Electrostatic Charging of Jumping Droplets on Superhydrophobic Nanostructured Surfaces:
Fundamental Study and Applications

by

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Condensation is a ubiquitous process often observed in nature and harnessed in many industrial processes such as power generation, desalination, thermal management, and building environmental control. Recent advancements in surface engineering have offered new opportunities to enhance condensation heat transfer by drastically changing the wetting properties of the condenser surface. Specifically, the development of superhydrophobic surfaces has been pursued to enhance condensation heat transfer, where the low droplet surface adhesion and small droplet departure sizes increase the condensation heat transfer coefficient. Specifically, when two or more small (≈10-100 μm) droplets coalesce on a superhydrophobic surface, they can spontaneously jump away from the surface due to the reduced droplet-surface adhesion and release of excess surface energy, which has been shown to increase heat transfer by 30 – 40% compared to that observed during gravitational shedding of droplets. While this droplet jumping phenomenon has been studied on a range of surfaces, past work has neglected electrostatic interactions and assumed charge neutrality of the droplets. Here, we show that jumping droplets on a variety of superhydrophobic surfaces, including copper oxide, zinc oxide, and silicon nanopillars, gain a net positive charge that causes them to repel each other mid-flight. The charge is determined experimentally by observing droplet motion in a uniform electric field. The mechanism for the charge accumulation is associated with the formation of the electric double layer at the droplet-coating interface and subsequent charge separation during droplet jumping governed by the fast time scales of droplet coalescence.
One application of this charging phenomenon is further enhancement of condensation heat transfer by preventing droplet reversal and return to the condenser surface due to the presence of vapor flow towards the surface, which increases the drag on the jumping droplets. This effect limits the possible heat transfer enhancement because larger droplets form upon droplet return to the surface that impede heat transfer until they can be either removed by jumping again or finally shedding via gravity. By characterizing individual droplet trajectories during condensation on superhydrophobic nanostructured copper oxide surfaces, this vapor flow entrainment is shown to dominate droplet motion for droplets smaller than $R \approx 30 \mu m$ at moderate heat fluxes ($q'' > 2 \text{ W/cm}^2$). Subsequently, electric-field-enhanced (EFE) condensation is demonstrated, whereby an externally applied electric field prevents jumping droplet return due to the positive charge obtained by the droplets upon jumping. As a result, with scalable superhydrophobic CuO surfaces, a 50% higher overall condensation heat transfer coefficient is demonstrated compared to a jumping-droplet surface with no applied field for low supersaturations (<1.12).

Another application of charged jumping droplets is use of these droplets for electrostatic energy harvesting. Here, the charged droplets jump between superhydrophobic copper oxide and hydrophilic copper surfaces to create an electrostatic potential and generate power during formation of dew under atmospheric conditions. Power densities of $-0.06 \text{ nW/cm}^2$ are demonstrated, which, in the near term, can be improved to $-1 \mu \text{W/cm}^2$. This work demonstrates a surface engineered platform that is low cost and scalable for atmospheric energy harvesting and electric power generation. These applications of charged jumping droplets offer new avenues for improving the performance of self-cleaning and anti-icing surfaces as well as thermal diodes, and may also provide a competitive mode of energy harvesting from temperature gradients.
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Chapter 1

1. Introduction

1.1 MOTIVATION

Vapor condensation is a familiar phenomenon which routinely occurs in nature [1-4]. An everyday example of condensation is the droplets of water which form on the container of a cold beverage left out on a warm, humid day. Condensation is also an essential consideration in industry for power generation [5], thermal management [6, 7], water desalination [8, 9], and environmental control [10]. For example, the steam cycle is responsible for over 90% of electrical power generation worldwide, and condensation heat transfer performance directly influences the thermal efficiency of the steam cycle [11]. If the heat transfer performance of the condenser shown schematically in the steam cycle in Figure 1 were improved, the bottoming cycle temperature, $T_{LOW}$, could be lowered while keeping $T_{HIGH}$ the same. The efficiency of the cycle is related to the ratio of the high to the low temperature, where a higher temperature ratio $T_{HIGH}/T_{LOW}$ is expected to result in higher cycle efficiency. Therefore, lowering $T_{LOW}$ increases $T_{HIGH}/T_{LOW}$ and translates to an efficiency improvement. In addition to improved cycle efficiency, a higher condensation heat transfer rate could mean that a smaller condenser is required, potentially decreasing the capital cost associated with construction of power plants that operate with steam cycles.

