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Effects of structural and chemical anisotropy of nanostructures on droplet spreading on a two dimensional wicking surface

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When a liquid droplet is deposited onto an array of nanostructures, a situation may arise in which the liquid wicks into the space between the nanostructures surrounding the droplet, forming a thin film that advances ahead of the droplet edge. This causes the droplet to effectively spread on a flat, composite surface that is made up of the top of the nanostructures and the wicking film. In this study, we examined the effects of structural and chemical anisotropy of the nanostructures on the dynamics of droplet spreading on such two-dimensional (2D) wicking surfaces. Our results show that there are two distinct regimes to the process, with the first regime characterized by strong anisotropy in the droplet spreading, following the asymmetric structural or chemical cues provided by the nanostructures. The trend reverses in the second regime, however, as the droplet adopts an increasingly isotropic shape with which it eventually comes to rest. Based on these findings, we formulated a quantitative model that accurately describes the behaviour of droplet spreading on 2D wicking surfaces over a wide range of conditions. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4890504]

I. INTRODUCTION

The spreading of a liquid droplet on a solid surface is a fundamental aspect of the interaction between solid and liquid phases and has been a key area of research for the past few decades.^{1–10} In particular, the most basic form of this interaction, the wetting of a liquid drop on a flat, homogeneous solid surface, has been intensively studied,^{1–5} yielding results that show that the spreading dynamics are dominated by the balance between Laplace pressure and droplet inertia (capillary-inertia regime) in the early stages of wetting,^{3,5} and then by the balance between capillary energy and viscous dissipation (capillary-viscous regime) in the later stages.^{2,3,5} The displacement (*a*) versus time (*t*) relationship of the droplet edge follows a power law for both regimes $(a \propto t^n)$, with *n* being 0.3–0.5 in the capillary-inertia regime.²

Most surfaces, however, are far from being perfectly flat and therefore, studies extending to droplet spreading on rough surfaces are important. It is known that when a droplet is deposited onto a rough substrate, the droplet may infiltrate the roughness of the surface so that it spreads over an uneven surface of homogeneous chemistry (Wenzel state)¹¹ or the droplet may "sit" on top of the rough surface, wetting only the tip of the roughness and effectively spreading over a flat surface of composite chemistry, made up by air spaces and the substrate material (Cassie-Baxter state).^{12,13} A third form of wetting is also possible. This involves the droplet liquid seeping into the roughness of the surface forming a wicking film that advances ahead of the droplet edge.^{14–18} The wicking film wets the sides but not the tips of the roughness. This causes the droplet to spread on a flat composite surface made up of solid and liquid phases and can be considered as a combination of Wenzel and Cassie-Baxter states of wetting. This form of wetting is also known as hemiwicking or 2D wicking, and the condition under which it will take place, as established by Bico *et al.*,¹⁴ is

$$\cos \theta > \cos \theta_c = \frac{1 - \phi_s}{r - \phi_s},\tag{1}$$

where θ is the contact angle the liquid makes with a flat surface of the substrate material, θ_c is the critical angle $(0^\circ \le \theta_c \le 90^\circ)$, *r* is the roughness of the textured surface (ratio of the actual surface area to projected area) and ϕ_s is the ratio of the area of the top of the nanostructures (which is not wetted by the wicking film) to the projected area.

Unlike Wenzel and Cassie-Baxter states, however, the dynamics of droplet wetting on 2D wicking surfaces is not well-studied. In particular, the effect of surface roughness anisotropy on droplet spreading for 2D wicking surfaces has yet to be reported despite the fact that such surface roughness anisotropy has been shown to have a significant influence on droplet spreading for Wenzel^{19,20} and Cassie-Baxter states.¹³ The motivation of this paper, therefore, is to conduct a systematic study on how structural and chemical anisotropy of

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the surface roughness affect the spreading dynamics of a droplet deposited onto a 2D wicking surface.

