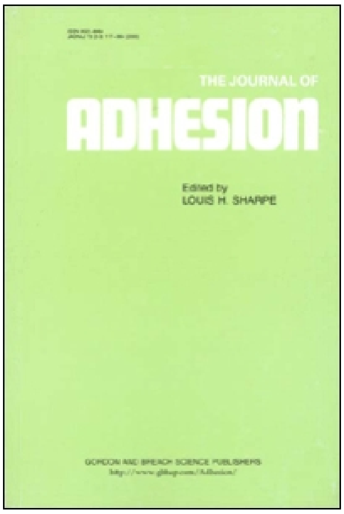

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Chemical Wetting Hysteresis*

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Experiments performed on model systems show that the contact angle of a liquid on a solid depends strongly on very small-sized chemical heterogeneities of the solid surface. The measurement of the maximum advancing and minimum receding contact angles of liquid Sn on Si-SiO_2 surfaces was performed by stretching and compressing a liquid bridge between two parallel plates. The shape and distribution of the micro-defects are controlled by fabricating model chemically-heterogeneous surfaces. The wetting hysteresis is found to depend on the linear density of the chemical defects as the chemical pinning of the triple line occurs in only one (advancing or receding) spreading direction. Moreover, the inversion of the chemistry of the substrate and the defect leads to different width of the hysteresis. These results agree fairly well with the recent theoretical descriptions of wetting phenomena.

KEY WORDS: wetting hysteresis; controlled chemical defects; liquid Sn/Si-SiO_2 substrate; maximum advancing and minimum receding contact angles; liquid bridge; cooperative pinning of the triple line.

1 INTRODUCTION

The equilibrium position (referenced to an arbitrary lateral position), $x = x_e$, of the solid-liquid-vapor edge (triple line) of a liquid on a perfect (*i.e.* smooth and homogeneous) solid surface, corresponds to the minimum value of the total interfacial free energy, E, of the solid (S), liquid (L), vapor (V) system in thermodynamic equilibrium:

$$\frac{dE}{dx} = (\gamma_{SV} - \gamma_{SL})\frac{dA_{SV}}{dx} + \gamma_{LV}\frac{dA_{LV}}{dx} = 0 \qquad (1a)$$

and

$$\frac{d^2E}{dx^2} < 0 \qquad (1b)$$

These relationships are equivalent to the equilibrium wetting condition given by the Young- Dupré equation:

$$\cos\theta^e = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad (2)$$

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[**] associé aux Universités d'Aix-Marseille 2 et 3.

When a surface has a chemical defect, the interfacial free energies of the solid, γ_{SV} and γ_{SL}, change locally (as the solid changes) and the contact angle, θ_d^e, on the area of the defect is different from that of the matrix. If a triple line lies partly on a matrix surface and partly on its defect, the macroscopic contact angle, θ_M, is changed. In order to understand this feature, we describe the behaviour of the triple line very slowly moved on a solid surface with such a defect.

When the surface is homogeneous, at every point of the triple line the contact angle is θ^e. When a part of the triple line contacts the defect at x_d, a distortion of the triple line occurs in two different ways as explained below in the case of an advancing triple line.

If $\theta^e < \theta_d^e$, the part of the triple line on the defect is stopped while the part of the triple line on the matrix surface is advancing (Fig. 1a). An increasing distortion of the triple line develops, which should be extended until the contact angle on the defect is θ_d^e. But the increase of the length of the triple line produces an increase of the liquid free area. Depinning should occur when the increase of the liquid surface free energy (second term of Eq. (1a)) is no longer balanced by the gain of wetting free energy (first term on Eq. (1b)).

If $\theta^e > \theta_d^e$, while the part of the triple line contacts the defect, it spontaneously advances on it as the liquid should have a smaller contact angle on this area (Fig. 1b). The distortion of the triple line occurs under the same energetic constraints as those described in the previous case, but the extension of the distortion is generally limited by the length of the defect, L_d. Indeed, the spreading of the liquid on the defect is stopped when the triple line contacts the matrix at $x_d + L_d$. A further advance of the part of the triple line on the matrix from x_d reduces the distortion of the triple line.