![Figure 1. Schematic representation of an ideal steam cycle. Starting from the liquid phase inside of the condenser, the fluid is pumped to high pressure, converted to vapor by the addition of heat at $T_{HIGH}$ in the boiler, expanded through the turbine back to the condenser pressure while producing work, and then condensed from vapor back to the starting liquid phase by removal of heat at $T_{LOW}$.](image-url)
Heating, ventilation, and air conditioning (HVAC) systems, which account for ≈20% of the total energy consumption in developed countries [12], also must be designed with condensation heat transfer performance in mind to limit the buildup of condensate and improve efficiency. Yet another area where condensation is important is in the transmittance of light into greenhouses, where condensate formation on windows can result in losses of up to 40% during the winter [13].

1.2 BACKGROUND

For these applications, heterogeneous condensation occurs on condenser walls as opposed to directly in the vapor phase because of reduced energy barriers for heterogeneous nucleation relative to homogeneous nucleation [14]. In typical industrial systems, the condensed vapor forms a thin liquid film on the condenser surface due to the high surface energy associated with the majority of industrial heat exchanger materials (i.e., clean metals and metal oxides). This mode, known as filmwise condensation, (Figure 2), is not desired due to the large thermal resistance to heat transfer [15]. However, on low surface energy materials, the condensed vapor forms discrete liquid droplets. During this dropwise condensation, droplets roll off at sizes approaching the capillary length (~2 mm for water) and clear the surface for re-nucleation as shown in Figure 2 [16].

Dropwise condensation can be achieved if the condensing surface is functionalized with a hydrophobic coating, for example a long-chain fatty acid, wax, or polymer coating [17-20]. Compared to filmwise condensation, dropwise condensation allows 5–7x higher heat transfer performance, as illustrated in Figure 3. The heat flux, $q''$, is the most commonly used metric for quantifying the amount of latent heat.

Figure 2. Filmwise condensation on a bare copper condenser tube (left) and dropwise condensation on a copper tube functionalized with a monolayer hydrophobic coating (right).
Figure 3. Condensation mode regime map shown with heat flux as a function of temperature difference between the condenser surface and surrounding vapor. The green area indicates potential improvement in heat transfer coefficient over state-of-the-art dropwise condensation.

of phase change removed by the surface during condensation at a given driving potential (temperature difference), $\Delta T = T_{\text{sat}(P_v)} - T_{\text{wall}}$, where $T_{\text{sat}(P_v)}$ is the saturation temperature of the surrounding vapor and $T_{\text{wall}}$ is the condenser wall surface temperature.

Achieving dropwise condensation on common industrial materials has been a topic of significant interest for the past eight decades [21, 22], with an emphasis on creating non-wetting surfaces via application of promoter coatings for easy droplet removal. While robust coatings continue to pose a challenge and require further development [21], recent advancements in nanofabrication have allowed for further tailoring of surface wetting properties and condensation behavior to enhance heat transfer performance above that of dropwise condensation on a flat surface. Three important properties that affect the condensation heat transfer coefficient, $h_c = q''/\Delta T$, are nucleation density, advancing contact angle, and departure radius [23, 24]. Heat transfer increases with nucleation density due to the increasing number of small droplets that have low conduction thermal resistance due to their size. Conversely, high apparent contact angle can lead to an increase in conduction resistance through the droplet due to the reduced size.
of the droplet base [23, 25], which hinders the overall heat transfer performance. Finally, larger droplets have increased thermal resistance and thus larger droplet departure size results in a lower overall condensation heat transfer coefficient.

