Condensation on Surface Energy Gradient Shifts Drop Size Distribution toward Small Drops

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Supporting Information

ABSTRACT: During dropwise condensation from vapor onto a cooled surface, distributions of drops evolve by nucleation, growth, and coalescence. Drop surface coverage dictates the heat transfer characteristics and depends on both drop size and number of drops present on the surface at any given time. Thus, manipulating drop distributions is crucial to maximizing heat transfer. On earth, manipulation is achieved with gravity. However, in applications with small length scales or in low gravity environments, other methods of removal, such as a surface energy gradient, are required. This study examines how chemical modification of a cooled surface affects drop growth and coalescence, which in turn influences how a population of drops evolves. Steam is condensed onto a horizontally oriented surface that has been treated by silanization to deliver either a spatially uniform contact angle (hydrophilic, hydrophobic) or a continuous radial gradient of contact angles (hydrophobic to hydrophilic). The time evolution of number density and associated drop size distributions are measured. For a uniform surface, the shape of the drop size distribution is unique and can be used to identify the progress of condensation. In contrast, the drop size distribution for a gradient surface, relative to a uniform surface, shifts toward a population of small drops. The frequent sweeping of drops truncates maturation of the first generation of large drops and locks the distribution shape at the initial distribution. The absence of a shape change indicates that dropwise condensation has reached a steady state. Previous reports of heat transfer enhancement on chemical gradient surfaces can be explained by this shift toward smaller drops, from which the high heat transfer coefficients in dropwise condensation are attributed to. Terrestrial applications using gravity as the primary removal mechanism also stand to benefit from inclusion of gradient surfaces because the critical threshold size required for drop movement is reduced.

INTRODUCTION

Condensation can be categorized as either filmwise or dropwise, with dropwise condensation being preferred because the overall heat transfer coefficient is often much higher. In filmwise condensation, a poorly conducting liquid film in contact with the condensing surface acts as a resistance to heat transfer between the steam and the surface that can greatly increase the costs associated with energy management. There are several applications covering many length scales where efficient heat transfer is important: heat pipes, the cooling of microelectronics, the cooling of nuclear power reactors, and temperature control on board spacecraft. In all these systems, heat transfer occurs when latent heat is released as hot vapor condenses on a cold surface. However, the inability to maintain a steady dropwise condensation state has prevented the widespread use of dropwise condensation on an industrial scale. One of the main barriers is the design of long-lasting surfaces whose coatings do not degrade or foul. The degradation of surface treatments over time typically leads to the transition from dropwise to filmwise condensation.

In addition to surface degradation, clearing the surface of larger drops quickly to expose fresh surface for nucleation of new drops can be a significant challenge during dropwise condensation. A common way to promote the removal of drops is to either tilt or vertically orient the surface to take advantage of gravity to clear the surface once the characteristic length of the drop exceeds the capillary length scale (about 2.4 mm for pure water). However, the challenge of removal becomes more complicated in low gravity environments and at small length scales where surface tension dominates inertia. In these cases, one needs to employ other methods to clear the surface.

There have been many efforts to move drops on a surface by deliberately disturbing the liquid–gas interface in the vicinity of the contact line to create a force imbalance between the leading and trailing edges of a drop. These methods can be classified as either active or passive, depending on whether external energy needs to be supplied to the system. The most commonly employed passive method uses a surface energy gradient, created by chemically patterning the surface.
chemically coating a physically textured surface. A comprehensive review of techniques to fabricate chemical and physical gradients is provided by Genzer et al. Some of the active methods include temperature gradients (thermocapillary), electrostatic potential gradients (electrocapillary), and a periodic asymmetric oscillation of a substrate. Combinations of these methods have also been used to further enhance drop speeds.

Passive methods have the advantage of requiring no external energy input. A molecular dynamics simulation has predicted drop speeds on the order of 1 m/s for water nanodroplets on a chemical gradient created with self-assembled monolayers. To date, the maximum speed achieved experimentally for a water drop ($V = 2 \mu L$) with a gradient surface is 45 cm/s. Furthermore, the minimum diameter required for a drop to move on a chemical gradient surface is about 1 mm or half the capillary length scale. Lowering the minimum diameter required for movement helps to limit the total area of the condensing surface covered by liquid so that more surface area is available for steam condensation. Thus, even in applications that have the advantage of gravity for drop removal, employing a surface energy gradient could still increase terrestrial heat transfer (and improve efficiency) by shifting the drop size population.