When a distortion of the triple line occurs, the contact angle is no longer constant along the triple line, but a macroscopic contact angle, θ_M, can be defined from the mean position of the triple line. The wetting hysteresis characterizes the dependence of the macroscopic contact angle on the surface defects when a liquid spreads (advances or recedes) on a surface. At zero speed, *i.e.* in a thermodynamic state, the maximum width of the wetting hysteresis can be measured. The wetting hysteresis should be decreased by the consumption of the kinetic energy of the triple line when spontaneous spreading occurs.

The previous description of the role of a chemical defect on the wetting of a solid surface synthesizes simple experimental observations and original ideas of different authors. It supposes that the wetting hysteresis should depend on the local contact angles on the defect and on the matrix, and on geometric characteristics of the defect. The dependence of the contact angle on the local equilibrium of the liquid on the solid at the scale of the defects was proposed 45 years ago.[1,2] The first models[3-6] used thermodynamics to describe the equilibrium state of a liquid on a surface with defects parallel to the triple line. They showed the existence of metastable states of the triple line between two extreme possible positions. More recent theoretical works have been performed by using a mechanical approach. They have included a description of the deformation of the liquid surface which results from the distortion of the triple line due to the different wettability of the defects.[7-12] This treatment confirms the prediction[13] of a stick-and-slip motion of the triple line when it moves on the heterogeneous surface.

Few experiments are available to discuss the validity of the theoretical models because the triple line can stick on very small defects: micron-size heterogeneities were recently shown to anchor the triple line on a macroscopic scale.[14,15] Since then,

