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Droplets on Soft Surfaces Exhibit a Reluctance to Coalesce due to an Intervening Wetting Ridge

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Microscale interactions with deformable substrates are of fundamental interest for studying self-assembly processes and the mobility of cells on soft surfaces, with applications in traction force microscopy. The behavior of microscale water droplets on a soft polymer substrate is investigated. Droplets formed by condensation on the soft substrate are reluctant to coalesce, which leads to coverage of the surface with clusters of droplets assembled in a honeycomb-like pattern. Cryogenically fixed in this state, scanning electron microscopy of these droplets reveals the presence of an intervening wetting ridge of the polymer that acts as a barrier between neighboring droplets and prevents coalescence. A linear elastic deformation model is developed to predict this surface profile and corroborate the observed behavior.

1 Introduction

Understanding the interactions of droplets with surfaces is important for a variety of self-cleaning,^[1,2] heat transfer enhancement,^[3,4] and anti-icing^[5] applications. Such interactions are strong functions of the surface wettability and are dictated by the shape and size of the droplets. Droplets on a rigid surface follow Young's equation which determines their static contact angles. However, on soft solid surfaces (Young's modulus, $E \sim$ few kPa), surface tension and Laplace pressure forces can deform the underlying substrate and Young's equation is no longer valid. The vertical component of the liquid surface tension force at the three-phase contact line pulls up the pliable substrate and forms a so-called wetting ridge.^[6,7] This wetting ridge can attain a significant deformation height (on the order of the elastocapillary length, $l_c = \gamma/E$, where γ is the surface tension) which engenders interesting droplet behaviors.

Several prior works have experimentally investigated the deformation of soft substrates due to the presence of a droplet and explained the phenomenon by modeling the substrate as a linear elastic material.^[6–13] Experimentally observed deformation profiles have been used to infer surface elastic constants.^[14,15] Ideally, the substrate deformation is symmetric about the center of a single droplet. However, inhomogeneity in the substrate properties can break this symmetry.

Asymmetry in the substrate deformation generates forces that act on the droplet and can cause motion; e.g., droplets can self-propel when subjected to a substrate stiffness gradient.^[16–19] Such asymmetry can also be induced by the presence of multiple droplets. The dynamic interactions between multiple droplets due to the formation of wetting ridges on a soft substrate differ significantly from droplet interactions that occur on a flat rigid substrate. The attraction or repulsion between droplets on soft surfaces has been termed the inverse Cheerios effect,^[20–22] due to the analogous behavior of rigid objects on liquid surfaces (that has been called the Cheerios

effect)^[23]. The influence of using soft substrates on droplet behaviors has also been probed during droplet impact,^[24,25] dropwise condensation,^[26,27] and droplet evaporation^[28] on such surfaces. Investigation of the interactions between droplets on viscoelastic liquids^[22] has been sparse, but observations suggest that the behavior is very similar to that on elastic surfaces.

Improved understanding of the behavior of multiple droplets on elastic surfaces is important to a variety of potential applications. Studying the interactions of multiple objects on a soft surface would explain the dynamics of processes such as self-assembly^[29] and in applications such as traction force microscopy.^[30] Understanding the mechanisms governing such interactions will improve predictive capabilities for other processes such as droplet condensation and evaporation on soft surfaces. A knowledge of how these interactions depend on the bulk and surface properties can help guide the design and fabrication of substrates that offer application-specific functionality. In this work, we investigate the interactions between microscale water droplets, which are formed by condensation, on a soft surface. Coalescence of droplets is severely hindered, and groups of clustered droplets form a honeycomb-like pattern. The droplets are cryogenically frozen to preserve their instantaneous wetting state and viewed in a scanning electron microscope to reveal the presence of intervening wetting ridges. The linear elastic equations governing the deformation of the substrate are solved to explain the observed reluctance to coalesce.