II. EXPERIMENTAL PROCEDURES

To obtain structurally anisotropic surface roughness, eight separate hexagonal arrays of Si nanofins were fabricated over an area of 1 cm² using interference lithography (IL) and metal assisted chemical etching (MACE). The details of the fabrication process and experimental methodology can be found in our previous paper¹⁸ and the dimensions of nanofins for each of the eight samples can be found in Table I. Briefly, the IL system was first used to expose 400 nm of spin-coated photoresist (Ultra-i-123) on a Si substrate twice, with each exposure at less than right angles to one another. After development with a commercial developer, Microposit MF CD-26, photoresist ellipses will be left on the Si surface. Oxygen plasma processing was then employed to remove the residual photoresist between the ellipses. To carry out the MACE process, 30 nm of Au was deposited onto the surface using a thermal evaporator. Next, the photoresist was removed using acetone and ultrasonication, leaving behind an Au mesh with a hexagonal array of elliptical holes. Placing the samples into a bath containing 0.44 M of H₂O₂ and 4.6 M of HF will then cause etching of Si under the Au mesh, leaving behind Si nanofins which protrude from the elliptical holes in the Au mesh.²¹ The height of the nanopillars can be controlled by the etching duration. Finally, the Au mesh was removed with a commercial Au etchant. Figs. 1(a) and 1(b) show SEM images of some of the Si nanofins employed in this study. Note that in Fig. 1(b), we have also defined the X- and Y-axes to be parallel to the long side and short side of the nanofins, respectively. This convention shall be used throughout the paper.

Besides structural anisotropy, the effect of chemical asymmetry of the nanostructures on the dynamics of droplet spreading was also investigated. Here, we have employed the use of structurally isotropic Polystyrene (PS) nanopillars fabricated with interference lithography and O_2/CF_4 plasma etching. The surface energy of the PS nanopillar surface can

TABLE I. Geometric properties of Si nanofins and nanopillars used in this study. The various geometric parameters, *p*, *q*, *m*, and *n* can be found annotated in the diagram Fig. 5. All nanofins are Si and deposited with silicone oil ($\gamma = 3.40 \times 10^{-2}$ N/m, $\mu = 3.94 \times 10^{-2}$ Pas, $\theta = 18^{\circ}$) while all nanopillars are PS and deposited with deionized water ($\gamma = 0.072$ N/m, $\mu = 8.9 \times 10^{-4}$ Pas, $\theta = 56.3^{\circ}$). Pillar 1 refers to the sample with hydrophilic PS and Pillar 2 refers to the sample with hydrophobic PS.

	<i>p</i> (µm)	q (µm)	<i>m</i> (µm)	n (µm)	<i>h</i> (µm)	ϕ_s	$V (\rm mm^3)$
Fin A	0.63	0.86	0.11	0.75	2.21	0.044	2.3
Fin B	1.21	0.94	0.30	0.70	3.29	0.133	2.5
Fin C	0.47	1.52	0.19	0.81	5.46	0.035	2.9
Fin D	1.28	0.94	0.33	0.63	2.33	0.157	2.3
Fin E	0.35	0.07	0.18	0.27	0.30	0.257	1.5
Fin F	0.40	0.17	0.18	0.26	0.46	0.229	3.4
Fin G	1.21	1.08	0.28	0.69	2.10	0.119	3.2
Fin H	1.13	1.05	0.27	0.64	1.15	0.120	2.0
Pillar 1	0.05	0.58	0.05	0.58	1.14	0.005	1.0
Pillar 2	0.12	0.51	0.12	0.51	1.30	0.028	1.0



FIG. 1. SEM images of nanofins viewed at (a) 40° tilt and (b) without tilt. Scale bars represent 2 μ m. (c) Anisotropic and (d) isotropic droplet shapes at different times of wetting. Scale bars represent 1 mm. The dotted arrow points to droplet edge and regular arrow points to edge of wicking film which is just emerging. The axes depicted are for illustration purposes only and are not the actual axes used for measurements.