While there has been a lot of work discussing the use of gradients in applications on small length scales to transport small quantities of liquid (e.g., microfluidics, DNA analysis, biological and chemical sensing), the utilization of these surfaces for dropwise condensation has not been thoroughly explored. More specifically, it has not been determined how a gradient surface changes the time evolution of a distribution of drop sizes during condensation. Our experimental study quantifies how populations of drops evolve differently over time on a chemical gradient surface relative to a uniform contact angle surface.

Early work in the area of drop size distributions focused on both modeling the drop size distributions by assuming a neutrally wetting surface and condensing onto uniform surfaces prepared to have a contact angle close to 90°. More recent work has relaxed the neutral contact angle constraint. Kim et al. modeled the steady-state distribution on a superhydrophobic surface for both small and large drops. They concluded that the surface wettability affects both the distribution and consequently the heat transfer. Very small drops (<5 μm) were found to be largely responsible for heat transfer. The work of Leach et al. focused on the growth rate mechanisms for different sized drops, and a single bimodal distribution was reported for a regime where large drops generated first and a population of small drops generated later coexisted. Experimental and computational examination of the transient drop size distributions for an inclined uniform contact angle surface showed that the distribution shape remained the same because of frequent periodic sweeping of the surface by gravity. Simulation of the time evolution of a population of drops on a surface energy gradient surface showed that because sweeping is more frequent on a gradient surface than on a slightly (5°) inclined surface, many more small drops resulted. However, the time evolution of drop size distributions was never quantified. To this end, we seek to create gradient surfaces that not only promote dropwise condensation but also shift the drop size distributions toward smaller drops. We then characterize the time evolution of drop size distributions on these surfaces.

The current work investigates the progression and underlying physics of dropwise condensation on both a gradient surface, which has been chemically patterned with a radial surface energy gradient (i.e., contact angle varies as a function of position), and a uniform surface (i.e., contact angle is spatially independent). Two different dropwise condensation modes are explored for both types of surfaces. In mode A, the surface is exposed to a transient steam source and the backside is not cooled. In mode B, the surface is exposed to a constant steam source and the backside of the surface is cooled. Mode A experiments elongate the time scale of condensation so that the effects of surface functionalization on condensation can be assessed. Mode B experiments show how frequent sweeping of the surface with a surface energy gradient changes the progression of the drop size distributions. Additionally, the conditions of mode B are similar to anticipated operating conditions of a condensing surface in an actual heat transfer application. Because of this, an accurate assessment of how a condensing surface would actually perform can be obtained for these experiments. Surfaces are characterized by the time evolution of the number density of drops, the fractional coverage, the drop size distributions, and the median drop size.

### MATERIALS AND METHODS

**Surface Preparation and Treatment.** Substrates were chemically treated to yield either a spatially uniform surface or a radial energy gradient surface. In preparation for treatment, circular polished glass substrates (Technical Glass Products) made of G.E. 124 fused quartz were cleaned in piranha solution, 70% H$_2$SO$_4$ and 30% of 50 wt % H$_2$O$_2$ by volume, for 25 min to remove any organic impurities on the substrate and to hydroxylate it in preparation for reaction with the silane. After quenching the reaction with deionized (DI) water, the substrates were removed from the piranha solution and submerged in a beaker full of DI water. The beaker was then continuously flushed with DI water for 5 min to remove any trace amounts of piranha solution on the surfaces of the substrates. Just prior to treatment, the substrates were removed from the beaker one at a time and rinsed with DI water for 5 min and then dried with nitrogen.

The uniform surfaces were treated with one of the three following silanes: 3-aminopropyltriethoxysilane (APTES), dodecyltrichlorosilane (dodecyl), or (heptadecafluoro-1,1,2,2-tetrahydroxydicyclohexyl)trichlorosilane (fluoro). The hydrophilic surfaces were created by liquid deposition of APTES to deliver static contact angles, $\theta_s$, of either 64° or 80°. A clean substrate was submerged in a solution of 8% APTES and 92% acetone for 20 min. The surface was then removed from the solution and rinsed with acetone for about 1 min to rinse off any unreacted silane. The surface was baked at 80 °C for 1 h to ensure complete bonding of the silane with the surface. The hydrophobic surfaces were created by vapor deposition of either dodecyl or fluoro to deliver static contact angles of 98° and 103°, respectively. For the dodecyl treatment, a mixture of 6 g of light mineral oil and 30 μL of dodecylsilane was used, and for the fluoro treatment, 6 g of light mineral oil and 6 μL of fluorosilane were used. Each mixture was degassed in a desiccator for 30 min to remove any dissolved air. Otherwise, the silane would react with both the air and water vapor to produce silicon dioxide solids, rendering it unreactive. After degassing, the desiccator was opened, and the substrate was suspended directly over the mixture, parallel to the free interface. A final vacuum was pulled on the system before letting the substrate react with the silane for 2 h. Finally, the surface was removed from the desiccator and baked in an oven at 80 °C for 1 h to ensure complete reaction.