2 Condensation Experiments

Soft substrates are prepared using a silicone gel (CY 52-276 A and B) and placed with their soft layer facing up on a thermoelectric cooler set to a temperature of 0 °C for all condensation experiments in this work (details of the substrate preparation and the condensation experiments are included in the Experimental Section). Water vapor from the surrounding ambient (~ 21 °C, ~38

% RH) condenses onto the surface. **Figure 1** shows image sequences from the videos of the condensation process on silicone gel layer thicknesses of a) 1 μm and b) 90 μm . These two samples have the same material wettability characteristics, but offer contrasting effective stiffness. The 1 μm -thick layer is an order of magnitude smaller in scale than the condensate droplet size and therefore behaves mechanically just like the rigid underlying glass substrate; the 90 μm -thick layer, on the other hand, acts as a bulk soft substrate composed of the silicone gel. A static contact angle of 97.8 deg, as measured for a 2 μl water droplet placed on the effectively stiff 1 μm -thick layer of silicone gel coated onto a substrate, is taken as the Young's contact angle and indicates that the silicone gel coating is intrinsically hydrophobic. On the thin layer, water droplets nucleate, grow in size, and coalesce to form bigger droplets, exhibiting the typical progression expected of dropwise condensation. However, on the thick layer, droplets are reluctant to coalesce, eventually assuming unconventional shapes with non-circular footprints due to the tight clustering of many droplets. A sequence of images showing the formation of such a cluster comprising four droplets on the 90 μm -thick silicone-gel layer is shown in Figure 1 c). Clustered droplets can remain in this configuration and continue to grow for a long time before they eventually coalesce, for example as shown in Figure 1 d) where five different droplets on the 90 μm thick layer coalesce into one big droplet with a ~ 200 s delay after clustering. At later stages of condensation, extreme clustering is eventually observed on the relatively soft thick layer, with droplets forming a dense honeycomb-like pattern; as shown in Figure 1 b) (at $t = 1818$ s). The observed behavior is very similar to the inverted Cheerios effect.^[20] A similar observation of delayed coalescence between condensing water droplets on a soft surface was made by Sokuler *et al*^[26]. The number of coalescence events during condensation on the two substrates is compared. Coalescence events, defined as the merging of two or more droplets into one bigger droplet, are counted during the time period from $t = 365.2$ s to $t = 418.6$ s. The

number of coalescence events over the specified time duration is 62 on stiff substrates versus 8 on soft substrates. Thus, the corresponding rates of coalescence (defined as the number of coalescence events per unit time) are starkly different, indicative of the reluctance to coalesce exhibited by soft surfaces.

3 Cryo-SEM

Cryogenic scanning electron cryomicroscopy (Cryo-SEM) is used in order to preserve the instantaneous wetting state of the droplets and visualize the physical features in the intervening region between non-coalesced droplets (Cryo-SEM details in the Experimental Section). An SEM of the frozen droplets and substrate is shown in **Figure 2 a**), along with a schematic representation of the side-view cross-section below. Droplets within the cluster assume unconventional polygonal footprints. Between the droplets, the presence of intervening polymer is evident in the image. The width of this intervening wetting ridge is $\sim 1.5 \mu\text{m}$. Because the three-phase contact line is visible from this top-down view, this indicates that the apparent contact angle of the droplets, defined as the angle between the liquid-vapor interface and the horizontal, is less than 90 degrees. Thus, on either side of the wetting ridge the liquid-vapor surface tension pulls the ridge and bends the substrate. The ridge, in turn, forces the droplets away from each other (equivalently, their apparent contact angle reduces) which prevents droplet-droplet contact, effectively hindering coalescence.

The cryo-SEM imaging was repeated multiple times to confirm this droplet and substrate morphology. In some runs, the frozen droplets detached from the surface, presumably either by sublimation as a result of heating during sputter-coating or by mechanical vibration while transferring samples from the cryo-preparation chamber to the imaging chamber. Imaging with the droplets removed provides greater clarity into the shape of the embossed polymer substrate

