Thermal transport to droplets on heated superhydrophobic substrates

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Abstract

This paper reports on measurements of thermal transport to solitary sessile water droplets placed on heated superhydrophobic substrates maintained at constant temperature. A single water droplet of nominally 3 mm diameter is placed on a preheated substrate and allowed to evaporate completely while being imaged from two angles with video cameras and an infrared camera. Substrate temperatures are varied from 60°C to 230°C and total evaporation time and heat transfer rate are determined. Three different rib-patterned superhydrophobic substrates are investigated of 0.5, 0.8, and 0.95 cavity fraction (relative projected cavity area of substrate to total projected surface area). The rib features range in width from 2 to 30 μm and in height from 15 to 20 μm . Results are also obtained for a smooth hydrophobic substrate for comparison. Droplet evaporation times increase with substrate cavity fraction while overall heat transfer rates decrease. At subcritical substrate temperatures the Nusselt number is larger for lower cavity fraction substrates. For supercritical substrate temperatures, as the cavity fraction increases nucleate boiling is delayed to higher substrate temperatures and the Leidenfrost point occurs at lower temperature. At the highest cavity fraction explored nucleate boiling does not occur at any substrate temperature. At temperatures above the Leidenfrost point the influence of cavity fraction is negligible.

Keywords:

superhydrophobic, droplet evaporation, heat transfer, structured substrate

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NOMENCLATURE

A_c	Projected droplet-substrate contact area
$\overline{A_p}$	Average projected area of droplet surface intercepting radiation from substrate
A_u	Exposed upper-surface area of droplet
c_p	Specific heat capacity of water
d_i	Diameter of a single-pixel thick droplet slice from CCD images
d_l	Width of droplet at droplet-substrate interface longitudinal to ribs
d_t	Width of droplet at droplet-substrate interface transverse to ribs
F_c	Substrate cavity fraction
g	Acceleration due to gravity
Gr	Grashof number
h_{conv}	Convective heat transfer coefficient for external water-air interface
h_{fg}	Latent heat of vaporization of water
h_p	Height of one pixel in CCD images
h_s	Heat transfer coefficient representing all modes of heat transfer from the substrate to the droplet
k	Thermal conductivity of water
Nu	Nusselt number
Nu_0	Nusselt number for smooth hydrophobic substrate
$Nu_{0.5}$	Nusselt number for $F_c = 0.5$ substrate
$Nu_{0.8}$	Nusselt number for $F_c = 0.8$ substrate
$Nu_{0.95}$	Nusselt number for $F_c = 0.95$ substrate
Pr	Prandtl number
$\dot{q}_{conv}$	Convective heat transfer rate at external droplet-air interface
$\dot{q}_{evap}$	Evaporative heat transfer rate at external droplet-air interface
$\dot{q}_{rad}$	Radiative heat transfer rate at external droplet-air interface
$\dot{q}_s$	Heat transfer rate at droplet-substrate interface
$\dot{q}_{sens}$	Rate of sensible heat change within droplet
$\overline{\dot{q}_{s,rad}}$	Average radiative heat transfer rate at droplet-substrate interface
t	Time
t_e	Time at point of critical heat flux
T_d	Droplet temperature
T_s	Substrate temperature
T_{sat}	Local saturation temperature of water

T_∞	Ambient air temperature
V	Droplet volume
V_0	Volume of spherical droplet with 3 mm diameter
w_c	Substrate cavity width
w_r	Substrate rib width
β	Volumetric thermal expansion coefficient of water
ϵ	Emissivity of water
ϵ_s	Emissivity of solid substrate
ν	Kinematic viscosity of water
θ	Contact angle
ρ	Density of water
σ	Stefan-Boltzmann constant

1. Introduction

Evaporation of a water droplet is a common, natural occurrence, yet it is a complex process where both heat and mass transfer occur as the water evaporates into the surrounding unsaturated air. Droplet evaporation from substrates is a regularly studied phenomenon due to its multiple applications including ink-jet printing [5, 34], micro/nano fabrication [6, 50], thin film coatings [23], and spray cooling [20]. Recently, droplet evaporation on superhydrophobic (SH) substrates has captured interest due to the significant alteration of heat transfer dynamics on these substrates caused by very high contact angles and micro/nanoscale surface structuring.

