provides a simple measurement of the surface roughness $r$. Practically, it would require long samples (or larger spikes), which are not easy to build.

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[10] Let us stress that for these "two-levels" surfaces, $r$ and $\phi_S$ can be treated as independent: for example, increasing the height of the spike keeping everything else constant makes $r$ increase at a constant $\phi_S$. This opens the possibility for a fine tuning of the wetting properties of a solid. First realizations of such surfaces are described in Öner D. and McCarthy T. J., *Langmuir*, **16** (2000) 7777.
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