The radial gradient surface was created with dodecyl only. A 1.4 μL dodecyl drop was deposited onto a fluoro-treated silicon wafer and then suspended over the substrate at ambient conditions for 4 min. Because the gradient geometry crucially depends on the shape of the vapor diffusion front, a large Pyrex dish was used to cover the system.
Surface Characterization. The uniform surfaces were characterized by static, advancing, and receding contact angles. The contact angle hysteresis of a surface ($\Delta \theta$) is defined as the difference between the advancing and receding contact angles. Prior to measurement, the surface was rinsed to remove any debris (e.g., dust). First, the surface was rinsed with acetone and DI water and then dried with nitrogen. For the static contact angle experiments, static images of 2 µL sessile drops in ten different locations were acquired with a Redlake HS-3 high-speed camera. For the advancing and receding contact angle experiments, the volume of a sessile drop was increased and decreased by hand with a micrometer syringe (Gilmont Instruments, GS-1200) in seven different locations. Movies capturing the motion of the contact line were acquired. All images were analyzed using an in-house Matlab script consisting of an image analysis routine that uses gray scale thresholding to determine the liquid–gas interface and the Nelder–Mead multivariate optimization method to determine $\theta_a$, $\theta_r$, and $\theta_e$. Assuming the Bond number, $B = \rho g e^2 / \sigma$, where $\rho$ = liquid density (1000 kg/m$^3$), $g$ = gravity (9.81 m/s$^2$), $e$ = footprint radius (0.92 mm for $V = 2$ µL and $\theta_e = 98^\circ$), and $\sigma$ = liquid–gas surface tension (0.072 N/m), is very small ($B \approx 0.1 < 1$), then the effect of gravity on the shape of the drop can be safely neglected. After setting $B \approx 0$, the optimization method finds $\theta_e$ by minimizing the least-squares difference between the experimentally determined profile and the numerically integrated Young–Laplace equation.40

The gradient surfaces were characterized by a dynamic contact angle, $\theta_g$. The dynamic contact angle can be calculated from measurements of the advancing, $\theta_a$, and the receding, $\theta_r$, contact angles at the leading and trailing edges of the drop, respectively, as it translates.31

$$\cos \theta_i = \frac{1}{2} \left( \cos \theta_a + \cos \theta_r \right)$$

Several drops of different volumes were deposited one at a time with a micrometer syringe (Gilmont Instruments, GS-1200) at the beginning of the gradient, and their motion down the gradient was recorded with high-speed imaging. The same in-house Matlab routine was used to find $\theta_a$ and $\theta_r$ at several locations along the gradient (cf. Figure 1). The measured strength of the gradient was $|\Delta \theta| / \Delta x = \frac{22^\circ}{mm}$.

Condensation Chamber. The important features of the experimental setup, including details of the condensation chamber, are shown in Figure 2. Steam is generated by boiling DI water in an Erlenmeyer flask with a hot plate. Stainless steel tubing connects from the flask to the inlet of the condensation chamber. One inch thick fiberglass insulation encloses the tubing to maintain the inside wall temperature close to the steam temperature. This minimizes condensate buildup over the course of the experiment. A condensate vent was installed prior to the steam inlet to drain off the condensate that always occurs at startup when the steam first encounters the cold tubing walls. The condensation chamber rests on an inverted glass Petri dish to allow for viewing and to protect the optical setup below from falling drops. The experiment is imaged from above and illuminated from below using collimated light. The collimated light backlights the drops for all contact angles so that the boundaries can be detected using image analysis. The light bulb in the collimated light train is powered by a 30 V DC power supply (GW Laboratory DC Power Supply, Model GPS-3030D). A Sterilite container served as the holding tank for the coolant, tap water and ice. The temperature of the coolant was maintained at 1 °C by excess ice. The water was pumped around at a volumetric flow rate of 2.9 mL/s by a circulator pump (Fisher Scientific, Model 73).

The condensation chamber was fabricated out of a solid piece of polycarbonate so that it was hollow on the inside. The chamber is about 81 mm tall with a 52 mm i.d. and 85 mm o.d. The chamber consists of three sections. The coolant flows through section 2. A circular polished glass substrate 2.5 in. in diameter and 0.0625 in. thick separates sections 1 and 2. The glass substrate contains the coolant from above and also acts as a window for visualization of the treated surface below. The downward facing treated surface, with the same hydrophobic part of the gradient is qualitatively represented by the dashed horizontal line, whose value is an average of five measurements taken at different locations. (upper right) Angle $\theta_g (\Delta \theta)$ is calculated from eq 1 using a subset of the data. (lower right) Top view of the gradient with side views of two drops at different locations on the surface to illustrate the spatial dependence of the contact angle. During the deposition process to block out convection currents. Finally, the surface was baked in an oven at 80 °C for 1 h.