underneath the droplets, as shown in Figure 2 b). The polymer underneath each droplet is shaped like a concave pit. The high Laplace pressure inside these microscale droplets (e.g., a droplet of diameter 25 μm would have an excess pressure of ~ 11.5 kPa) is able to deform the soft substrate appreciably, leading to the formation of these concave pits. Upon closer inspection of the underlying polymer substrate, as shown in **Figure 3**, ruptures in the subsurface portions of the wetting ridges are revealed. This indicates that the intervening polymer is squeezed to become very thin between the droplets, and hence ruptures as a result of droplet freezing and expansion during cryo-SEM sample preparation. It is important to note that there is no evidence that the polymer ridges rupture during condensation, as this would result in readily coalescing droplets. Assuming that the linear coefficient of thermal expansion of the silicone gel is similar to that of the chemically similar PDMS, equal to $3.1 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ ^[31,32], and that this value is valid at these extremely low temperatures, the linear thermal expansion ratio for a temperature change of ~ 170 $^\circ\text{C}$ is 0.053. Relative to the elastocapillary length ($l_c = \gamma/E$) of 24 μm , the corresponding change in length is 1.27 μm , which is an order of magnitude smaller than the expected deformation. Thus it is reasonable to conclude that the deformations observed are mainly due to the surface tension and Laplace pressure forces exerted by the droplets, rather than thermal expansion and/or contraction during cryo-fixation. In addition, the wetting ridges are observed to be widest at the top of the ridge. The Laplace pressure pushes the ridge away from the droplet center while the surface tension at the contact line pulls the top of the ridge towards the droplet center. The top of the ridge where surface tension acts is hence expected to be wider than other regions of the ridge below the contact line where the Laplace pressure is dominant.

4 Linear Elastic Deformation Model

4.1 Governing Equations and Boundary Conditions

The liquid-vapor interface curvature and apparent contact angle (ACA) of a droplet on a soft substrate are strong functions of the deformed surface profile. A linear elastic deformation model is developed to simulate the deformation profile of the soft surfaces and to explain the low ACAs observed. The forces exerted by a droplet on the solution domain of the substrate are shown in **Figure 4**. The domain has a thickness of h in the z -direction and is infinitely long in the x -direction. The liquid-vapor surface tension (γ_{lv}) results in the point loads (depicted by red arrows) at the contact lines, $x = \pm R$, in both the x and z directions, where R is the radius of the base of the droplet. The horizontal and vertical components are $\gamma_{lv} \cos \theta$ and $\gamma_{lv} \sin \theta$, respectively. The static contact angle of a droplet on a thin ($\sim 1 \mu\text{m}$) silicone gel substrate is used as the Young's contact angle, θ , because the intrinsic material wettability is independent of the substrate thickness. The Laplace pressure within the droplet ($2\gamma_{lv} / R_d$, where R_d is the radius of curvature of the liquid-vapor interface) pushes down on the substrate between $x = -R$ and $x = R$ (depicted by blue arrows). The deformation field is computed by solving the static equilibrium equations for a linear elastic body in the two dimensions x and z .

$$(1 - 2\nu) \nabla^2 \underline{u} + \underline{\nabla} (\underline{\nabla} \cdot \underline{u}) = 0 \quad (1)$$

where $\underline{u} = (u_x, u_z)$ is the deformation field at any point (x, z) and ν is the Poisson's ratio.

Similar to a liquid-vapor interface, the solid-vapor interface of a soft solid has surface stresses which cause a jump in the stress across the interface represented by the relation

$$[\underline{\underline{\sigma}} \cdot \underline{\underline{n}}]_{-}^{+} = -\underline{\underline{\nabla}}^s \cdot \underline{\underline{\Upsilon}} \quad (2)$$

where $[\underline{\underline{\sigma}} \cdot \underline{\underline{n}}]_{-}^{+}$ is the jump in the normal bulk stress to the external stress and $\underline{\underline{\nabla}}^s$ is the surface gradient operator acting on the surface stress $\underline{\underline{\Upsilon}}$. The solution procedure employed here has been previously developed and described in detail by Style and Xu.^[33] The surface stress is represented by a linear-elastic constitutive relationship

$$\underline{\underline{\Upsilon}} = \Upsilon_0 \underline{\underline{I}} + 2\mu^s \underline{\underline{\varepsilon}}^s + \lambda^s \text{Tr}(\underline{\underline{\varepsilon}}^s) \underline{\underline{I}} \quad (3)$$

where Υ_0 is the residual stress in the absence of any strain, μ^s and λ^s are the two surface Lamé constants, $\underline{\underline{\varepsilon}}^s$ is the infinitesimal surface strain tensor, $\text{Tr}(\underline{\underline{\varepsilon}}^s)$ is its trace and $\underline{\underline{I}}$ is the identity tensor. The surface Lamé constants are different from the bulk Lamé constants; the latter are known functions of the bulk Young's modulus and Poisson's ratio for a linear elastic material. The jump in stress across the solid-air interface gives the boundary conditions at the top surface. Substituting equation (3) into equation (2) we get the required boundary condition at $z = h$

$$\underline{\underline{\tau}} - \underline{\underline{\sigma}} \cdot \underline{\underline{z}} = -\frac{\partial^2}{\partial x^2} \begin{pmatrix} \Lambda u_x \\ \Upsilon_0 u_z \end{pmatrix} \quad (4)$$

