

Wetting of textured surfaces

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Abstract

We discuss quantitatively the wetting of a solid textured by a designed roughness. Both the hydrophilic and the hydrophobic case are described, together with possible implications for the wetting of porous materials. © 2002 Elsevier Science B.V. All rights reserved.

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1. The Kao experiment

Shibuichi et al. from the Kao Corporation recently made a remarkable series of experiments where they could show how texturing a surface modifies the contact angle, as a function of the chemical wettability of the solid [1]. Their results are shown in Fig. 1, where the value of the measured apparent contact angle θ^* on a rough surface is plotted versus θ , the Young contact angle determined on a flat surface of the same chemical composition. Both angles are expressed by their respective cosine.

Different regimes can be observed, together with an asymmetry between the hydrophobic side ($\theta > 90^\circ$) and the hydrophilic one ($\theta < 90^\circ$). (1) As soon as the substrate becomes hydrophobic, $\cos \theta^*$ sharply decreases, corresponding to a jump

of the apparent contact angle θ^* to a value of the order of 160° . It is also observed that very few values are available on this side, because of the practical difficulty of achieving flat surfaces of large hydrophobicity (i.e. large contact angle θ), as stressed long ago by Zisman [2]. Thus, the only way for realizing ultra-hydrophobic surfaces indeed consists in designing textured (hydrophobic) surfaces. (2) On the hydrophilic side, the behaviour is quite different: in a first regime, the cosine of the apparent contact angle increases linearly with $\cos \theta$, with a slope larger than 1 (in agreement, as we shall see further, with the so-called Wenzel's relation [3]). Thus the effect of the roughness is found in this case to improve the wetting. But the resulting line does not intercept the line $\cos \theta^* = 1$, which means that a wetting transition is not induced by the solid roughness. Indeed, in a second regime (concerning small contact angles), $\cos \theta^*$ is also found to increase lin-

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early with $\cos \theta$, but with a much smaller slope. Complete wetting ($\theta^* = 0$) is only reached if the substrate itself becomes wettable ($\theta = 0$). Our aim is here to describe these successive behaviours.

2. Super-hydrophobic solids

For hydrophobic solids ($\theta > \pi/2$), the dry solid has a surface energy γ_{SV} lower than the wet one γ_{SL} (as derived from the Young equation $\gamma \cos \theta = \gamma_{SV} - \gamma_{SL}$, denoting the liquid/vapour surface tension by γ). Thus, the surface energy can be lowered if air is trapped below the drop. For roughnesses of the order of $30 \mu\text{m}$ (a typical scale for some plant leaves [4]), these air pockets can be directly observed through the drop, which acts as a magnifying glass. A drop eventually sits on a patchwork of solid and air, which allows us to calculate the apparent contact angle [5]. We consider for simplicity a surface with crenellations (or spikes), as shown in Fig. 2. The liquid/vapor interfaces are drawn straight, because of the constant radius of curvature of the drop, much larger than the size of the texture. Note also that the existence of such interfaces below the drop is due to a possible pinning on the corners of the crenellations. More generally, such a pinning is possible on a textured surface, providing that it is rough enough, as discussed by Johnson and Dettre [6].

The contact angle can be obtained by considering a small displacement dx of the contact line. The change dF in surface energy per unit length associated with this displacement writes:

$$dF = \phi_S(\gamma_{SL} - \gamma_{SV})dx + (1 - \phi_S)\gamma dx + \gamma dx \cos \theta^* \quad (1)$$

where ϕ_S is the fraction of the solid/liquid interface below the drop. Using Young's equation, the minimum of F leads to:

$$\cos \theta^* = -1 + \phi_S(\cos \theta + 1) \quad (2)$$

Some corrections to this form have been proposed by Herminghaus, taking into account a possible roughness of the solid/liquid interface [7]. But the basic conclusions remain the same: (1) The contact angle discontinuously jumps to a value close to π (but smaller) as soon as air