![Figure 1](dx.doi.org/10.1021/la404057g) | Langmuir 2014, 30, 1788–1798
are six holes drilled in the circumference of the chamber so that screws can be threaded into both sides of section 2 to compress the chamber and hold everything in place. All of the experiments are pendant mode dropwise condensation. Gravity is the removal mechanism for a drop that has had sufficient time to reach the critical radius corresponding to instability.

Methods. Condensation experiments were run in two different modes: (A) transient steam exposure and no cooling and (B) constant steam exposure and cooling (cf. Table 1). Only uniform surfaces were tested for mode A because the driving force of condensation proved to be insufficient to move drops on a gradient surface.

Table 1. Summary of Experimental Operating Conditions for the Two Different Modes

<table>
<thead>
<tr>
<th>mode</th>
<th>description</th>
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<tbody>
<tr>
<td>A</td>
<td>transient steam, no cooling</td>
</tr>
<tr>
<td>B</td>
<td>constant steam, constant cooling</td>
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For mode A experiments, the treated surface was exposed to a transient steam source and the backside was not cooled. In the absence of active cooling, the surface can only cool by radiating heat into section 2. As a result, the temperature of the air in section 2 increases, condensate forms on the window, and visualization becomes obscured. To avoid this, the window was removed. Next, DI water was boiled using a kettle (Hamilton Beach; Model K6080). The chamber was placed in a Pyrex dish where 300 mL of boiling water was poured into the dish up to a height where it made contact with the perimeter of the chamber. This created a small pocket of air inside the chamber which trapped the steam. The boiling water was allowed to cool down over a period of about 15 min. A pixelink camera (Model: PL-A741) was used to record images at 1 fps with a resolution of 1280 × 1024. For this mode, the driving force decreases substantially over time, and the drops never reach the critical instability radius for detachment by gravity.

For mode B experiments, the treated surface was exposed to a constant steam source and was constantly cooled on the backside. The temperature of the coolant was maintained at 1 °C by excess ice. To perform this type of condensation experiment, a 500 mL Erlenmeyer flask was filled with 350 mL of DI water. The hot plate was turned on to 450 °C to boil the DI water and produce steam. At the first sight of bubble nucleation, a heat gun is turned on to the highest setting and aimed at the inverted glass Petri dish. By heating up the glass, the steam will not condense onto the glass Petri dish but, instead, on the treated surface. This step was necessary because any condensate buildup on the Petri dish will obscure the field of view. Once a rolling boil is established, the pump is turned on to start cooling the slide. Eventually the steam enters the chamber via section 3, and a Redlake HS-3 high-speed camera is manually triggered to record at the first signs of nucleation at a rate of 30 fps with a resolution of 1280 × 1024 for about 2 min. Toward the end of the experiment, there is drop detachment as a result of gravity for the uniform contact angle surfaces only. In the case of a gradient surface, there is no dripping because drops are removed at a critical radius that is much smaller than that at the onset of instability by gravity. After the drops are swept off the

Figure 2. Experimental setup. Condensation chamber (sections 1, 2, and 3) is imaged from above and illuminated from below. A hot plate (left) boils DI water to produce steam (dots). Condensate buildup drains out through the condensate vent and into a beaker. Chamber sections 1 and 2 are separated by a window, coolant flows through section 2, a downward facing treated surface (cross-hatch) separates sections 2 and 3, and the steam enters into section 3. A diffuser piece at the steam inlet evenly distributes the steam.
The gradient, they collect in a puddle at the perimeter of the gradient (where the contact angle is very small), and the liquid eventually drips from the surface and/or runs down the side of the chamber.

**RESULTS AND DISCUSSION**

The goal of the mode A experiments was to investigate how wettability affects the time progression of condensation through alteration of the physics involved in coalescence. For mode B experiments, the objective was to see how the presence of a frequent and periodic removal mechanism, such as that present on a gradient surface, alters the drop populations. Metrics such as how many drops were present on the surface at any point in time, the drop sizes, and how they were distributed were used to compare and contrast the two different types of surfaces. Analysis for both modes was restricted to drops larger than about 80 μm. The cutoff is a compromise between the two types of cameras used and their different resolutions.

**Growth Curves.** A growth curve is a time course of the number of drops per unit surface area (i.e., number density). This course characterizes the progression of a condensation experiment. Each growth curve can be separated into at least three regions:

- **Region 1:** The initial formation of drops.
- **Region 2:** The growth of drops due to condensation.
- **Region 3:** The stabilization of the drop population.