Equation (4) signifies that the jump from the stress in the body, $\underline{\underline{\sigma}}$, to the externally applied stress, $\underline{\underline{\tau}}$, is given by the gradients of the displacements at the interface. Here $\Lambda = \lambda^s + 2\mu^s$ and $\underline{\underline{z}}$ is the unit vector in the z -direction. The soft polymer layer is fixed to a stiff substrate and hence has no deformation at $z = 0$, which translates to the boundary conditions $u_x(x, z = 0) = u_z(x, z = 0)$. The scalar components of equation (1) are solved in Fourier space using the boundary conditions at $z = 0$ and $z = h$. The displacements and the externally applied stresses are described by the linear relation

$$\hat{u}_i(\alpha, z) = QS_{ij}^{-1}(\alpha, z)\hat{\tau}_j \quad (5)$$

where $\hat{u}_i(\alpha, z)$ is the displacement at z and $\hat{\tau}_j$ is the externally applied stress on the top surface in Fourier space, and QS_{ij} is the spring constant. The externally applied stresses due to surface tension at the contact line and the Laplace pressure inside the droplet are represented as

$$\begin{aligned} \tau_x &= \gamma_{lv} \cos \theta (\delta(x+R) + \delta(x-R)) \\ \tau_z &= \gamma_{lv} \sin \theta (\delta(x+R) + \delta(x-R)) - \frac{2\gamma_{lv}}{R_d} (H(x+R) - H(x-R)) \end{aligned} \quad (6)$$

where the point loads due to surface tension are expressed using the Dirac delta functions $\delta(x+R)$ and $\delta(x-R)$ acting at $x=-R$ and $x=R$, respectively. H is the Heaviside unit step function and is used to express the Laplace pressure acting between $x=-R$ and $x=R$.

The elasticity, E , of the substrate is taken as 3000 Pa as reported in the literature.^[7–9,14,34] The surface Lamé constants, $\Lambda = 0.45 \text{ Nm}^{-1}$ and $\Upsilon_0 = 0.02 \text{ Nm}^{-1}$, are obtained by fitting the model to experimental surface deformation profile data obtained from confocal microscopic imaging of a single glycerin droplet on a silicone gel-coated substrate (details in the Supporting Information section 1). For all cases investigated using the model, the thickness of the polymer is taken as $h = 20 \text{ }\mu\text{m}$. The direction and magnitude of forces at the contact line are determined by Young's contact angle ($\theta = 97.8 \text{ deg}$).

4.2 Model Results

The deformations of nominally stiff ($1 \text{ }\mu\text{m}$ thick) and soft ($20 \text{ }\mu\text{m}$ thick) silicone-gel substrates induced by a droplet of $25 \text{ }\mu\text{m}$ base radius (representative of the size of droplets observed in Figure 1 and Figure 2) are evaluated using the model and shown in **Figure 5**. The green area represents the silicone-gel substrate and the surface ($z = h$) deformation profile is indicated by the bold green lines. The blue area represents the water droplet, with the the liquid-vapor interface

indicated by bold blue lines. The governing equilibrium equations for the polymer substrate do not provide any information about the liquid-vapor interface shape or the apparent contact angle (ACA) of the droplet, which is defined as the angle between the liquid-vapor interface at the contact line and horizontal, after deformation. The liquid-vapor interface profile and hence the ACA on the deformed substrate is determined by equating the volume of the droplet to that on the undeformed substrate (i.e., conservation of the droplet volume). The volume of the droplet on the undeformed substrate is known based on the locations where the point loads are applied (or equivalently the base radius) and the Young's contact angle. In the deformed configuration, the contact lines are at the x -locations of the peaks in the surface profile, which in turn determine the droplet base radius after deformation. The ACA of the droplet after surface deformation is then uniquely determined by the droplet volume. A detailed discussion of the calculation of the ACA on the deformed substrate is included in the Supporting Information section 2.