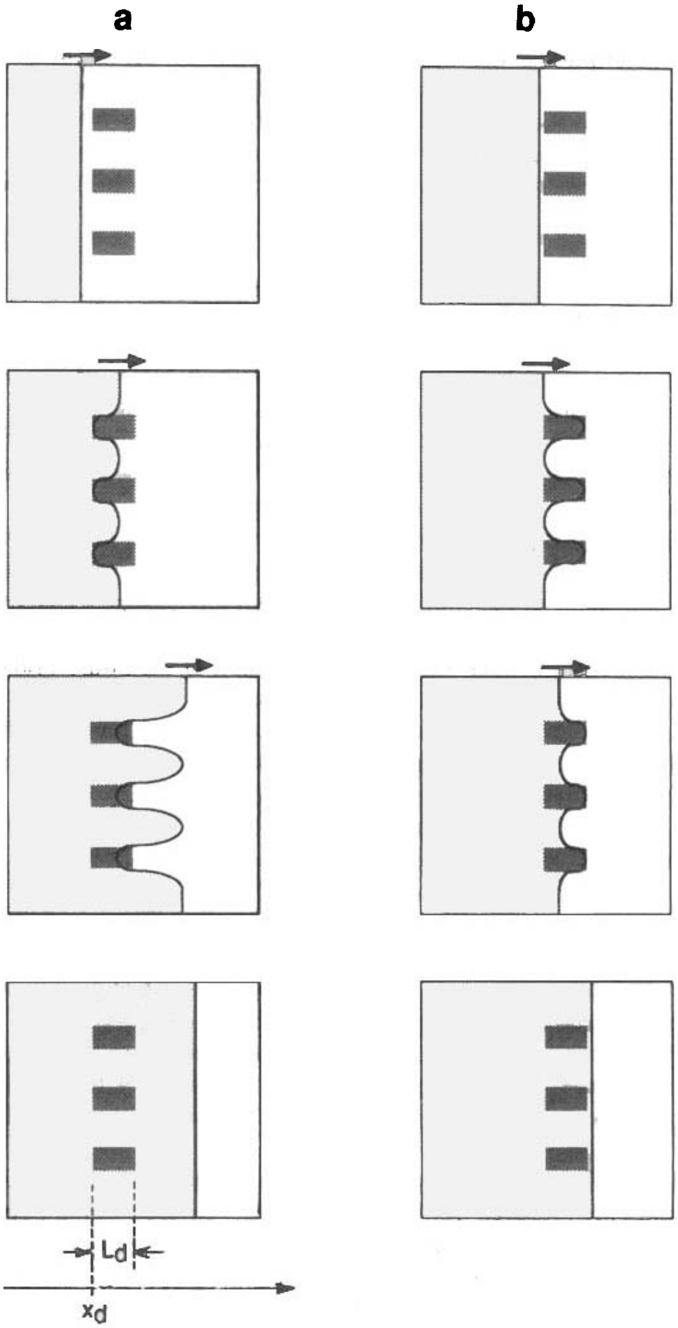

FIGURE 1 Schematic behaviour of an advancing triple line when it encounters a) a defect less wettable than the matrix ($\theta^e < \theta^e_d$), b) a defect more wettable than the matrix ($\theta^e > \theta^e_d$).

experimental studies have focused on the wetting of surfaces with controlled defects. These studies revealed the shape of the triple line on a single defect[14,15] and provided a qualitative description of the stick-and- slip motion of a triple line in the defect field.[16] Quantitative measurements are still needed to determine the chemical and physical parameters of the defects on which the width of the wetting hysteresis depends. Liquid Sn on Si-SiO_2 substrates was found to be a good model system since the defects can be controlled at the micrometer scale, and the wetting of Sn on Si and SiO_2 are very different.

EXPERIMENTAL METHOD

A liquid bridge located between two parallel plates is successively compressed and stretched very slowly. Figure 2 presents a typical experiment, the important steps of which are described below. The four macroscopic contact angles, the two contact area diameters and the height of the "sandwich-drop" are simultaneously measured. Details and experimental set-up are given in another paper.[17]

The liquid bridge is compressed from steps A to C (Fig. 2). The contact angles and areas increase until the liquid bridge is symmetrical. From B to C, the compression produces an increase of the contact areas without any change of the contact angles. They have the value of the maximum advancing macroscopic contact angle, $\theta_a^{\max}$. This angle is measured in C after a 0.5 mm compression of the liquid bridge in the $\theta_a^{\max}$ configuration. Actually, although the compression speed is constant, the increases of the contact areas are discontinuous; stick-slip motions of the triple lines occur as observed by Di Meglio.[16] This mainly explains the scattering of $\theta_a^{\max}$ values on the maximum advancing contact angle plateau between B and C.

From C to F the liquid bridge is stretched. Until D, the contact angles continuously decrease, from the maximum advancing macroscopic contact angle, $\theta_a^{\max}$, to the minimum receding macroscopic contact angle, $\theta_r^{\min}$, without any change in the contact areas. In D, $\theta_r^{\min}$ is measured. From D to E, the contact areas decrease by stick-slip motions of the triple lines, whereas the contact angles have the constant value $\theta_r^{\min}$. Upon stretching after E, the liquid bridge becomes sensitive to gravity, which induces the dissymmetry and the breaking up of the sandwich-drop.

The equilibrium contact angles, θ^e, on the pure substrates are obtained by two paths: after the spontaneous advancing and receding motions of the triple line, at the beginning and the end of the "sandwich-drop" experiment in the sessile drop configuration.

The defects of the studied surfaces were prepared using microelectronic technology. The substrates are prepared from wafers of Si (100) covered with a 28 nm thermally-grown SiO_2 layer. From these samples, different groovings allow one to obtain either SiO_2 cylinders in relief on a Si (100) matrix surface or cylindrical holes of Si (100) in the amorphous layer of SiO_2. Circular (°) or square (□) shapes (60 μm large) and single (°) or double (°°) densities of the defects (100 or 200 μm on center apart) were studied. The photographs of Figure 3 show an example of such a surface. The metal sample is a piece of tin, 99.999% pure, of a few hundred mg in weight. The experiments are performed in a 10^{-5} Pa vacuum at 1173 K.