Superhydrophobic (SH) surfaces exhibit internal contact angles with water in excess of 120° and contact angles up to 177° have been reported [9]. This non-wetting behavior occurs in nature with such examples as the lotus leaf [2]. Artificial SH surfaces are manufactured by combining micro and/or nanoscale surface roughness with a non-wetting surface coating such as Teflon. Manufacturing methods include, among others, deep reactive ion etching, wax film growth, alumina gel film preparation, and vapor deposition of fluoroalkyl silanes [4]. The left panel of Fig. 1 is an SEM image of a rib/cavity structured surface created using common photolithographic techniques. If the distance between roughness features is minimal, and the Laplace pressure is not exceeded, liquid above the cavities will form menisci between roughness features and rest above the cavities (Cassie-Baxter state [7]), significantly increasing the contact angle and altering the fluid flow and

Figure 1: Left panel: SEM image of an $F_c = 0.8$ SH surface. Right panel: Sessile droplet placed on a heated SH surface (note the ribs are not to scale as the droplet with a 3mm diameter would be in contact with hundreds of ribs). Convection, conduction, and radiation (not shown) occur at the base of the droplet, while free convection, radiation, and evaporative cooling occur at the upper surface of the droplet.

heat transfer behavior of liquids on the surface. SH surfaces can be characterized by the cavity fraction, defined as the ratio of the projected area of the cavities to the overall projected area of the surface. Significant research has been focused on the hydrodynamics of fluid interactions with SH surfaces (channel flow [24, 28, 32, 33, 48, 49], jet impingement [21, 29, 36, 37], and droplet motion [38, 40, 45, 47]). More recent research has explored heat transfer dynamics (channel flow [11, 27], condensation [8, 15, 31] and ice formation [25, 46]). However, much less research has been published regarding the heat transfer behavior with regard to droplet evaporation dynamics on a heated SH substrate [13].

Droplet evaporation rate is a function of the relative humidity of the surrounding air, the surface area in contact with the air (a function of the liquid-solid contact angle), and the substrate temperature and thermal conductivity of the material [14, 39]. During evaporation, two distinct modes can occur; constant contact angle and constant contact line, where in the latter the surface area of the droplet in contact with the substrate remains nominally constant [26, 30, 35, 51]. During evaporation of droplets from most hydrophilic surfaces the constant contact line mode prevails due to the droplet being pinned to the surface. Pinning may also occur for some hydrophobic and SH surfaces [10, 51]. However, more commonly hydrophobic and SH surfaces exhibit the constant contact angle mode which is characterized by a retreat of the liquid-solid contact line accompanied by the maintenance of

the liquid-solid interior contact angle.

For a sessile droplet on a smooth hydrophobic surface it has been shown that the evaporation rate is linearly proportional to the radius of the liquid-solid contact area between the droplet and the hydrophobic surface [3, 19]. As hydrophobicity or superhydrophobicity increases, the evaporation rate decreases due to water vapor being trapped near the contact line of the droplet between the sides of the droplet and the substrate [41–44].

When the substrate is heated the evaporation process is enhanced on both hydrophobic and hydrophilic surfaces. Complex circulations due to temperature gradients within the droplet alter the evaporation dynamics and the evaporation rate on hydrophilic surfaces is underestimated when a diffusion-only model is applied [12, 18]. At surface temperatures greater than the saturation temperature, the dynamics in the liquid change dramatically as nucleate boiling begins to occur. Above the Leidenfrost temperature the vapor layer between the droplet and substrate acts as a barrier to heat transfer resulting in a significant drop in evaporation rates.

For liquid droplets on metal SH surfaces with droplets in the Cassie-Baxter state there will be regions of high heat transfer (above the microstructure) interspersed with nearly adiabatic regions (above the air cavities). This nonuniform heating due to the droplet sitting atop the microstructured surface significantly decreases the expected droplet temperature and subsequently decreases the evaporation rate [13]. Dash and Garimella created a simple model to estimate the actual interface temperature, which when used with the common vapor-diffusion-only model more accurately estimates the slower evaporation rates observed on SH surfaces for surface temperatures up to 60°C [13]. We expect as the SH substrate temperature continues to increase the dynamics will be altered even further as the saturation temperature is approached and exceeded. Above the saturation temperature, at supercritical temperatures, heat transfer and droplet boiling dynamics on a SH surface has received only limited prior attention.

In this paper we expand the current understanding of the influence of surface temperature and topography on droplet evaporation and heat transfer rates by characterizing static water droplet evaporation on heated SH surfaces. Experiments are presented for various surface types and over a wide range of surface temperatures. Temporal variation of the droplet geometry and temperature are characterized as a function of the controlling variables. Further, the influence of topography and surface temperature on evaporation rate, interfacial heat flux, droplet boiling behavior, and Leiden-

frost point temperature are presented.