be controlled using the concentration of CF₄ in the plasma. One sample was fabricated with hydrophilic ($\theta = 75^{\circ}$) PS nanopillars and another fabricated with hydrophobic ($\theta = 115^{\circ}$) PS nanopillars. These nanopillars were then subjected to oblique angle deposition of Al along the arbitrarily named *Y*-axis so that only one side of each nanopillar and its top would be coated with Al. The details of the fabrication procedure can be found in our previous paper.²⁰

To examine the droplet spreading behaviour, deionized water ($\rho = 1000 \text{ kg/m}^3$, $\gamma = 0.072 \text{ N/m}$, $\mu = 8.9 \times 10^{-4} \text{ Pas}$, $\theta = 56.3^{\circ}$) or silicone oil ($\rho = 1065 \text{ kg/m}^3$, $\gamma = 3.40$ $\times 10^{-2}$ N/m, $\mu = 3.94 \times 10^{-2}$ Pas, $\theta = 18^{\circ}$) was deposited quasistatically (~ 1 mm/s) onto the center of the samples by means of a micropipette. Here, ρ , γ and μ refer to the density, surface tension and viscosity of the liquid respectively. A microbalance was employed to measure the exact amount of liquid that was deposited. The droplet spreading process was recorded by a high speed camera (Photron Fastcam SA5) at 100 fps (frames per second), which is sufficiently fast for the scope of this study. Higher frame rates were not used due to memory limitations of the camera, which would have undesirably restricted the period of video capture. Measurements of a, the distance from the center of the droplet to its edge, with respect to time, t, were then carried out on the captured video using the free software, Tracker.

III. RESULTS AND DISCUSSION

A. Effects of structural anisotropy

When 1 to 3 μ l silicone oil droplets were deposited on the Si nanofins, the oil droplets were initially observed to spread rapidly in an anisotropic manner for a relatively short period of time (t < 0.05 s), becoming longer in the X-axis than the Y-axis (Fig. 1(c)). No wicking film was observed at this stage. As wetting proceeds, however, the droplet began to adopt an increasingly isotropic profile until the distance between the droplet edge and the droplet centre, a, is the same for both X- and Y-axes (Fig. 1(d)). A wicking film that advances ahead of the droplet edge can be found at this stage.

The quantitative measurements of *a* vs *t* were found to reflect the qualitative observations described above. In the absence of external interference, the *a*-*t* plot of the droplet in the *Y*-axis was always displaced by a positive Δt with respect to that of the *X*-axis as a result of the initial anisotropic shape of the droplet. Moreover, the *a*-*t* plots of both the *X*- and *Y*-axes for t > 0.05 s fit closely to the displacement-time equation derived for an isotropic droplet spreading on nanostructures imbibed with a wicking film (Figs. 2(a) and 2(b)),¹⁸

$$t \approx \frac{3\mu}{\delta\gamma} \left[\frac{\pi^2}{64V^2} a^8 + \frac{\pi^4 \phi_s (1 - \cos\theta)}{896V^4} a^{14} \right] + \Delta t = \frac{3\mu}{\delta\gamma} \psi + \Delta t, \quad (2)$$

where V is the volume of droplet and δ refers to the height of the liquid wedge formed by the droplet near the triple phase contact line (see Ref. 18 for a more detailed description). According to de Gennes' analysis,^{1,7} viscous dissipation during droplet spreading takes place mainly within this wedge. δ in Eq. (2) can be empirically determined from the gradient of the experimental t vs ψ plots, an example of which is shown in Fig. 2(b). For all our samples, it was found that the gradients of the t- ψ curves are similar for the X- and Y-axes (Fig. 2(b)), implying that δ is of approximately the same value for both axes.