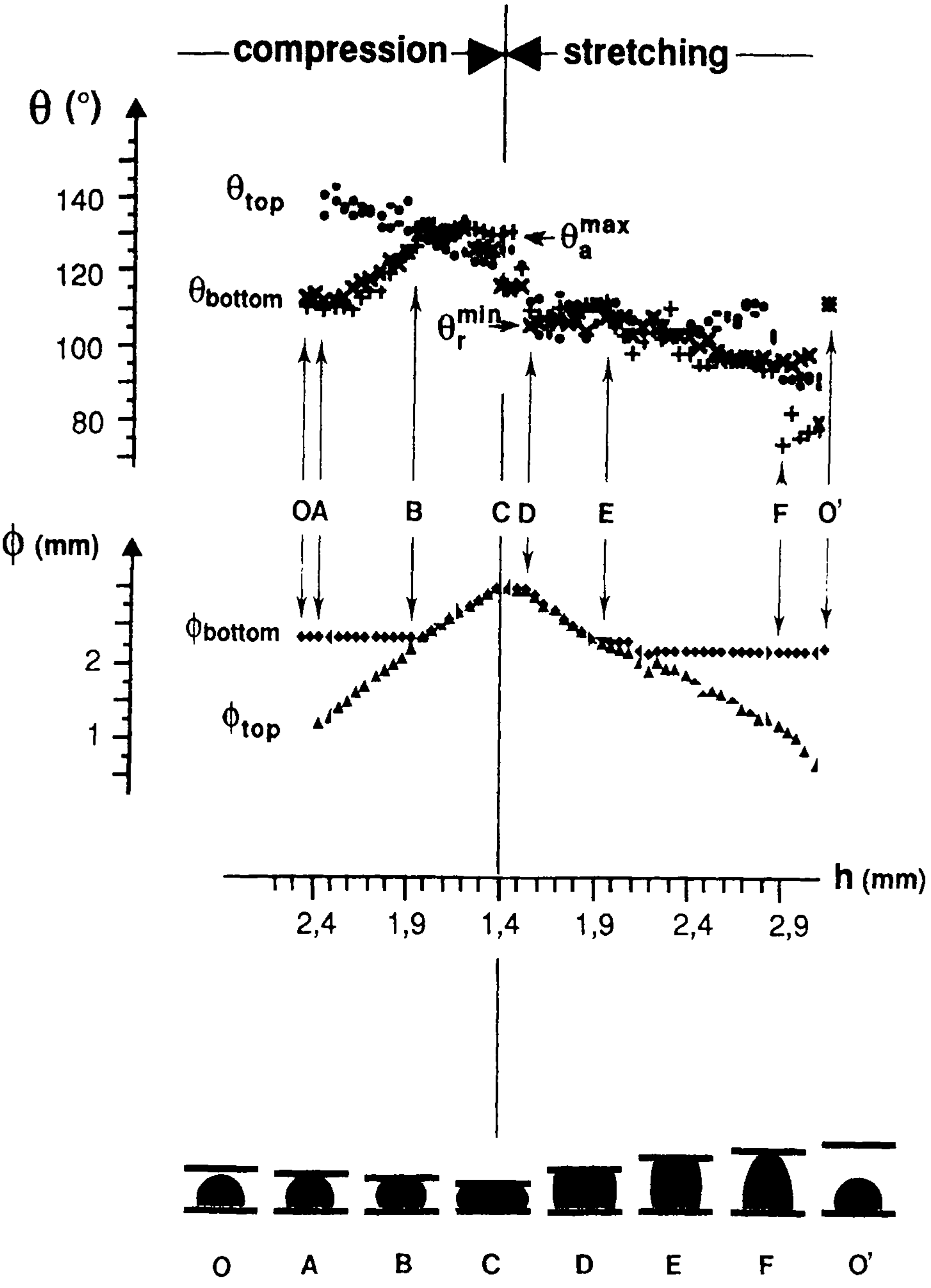

FIGURE 2 Contact angles (θ) and solid-liquid area diameters (ϕ) of a sandwich drop of Sn between two plane, identical, randomly-rough SiO_2 substrates at 1173 K as a function of the height of the liquid bridge (h) during a 0.5 mm·mm^{-1} continuous compression-stretching cycle (from Ref. 17). Different configurations are shown to illustrate the experiment. The volume of the drop is about 1 cm^3 so that the height of the sessile drop is of the order of the capillary length ($l_c \simeq 2$ mm).