Superhydrophobic surfaces [26, 27], where nearly spherical water droplets with high mobility and minimal droplet adhesion are energetically favorable, have been studied in detail due to their potential to enhance condensation performance by reducing droplet departure sizes (≤3 mm) and enabling faster clearing of the surface by drop shedding for re-nucleation. The ability to alter wetting characteristics to create superhydrophobic surfaces via surface structuring is well documented [28-31]; however, the potential increase in condensation heat transfer from easier droplet shedding and the resulting smaller droplet departure radius on superhydrophobic surfaces is offset by the increased resistance due to the high contact angle of droplets on these surfaces during typical gravitational shedding.

Interestingly, careful tailoring of the chemistry and roughness of a superhydrophobic surface can result in shedding of droplets at length scales smaller than those observed during gravitational shedding, where droplets jump away from the surface at small length scales (< 100 μm). The heat transfer performance during condensation has been demonstrated to exceed the highest values reported for dropwise condensation (Figure 3) into the regime of previously untapped potential for this jumping mode of condensation. In this work, we show that the droplets ejected during this heat-transfer-enhancing jumping droplet condensation attain a positive electrical charge, a phenomenon which can be leveraged to further enhance heat transfer or even harvest energy.

1.3 THESIS OBJECTIVES AND OUTLINE
The objective of this thesis is focused on the discovery, quantification, and potential applications of the net positive charge attained by jumping droplets. These jumping droplets obtain electrostatic charge due to the formation of the electric double layer at the droplet-coating interface and subsequent charge separation during droplet jumping governed by the fast time scales of droplet coalescence.

One application for this charging mechanism is further enhancement of condensation heat transfer by preventing droplet reversal and return to the condenser surface due to the existence of vapor flow towards the surface, which increases the drag on the jumping droplets. We experimentally demonstrate a 50% higher overall condensation heat transfer coefficient compared to that on a jumping-droplet surface with no applied field for low supersaturations (<1.12), defined as the ratio of the vapor pressure to the saturation pressure at the surface temperature, $S = \frac{P_{\text{vap}}}{P_{\text{sat}}(T_{\text{wall}})}$. 

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Another application of charged jumping droplets is use of these droplets for electrostatic energy harvesting. Here, we show experimentally obtained power densities of \(-0.06\, \text{nW/cm}^2\), which, in the near term, can be improved to \(-1\, \text{µW/cm}^2\) by tuning the harvesting device. The structure of this thesis is outlined below:

In Chapter 1, the motivation for studying and improving condensation heat transfer was discussed. Previously studied modes of condensation and significant contributions to the field were explored.

In Chapter 2, condensation on superhydrophobic surfaces and the effects of surface geometry and chemistry are reviewed.

In Chapter 3, the experimental setup used for the results presented in this thesis is detailed and the experimental heat transfer measurement technique is discussed, including previously obtained results for jumping droplets which show improved heat transfer coefficient compared to dropwise condensation.

In Chapter 4, experimental quantification of the charge by observing droplet motion in a uniform electric field is discussed. The mechanism for the charge accumulation is explained.

In Chapter 5, jumping droplet return to the condenser surface due to vapor drag is overcome by application of electric fields, resulting in improved heat transfer and elimination of progressive flooding.

In Chapter 6, charged jumping droplets are demonstrated to be a viable method for energy harvesting from a temperature gradient.
To achieve superhydrophobicity, a surface must be both chemically hydrophobic and topographically rough. The maximum theoretical contact angle of water on a molecularly flat surface is approximately 133°, which would occur on a surface of perfectly aligned $-\text{CF}_3$ groups (which has the minimum attainable surface energy of $\approx 6 \text{ mN/m}$), where the water-solid interfacial tension is approximated as $\approx 56 \text{ mN/m}$ by the Girifalco-Good-Fowkes approximation [32, 33]. Since superhydrophobicity is defined as a contact angle of greater than 150° for a water droplet resting on a surface, chemical hydrophobicity alone cannot result in superhydrophobicity. The addition of surface roughness, such as micropillars or nanowires, changes the wettability of a surface by forcing a water droplet placed on the surface to interact with more solid area and changing the apparent surface energy of the water-solid interface. Typically, for surfaces composed of a material which would have an intrinsic contact angle greater than 90° if it were flat, the contact angle will increase with increased surface roughness; therefore, the combination of roughness and chemical hydrophobicity (contact angle $> 90^\circ$ on a flat surface) can result in surfaces with apparent water contact angles greater than 150°, or superhydrophobic surfaces. These surfaces exhibit low droplet adhesion, particularly when droplets do not completely wet the solid substrate, and as such can result in novel modes of condensation where droplet departure size is decreased.