The remaining sections of the paper are as follows. First the experimental methods used to analyze an evaporating droplet, including hardware used, methods for collection of data, and data analysis are outlined. The next section presents results from the experiments and a quantitative analysis of the heat transfer for various surfaces and temperatures explored. Finally, conclusions are drawn and implications of the work discussed.

2. Experimental Methodology

2.1. Substrates

A smooth hydrophobic substrate and three different SH substrates manufactured from silicon using photolithographic processes were used. Figure 1 (left panel) shows an SEM image of a rib and cavity microfeatured SH surface created for use in the current research. Rib widths range from 2 to 20 μm , heights from 15 to 20 μm , and spacing between the ribs (cavities) ranges from 20 to 38 μm . All SH surfaces have a thin (≈ 100 nm) layer of chromium to promote adhesion with Teflon which renders the surfaces superhydrophobic.

A common metric indicating the degree of superhydrophobicity of a given substrate is the cavity fraction, F_c . It is defined as the relative projected cavity area to total projected area of the surface. For rib and cavity structures this yields

$$F_c = \frac{w_c}{w_c + w_r} \quad (1)$$

where w_c is the width of a cavity and w_r is the width of a rib. Cavity fractions of the SH surfaces used here are $F_c = 0$ (smooth), 0.5, 0.8, and 0.95. For these surfaces, the corresponding initial interior static contact angles with water were approximately 108° , 120° , 123° , and 140° , respectively.

2.2. Experimental Setup

Experiments consist of a sessile distilled water droplet with initial diameter of nominally 3 mm undergoing evaporation on a heated substrate. Three trials were recorded at each surface temperature ranging from 60°C to 230°C and for each surface type. A schematic representation of the experimental setup is shown in the left panel of Fig. 2. A patch heater is affixed to the underside of an aluminum block which is then seated in a block of insulating foam. The heat output of the patch heater is controlled by a voltage transformer. Silicon wafers are affixed to the top of the heated aluminum block

Figure 2: Left panel: Experimental setup including heated substrate apparatus, cameras, and other sensors used for measurement. Right panel: Droplet images directly from the camera (top) and final binary image (bottom).

using thermal paste. A droplet of distilled water is placed on the substrate using a glass syringe with a Teflon needle to minimize particulate contamination from metals which can cause droplets to prematurely pin to the surface during evaporation. Two CCD cameras are used to film the droplet from the sides and a thermal imaging camera captures the temperature of the top of the droplet. In addition, for supercritical substrate temperatures, high speed camera video images of the droplet were captured at 10,000 FPS. High-speed footage was not post-processed to produce quantitative data, but instead was reviewed for qualitative observations of boiling and Leidenfrost behavior.

A K-type thermocouple embedded 3 mm below the top surface of the aluminum block measured the silicon substrate temperature, T_s , with an uncertainty of $\pm 0.5^\circ\text{C}$. A correlation between the temperature measured by this thermocouple and the true temperature of the upper surface of the substrate was found using a flat-black painted silicon wafer and an infrared camera oriented normal to the surface of the wafer. Using various steady-state temperatures a linear relationship between the thermocouple and infrared camera temperatures was found with a coefficient of determination, $R^2 = 0.9998$.

An infrared camera normal to the substrate surface focused on the top of the evaporating droplet measured the droplet surface temperature, T_d , through time. This temperature is not to be understood as an average or minimum droplet temperature, but rather a representative droplet temperature. Uncertainty in T_d introduced by the infrared camera is nominally

$\pm 3.2^\circ\text{C}$. Additionally the ambient air temperature, T_∞ , was measured using a thermocouple with an uncertainty of $\pm 0.4^\circ\text{C}$.

Two CCD cameras parallel to the substrate surface, one aligned parallel to the microribs on the surface and the other perpendicular, image the geometry of the droplet through time. After filming, a grayscale intensity threshold is determined that distinguishes the droplet from the rest of the image and a binary operation is applied to isolate the droplet as illustrated in the right panel of Fig. 2. Droplet volume was estimated assuming an axisymmetric droplet with a local diameter defined by the length of each horizontal row of pixels within the droplet such that

$$\Delta V_i = \frac{\pi d_i^2 h_p}{6} \quad (2)$$

Here d_i is the distance, in physical units, between left and right droplet edges at a particular vertical pixel location, and h_p is the height, in physical units, of one pixel. Total droplet volume is then found by summing the individual volumes for each pixel row of the droplet. Any asymmetry in the droplet can be accounted for by averaging together the volumes determined from the two camera images, although the difference in measured volume was always within $\pm 2\%$.