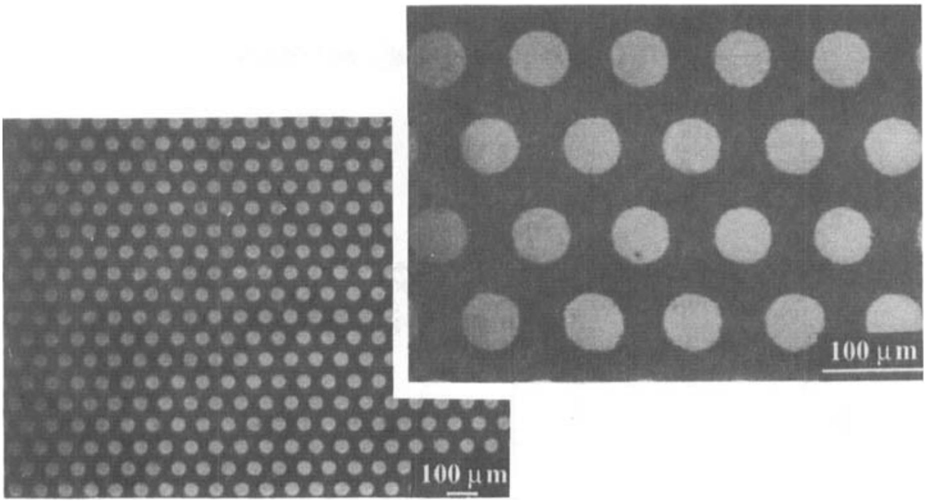

FIGURE 3 Photographs by optical micrography of a two-phase substrate composed of (100) Si disks on a thermally-grown SiO_2 matrix surface.

CHEMICAL WETTING HYSTERESIS: RESULTS AND DISCUSSION

Previous experiments showed that a perpendicular step parallel to the triple line cannot anchor the triple line if its height is very small compared with the capillary length.[17] This behaviour could be due to its thermal wandering which allows this linear defect to be jumped easily by a mechanism of nucleation.[18,8] Then, on the Si-SiO_2 substrates which have perpendicular steps 28 nm high between the matrix surface and the defects, the measured hysteresis should only depend on the 2D characteristics of the defects as the capillary length of tin is some millimeters.

Sandwich-drop experiments were performed at 1173 K with Si-saturated Sn on $SiO_{2\circ}$/Si, $SiO_{2\circ\circ}$/Si, $SiO_{2\square}$/Si, $Si_{\circ}/SiO_2$, $Si_{\circ\circ}/SiO_2$ and $Si_{\square}/SiO_2$ substrates. The equilibrium contact angles, θ^e, of Si-saturated Sn at 1173 K on pure Si and pure thermally-grown SiO_2 are, respectively, equal to $40 \pm 2°$ and $111 \pm 2°$. Then the wetting hysteresis of a liquid drop of Sn on a solid surface composed of Si and SiO_2 could be as large as 71°. That corresponds to a change in a ratio of 1.87 of the contact area diameter of a sessile drop. Then the size of the defects is two orders of magnitude less than the possible variation of the contact.diameter of a millimeter-size sessile drop. As the triple line should be pinned on the closest defects (to minimize the increase of the liquid surface area),[9] the distortion of the triple line should not be visible at the scale at which the macroscopic contact angle is measured.