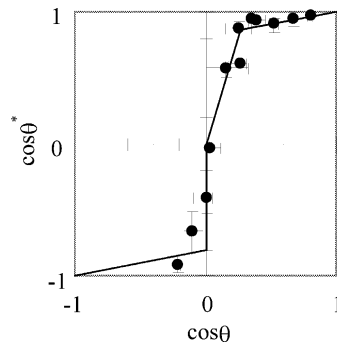


Fig. 1. Experimental results of the Kao group (from [1]). The cosine of the effective contact angle θ^* of a water drop is measured as a function of the cosine of the Young angle θ (determined on a flat surface of the same material and varied using different liquids). The results are obtained on hydrophobic ($\cos \theta < 0$) and hydrophilic ($\cos \theta > 0$) situations. In both cases, the roughness is found to affect dramatically the contact angle, but differently. The thin straight lines are respectively Eq. (2), Eq. (4) and Eq. (9), reading from left to right.

trapping is possible, and then varies very slowly with θ (since we expect ϕ_S to be much smaller than 1, on a very rough surface); (2) A total drying cannot be achieved by texturing a surface: $\theta^* = \pi$ implies either $\phi_S = 0$, which is not possible statically, or $\theta = \pi$, in which case it is not necessary to modify the surface to make it hydrophobic. Denoting by ε the difference between π and θ^* , we find from Eq. (2) that ε varies as $\sqrt{\phi_S}$ in the vicinity of $\theta^* = \pi$. This function is critical close to $\phi_S = 0$ (i.e. it varies quickly with ϕ_S in this limit), which stresses how difficult it is to reach values of θ^* very close to π . Note finally that the contribution due to the line tension was neglected in Eq. (1). For each spike (of size b), the surface energy is of order γb^2 , while the line energy is of order τb . The order of magnitude of τ is γa , where a is a microscopic length—thus, the

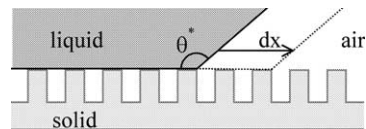


Fig. 2. Liquid deposited on a model surface with holes or spikes: for contact angles larger than $\pi/2$, air is trapped below the liquid, inducing a composite interface between the solid and the drop.

line tension should not have any effect in this problem as long as $b > a$, i.e. for spikes of supramolecular size.

These results qualitatively agree with the data displayed in Fig. 1. The value which can be deduced from this experiment is $\phi_s \approx 0.2$ —which expresses that only 20% of the solid surface below the drop are in contact with the liquid. The discussion also implies that a super-hydrophobic surface does not necessarily need to be highly rough. Model surfaces can have the same kind of properties, provided that the texture is designed in such a way that it favours air trapping [5]. Even a hydrophilic surface can be made super-hydrophobic, if the texture consists of mushroom-like patterns, with overhangs on which the contact line can be pinned [7]—but this state is only metastable, since a hydrophilic solid gains energy being covered by the liquid.

This last remark on metastability is more general. The asymmetry between the hydrophilic and hydrophobic sides stressed in Fig. 1 comes from the facts that the solid is initially dry before depositing a drop on it, and that pinning of the contact line is possible. But it is not obvious that the resulting state has a surface energy lower than the so-called Wenzel configuration, for which the solid/liquid interface follows the accidents of the solid surface. Denoting by r the solid roughness (i.e. the ratio of the actual surface over the projected one), a displacement of a curvilinear quantity rdx of the contact line implies a change in energy per unit length:

$$dF = r(\gamma_{SL} - \gamma_{SV})dx + \gamma dx \cos\theta^* \quad (3)$$

since the liquid/vapour interface is not affected by the solid roughness. F is minimal at equilibrium, which yields to Wenzel's relation [3]:

$$\cos\theta^* = r\cos\theta \quad (4)$$

where θ is Young's angle. For a flat surface ($r = 1$), Eq. (3) and Eq. (4) indeed define θ .