![Figure 3](image1.png)

**Figure 3.** (left) Growth curve for a uniform dodecyl surface exposed to a constant source of steam and constant cooling (mode B). (right) Images just before (red) and just after (blue) a large scale coalescence event, also indicated by arrows in inset of sawtooth. A sharp decrease in the number density coincides with clearing a large surface area.

![Figure 4](image2.png)

**Figure 4.** Mode A. Uniform surface. Time evolution of number density (left) and fractional coverage (right) for dropwise condensation on a treated surface that was exposed to transient steam and was not cooled for three surface treatments: APTES ($\theta_s = 80^\circ$; $\Delta \theta = 42^\circ$; black), dodecyl ($\theta_s = 98^\circ$; $\Delta \theta = 22^\circ$; red), and fluoro ($\theta_s = 103^\circ$; $\Delta \theta = 18^\circ$; green). ($\bigtriangleup$), ($\bigcirc$), and ($\square$) denote the first, second, and third trials, respectively. Time $t = 0$ s corresponds to the first instant when a statistically significant number of drops have populated the surface, yielding a drop size distribution with a distinct shape. Reported contact angle hysteresis values were measured on slides that were treated and prepared in the same way.
two regions, regardless of the mode of operation and surface treatment (cf. regions 1 and 2 of Figure 3). There is an additional region when the treated surface is cooled (cf. region 3 of Figure 3). In region 1, the total number of drops increases as they nucleate and coalesce on a small length scale to produce drops of increasing size that come into view. In region 2, there is a net decrease in the total number of drops because the number of coalescence events exceeds the number of nucleation events. The presence of first generation drops leaves less surface area for drops to nucleate. Regions 1 and 2 are separated by a peak which corresponds to the maximum number density. The peak signifies a transition from nucleation domination in region 1 to coalescence domination in region 2. Finally, region 3 is characterized by a sawtooth wave. Here, large-scale coalescence events remove many smaller drops in a single coalescence event which are then replenished in time until another large scale coalescence event occurs (cf. Figure 3; blue image).

The driving force for condensation is dictated by both the temperature difference between the steam and the surface and the amount of steam present. Running an experiment without cooling the surface or replenishing steam (mode A) elongates the time scale of condensation and allows for easier observation of how surface wettability affects the time needed to reach the maximum number density. On the left side of Figure 4, the growth curves are plotted for mode A for three uniform surface treatments: APTES ($\theta_i = 80^\circ$), dodecyl ($\theta_i = 98^\circ$), and fluoro ($\theta_i = 103^\circ$). Comparing these cases, we can see that as $\theta_i$ increases, it takes more time to reach the maximum number density, indicating that the less hydrophobic a surface is, the easier it is to nucleate. Therefore, more hydrophilic surfaces have a head start on growing the first generation of drops relative to less hydrophilic surfaces. Because transition from region 1 to region 2 is affected by the ratio of area available for nucleation and area taken up by existing drops, one also needs to consider how the wettability of the surface affects the drop footprint and coalescence.

For example, a drop with volume $V$ on a hydrophilic surface will have a larger perimeter (i.e., footprint area) than a similar drop on a hydrophobic surface. The most significant difference, though, between the hydrophobic (dodecyl and fluoro) and the hydrophilic (APTES) surfaces is in the details of the coalescence events. On the APTES surface, coalescence events typically involved two or maybe three drops whereas coalescence events on the dodecyl and fluoro surfaces usually involved more than three drops within the observed frame rate of 1 s. Additionally, after coalescence on an APTES surface, the contact line of the new drop remained mostly pinned (cf. Figure 5; top row), whereas on a hydrophobic surface, the contact line was more mobile and retracted immediately after coalescence (cf. Figure 5; bottom row). Qualitatively, pinning of the contact line on a hydrophilic surface suggests a higher contact angle hysteresis relative to a hydrophobic surface. Quantification of the hysteresis showed that it was highest for an APTES surface ($\Delta \theta = 42^\circ$) and lowest for a fluoro surface ($\Delta \theta = 18^\circ$). Consequently, less surface area was regenerated for an APTES surface compared to either a dodecyl or a fluoro surface. These three features (i.e., larger perimeter, less sweeping because coalescence events involve few drops, and pinned contact lines) catalyze the transition from region 1 to region 2 for an APTES surface by blocking active nucleation sites with footprint areas that are larger than their hydrophobic counterparts. These results are in agreement with previously published results that also examined the effects of wettability on drop growth and condensation by utilizing a weak gradient surface. However, contact line motion is biased on a gradient surface. For this reason, we chose to isolate the effects of wettability from the effects of the gradient dynamics on drop growth by performing a set of experiments on uniform contact angle surfaces ranging from hydrophilic to hydrophobic.