### 2.1 Effects of Surface Roughness

Hydrophobic surfaces with structures or roughness features smaller than the capillary length scale (Bond number for the structures is much less than unity, $Bo = \rho g L^2 / \gamma_w << 1$) have been proposed to enhance condensation heat transfer performance [23, 34-42]. By altering the surface structure, wetting properties can be tuned to manipulate condensation behavior, with morphologies ranging from highly pinned, i.e., Wenzel state [43], to superhydrophobic, i.e., Cassie state [44].

The Wenzel and Cassie states can be understood through energy minimization for a droplet on a structured surface. First, a flat surface is considered to define the equilibrium contact angle, a property of the three phases that come into contact. A droplet deposited on a flat surface can either spread and wet the surface or form a discrete droplet depending on the surface energies of the three interfaces. Young (1805)
first proposed that the equilibrium contact angle for a discrete droplet, $\theta_{eq}$, is dictated by a force balance at the three phase contact line:

$$\cos \theta_{eq} = \frac{\gamma_{sv} - \gamma_{st}}{\gamma_{lv}},$$

where $\gamma_{sv}$, $\gamma_{st}$ and $\gamma_{lv}$ are the solid-vapor, solid-liquid, and liquid-vapor surface tensions, respectively (Figure 4(a)). Building on Young's work [45], Wenzel and Cassie extended the wetting analysis to rough and porous surfaces. For a surface with roughness, $r$, defined by the ratio of the total surface area to the projected area (Figure 4(b,c)), Wenzel (1936) showed for a fluid which wets the total surface area (Figure 4 (d,e)) that the apparent contact angle in the Wenzel state, $\theta_W$, is defined by:

$$\cos \theta_W = r \cos \theta_{eq}.$$  

For the contrasting case where the droplet rests on the tips of the roughness (Figure 4(f,g)), Cassie and Baxter (1944) showed that the apparent contact angle in the Cassie state, $\theta_C$, is defined by:

$$\cos \theta_C = \phi (1 + \cos \theta_{eq}) - 1.$$  

Figure 4. (a) Schematic of the equilibrium contact angle. (b) Side view and (c) top view of structured surface with evenly spaced pillars on a square grid. (d) Schematic and (e) image of droplet in Wenzel wetting state. (f) Schematic and (g) image of droplet in Cassie-Baxter wetting state.
where the solid fraction $\varphi$ is the ratio of the structure or roughness area contacting the droplet to the projected area. The Wenzel state is typically less useful for condensation due to the higher adhesion associated with this wetting state [26]. Consequently, many studies have focused on creating and understanding superhydrophobic Cassie-stable surfaces to limit adhesion and increase fluid repellency [46, 47]. It is important to note, however, that in the case of condensation, the nucleation of droplets from the vapor phase can initiate within the roughness, which may render equations 2 and 3 invalid; this is discussed further in Section 2.3.

Structured surfaces used in past studies on condensation include highly ordered structures such as arrays of silicon pillars fabricated in a cleanroom environment, more disordered but often more scalable metal oxide structures grown hydrothermally or with chemical vapor deposition (CVD) or plasma-based approaches, or hierarchical combinations of ordered and disordered structures. Current techniques allow fabrication of structures with sizes ranging from the microscale (~10 $\mu$m) to the nanoscale (~1 nm). The highly ordered cleanroom-fabricated structures allow for more control and accurate modeling, but the tradeoff is typically a loss of applicability on large industrial scales.