The 'air pockets state' considered up to now is thermodynamically stable if the energy variation expressed by Eq. (1) is smaller than the one leading to Wenzel's relation, given by Eq. (3). Hence, the condition of stability for this state is:

$$\cos\theta < \frac{\phi_s - 1}{r - \phi_s} \quad (5)$$

Thus, the solid must be hydrophobic enough (θ large enough), for air pockets to be stable. This condition is all the less restrictive since the solid is rough (for r large, Eq. (5) just expresses the usual condition of hydrophobicity: $\cos\theta < 0$). For a Young contact angle between $\pi/2$ and the threshold value given by Eq. (5), air pockets should be metastable. It would be interesting to test these predictions by forcing an impregnation in such a case (for example, immersing a rough hydrophobic sample at a large depth in a bath to study if an air film can displace the liquid). Similarly, the observed contact angle should depend on the way the sample is prepared: if condition 5 is not satisfied, the contact angle should not be the same if the drop results from the coalescence of micro-droplets deposited from a vapor (in which case the vapor or the micro-droplets can penetrate the roughness, of larger size) or if it is simply a large drop which is deposited.

3. Super-hydrophilic solids

For hydrophilic solids, the situation is quite different because the solid/liquid contact is favoured ($\gamma_{SL} < \gamma_{SV}$). Thus, the solid/liquid interface is likely to follow the roughness of the solid, which leads to a Wenzel contact angle Eq. (4). Since we have $r > 1$ and $\theta < \pi/2$, Eq. (4) implies $\theta^* < \theta$: the solid roughness makes the solid more wettable. The linear relation found in Eq. (4) is in good agreement with the Kao data Fig. 1, in the first part of the hydrophilic side. We can even deduce from the data the solid roughness, which is for this particular experiment found to be of the order of 3—a high value, as stated by the authors who emphasized the fractal nature of this surface [1].

But a second phenomenon can occur in the hydrophilic case, which deserves a special discussion. Since the solid is textured, it can be considered as a kind of porous material, in/on which the liquid can be absorbed [8]. This is a rather particular imbibition, since this porous material is close to be 2d (unlike usual 3d porous media). Conse-

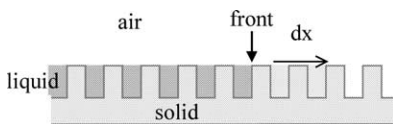


Fig. 3. Liquid film invading the texture of a solid decorated with spikes (or microchannels). The front is marked with an arrow. In the case of partial wetting, the top of the spikes remain dry—we call ϕ_s the emerged fraction of solid, corresponding to islands above the film level.

quently, a liquid/air interface must develop during the imbibition: following a suggestion of Steven Garoff, we could call this situation *hemi-wicking*, since it is intermediate between spreading and imbibition. Thus, the condition for this process to take place is expected to be intermediate between the spreading and imbibition criteria ($\theta = 0$ and $\theta < \pi/2$, respectively). Besides, if a film propagates from a deposited drop, a small amount of liquid is sucked into the texture, and the remaining drop sets on a patchwork of solid and liquid—a case very similar to the super-hydrophobic one, except that here the vapor phase below the drop is replaced by the liquid phase. We successively discuss the condition for hemi-wicking to occur, and the value of the resulting contact angle.

Let us consider for simplicity a model surface such as the one sketched in Fig. 3, in which hemi-wicking takes place, in a partial wetting situation ($0 < \theta < \pi/2$).