The deformations of the two different substrates shown in Figure 5 are clearly different. The behavior of the droplet on a 1 μm -thick substrate is almost the same as that on a perfectly stiff substrate. In the magnified view of Figure 5 a), a black dashed line representing the liquid-vapor interface on an undeformed stiff substrate shown as a horizontal solid black line almost overlaps with the liquid-vapor interface on the deformed substrate. The ACA (94.3 deg) is only slightly lesser than the Young's contact angle (97.8 deg). In contrast, a similar comparison for the 20 μm -thick substrate shows that the liquid-vapor interfaces on the undeformed and deformed substrates are significantly different. The pliability of the 20 μm -thick substrate is immediately evident from its deformation in the z -direction which is comparable to the droplet size. The two noteworthy features of the deformed substrate are (1) the depression under the droplet caused by the Laplace pressure, and (2) the protrusion perpendicular to the undeformed surface at the contact line, called the wetting ridge, caused by the liquid-vapor surface tension. The droplet

embeds into the soft substrate due to the compounding effects of these deformations and assumes an ACA of 50.5 deg that is significantly lower than on the stiffer substrate.

These results indicate that the interaction between neighboring droplets (and their tendency to coalesce) on soft substrates would be significantly different than on stiff substrates of identical material wettability. It is known that neighboring droplets will coalesce on a stiff substrate regardless of the static contact angle^[35,36], whereas the wetting ridges formed on a soft substrate will hinder the coalescence of neighboring droplets. The ACA of the droplet provides insight into the tendency of droplets to coalesce on soft substrates and serves as a metric for quantifying the propensity of droplets to coalesce by contacting each other above the wetting ridge. If the ACA of a droplet is less than 90 deg, it is not likely to coalesce with other droplets in close proximity. An ACA greater than 90 deg indicates that the droplet interface extends beyond the contact line and the droplet is prone to contacting neighboring droplets despite the existence of the wetting ridge. It must be pointed out that the shapes of the liquid-vapor interfaces of a 25 μm radius droplet on thicker substrates, such as a 90 μm thick substrate, are convex ($\text{ACA} < 0$) and not in line with the experimental observations of concave interfaces. We note that the linear elastic model described by equation (1) employs linear elasticity which inherently assumes small strains and may not necessarily be true for elastomers. The discrepancy between the experimental observations and model predictions for thicker substrates can be addressed by taking into account non-linearities. Nevertheless, we believe that the current modeling approach still provides valuable insight that allows interpretation of the mechanism underlying the reluctance to droplet coalescence.

The effect of droplet size on the ACA on the deformed substrate is considered next by comparing the deformation shown in Figure 5 b) to the deformation caused by a larger droplet of base radius of 50 μm . Profiles of the deformed substrate and the liquid-air interface are shown in **Figure 6** for single droplets of base radii a) 25 μm and b) 50 μm on a 20 μm -thick silicone gel layer. The ACAs in both cases are less than 90 deg (50.5 deg and 81.8 deg, respectively) implying that the liquid-vapor interface pulls the wetting ridge and bends the substrate. The height of the wetting ridge above the undeformed polymer surface is quite similar in both cases, 8.9 μm and 9.8 μm for the 25 μm and the 50 μm droplet, respectively. The Laplace pressure depresses the substrate underneath the droplet and a portion of the droplet volume embeds itself in the substrate to a level below the peaks in the surface profile at the wetting ridge. The base radius of the droplet in the deformed state is also greater than in the undeformed state, as is evident from the x -location of the peaks in the deformed top surface (namely, the base radii of the 25 μm and 50 μm droplets respectively increase to 26.6 μm and 51.8 μm). These deformation effects force the ACA to be smaller than the contact angle on a flat, rigid substrate. The Laplace pressure is higher for the smaller droplet and consequently the depression of the substrate is far more pronounced than for the bigger droplet. As a result, a significantly greater portion of the total droplet volume is below the wetting ridge for the smaller droplet (60%) compared to the larger droplet (25%). This is reflected in the lower ACA of the smaller droplet (50.5 deg) compared to the larger droplet (81.8 deg).

The deformed substrate and the liquid-air interface profiles are also predicted for cases of two neighboring droplets in Figure 6, each of droplet base radii c) 25 μm and d) 50 μm . The separation distance between the three-phase contact lines of the two droplets in the undeformed state is set to 2.2 μm such that the predicted width of the intervening wetting ridge is similar to that observed in the cryo-SEM images ($\sim 1.5 \mu\text{m}$).