To briefly recap the derivation of Eq. (2), we first note that the incentive for droplet spreading is the lowering of the total surface energy of the droplet-substrate system. This excess capillary energy acts as the driving force for the flow of the droplet outwards, which was modelled as Poiseuille's flow, leading to the expression¹⁸

$$U = \frac{\delta\gamma}{3\mu a} \left[\frac{2H^2}{a^2 + H^2} - \phi_s(1 - \cos\theta) \right],\tag{3}$$

where U refers to the velocity of the droplet edge and H refers to the maximum height of the droplet measured from the substrate surface. Since $a/H \gg 1$ in the second regime (after the emergence of the wicking film ahead of the droplet edge) for which Eq. (2) is valid for, the conservation of droplet volume will give $H \approx \frac{2V}{\pi a^2}$, which, together with $U = \frac{da}{dt}$, can be substituted into Eq. (3) to give

$$\frac{\pi^2 a^7}{8V^2 \left[1 - \frac{\pi^2 \phi_s (1 - \cos \theta)}{8V^2} a^6\right]} \frac{da}{dt} = \frac{\delta \gamma}{3\mu}.$$
 (4)

Integrating Eq. (4) then yields Eq. (2). Additional details of the derivation can be found in Ref. 18.

The above observations hold true even when the droplet was artificially elongated in the Y-axis initially (Figs. 2(c) and 2(d)). Using the tip of the pipette, the droplet was smudged in the Y-axis so that it becomes longer than the X-axis in the initial phase. As a result, the *a*-*t* curve of the X-axis becomes displaced by a positive Δt with respect to the Y-axis. However, both *a*-*t* curves remain in good agreement with Eq. (2) and there is, again, no significant difference between the gradients of the *t*- ψ curves for both axes (Fig. 2(d)).

1. The two regimes

These results clearly show that there are two distinct regimes for droplet spreading on 2D wicking surfaces. In the first regime (t < 0.05 s), the droplet rapidly adopts an elliptical cap shape upon contact with the nanofins. Recent evidences¹⁸ have suggested that during the early stages of droplet spreading on a 2D wicking surface, the wicking film has yet to advance ahead of the droplet edge, which basically means that the droplet is spreading in the Wenzel state. Indeed, a comparison between the elliptical cap shape shown in Fig. 1(c) with the shape of droplets deposited on nanofins that do not cause 2D wicking (i.e., droplet stays in Wenzel



FIG. 2. Representative (a) a-t plot and (b) t- ψ plot of a 2 μ l silicone oil droplet on nanofins. (c) a-t plot and (d) t- ψ plot of a 2 μ l silicone oil droplet that was artificially made longer in the Y-axis than the X-axis in the initial stages.

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state throughout wetting process)²⁰ shows that they are similar.

The anisotropic wetting of the droplets in the first regime can then be attributed to uneven pinning forces on the contact line in the X- and Y-axes as it was previously demonstrated that, for the parameters of our study, the longer edge of the nanofin normal to the Y-axis causes a longer pinning length which translates to a stronger resistance to wetting in the Y-axis.²⁰

As this Wenzel spreading regime transits into the next regime, however, the emergence of the wicking film ahead of the droplet edge changes the rough, chemically homogeneous surface that the droplet was spreading on to a flat, solid-liquid composite surface made up of the top faces of the nanostructures and the top of the wicking film. Note that the wicking film wets the entire height of the nanostructures except for their top faces. As mentioned earlier, the consequence of this is that the droplet spreading dynamics is changed to one that can be described by Eq. (2). Since Eq. (2) was originally derived for an isotropic droplet (spherical cap shape),¹⁸ the good fit between the experimental and calculated *a-t* trends is rather unexpected. This is most likely due to the relatively low anisotropy of the droplets exhibited on nanofins, which makes Eq. (2) a valid estimation for the *a*-*t* relationship of droplets spreading on such 2D wicking surfaces. Also, since the droplet approaches a spherical cap shape as wetting proceeds, Eq. (2) becomes more and more accurate over time.