Projected droplet-substrate contact area can be found by assuming an elliptical droplet footprint on the substrate and using

$$A_c = \frac{\pi d_l d_t}{4} \quad (3)$$

where d_l and d_t are the distance between the edges of the droplet at the droplet-substrate interface for camera views longitudinal and transverse to the microrib structures. An alternative method is to assume the droplet footprint is circular and average the contact areas found using each camera view independently. This results in an order $\pm 0.1\%$ difference in area. More anisotropic surfaces (higher F_c) yield larger differences in d_l and d_t . For example, the $F_c = 0.95$ substrate yields a difference between d_l and d_t of nominally 10% whereas the smooth hydrophobic substrate yields a difference of nominally 1%.

We note that when placing the droplet on a heated substrate at supercritical temperatures, droplets begin to translate freely, making data collection very difficult. To mitigate this problem, the smooth hydrophobic surface was constructed by forming a slightly concave region in an aluminum plate,

coated in Teflon, with a large radius of curvature such that changes in contact angle or evaporation dynamics are negligible. Gravity keeps the droplet centered, making data collection feasible. For SH surfaces droplet boiling is much less violent, reducing the need for external stabilization of the droplet. In addition, temporary pinning on ribs stabilizes the droplet, the effects of which are discussed in the Results section.

To estimate the contact angle at the surface an ellipse is fit to the shape of the bottom portion of the droplet in the binary image, below the maximum diameter. At the contact point the slope of the ellipse is calculated, from which the contact angle is computed.

2.3. Experimental Model

Heat is exchanged between the substrate and the droplet via conduction through the ribs and convection and radiation through the cavities, as depicted in the right panel of Fig. 1. An overall heat transfer rate from the substrate to the droplet can be estimated by

$$\dot{q}_s = h_s A_c (T_s - T_d) \quad (4)$$

where A_c is the total projected contact area between the droplet and the substrate, T_s is the substrate temperature, and h_s is an overall convection coefficient representing all modes of heat transfer between the substrate and the droplet through the projected area.

Heat is subsequently transferred from the droplet to the ambient air via convection, radiation, and mass transfer of water vapor. Newton's Law of Cooling can be applied to the free convection between the free surface of the droplet and the surrounding medium to yield

$$\dot{q}_{conv} = h_{conv} A_u (T_d - T_\infty) \quad (5)$$

where $\dot{q}_{conv}$ is the heat transfer rate due to free convection, h_{conv} is the free convection coefficient between the droplet free surface and the surrounding medium, A_u is the surface area of the droplet, and T_∞ is the temperature of the surrounding medium.

Estimating the radiative exchange between the droplet and the surroundings with the Stefan-Boltzmann Law yields

$$\dot{q}_{rad} = \epsilon \sigma A_u (T_d^4 - T_\infty^4) \quad (6)$$

where $\dot{q}_{rad}$ is the heat transfer rate due to radiation between the droplet and the surroundings, ϵ is the emissivity of the droplet free surface, and σ is the Stefan-Boltzmann constant.

The heat of evaporation can be modeled by

$$\dot{q}_{evap} = h_{fg}\rho \frac{dV}{dt} \quad (7)$$

where $\dot{q}_{evap}$ is the heat transfer rate due to evaporation, h_{fg} is the latent heat of vaporization of the droplet liquid, ρ is the density of the droplet liquid, and dV/dt is the time rate of change of droplet volume.

Sensible heat change within the droplet can be modeled by

$$\dot{q}_{sens} = c_p\rho V \frac{dT_d}{dt} \quad (8)$$

where $\dot{q}_{sens}$ is the energy storage rate due to sensible heat, c_p is the specific heat capacity of the droplet liquid, V is the droplet volume, and dT_d/dt is the time rate of change of droplet temperature. An energy balance on the drop requires that $\dot{q}_s = \dot{q}_{conv} + \dot{q}_{rad} + \dot{q}_{evap} + \dot{q}_{sens} = \dot{q}_{tot}$.

A representative analysis of the relative importance of the four modes of heat transfer outlined in (5) to (8) is shown in Fig. 3. These are results of a single experiment but are representative of all experiments conducted. Heat transfer rates are normalized by the overall heat transfer rate and shown as a function of time normalized by total evaporation time. An initial heat-up period exists where heat transfer due to sensible heat is significant. However a quasi-steady state is achieved rapidly and the heat transfer due to mass transfer of water vapor dominates all other terms, representing greater than 95% of the total heat loss. Consequently, the heat transfer due to convection and radiation from the upper surface of the droplet along with the sensible heat change within the droplet are neglected in the subsequent results and analysis.