The height of the wetting ridge (measured from the top horizontal surface of the undeformed polymer) is amplified in the presence of two droplets to 16.7 μm and 17.7 μm for the 25 μm and 50 μm droplets, respectively. This increase is expected because the deformation profile is a superposition of the effects of individual forces. As a consequence of this increased ridge height, the ACA is even lower than that for the case of a single droplet as shown in Figure 6 (32.2 deg for the 25 μm droplet and 73.1 deg for the 50 μm droplet).

As droplets condense on a soft polymer and grow in size, they initially have small ACAs and exhibit extreme reluctance to coalesce due to the large relative height of the wetting ridge. As they increase in size, the droplets become more prone to coalescence as they attain higher ACAs and the wetting ridge acts as a relatively shorter barrier (compared to the size of the droplets). At a certain threshold radius, the liquid-vapor interfaces of the neighboring droplets will touch, which would be indicative of coalescence. This corroborates the experimental observations shown in movie S2 in the Supporting Information and depicted in Figure 1 d), where droplets initially resist coalescence and assemble into groups when they are small, but eventually merge after they grow to larger sizes. With refinements in our model to account for non-linearities, viscoelastic properties, and consideration of system energy, prediction of such a threshold radius can be explored, and presents a direction for future research.

In the predictions shown in Figure 5 and Figure 6, the wetting ridge is narrowest at the peak, unlike the cryo-SEM observations that revealed a greater width of the ridge at the top. In the experiments, as a droplet deforms the substrate, the directions and locations of the Laplace pressure and surface tension forces acting on the polymer reconfigure dynamically. Based on the low ACA, the top of the polymer ridge would be pulled in towards the center of the droplet by surface tension, increasing its width. This dynamic reconfiguration of the droplet forces acting

on the substrate is not considered in the simplified static equilibrium model. A potential avenue for future work is consideration of a dynamic elastic model or system energy calculations to further explain the exact shape of the wetting ridge that impedes coalescence between droplets on a soft surface.

5 Conclusions

The reluctance to coalescence exhibited by droplets on soft surfaces has been investigated. Water droplets are condensed on a silicone gel-coated substrate and their behavior is observed and reported. Compared to the behavior on rigid substrates, for which neighboring droplets readily coalesce along the intersection of their three-phase contact lines, droplets on soft surfaces are extremely reluctant to coalesce and form clusters of densely crowded droplets in a honeycomb-like pattern. Condensed water droplets are cryogenically frozen in this state to observe the intervening region between neighboring droplets via scanning electron cryomicroscopy. The cryo-SEM images clearly reveal a tall wetting ridge formed by deformation of the soft polymer substrate that arises between neighboring droplets and acts to impede droplet coalescence. A linear elastic deformation model is developed to understand the contrasting behaviors of droplets on nominally stiff versus soft substrates and explain the low apparent contact angles of droplets on the soft substrates, providing insight into the reduced tendency of droplets to coalesce. In addition to strengthening our current understanding of how droplets interact on soft surfaces, the model can assist in applications which rely on the interaction of droplets and other objects with soft surfaces. Further improving the model by considering non-linear elasticity, deformation dynamics of the process by inclusion of viscoelasticity, and system energy could better predict the exact shape of the deformed surface. This would in turn improve our capability to predict the

dynamics of processes such as coalescence during condensation, evaporation, and droplet motion on soft surfaces.

6 Experimental Section

Substrate Preparation: Soft substrates are prepared by coating a layer of a silicone gel (Dow Corning DOWSIL CY 52-276 A and B) on top of a stiff solid substrate. The stiff substrate (either glass or Thermanox coverslips) is first cleaned with acetone and methanol. A mixture of CY 52-276 A and B is prepared in a 1:1 ratio. The mixture is then desiccated and spin-coated on the clean substrate. A spin-speed of 500 rpm for 40 s results in a layer thickness of ~ 90 μm . As an alternative process to achieve a much thinner ~ 1 μm -thick layer, the substrate is immersed for 30 mins in a 1% wt/wt solution of the silicone gel mixture in hexane. For both processes, the silicone gel-coated substrate is then placed on a hot plate maintained at 100 $^{\circ}\text{C}$ for 1 hr. The thicknesses of the coated layers are measured using a 3D optical profiler (Zygo NewView 6200).