Because the wetting is only partial, the top of the spikes in Fig. 3 remains dry, as the imbibition front (marked with an arrow) progresses. We call ϕ_s the solid fraction remaining dry (note that for this particular texture, ϕ_s has the same value as in Fig. 2, in the super-hydrophobic regime). If the imbibition front progresses by a quantity dx towards the right, the corresponding change in interfacial energy writes per unit length:

$$dF = (\gamma_{SL} - \gamma_{SV})(r - \phi_s)dx + \gamma(1 - \phi_s)dx \quad (6)$$

where the factor $(r - \phi_s)$ expresses that the inside of the texture is invaded, but not the top. The second term is unusual in impregnation processes, since it is due to the creation of a liquid/vapor interface as the film moves.

Hemi-wicking should occur if dF is negative. Together with Young's relation, this yields as a criterion:

$$\theta < \theta_c, \quad \text{with } \cos \theta_c = \frac{1 - \phi_s}{r - \phi_s} \quad (7)$$

As expected, this condition is intermediate between the ones for spreading and for imbibition. Both these cases can be seen as limiting expressions of criterion 7. (1) For a flat surface ($r \rightarrow 1$), we find $\theta_c = 0$: spreading on a flat surface occurs if the contact angle vanishes. (2) For porous media ($r \rightarrow \infty$), we find $\theta_c = \pi/2$, which is the classical condition for capillary rise. More generally, we have $r > 1$ and $\phi_s < 1$ so that condition 7 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 design. For a given surface composition and liquid (i.e. fixing θ), the nature of the texture (which determines r and ϕ_s) decides if condition 7 is satisfied, or not. In the general case of disordered surfaces, the parameters r and ϕ_s are deeply intricate, and ϕ_s may depend on θ . Conversely, micropatterned surfaces such as the one sketched in Fig. 3 allow to decouple these two parameters, and even to treat them as independent. As an example, Öner and McCarthy recently produced beautiful micropatterned surfaces of variable height, but constant spike dilution (i.e. variable r and fixed ϕ_s) [9].

Finally, the value of the contact angle can be discussed. If the surface composition is such that $\pi/2 > \theta > \theta_c$, the solid remains dry beyond the drop, and the Wenzel's relation Eq. (4) applies. On the other hand, if the contact angle is smaller than θ_c , a film develops in the texture and the drop sits upon a mixture of solid and liquid Fig. 4.

Once again, the value of the apparent contact angle can be deduced from a small displacement

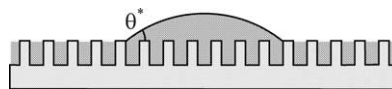


Fig. 4. In the case where a film invades the solid texture, a drop lies on a solid/liquid composite surface. Then, the apparent contact angle θ^* is found to be intermediate between 0 (which would be observed if the substrate would only consist of liquid) and θ (which is the contact angle on a flat homogeneous solid).

dx of the contact line of the drop. The associated change in surface energy writes per unit length:

$$dF = (\gamma_{SL} - \gamma_{SL})\phi_S dx - \gamma(1 - \phi_S)dx + \gamma \cos\theta^* dx \quad (8)$$

where the second term on the right-hand side is related to the suppression of liquid/air interfaces as the drop spreads. The equilibrium condition $dF = 0$ together with Young's relation yields:

$$\cos\theta^* = \phi_S \cos\theta + 1 - \phi_S \quad (9)$$

This expression shows that the film beyond the drop indeed improves the wetting ($\theta^* < \theta$), but it does so less efficiently than with the Wenzel scenario: for $\theta < \theta_c$, the angle deduced from Eq. (9) is significantly larger than the one derived from Eq. (4). Physically, this can be understood as the smoothing effect of the film, which erases the solid roughness and thus prevents the Wenzel effect to take place. Furthermore, Eq. (9) (unlike Eq. (4)) shows that it is not possible to induce a wetting transition by texturing a solid: complete wetting of a rough surface ($\theta^* = 0$) is only achieved for $\theta = 0$.