A useful aspect of Eq. (2) is that it can explain the increasing isotropy in the droplet shape in the second regime. Differentiating Eq. (2), it can be seen that the speed of advance by the droplet edge, da/dt, is inversely related to a. In the absence of external interference, the droplet adopts an initial anisotropic shape in the first regime where a (*Y*-axis) is smaller than a (*X*-axis). This causes da/dt (*Y*-axis) to consistently be greater than da/dt (*X*-axis) until $t \gg \Delta t$, when a (*Y*-axis) $\approx a$ (*X*-axis). In other words, the rate of

advance of the droplet edge in the *Y*-axis will always be faster than that in the *X*-axis in the second regime, so that the initially anisotropic shape of the droplet gradually becomes isotropic (Figs. 2(a) and 2(c)).

2. Effect of nanoscale geometry on the microscopic shape of droplet edge

Next, we investigated the influence of the composite surface chemistry on δ which is obtained from the gradients of t- ψ plots. This surface chemistry can be characterized by θ^* , the thermodynamic equilibrium contact angle of the surface that is given by¹⁴

$$\cos\theta^* = 1 - \phi_s(1 - \cos\theta). \tag{5}$$

Plotting δ against θ^* in Fig. 3(a), we obtained the relationship $\delta = K/\theta^*$, where K = 0.0129 mm rad, which is consistent with the relationship previously derived by Joanny *et al.*²² To further validate this correlation, we make use of the results of Choi *et al.*'s study,¹³ which shows SEM pictures of PDMS droplets on Si microstructures. The height of the droplet foot/ wedge, determined from the SEM pictures, was measured to be 30 μ m, 13.5 μ m, 10.8 μ m, and 9.8 μ m for $\theta^* = 28^\circ$, 110°, 119°, and 135°, respectively. Using the empirical relationship above, we can obtain $\delta = 26.4 \,\mu$ m, 6.7 μ m, 6.2 μ m, and 5.5 μ m following the same order, which agrees reasonably well with the trend of the experimental values.

Physically, Fig. 3(a) suggests that viscous dissipation takes place increasingly in the bulk of the droplet (because δ increases rapidly) as the composite surface that the droplet is spreading on becomes more hydrophilic (i.e., θ^* falls). This is not entirely unexpected as reports have indicated that a completely wetting surface ($\theta^* = 0^\circ$) will cause a deposited droplet to form a wetting layer of macroscopic thickness within which viscous dissipation occurs throughout.⁶ In this



FIG. 3. (a) Plot of δ vs θ^* . (b) Plot of a/H vs ϕ_s . Schematic diagrams illustrating (c) contact line pinning for wetting in the Wenzel state and (d) lack of contact line pinning for wetting on a 2D wicking surface in the second regime due to the presence of a wicking film. Orange—side view of nanostructure. Blue—liquid. Black line—liquidvapour interface.

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extreme case, δ should be equivalent to the thickness of the wetting layer which therefore, represents the maximum value of δ that the relationship $\delta = K/\theta^*$ is valid for. Of more immediate relevance, $\delta = K/\theta^*$ gives the reason for the identical gradients of the *t*- ψ plots for *X*- and *Y*-axes of the same sample; since θ^* is the same for both axes, therefore δ is the same.

In addition, the result in Fig. 3(a) is important because we had previously suggested that the first term of Eq. (2), which does not contain surface dependent parameters such as ϕ_s and θ , could possibly be used to estimate droplet spreading dynamics on 2D wicking surfaces made up of irregular arrays of nanostructures or nanostructures of mixed hydrophilicity.¹⁸ Fig. 3(a) shows that this is not the case as a change in ϕ_s or θ will affect θ^* which influences the value of δ , thereby making the first term of Eq. (2) indirectly dependent on surface properties.