As the shape (circle or square) of the defects does not change the advancing and receding contact angles when the density of the defects is constant, all the results are plotted in Figure 4. The axes were chosen to show clearly the physical quantities on which the wetting hysteresis depends. The advancing and the receding wetting hysteresis are written:

$$\Delta W = \cos\theta_M - \cos\theta^e_{\text{matrix}} \tag{3}$$

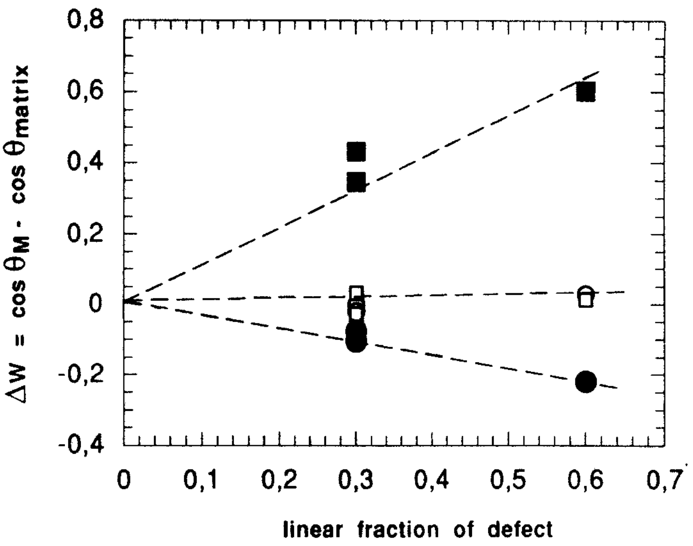

FIGURE 4 Maximum advancing and minimum receding *chemical* wetting hysteresis of tin on the two-phase Si-SiO_2 substrates at 1173 K as a function of the maximum linear fraction of defects. θ_M is θ_a^{max} or θ_r^{min}. For eliminating the intrinsic wetting hysteresis due to the roughness of the substrate (existing for both pure and heterogeneous substrates), these advancing and receding contact angles are, respectively, referred to the advancing and receding contact angle of tin measured on the pure matrix: θ_{matrix} are θ_a^{max}(matrix) θ_r^{min} (matrix), respectively, instead of θ^e on the pure matrix. Experiments on the SiO_2 matrix are plotted with squares: □ $\cos\theta_a^{max} - \cos\theta_a^{max}(SiO_2)$ with $\theta_a^{max}(SiO_2) = 126 \pm 2°$, ■ $\cos\theta_r^{min} - \cos\theta_r^{min}(SiO_2)$ with $\theta_r^{min}(SiO_2) = 105 \pm 2°$. Experiments on the Si matrix are plotted with circles: ● $\cos\theta_a^{max} - \cos\theta_a^{max}(Si)$ with $\theta_a^{max}(Si) = 44 \pm 1°$, ○ $\cos\theta_r^{min} - \cos\theta_r^{min}(Si)$ with $\theta_r^{min}(Si) = 35 \pm 1°$.

where θ_M is θ_a^{max} or θ_r^{min}. Classically, wetting hysteresis refers to $(\theta_a^{max} - \theta_r^{min})$. Here, ΔW is preferred as in the theoretical works,[7–9] because the equilibrium is governed by the minimisation of the energy which displays the cosine of the contact angle (Eq. (1a), and (2)). Advancing and receding ΔW are shown as a function of the maximum linear fraction of the defects, f_d^{max}. This quantity supposes that the triple line lies on the closest defects and maximizes its length on them. It should be noted that the measured values of θ_a^{max} and θ_r^{min} on the pure substrates are not strictly equal to θ^e because these substrates always have an intrinsic roughness. To get rid of this roughness hysteresis and to discuss only the chemical hysteresis, the value of ΔW is calculated from the values of θ_a^{max} and θ_r^{min} on the heterogeneous substrates refered to θ_a^{max} (matrix) and θ_r^{min} (matrix) respectively, instead of to θ^e in Equation (3).

Figure 4 shows that the advancing wetting hysteresis is very different if Si is the matrix or the defect. Si defects on SiO_2 produce a large wetting hysteresis, but the same geometrical SiO_2 defects on Si produce no hysteresis. These results are consistent with the previous qualitative description of the behaviour of the triple line when it encounters a chemical defect that is less wettable or more wettable than the matrix, respectively. Hysteresis appears when the triple line is pinned on the defects. In the case of our experiments, the defects are very close to each other and the distortions of the triple line interfere. A cooperative effect increases the hysteresis as multi-pinning reduces the deformation of the liquid surface. In the case of pinning of the triple line by the matrix at the end of the defect, the wetting hysteresis is too small to be detected in our experiments as the length of the defect, L_d, is very small.