Note finally that the crossover between the Wenzel and the film regimes indeed takes place for $\theta = \theta_c$ (and thus depends on the design of the texture): Eq. (4) and Eq. (9) give the same apparent contact angle for $\theta = \theta_c$. These behaviours fairly agree with the Kao data (Fig. 1), where two linear regimes are successively observed in the hydrophilic regime, with slopes respectively larger and smaller than 1. It is also found experimentally that the apparent contact angle does not vanish on a rough surface, if the Young angle itself remains larger than zero, in agreement with our conclusions.

4. Applications to porous media

Very often, the properties of a porous medium are (over)simplified by considering that such a medium can be considered as an array of capillary tubes. For example, both the capillary rise in a tube and in a porous material are often found to follow the so-called Washburn law (the height increases as the square root of time, for small

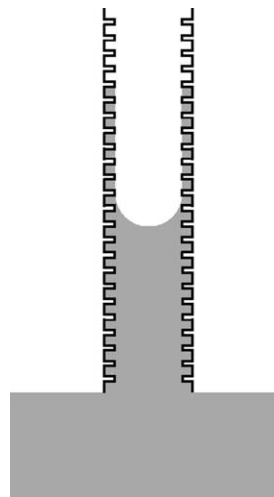


Fig. 5. Tube decorated with spikes, as an example of modelization of a porous material. Two different capillary rises are likely to take place in such a tube: one in the main part, and the other inside the spikes. The film in the spikes propagates faster than the main meniscus, which leads to a broadening of the front. This should mimic porous materials where (at least) two different length scales are generally present.

heights [10]), from which an equivalent tube radius can be deduced for characterizing the porous structure. This approach is sometimes useful, but cannot explain many experimental facts related to the complex nature of the porous material. For example, it was reported that the width of a liquid front (defined as the distance between the most advanced and the less advanced parts) gets larger with time in most imbibition processes in a paper or in a fabric [11].

Here we propose to consider a tube decorated with a texture Fig. 5. Most porous media are similarly characterized by two different length scales (intervals between fibers and between yarns in a fabric, for example), and such a description should be relevant for these kinds of materials.

We take the two length scales much smaller than the capillary rise, so that a wetting liquid should invade both the tube itself and the texture, if condition 7 is satisfied. Although the scale of the texture is much smaller than the one of the tube, the film should propagate faster along the decorations than in the tube, because the latter acts as a reservoir for the film. As long as gravity

can be ignored, both the rises obey the Washburn equation (diffusive-type law) [8,10], so that the front should become wider and wider as time goes on.

On the other hand, the main front (the one in the tube) raises along a composite surface, made of solid and liquid, and the apparent contact angle on the tube is given by Eq. (9). In the limit of small velocities (for which dynamic corrections can be ignored for the contact angle) and as shown by Washburn, the value of this angle influences the dynamics of the rise. Since the presence of a texture affects the value of the contact angle, the value deduced from the dynamics of the rise could be different from the one measured on flat surface of the same material. Thus, considering a textured tube could also explain some discrepancies reported in the literature, where anomalously low values for the contact angle have sometimes been found.

5. Conclusions

We have shown that the simplest possible description of the wetting (or dewetting) of a textured surface implies two dimensionless parameters, namely the surface roughness and a surface fraction characterizing the ratio between the two levels of such a surface. The apparent contact angle could be calculated on such a surface, as a function of these parameters and of the Young contact angle, fixed by the chemical nature of the solid and the liquid.

In the hydrophobic case, it was found that if the contact line can pin on the texture (thanks to the presence of sharp corners, for example), a super-hydrophobic behaviour can be generated, of

obvious practical interest: a drop does not stick on such a surface, and can be easily removed. The question of the possible metastability of such super-hydrophobic states was also addressed.

In the hydrophilic case, the drop either follows the topography, which generates an efficient decreasing of the contact angle, or it spreads inside the solid texture, and then coexists with the solid filled with liquid. There again, the contact angle is decreased, but remains strictly larger than zero in a situation of partial wetting, because of the presence of emerged islands.

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