Conservation of energy for the evaporating droplet in the quasi-steady state regime can now be approximated with a balance of heat transfer from the surface to the droplet (4) and droplet evaporation (7)

$$h_s A_c (T_s - T_d) = h_{fg}\rho \frac{dV}{dt} \quad (9)$$

Thus, the total heat transfer to the droplet can be estimated by measuring the heat lost to evaporation and h_s can be determined as,

$$h_s = \frac{h_{fg}\rho dV/dt}{A_c(T_s - T_d)} \quad (10)$$

Figure 3: Ratio of each mode of heat transfer to the total heat loss as a function of time normalized by the total evaporation time for a representative scenario.

3. Results

First we present qualitative results which capture the nature of droplet boiling and vaporization at temperatures greater than the saturation temperature. Then we quantify the droplet volume, contact angle and area, and total phase change time. Next, heat transfer rates are presented. Finally, Nusselt number relations are presented for the scenarios with subcritical substrate temperatures (Nu cannot be quantified at supercritical temperatures due to the boiling and bouncing of the droplets rendering contact area calculations impossible).

3.1. Qualitative Observations at Supercritical Substrate Temperatures

High-speed images of droplets resting on the smooth hydrophobic surface for a range of substrate temperatures are shown in Fig. 4. Frames were sampled at 0.0005 s intervals. In the top row, the surface temperature is approximately 85°C, which is 10°C below the local saturation point of water, $T_{sat} = 95.0^\circ$. Boiling is notably absent, as expected. The second row of the figure shows the surface at approximately 105°C. This is near the onset of nucleate boiling, and the droplet shows signs of boiling with observable surface agitation. In the third row of images, the surface is at approximately 125°C, near the critical heat flux temperature. Surface agitation is most pronounced in this set of images, thus it is expected the maximum heat transfer rate is near this substrate temperature. Droplet bouncing also occurs at this

Figure 4: High speed images of droplet evaporation on the smooth hydrophobic surface ($F_c = 0$) at various supercritical substrate temperatures. Images were taken at 0.0005 s intervals. Each row is from a different substrate temperature, as noted.

temperature. The last row shows the surface at a much higher substrate temperature, 180°C. Notably, the surface agitation is lessened as the droplet nears the Leidenfrost point at nominally 200°C, where these surface agitations are expected to die out completely as a stable vapor layer forms between the droplet and the substrate.

High-speed imaging also provides visual evidence that heat transfer to the droplet decreases with increasing cavity fraction. Figure 5 shows a series of frames at 0.0005 s intervals from each substrate at 125°C. The top row is recreated from the third row of Fig. 4. Again note the presence of rapid droplet surface agitation, indicative of nucleate boiling. Surface agitation markedly decreases in the second row where $F_c = 0.5$. In the third row, $F_c = 0.8$, only a small degree of surface agitation is still present and nucleate boiling is notably absent. Finally, in the bottom row of images which show a droplet evaporating on the $F_c = 0.95$ surface, no surface agitation is present, indicating a tremendous reduction in heat transfer relative to the smooth and lower cavity fraction cases.

Figure 5: High speed images of droplet evaporation at $T_s \approx 125^\circ\text{C}$. Images were taken at 0.0005 s intervals. Each row is from a different substrate type: smooth hydrophobic (top), $F_c = 0.5$ (second), $F_c = 0.8$ (third), and $F_c = 0.95$ (bottom).

3.2. Droplet Evaporation Dynamics

Droplet temperature as a function of time for a single test case of each substrate is shown in Fig. 6. These results are for $T_s = 80^\circ\text{C}$ but are representative of all cases where the substrate temperature is less than the water saturation temperature. There is an initial period of nominally 10 s during which the temperature quickly rises followed by a relatively long period of modestly declining droplet temperature. This period is the primary focus of the current research. In general, T_d decreases with increasing F_c , which is the same trend observed by Dash and Garimella at lower surface temperatures [13]. Near the end of the droplet evaporation process, T_d experiences drastic changes caused by rapid vaporization as the droplet vanishes.

Projected droplet-substrate contact areas as a function of time, for the same representative case of Fig. 5, are shown in the left panel of Fig. 7. Note the contact area decreases nearly linearly with time which is analogous to the D^2 law of suspended evaporating droplets [17]. If the substrate is unheated, the driving force for evaporation is the difference in water concentration between the droplet surface and the ambient air [16]. As the substrate is heated, however, the substrate temperature itself becomes the important

Figure 6: Transient droplet temperature as a function of time for substrate temperature of nominally 80 °C and for all substrates considered.

variable in droplet evaporation. Adding heat to the evaporating droplet serves to accelerate the process, but the effects of evaporative cooling keep the droplet temperature well below that of the substrate.