Fractional coverage, the ratio of the cumulative “wetted” area covered by drop footprints to the total surface area, is another way of plotting the growth curves and shows how much of the surface is covered by liquid. On the right side of Figure 4, we see that in the absence of frequent drop removal on a horizontal surface all surfaces approach a high fractional coverage (fluoro: 45%; dodecyl: 50%; and APTES: 70%) consisting of drops whose radii are all greater than 80 $\mu$m. A high fractional coverage of large drops is undesired because conduction through the liquid is the largest resistance to high heat transfer between the steam and the condensing surface. Also, regions 1 and 2 of the growth curves are characterized by different slopes separated by a transition point. The transition point corresponds to the maximum number density on the growth curve. The steeper slope corresponding to region 1 is hypothesized to correspond to mass transfer limitations and how quickly the drops nucleate and grow continuously mainly by direct condensation onto the liquid–gas interface, as opposed to absorption of weakly adsorbed water molecules on the surface at the drop perimeter. Drops in this region also experience discrete growth due to small scale coalescence events. The smaller slope corresponding to region 2 is hypothesized to coincide with diffusion limitations in the sense of how quickly the drops “diffuse” and/or convect (for the gradient surface) as they experience discrete growth by coalescence (over a larger scale) with neighboring drops to clear the surface for renucleation. The sawtooth region is absent for all three surface treatments under conditions of mode A because of the low condensation driving force. The driving force is low because the steam depletes and the surface heats up.

Figure 5. Example highlighting the differences in contact line mobility of the newly formed drop after a coalescence event on APTES (top row) and dodecyl (bottom row) treated surfaces subjected to conditions of mode A. The contact line of newly formed drop 1 on the APTES surface is highly irregular and appears to retain some features of previous unmerged drops 1, 2, and 3. Elapsed time between images in both the top and bottom rows is 1 s.
quickly. Consequently, there are very few coalescence events occurring toward the end of the experiment.

Now we compare the results between uniform and gradient surfaces exposed to a constant generation of steam with the back side constantly cooled (mode B). Several differences arise (cf. Figure 6, left). For a uniform surface, the growth curve monotonically increases in region 1 until peaking at a maximum value, beyond which it decreases in region 2 for a short time before transitioning to a downward trending sawtooth wave in region 3 (inset in Figure 6). For a gradient surface, while the growth curve is largely similar up to the peak, there are several important differences beyond that point. After a short decrease, the number density transitions to a sawtooth wave with a mean slightly below the maximum value. This behavior indicates that dropwise condensation has essentially reached a steady state and will continue until the steam source is removed or the surface fouls. A constant number density corresponds to a constant fractional coverage (cf. Figure 6, right). In contrast, for a uniform surface, the fractional coverage monotonically increases at a faster rate than mode A. Here, the fractional coverage reaches 70% for dodecyl and 80% for APTES surfaces after only 2 min. Again, the large fractional coverage consists of drops larger than 80 μm. A constant low fractional coverage, such as that for a gradient surface, means that the majority of the surface will always be available for the nucleation of many small drops, favoring efficient heat removal.

Note that because of the method we use to generate the radial gradient, there is a region in the center that is hydrophobic (cf. Figure 1). Here, drop motion is not influenced by the surface energy gradient. Drops in this central region are stationary and grow only by coalescing randomly with other nearby drops in this region, akin to coalesce on a uniform surface. Because of the existence of this “dead” uniform region, there is a very slight increase (from the constant value) in the fractional coverage (i.e., minor decrease in number density) at longer times. Essentially, drop coalescence in the central hydrophobic central region increases the coverage while decreasing the total number of drops, until they are large enough to drip off the surface. An ideal gradient would minimize the radius, r_{15}, of this flat hydrophobic zone (cf. Figure 1, lower right). But to achieve such a gradient would require more complex fabrication methods than are presently available to us.

In comparison to the two uniform surfaces, the gradient surface has a slightly lower maximum number density. The peak corresponds to an instant in time when a large number of drops located on or near the gradient have reached the threshold radius required for movement. Drops move when the force from the surface energy gradient exceeds the resisting forces of hysteresis and drag. Because of the radial geometry of the gradient pattern, the drops sweep large sectoral areas of the surface and coalesce with other drops in their path (much like the spokes of a bike wheel) as they depart. This frequent sweeping results in a noticeable reduction in the number density when compared to the uniform dodecyl-treated surface.