3. Resting shape of the droplets

The shapes of the droplets after they have come to rest were also characterized. We then compare them to the expected shapes using¹⁸

$$\frac{a}{H} = \sqrt{\frac{2}{\phi_s(1 - \cos\theta)} - 1},\tag{6}$$

which describes the shape of the droplet when the gain in capillary energy, the driving force for droplet spreading, from wetting an additional distance of *da* is zero. The validity of Eq. (6) can be checked by considering the extremes. On one hand, if the droplet is spreading on a completely liquid surface ($\phi_s = 0$), Eq. (6) yields $a/H \rightarrow \infty$, which is reasonable, considering the droplet will simply merge into the liquid surface, forming an infinitely thin film. On the other hand, if the droplet is spreading on a completely solid surface ($\phi_s = 1$), Eq. (6) yields $a/H = [(1 + \cos\theta)/(1 - \cos\theta)]^{1/2}$. This a/H ratio corresponds to the case where the droplet makes a contact angle of θ with the surface, which is the expectation for $\phi_s = 1$. From Fig. 3(b), it can be seen that the experimentally measured values of a/H agree very well with the calculated values.

It is worth noting that the droplet shape described by Eq. (6) corresponds to the thermodynamic equilibrium shape (i.e., Eqs. (5) and (6) actually describe the same droplet shape),¹⁸ implying that the droplets on 2D wicking surfaces come to rest at their most stable states. This is a unique result that is in marked contrast to Wenzel and Cassie–Baxter states of wetting, where droplets come to rest in metastable shapes as a result of contact line pinning at the top of the nanostructures.^{13,19,20}

Using the example of Fig. 3(c), which shows a droplet in Wenzel state wetting a row of nanostructures, it can be seen that the driving force for wetting must be able to rotate the droplet edge by 90° to wet the nanostructure sidewall before the triple phase contact line can advance.²³ Once the driving force, which decreases as the droplet spreads, falls below this minimum level, wetting will stop. In other words, the droplet will come to rest before the driving force for wetting becomes zero. However, for 2D wicking surfaces, the wicking film essentially eliminates the need for the droplet edge to rotate its contact angle before it can advance (Fig. 3(d)). This is because the minimum contact angle required for the droplet edge to pass from the top of the nanostructure to the top of the wicking film is 0°. Since the local contact angle at the top of the nanostructure is always greater than 0°, the droplet edge does not experience any resistance to wetting in the form of contact line pinning and the droplet only stops spreading when it reaches its thermodynamic equilibrium shape, where the driving force for wetting is reduced to nothing.

B. Effects of chemical anisotropy

When 1 μ l of deionized water droplets were deposited onto structurally isotropic nanopillars with chemical anisotropy, it was found that the droplet, spreads more in the +*Y* direction than the -*Y* direction (Figs. 4(a) and 4(b)). Note that there is chemical anisotropy in the *Y*-axis (the Al side of the nanopillars faces +*Y* but the PS side faces -*Y*) (Fig. 4(b)) but not in the *X*-axis. Like the case of droplet spreading on nanofins, we observed anisotropic wetting in the initial stage of droplet spreading prior to the adoption of a more isotropic spherical cap shape by the droplet.

Once again, the wetting anisotropy in the initial stage is a direct result of the droplet being in the Wenzel state and the similarity between the droplet shapes observed here and the droplet shapes reported for Wenzel state wetting on the same nanostructures²⁰ lends support to the claim. Consistent with the analysis for nanofins above, the different extents of wetting (a(+Y) > a(+X) = a(-X) > a(-Y)) in the various directions in the first regime is caused by the differences in pinning strength on the contact line with the most hydrophilic side (Al coated) having the least strength and the most hydrophobic side (PS) having the most.²⁰

Interestingly, as the droplet became more isotropic, the anisotropy in wetting lengths appeared to remain intact (Fig. 4(c)). However, it should be noted that the values of *a* in Fig. 4(c) were obtained with respect to the original centre of the droplet (marked by the dashed white line in Fig. 4(a)) whereas *a* in Eq. (2) refers to the base radius of the droplet which is given by the distance from droplet edge to the instantaneous centre of the droplet. As can be seen in Fig. 4(a), the actual centre of the droplet was constantly shifting in the +Y direction during the wetting process. Compensating for this shift, we can modify *a* using *a* (*Y*-axis) = 1/2[a (+Y) + a (-Y)] so that *a* (*Y*-axis) now represents the base radius of the droplet in the *Y*-axis and comparisons between experimental *a-t* trends can be made with Eq. (2).