Inspection of the lines in Fig. 7 show a step-wise fashion of contact area decrease in some regions which is due to the pinning phenomenon described previously. For SH surfaces, this is explained physically by temporary pinning at a microrib until surface tension overcomes the pinning forces and the droplet then retracts and pins at a different rib. For the smooth hydrophobic substrate pinning likely occurs at imperfections on the surface resulting in unpredictable pinning behavior.

Droplet pinning and unpinning can also be observed in the contact angle, θ , dynamics shown in the right panel of Fig. 7. This is most prominent in the smooth hydrophobic case. For all surfaces the contact angle remains relatively constant over most of the evaporation process until the end of the droplet's life, when the droplet becomes pinned to the surface and contact angle decreases rapidly. This behavior is typical across all substrate types and temperatures, when boiling is not present, and is not dependent on substrate temperature. Studies of droplet evaporation have shown similar results of pinning and unpinning dependent on droplet size and surface structure [1, 10, 22, 30, 42, 51]. Specifically, Jung and Bhushan found variations in contact angle for microscale droplet evaporation due to changes in the state of the droplet from Cassie-Baxter to Wenzel [22]. However, in this paper we are focused on large droplets in the regime of nearly constant θ and T_d , and thus

Figure 7: Left panel: Projected droplet-substrate contact area as a function of time for substrate temperature of nominally 80 °C and for all substrates considered. Right panel: Internal droplet-substrate contact angle as a function of time for substrate temperature of nominally 80 °C and for all substrates considered.

the varying θ region at the end of the droplet life is not considered further.

Of particular note in the left panel of Fig. 7 is the difference in initial contact area between the various substrates. As F_c increases, θ increases (right panel), and the initial A_c decreases. This in part explains the increased droplet lifetimes with increasing F_c , since less heat is transferred from the substrate to the droplet as A_c becomes smaller.

Temporal droplet volume (V) data (smoothed) for the same representative cases depicted in Fig. 7, are shown in the left panel of Fig. 8. Results at a higher substrate temperature of $T_s = 120^\circ\text{C}$ are shown in the right panel. Volume data obtained for droplets in the nucleate and transitional boiling regimes tends to be very noisy due to rapid droplet oscillations. Thus all volume data were smoothed with a weighted, third degree polynomial, linear least squares regression, localized over no less than 1/4 of the span of the V data, and with $R^2 = 0.9999$. All data here and in subsequent figures was truncated by defining $t = 0$ as the condition when the droplet volume, V_0 is equivalent to that of a sphere with a 3 mm diameter.

As expected, the evaporating droplet volume decreases continuously with time. Additionally, the rate of volume decrease, dV/dt , also decreases as evaporation progresses. This general behavior was typical for all substrate types and temperatures. However, of note is the decrease in initial dV/dt as F_c increases, concomitant with a decrease in direct liquid-solid contact and leading to increased droplet lifetimes.

Figure 8: Droplet volume as a function of time for all substrates considered for $T_s = 80^\circ\text{C}$ (left panel) and $T_s = 120^\circ\text{C}$ (right panel).

Total evaporation times for droplets on each substrate as a function of substrate temperature are shown in Fig. 9, where evaporation time is defined as the time for a droplet to reach 10% of the initial volume. Three tests at each substrate temperature were averaged for the results shown. In the subcritical regime (left panel), as the substrate temperature increases, the evaporation time decreases due to increased heat transfer. The evaporation time also increases as F_c increases due to the decrease in both projected droplet-substrate contact area and physical droplet-substrate contact. The average decrease in evaporation times for the droplets on the SH surfaces compared to the smooth surface is 13%, 28%, and 40% for the $F_c = 0.5$, 0.8, and 0.95 surfaces, respectively. Power-law curve-fits for each substrate were determined and are shown in the left panel of Fig. 9. Of note is the observation that power-law curve fits intersect at about 25°C (ambient temperature) when extrapolated to the left of the figure, as expected.

At supercritical substrate temperatures (right panel of Fig. 9) the trend of decreasing vaporization time with increasing substrate temperature continues until it reaches a minimum at around $T_s = 120^\circ\text{C}$. This minimum in t_e corresponds to the critical heat flux point where heat input reaches a maximum. It is easily observed in the smooth substrate data whereas the $F_c = 0.95$ substrate data shows much less variation. Beyond the critical heat flux point evaporation time increases slightly corresponding to the transition from nucleate to film boiling (which is notably absent in the $F_c = 0.95$ scenario). Above $T_s \approx 160^\circ\text{C}$ there is no clear distinction in t_e between the hydrophobic and SH substrates.