**Drop Size Distributions.** Another major difference between uniform and gradient surfaces is the time evolution of the drop size distributions. For a uniform surface, each region of the growth curve (cf. Figure 3) has a unique drop size distribution (cf. Figure 7; red distributions). Additionally, the shape of the distribution can be used to determine the specifics related to the stage of condensation. When condensation begins, small drops nucleate and coalesce with one another until they are large enough to be detected by image analysis (i.e., drops larger than about 80 μm). These are the first generation of drops, represented by distribution I, which characterizes region 1 (cf. Figure 7). As the drops from the first generation continue to coalesce and grow, the area regenerated by the drops also increases and a population of small drops is born, but has not yet come into view (cf. Figure 7; distributions IIA and IIB). The first occurrence of distribution IIA corresponds to the peak between regions 1 and 2. Distribution IIA spans the beginning half of region 2 when coalescence first dominates over nucleation. Distribution IIB characterizes the latter half of region 2 where coalescence occurs over larger length scales. As time progresses through region 2, the small drops finally come into view by growing mainly by condensation onto the interface and by small scale coalescence events. Distribution III is bimodal and spans most of region 3. The distinct population of small drops is represented by a secondary peak at a smaller median radius and the broad distribution at the higher median radius corresponds to the first
generation of drops (cf. Figure 7; distribution III). There is one final transition, occurring somewhere near the end of region 3, to a final distribution resembling the initial distribution. Here, the number of first generation drops is substantially diminished to a handful of drops each almost large enough to drip from the surface. The rest of the surface is covered with lots of very small drops. The magnitude of the histogram bars, relative to the initial distribution, is about the same or a little less. The final
transition is not marked because it is difficult to accurately delineate the end of distribution III, as the shape progression is continuous in time.

Unlike a uniform surface where each region of the growth curve is uniquely characterized by the shape of the drop size distribution, there are only two shapes of distributions observed for a gradient surface (cf. Figure 7; lilac distributions). Hence, the shape of the distribution alone cannot be used to determine the stage of condensation. The observed shape shifts between points I and III for a uniform surface are absent for a gradient surface. This is because drops large enough to move on the gradient are present, and as they translate, they coalesce and remove drops in their path. Consequently, the first generation drops never have a chance to grow and form a distinct population with a large median radius. Similar results were found for an inclined uniform contact angle surface where gravity was the removal mechanism. The broadening of the initial distribution is a result of the large hydrophobic center where larger drops are trapped and will never reach the gradient (cf. Figure 7; distribution IIIB). As time progresses and these drops coalesce with one another, the number of drops will decline and the regenerated area will give rise to more nucleating drops. Eventually, a single large drop will be left in the center that can only depart from the surface by dripping. Dripping occurs when the pendant drop goes unstable because the force of gravity exceeds the force of surface tension. For an ideal gradient surface with no hydrophobic central region, we expect the distribution shape to remain the same for the entire experiment because drops would be removed before they reach the critical size for dripping.

To recapitulate our findings, the main difference between the gradient and uniform surfaces with regards to the drop size distributions is the absence of a bimodal distribution in region 3 for a gradient surface (cf. Figure 7; distribution III). For a uniform surface, the peak at the large drop radius corresponds to the first generation of drops whereas for the gradient surface, this generation is absent because they are removed by the gradient. The frequent sweeping on a gradient surface induces a steady state which essentially freezes the drop distribution at the shape of the initial distribution.

The population of drops on the gradient surface in region 1 summarizes the results of Figure 4 (cf. Figure 7, lilac inset photo for distribution I). The annuli (white perimeter, dark gray) of different color intensity encircling the light gray circular region further corroborate the effects of wettability on the time scale of nucleation and coalescence. The majority of the light gray circle corresponds to the hydrophobic part of the surface with the balance corresponding to the start of the steep part of the gradient. The dark gray ring corresponds to the rest of the gradient. Here, the gradient is initially shallower than the preceding part of the gradient. However, the gradient returns to being steep at the outermost part of the dark gray ring (cf. Figure 1). Finally, the irregularly shaped drops on the perimeter of the image that appear to be mostly white reside on the most hydrophilic part of the surface ($\theta_1 \approx 30^\circ$). The drops in the more hydrophilic region are much larger in size than those in the more hydrophobic regions, meaning that condensation has progressed further. In other words, at any point in time, the more hydrophilic the surface is, the further along the growth curve you are.