From Fig. 4(d), it can be seen that when *a* (*Y*-axis) is plotted in the stead of *a* (+*Y*) and *a* (-*Y*), all of the four *a*-*t* curves in Fig. 4(d) collapses into a single curve that follows Eq. (2). The implication of this is that, like structural anisotropy, chemical anisotropy causes wetting asymmetry in the first regime as the droplet spreads in the Wenzel state. In the second regime, however, the wetting anisotropy reverses due to the emergence of the wicking film, which causes the droplet to spread in each axis according to Eq. (2). The spreading



FIG. 4. (a) Time resolved pictures of droplet wetting on a chemically anisotropic 2D wicking surface. The droplets have been traced out in white dotted lines in the first two pictures to enhance visibility. Red diamond indicates the instantaneous center of the droplet. Scale bars represent 1 mm. Orientation of chemical anisotropy also shown in the schematic diagram depicting the top view of a nanopillar. Green—PS. Yellow—Al coating. (b) Schematic diagram showing the asymmetry in wetting. (c) a vs t plots in +Y, -Y and the X-axis for hydrophilic (sample 1) and hydrophobic (sample 2) PS nanopillars. (d) a vs t plot using the modified value of a (Y-axis). For the calculated plot, $\delta = 10 \, \mu m$ was used.¹⁸

velocity, da/dt, will therefore be faster for the axis where *a* is lower, thereby enabling it to catch up with the other axis so that the droplet eventually regains isotropy in its shape. Thereafter, the droplet can be observed to spread isotropically, which is expected since the wicking film effectively eliminates the chemical anisotropy of the nanostructures when it fills up the space between the nanopillars, leaving only an isotropic, flat, composite surface of Al and water for the droplet to spread on (Fig. 4(b)). It is for this same reason that the *a*-*t* plots for both hydrophobic and hydrophilic PS follow the same trend in Fig. 4(d).

It is also worth noting that the droplets deposited on chemically anisotropic 2D wicking surfaces eventually came to rest in the shape predicted by Eqs. (5) and (6). The experimentally observed contact angles for the samples with



FIG. 5. Schematic diagram of nanofins showing the various dimensions.

hydrophilic and hydrophobic PS are 3.2° and 3.7° , compared with the theoretical predictions of 1.6° and 3.7° , respectively. Note that the slight discrepancy between the theoretical predictions and experimental results for hydrophilic PS nanopillars is within measurement uncertainty. As with the case of structural anisotropy, this result indicates that chemical anisotropy introduces no contact line pinning forces that restrict the droplets from reaching their thermodynamically stable state when spreading on a 2D wicking surface.

IV. CONCLUSION

We have investigated the effects of structural and chemical anisotropy of nanostructures on the dynamics of droplet spreading on a 2D wicking surface. It was found that in the earliest stage of droplet spreading, the droplet adopts the Wenzel state during wetting and both structural and chemical anisotropy can individually cause the droplet shape to become anisotropic, elongating the droplet in the axis or direction with the least resistance to wetting. This is followed by the advance of a wicking film ahead of the droplet edge which causes the droplet to effectively spread on a composite surface of solid and liquid phases. The wicking film eliminates pinning forces so that the droplet can spread uninhibited in all directions, thus helping it regain isotropy in its shape over time. We have also shown that the rate of droplet spreading on a 2D wicking surface in the second regime can be simply described by a model that balances the gain in capillary energy of the system with the viscous losses of fluid flow, regardless of the type and level of anisotropy inherent in the nanostructures. This model has also been shown to accurately predict the shapes of the droplets when they come to rest and gives insights into the location of the droplet at which the viscous losses are taking place.

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