2.2 OBTAINING CHEMICAL HYDROPHOBICITY

Since most industrial metals, such as aluminum, copper, titanium, and stainless steel (and their corresponding oxides) have high surface energy, surface functionalization via a coating that can reduce surface energy is required on these materials to obtain dropwise condensation. Furthermore, the micro- and nanostructured surfaces described previously also must be coated to impart low surface energy (specifically, $\theta_{eq} > 90^\circ$) in order to take advantage of the benefits offered by the Cassie state. This is a particularly active area of research, as no solution has yet been proposed which satisfactorily addresses durability, cost, and performance concerns. Several approaches to obtaining suitably low surface energies are presented here with their advantages and disadvantages highlighted.

Self-assembled monolayers (SAMs) result from spontaneous physi- or chemisorption of a thin molecular film (~1 nm) comprised of individual molecules on the condensing surface. These molecules have hydrophobic tails pointing away from the surface that interact with the condensate and ligand heads that bind to the surface. This functionalization method does not introduce a significant thermal resistance; however, durability is a primary concern. Two common types of SAMs are sulfur-based ligand thiols and silicon-based ligand silanes. Thiols have been found to oxidize over short time scales upon exposure to ambient conditions or UV radiation and reduce to disulfides and sulfonates which can wash away from
the surface with polar solvents such as water [48]. Thiols are also less thermally stable than silanes [49]. Silanes show better stability due to covalent bonding with the surface [50]. Furthermore, self-healing strategies have recently been demonstrated based on fluorinated silane chemistries that could increase the longevity of these coatings [51, 52]. However, durability is still currently a major concern with silanes [53].

Polymer coatings such as polytetrafluoroethylene (PTFE), parylene, and silicones have been used as a functional coating to promote dropwise condensation [18, 54-56]. However, the required coating thickness to realize satisfactory durability results in an added thermal resistance which offsets the heat transfer improvement due to DWC [18]. This thickness requirement may be reduced with new binder materials to form a stronger bond between the polymer and substrate. In addition, initiated CVD of fluoropolymer thin films is another potential functionalization method which offers high coating conformality and potential robustness [53, 57].

Ion implantation promotes dropwise condensation through carbon, nitrogen, and oxygen ion implantation in copper, aluminum, titanium, and steel surfaces [58-60]. Sustained dropwise condensation was achieved on these surfaces over periods of multiple months [61]. However, this method is not commonly used because it is relatively expensive compared to SAMs and polymer coatings.

Noble metals applied as a thin functional coating are a robust approach to achieve dropwise condensation, with one paper demonstrating continuous DWC on gold for over five years [62]. Initially, gold was thought to be intrinsically hydrophobic [63]. However, subsequent experimental results showed that the contact angle on a clean gold surface with hydrocarbons desorbed and oxide removed by heating in a hydrogen gas stream with < 1 ppm hydrocarbons was 0° [64]. This claim was initially disputed [65], but subsequent studies demonstrated that gold, while intrinsically hydrophilic, rapidly adsorbs hydrocarbons from air resulting in increased contact angle and dropwise condensation [66-68].

2.3 CONDENSATION ON SUPERHYDROPHOBIC SURFACES
Superhydrophobic condensation was first investigated for its potential to shed droplets via gravity at small length scales due to decreased contact angle hysteresis [69]. Interestingly, on suitably designed superhydrophobic surfaces, small water droplets (∼10–100 µm) can undergo coalescence-induced droplet ejection or “jumping” during condensation due to the release of excess surface energy [34].
gravitational removal and jumping on superhydrophobic surfaces, designs can be optimized by considering the dominant wetting morphology present during condensation and its effect on heat transfer.