Condensation Experiments: Water is condensed onto the soft surface by keeping the substrate on a thermoelectric cooler set to 0 $^{\circ}\text{C}$. The condensation process is observed on the silicone gel-coated glass substrate using a lens (VH-Z100R, Keyence) attached to a CCD camera (EO-5023M 2/3" Monochrome, Edmund Optics). Videos of the condensation experiments are included in the Supporting Information.

Cryo-SEM: The substrate and condensed water droplets are instantaneously frozen in a cryogen and the sample is subsequently placed in a scanning electron microscope for observation in this fixed state. Cryo-SEM has been used previously for direct visualization of the wetting state of liquid droplets on other types of surfaces.^[37,38] Ambient water vapor is condensed on the 90 μm -thick silicone-gel coated substrates using a thermoelectric cooler as described in the preceding

sections. The substrate with condensed water is then immediately mounted with a cryo-sectioning medium (Tissue-Tek O.C.T. Compound) on a flat specimen holder and cryo-fixed by immersion in a nitrogen slush (Gatan Inc. Alto 2500 Cryo-Preparation System). Samples are immersed until the liquid nitrogen ceases to boil and then cryo-transferred into the cryo-preparation chamber set at $-180\text{ }^{\circ}\text{C}$. The samples are then immediately inserted into the SEM cryo-stage set at $-90\text{ }^{\circ}\text{C}$ to sublimate surface frost and for initial viewing. Once frost-free, samples are returned to the cryo-preparation chamber at $-180\text{ }^{\circ}\text{C}$, allowed to cool and halt sublimation, and then sputter-coated with platinum in the chamber. Platinum is sputter-coated at a current of 18 mA in two 60 s-long periods with a break of 60 s in between to minimize sample heating during sputtering.^[38] The platinum-coated sample is then re-inserted into the SEM cryo-stage for final SEM imaging which is performed at $-140\text{ }^{\circ}\text{C}$ (FEI Nova Nano 200 Series SEM).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1 Time-sequenced images of condensing water droplets on silicone gel layers of a) $1\text{ }\mu\text{m}$ and b) $90\text{ }\mu\text{m}$ thickness. c) Formation of a cluster of four non-coalescing water droplets and (d) delayed coalescence between clustered droplets on the $90\text{ }\mu\text{m}$ thick silicone gel layer. [1.5 columns wide]

Figure 2 Cryo-SEM images of a) a cluster of water droplets on a soft polymer substrate and b) the fixed underlying polymer after the frozen water droplets are detached from the surface. Representative side-view cross-sections are schematically represented in the sketches below the images. One selected intervening polymer ridge is indicated in each image by a white arrow. [1.5 columns wide]

Figure 3 Cryo-SEM images of the underlying polymer substrate after frozen droplets are detached. As shown in the magnified image, the subsurface portion of the wetting ridge is revealed to be an extremely thin membrane of intervening polymer (indicated by red arrows), which ruptures as a result of the cryo-fixation. [1.5 columns wide]

Figure 4 Schematic representation of the external forces acting on the substrate solution domain.

[1 column wide]

Figure 5 Linear elastic prediction of deformation of a silicone gel layer (green) of thicknesses a) 1 μm and b) 20 μm due to the forces exerted by a single water droplet (blue) of base radius 25 μm . The respective magnified views below show the region near the three-phase contact line with the corresponding apparent contact angle. The solid black line and the dashed black line

respectively represent the solid surface and the liquid-vapor interface in the undeformed configuration. [1.5 columns wide]

Figure 6 Linear elastic prediction of deformation of a 20 μm -thick silicone-gel layer (green) due to forces exerted by a single droplet of base radius a) 25 μm and b) 50 μm , and by two droplets of base radii c) 25 μm and d) 50 μm each. The accompanying magnified views show the region

near the three-phase contact lines with the corresponding apparent contact angles. [1.5 columns wide]

Intervening wetting ridges formed between neighboring water droplets during condensation on soft surfaces, which hinder droplet coalescence, are observed by cryogenic scanning electron microscopy. A linear elastic model is employed to predict the deformation of a soft surface by the droplets and explain the observed reluctance to coalesce.

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Droplets on Soft Surfaces Exhibit a Reluctance to Coalesce due to an Intervening Wetting Ridge

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