In Figure 8, the time progression of the median drop radius is plotted for modes A (left) and B (right). For the uniform surface treatment, regardless of the mode of condensation, the median radius increases monotonically for the first (i.e., largest in size) generation of drops. In contrast, for the population of smaller drops, the median radius tends to remain relatively constant. Recall that the coexistence of two distinguishable populations of drops corresponds to the bimodal distribution for a uniform surface (cf. Figure 7; distribution III). Additionally, the curvature in the data for the first generation of drops depends on the mode of condensation. The curvature is likely influenced by the growth rate, which is larger for mode B because of the higher condensation driving force. Comparison of the APTES results for mode A with results in the literature for a surface with a similar contact angle shows good qualitative agreement. Also, in the case of mode A, the emergence of a distinguishable population of small drops occurs earlier for a hydrophilic surface. This result agrees with that of Figure 4, which also shows that the more hydrophilic a surface is, the faster the condensation progresses. In the case of mode B, maturation of the first generation drops is truncated for a gradient surface. This result is in agreement with the constant number density and fractional coverage results of Figure 6 and with the frozen drop size distribution shapes of
Figure 7. These results show that in the case of a gradient surface, frequent periodic sweeping of the surface alters the time evolution of a population of drops relative to a uniform surface.

**Heat Transfer Implications.** The higher heat transfer coefficients found in dropwise condensation relative to filmwise condensation are often attributed to the presence of very small drops which balance the effects of conducting and dissipating heat to the surface while at the same time, not creating a large resistance. Accordingly, to maximize heat transfer, the chemical treatments for condensing surfaces should be designed to maintain the highest possible fractional coverage of very small drops (<5 μm) without transitioning to filmwise condensation. One strategy to achieve this design criterion is to pattern a chemical gradient onto the condensing surface to induce frequent sweeping by moving drops, as shown here. In doing so, a mostly stagnant distribution that is dominated by very small drops, relative to a uniformly coated hydrophobic surface, is achieved.

**CONCLUSIONS**

A radial surface energy gradient alters the time evolution of a population of drops by frequently sweeping the surface to remove large drops. As a result, maturation of the first generation of drops is truncated, and a bimodal drop size distribution is never observed. Furthermore, because the departure of large drops is staggered, there is a large population distribution is never observed. Furthermore, because the generation of drops is truncated, and a bimodal drop size population of drops by frequently sweeping the surface to remove large drops. As a result, maturation of the first generation of drops is truncated, and a bimodal drop size distribution is never observed. This essentially locks the shape of the drop size distribution at the initial distribution, which consists of small drops. The unchanging distribution shape indicates that dropwise condensation on a gradient surface has reached a steady state. The steady state corresponds to a balance between the “birth” of drops by nucleation and the “death” of drops by coalescence. In contrast, for a uniform contact angle surface, there are four shapes that the drop size distributions evolve through. They can be associated uniquely with each stage of condensation (i.e., location on the growth curve) and, whether unimodal or bimodal, how many distinguishable populations of drops are present.

Experiments conducted on the uniform contact angle surfaces for mode A revealed the effects of wettability on the time progression of growth. For decreasing contact angle, it takes less time to reach the maximum number density because of differences in perimeter availability for coalescence and also differences in the physics of coalescence. For hydrophilic surfaces, it also appears that there is some history of a coalescence event contained within the contact line of a new drop formed from coalescence. The irregularly shaped footprint contains features reminiscent of the individual contact lines of the coalesced drops. Furthermore, the contact line appears to be less mobile on a hydrophilic surface, which gives rise to a decrease in available surface area for nucleation.

Surface patterning (chemical and/or physical) for condensing surfaces should aim for a high fractional coverage of very small drops (<5 μm) to achieve high heat transfer rates. A properly designed surface would give all drops a chance to access the gradient at some point during their growth either by their position on the surface and/or by randomly sampling the gradient as a result of a shape fluctuation from coalescence. Gradient surfaces might be an effective tool in promoting and sustaining dropwise condensation for the management of large heat loads in regimes where gravity cannot be used as a drop removal mechanism. Examples include heat pipes and microelectronics that operate on small length scales where inertia is dominated by surface tension and in spacecraft, which present a low gravity environment. However, even terrestrial-based technologies stand to benefit from using surface energy gradient surfaces because the critical length scale required for movement of the drops is drastically reduced.

**ASSOCIATED CONTENT**

Supporting Information

Movie 1: dropwise condensation under conditions of mode B on a uniform contact angle surface treated with the dodecylsilane; area of condensation is about 1.7 cm², acquisition rate was 30 fps, playback is 25 fps. Movie 2: dropwise condensation under conditions of mode B on a gradient surface created with vapor diffusion of the dodecylsilane from a point source; drops move on the gradient when their size exceeds the critical threshold required for movement; in the center hydrophobic region, drops are “stuck” and never reach the gradient; here, they continue to grow by coalescence with neighboring drops; area of condensation is about 1.7 cm², acquisition rate was 30 fps, playback is 25 fps. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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