During condensation, droplet nucleation can initiate within the surface roughness and the droplet can undergo a non-equilibrium wetting process where Equations 2 and 3, for which equilibrium is assumed, may not apply. Studies on structured superhydrophobic surfaces with well-controlled geometries have demonstrated that, during condensation, highly adhered Wenzel droplets form that are distinct from the mobile Cassie droplets formed upon fluid deposition with a syringe [26, 70-72]. More recent work has shown that three different droplet morphologies exist during condensation: Wenzel (W) (Figure 5(a)), partially wetting (PW) (Figure 5(b)), and suspended (S) (Figure 5(c)) [23]. Both S and PW droplets are highly mobile relative to W droplets and, as such, are favorable due to their increased ability to depart from the surface. The emergent droplet morphology must be characterized and understood in order to tailor the surface structuring to optimize heat transfer [73].

Determination of the emergent droplet morphology (PW, S, or W) is based on structure geometry and nucleation density. While intricate liquid/structure interaction dynamics dictate droplet morphology for droplets nucleating within the structure, the energy barriers encountered by the droplet can be approximately predicted by comparing the energies of the non-equilibrium advancing Cassie and Wenzel states with a dimensionless energy ratio:

\[ E^* = \frac{\cos(\theta_c)}{\cos(\theta_W)} = \frac{-1}{r \cos(\theta_{eq})} \]  \hspace{1cm} (4)

where \( r = 1 + \pi dh/l^2 \) is the surface roughness, and \( \theta_a \) is the advancing contact angle on a flat surface. Equation 4 implies that when \( E^* > 1 \), W droplet morphologies are favored, while when \( E^* < 1 \), PW droplets should emerge [74]. In addition to this energy barrier criterion, the nucleation density must be low enough that the distance between nuclei of droplets is \( 2 - 5 \) the spacing between the structures \( (L/l > 2-5) \). If the nucleation density is too high such that \( (L/l < 2-5 \), the energy barrier associated with individual droplet growth (Equation 4) is overcome through coalescence events and condensate floods the surface, forming undesired W droplets. This result enables surface design based on defining the location of and distance between nucleation sites to favor formation of favorable PW droplet morphologies.
2.4 DROPLET DEPARTURE

Superhydrophobic surfaces have potential to enhance condensation performance by reducing droplet departure size (≤ 3 mm) and enabling faster clearing of the surface for re-nucleation. This is possible due to the low contact angle hysteresis exhibited by these surfaces, which in turn allows less pinning force to hold the droplet in place against the body force due to gravity. As such, smaller droplet departure sizes than those observed during dropwise condensation on a flat surface are expected. However, when a structured surface is suitably designed, coalescence-induced jumping condensation occurs and departure radii are orders of magnitude smaller (~10 μm) than those exhibited during typical dropwise condensation. The different departure mechanisms are discussed here.

2.4.1 Gravitational Shedding

During gravitational shedding, droplets depart once the gravitational body force overcomes the pinning force due to contact angle hysteresis. For example, on a vertical condenser surface, the gravitational body force is simply the weight of a droplet, while the pinning force arises from the difference in surface tension forces tangent to the vertical condenser surface arising from the difference in contact angle at the advancing (downwards) portion of the droplet contact line and the receding (upwards) portion of the droplet contact line. The gravitational body force scales with droplet volume, \( \sim r^3 \), while the pinning force scales approximately with the contact line length, \( \sim r \). Therefore, as the droplet grows, the gravitational body force eventually overcomes the pinning force when the droplet reaches the departure radius. From this illustration, it becomes clear that a lower contact angle hysteresis decreases the relative magnitude of the pinning force and thus results in a smaller departure radius; hence, superhydrophobic surfaces were considered for their markedly low contact angle hysteresis compared to flat surfaces [75, 76]. The key compromise is that superhydrophobic surfaces also have high contact angles, which can offset the heat transfer enhancement.
2.4.2 Droplet Jumping

When condensation occurs on a suitably designed superhydrophobic surface for which $E^* < 1$ and $(L)/l \geq 2–5$, nearly spherical droplets of condensate form. These droplets can spontaneously merge and jump away from the condensing surface at small sizes (~10–100 μm). This phenomenon was first reported for dropwise condensation of mercury on rough steel [77]. Jumping occurs due to a release of surface energy upon coalescence of two droplets, some of which is converted to kinetic energy manifested as the motion of the merged droplet perpendicular to the condensing surface while the rest is dissipated by viscosity during coalescence and subsequent droplet oscillation [34, 78-84]. The small droplet departure radius as observed during experimentation is observed in Figure 6; this offers the possibility to enhance heat transfer performance by lowering the average droplet thermal resistance [35, 73, 85-87].