Figure 9: Droplet evaporation time as a function of substrate temperature for all substrates considered and for all experimental runs. The left panel shows the evaporation time (log scale) for subcritical substrate temperatures as well as power-law curve fits. The right panel shows the evaporation time for supercritical substrate temperatures with polynomial fits to the experimental data.

3.3. Heat Transfer Rates

Total heat input is determined from (7) and averaging over the time domain corresponding to $V_0 \geq V \geq 0.1V_0$. This resultant average heat input, $\bar{q}_s$, is shown for subcritical substrate temperatures in Fig. 10 and supercritical temperatures in the left panel of Fig. 11 as a function of the surface temperature. Faired lines are also shown to view the data for each F_c more clearly. Additionally the right panel of Fig. 11 includes droplet images corresponding to each substrate for various temperatures defined by the ranges shown.

In the subcritical regime shown in Fig. 10 for all substrates $\bar{q}_s$ increases with increasing T_s . As F_c increases $\bar{q}_s$ decreases. The average decrease in the total heat transfer rates to the droplets on the SH surfaces (compared to the smooth surface) is 20%, 35%, and 45% for the $F_c = 0.5, 0.8$, and 0.95 surfaces, respectively. In the supercritical regime (left panel of Fig. 11) $\bar{q}_s$ continues to increase with T_s until it reaches a maximum, near $T_s - T_{sat} \approx 20^\circ\text{C}$ for the smooth substrate. This point corresponds well to the critical heat flux point in the classical boiling curve. Note the corresponding droplet image for $F_c = 0$ in region B in the right panel of Fig. 11 where rapid boiling is evident. Further increasing T_s on the smooth surface decreases the average heat input steadily until reaching a minimum near $T_s - T_{sat} \approx 90 - 100^\circ\text{C}$, corresponding to the Leidenfrost point.

Figure 10: Time-averaged droplet-substrate heat transfer rate as a function of substrate temperature, in the subcritical regime, for all substrates studied.

Figure 11: Time-averaged droplet-substrate heat transfer rate as a function of substrate temperature, in the supercritical regime, for all substrates studied. Note in the left panel the average heat transfer rate is plotted against $T_s - T_{sat}$. Regions A, B, C, and D correspond to temperature ranges for which images of the heated droplets are shown in the right panel for each substrate.

SH substrates exhibit some important differences from the smooth substrate. First, with increasing F_c the average heat input decreases for all temperatures below the Leidenfrost point temperature. This is most evident in Fig. 11 near $T_s - T_{sat} \approx 20-30^\circ\text{C}$ where nucleate boiling is occurring on the smooth and lower F_c substrates (see the corresponding snapshot of droplet in right panel) but not on the $F_c = 0.95$ substrate. Here the maximum heat transfer rate decreases from 1.9 W on the smooth surface to 1.4, 0.95, and 0.8 W on the $F_c = 0.5, 0.8$, and 0.95 surfaces respectively. Thus the air cavities of the SH surface not only hinder heat transfer at all substrate temperatures, but also dramatically alter the dynamics of nucleate boiling. Second, the images shown in the right panel of Fig. 11, show much less convection for the high F_c substrates at $T_s - T_{sat} \approx 30^\circ\text{C}$ or above and it seems nucleate boiling can be greatly minimized or eliminated when a SH substrate is employed.

We note here that the average rate of heat transfer to the droplet, $\overline{\dot{q}_s}$, is comprised of contributions from convection between the solid substrate and the liquid droplet and conduction and radiation through the air in the cavity regions. It can be estimated that radiation contributes

$$\overline{\dot{q}_{s,rad}} = \epsilon_s \sigma \overline{A_p} (T_s^4 - T_d^4) \quad (11)$$

where ϵ_s is the emissivity of the solid surface and $\overline{A_p}$ is the average projected area of the droplet surface that intercepts radiation from the solid surface below. If we assume the solid surface acts as a blackbody, $\epsilon_s = 1$. $\overline{A_p}$ can be approximated as $\pi \overline{D_d}^2 / 4$, where $\overline{D_d}$ is the average horizontal diameter of the sessile droplet. In this case, $\overline{D_d} \approx 1.5 \text{ mm}$. Using the extreme case of $T_s = 100^\circ\text{C}$ and $T_d = 70^\circ\text{C}$, $\overline{\dot{q}_{s,rad}}$ computes to 0.5 mW, which is three orders of magnitude smaller than the contributions of conduction and convection. Further, the conduction through the air layer can be estimated and is nominally 10-20 mW, also much smaller than the measured values. Thus the transport is dominated by convection from the solid ribs into the liquid.