Similar behaviour in the receding configuration is observed but for inverted positions of the defect and the matrix. They are controlled by the same physical phenomena. SiO_2 defects do not produce wetting hysteresis while Si defects on a SiO_2 matrix surface do.

The magnitude of the wetting hysteresis is now considered. Figure 4 shows a linear increase of the wetting hysteresis (in ΔW form) when the length of the pinned triple line increases. But, if the chemistry of the matrix and the defect are inverted, the width of the hysteresis changes. Considering the thermodynamic or mechanical equilibrium, the value of the wetting hysteresis should be interpreted in term of $\Delta W = \cos\theta_M - \cos\theta^e_{\mathrm{matrix}}$ as has been done in previous theoretical works.[7, 9] The defects are characterized by a sharp change of wettability at the edge between the defect and the matrix. They are the so-called "mesa-defects" described by Joanny and De Gennes.[7] The pinning strengths of the defects, defined as the difference of wetting between the matrix and the defect, $\Delta W^e (= \cos\theta^e_{\mathrm{defect}} - \cos\theta^e_{\mathrm{matrix}})$, are large: they are equal to $+1.12$ or -1.12 depending on whether Si is the defect or the matrix, respectively. But, for the same size and distribution of the defects having the same pinning strength in absolute value, Si defects on SiO_2 are 3 times stronger than SiO_2 defects on Si. This result can be interpreted if the pinning function of the defect is considered as a perturbation of the equilibrium shape of the liquid drop on the perfect matrix surface. Then, the wetting hysteresis has to depend on the wettability on the matrix surface. The experimental results show that this factor should give rise to an increase of the wetting hysteresis when $\theta^e_{\mathrm{matrix}}$ increases. It should be noted that for weak defects Robbins and Joanny proposed a factor $\sin\theta^e_{\mathrm{matrix}}$.[9]

WETTING HYSTERESIS ON REAL SURFACES

The aim of this paper was to present a method and a chemical system suitable for the quantitative study of the wetting hysteresis. To our knowledge, these experiments give the first quantitative results which can be used to discuss the thermodynamic parameters on which the wetting hysteresis depends. These results could be obtained by studying surfaces with one type of well-characterized defects. But this is only a first experimental step, as the results cannot be generalized. Indeed, another series of experiments is needed to understand the wetting hysteresis on other simple heterogeneous surfaces, such as those with defects whose size tends towards the capillary size, or those with a high or low density of defects.

One defect can be defined as an homogeneous smooth surface chemically different from the matrix surface and/or tilted towards it. A surface which has topological defects can be described as a matrix surface which is parallel to the mean plane on the solid, the defects of which are the plane areas tilted by an angle, α, from the matrix plane. The equilibrium contact angle on each tilted area is equal to $\theta^e + \alpha$. Real surfaces are generally randomly rough surfaces which have at least two types of defects. Then, they will show contact angle hysteresis in the two directions (advancing and receding) of motion of the triple line if one type of defect is more wettable ($\alpha < 0$) and the other type less wettable ($\alpha > 0$) than the matrix surface. This is the case of rough surfaces with hills and valleys parallel to the triple line. While the quantities on which the wetting hysteresis depends are now better defined, the prediction of the wetting hysteresis of a randomly rough surface is difficult due to the lack of determination of the relevant size of defects of the surface. Convenient experimental works on this subject could be performed with surfaces where several types of defects are mixed (for example large and narrow defects in variable proportion).

This work shows that the surface state at the micrometer scale is a very important parameter to know when an equilibrium contact angle is measured. Particularly, the Young relationship has to be used with caution if interfacial free energies of the solid have to be determined from contact angle measurements.

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