3.3.1. Nusselt Number Analysis for Subcritical Substrate Temperatures

Grashof number, Gr , Nusselt number, Nu , and Prandtl number, Pr were calculated for all data sets at subcritical substrate temperatures. Gr is defined here as

$$Gr = \frac{g\beta(T_s - T_d)V}{\nu^2} \quad (12)$$

where g is the acceleration due to gravity, and β and ν are the volumetric thermal expansion coefficient and kinematic viscosity of the liquid, respec-

tively. Here the cube root of droplet volume was chosen as the characteristic length scale. Nu is defined here as

$$Nu = \frac{h_s A_c^{1/2}}{k} \quad (13)$$

where k is the thermal conductivity of the liquid and the square root of the projected droplet-substrate contact area was used as the characteristic length scale for Nu , which represents the effective area through which convection occurs. Pr is defined as

$$Pr = \frac{\rho c_p \nu}{k} \quad (14)$$

We note that all fluid properties in (12) to (14) were determined at the droplet temperature.

For laminar free convection on a (vertical flat plate the Nusselt number is a function of $Gr^{1/4}$ and $Pr^{1/3}$. Thus, Nu as a function of $Gr^{1/4} Pr^{1/3}$ for the $F_c = 0.95$ substrate is shown in the left panel of Fig. 12. A least-squares power-law curve fit of the data is superimposed. Although the spread is as great as 30% above and 20% below the curve, this fit allows comparison among the substrates, which are shown in the right panel of Fig. 12. Equations defining each of these lines are

$$Nu_0 = 2.53 Gr^{1/4} Pr^{1/3} \quad (15)$$

$$Nu_{0.5} = 2.40 Gr^{1/4} Pr^{1/3} \quad (16)$$

$$Nu_{0.8} = 2.14 Gr^{1/4} Pr^{1/3} \quad (17)$$

$$Nu_{0.95} = 1.65 Gr^{1/4} Pr^{1/3} \quad (18)$$

where the subscripts represent the $F_c = 0, 0.5, 0.8$, and 0.95 substrates.

In general, Nu increases with $Gr^{1/4} Pr^{1/3}$ as expected. Further, for a given Gr , Nu is larger for smaller F_c . Nu decreases modestly (nominally 5%) for cavity fractions up to 0.5 but drops off dramatically as cavity fraction is further increased. For a cavity fraction of 0.8, Nu is decreased by nominally 15% from the smooth hydrophobic case, and for a cavity fraction of 0.95, Nu is decreased by nominally 35%. It should be noted that the definition of Nu employed here accounts for the decrease in droplet contact area that prevails for the different substrates through the use of $A_c^{1/2}$ as the characteristic length scale. Thus, comparison of Nu between the different surface types yields the amount of deviation in the convection coefficient that prevails due only to

Figure 12: Nu as a function of $Gr^{1/4}Pr^{1/3}$. In the left panel experimental data and a power-law curve fit for the $F_c = 0.95$ substrate are shown. In the right panel are power-law curve-fits for all substrates studied. Note the log-scale of the axes.

the trapped air in the cavity regions. Of course, the combined effect of more trapped air and smaller A_c as F_c increases combine to yield overall heat transfer rates that show greater deviation between surfaces, as illustrated in Fig. 10.

4. Conclusion

This paper has reported on experiments characterizing droplet-substrate convective heat transfer for sessile water droplets resting on rib-patterned superhydrophobic substrates. At a given substrate temperature, droplet temperatures tend to be lower for substrates with higher cavity fraction. This corresponds to decreased evaporation rates for subcritical substrate temperatures. These trends are explained by both the increase in contact angle and decreased physical contact between the droplet and the substrate due to the air cavities leading to lower projected total droplet-substrate contact areas.

At surface temperatures higher than the saturation temperature, increasing the cavity fraction decreases the heat transfer rate, delays the onset of nucleate boiling, and decreases the temperature where Leidenfrost behavior occurs. If the cavity fraction is increased enough ($F_c = 0.95$ for this paper), nucleate boiling is suppressed at all surface temperatures and the droplet exhibits Leidenfrost-like behavior near the classical critical heat flux point. This change may be explained by the presence of persistent vapor cavities on the SH surfaces. These cavities act to stabilize the vapor film beneath the

boiling droplet at lower supercritical temperatures.

Nusselt number data confirm that decreased heat flux exists for droplets on substrates of greater cavity fraction, with the effect increasing with increasing F_c . Near $F_c = 0.95$, even small changes in cavity fraction exhibit appreciable changes in Nu . Data presented here allow for the prediction of effective droplet-substrate heat transfer coefficients over a wide range of cavity fractions.

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