In addition to enhancing heat transfer performance, jumping condensation offers an alternative method for transportation of condensate in phase-change systems which is independent of gravity and does not require wicking structures [88, 89].

2.5 SUMMARY

The role of surface structure on wetting behavior was introduced in Section 2.1. Since a superhydrophobic surface must be structured and also chemically hydrophobic, several methods of surface functionalization were discussed in Section 2.2. Section 2.3 discussed the different droplet morphologies observed during condensation on superhydrophobic surfaces and how the surface can be tailored to obtain the desired PW morphology, and Section 2.4 covered the two modes of droplet departure from superhydrophobic surfaces during condensation, namely, gravitational shedding and droplet jumping.
Chapter 3

3. Experimental Setup and Heat Transfer Measurement

In this chapter, the experimental setup used throughout to observe condensation and measure heat transfer is presented. This setup consists of a vacuum chamber, a pure water vapor supply, and a chiller flow loop which is capable of cooling the condenser test section via internal chilled water flow. The chamber is instrumented with a vapor pressure gauge, a chiller water flow rate meter, and thermocouples used throughout the system to determine relevant temperatures, all connected to a data acquisition system. Past work conducted with this vacuum chamber to determine condensation heat transfer coefficients for filmwise, dropwise, and jumping droplet condensation is presented. Jumping droplet condensation is shown to exhibit 30% higher heat transfer than state-of-the-art dropwise condensation but is limited by the flooded mode of condensation, which occurs at elevated supersaturation.

3.1 EXPERIMENTAL SETUP

The custom environmental vacuum chamber used for this work (Kurt J. Lesker) consists of a stainless steel frame with a door (sealed with a rubber gasket), two viewing windows, and apertures for various components. Resistive heater lines were wrapped around the exterior of the chamber walls to prevent condensation at the inside walls and then insulated on the exterior walls. The output power of the resistive heater lines was controlled by a voltage regulator (Variac). Two insulated stainless steel water flow lines (Swagelok) were fed into the chamber via a KF flange port (Kurt J. Lesker) to supply cooling water to the chamber from a large capacity chiller (System III, Neslab). The cooling water flow rate was measured via an in-line liquid flow meter (0-5 L/min L-Series liquid flow meter, Alicat).

A secondary stainless steel tube line was fed into the chamber via a KF adapter port that served as the flow line for the incoming water vapor supplied from a heated steel water reservoir. The vapor line was wrapped with a rope heater (60 W, Omega) and controlled by a power supply (Agilent). The vapor reservoir was wrapped with another independently-controlled rope heater (120 W, Omega) and insulated to limit heat losses to the environment. The access tubes were welded to the vapor reservoir, each with independently-controlled valves. The first valve (Diaphragm Type, Swagelok), connecting the bottom of the reservoir to the ambient, was used to fill the reservoir with water. The second valve (BK-60, Swagelok), connecting the top of the reservoir to the inside of the chamber, provided a path for vapor
inflow. K-type thermocouples were located along the length of the water vapor reservoir to monitor temperature.

A bellows valve (Kurt J. Lesker) was attached to the chamber to serve as a leak port between the ambient and inside of the chamber. In order to monitor temperatures within the chamber, K-type thermocouple bundles were connected through the chamber apertures via a thermocouple feed through (Kurt J. Lesker). To provide electrical connections inside the chamber for LED lighting and electric field generation, insulated copper electrical wires were connected through the chamber apertures via an electrical feed through (Kurt J. Lesker). A pressure transducer (925 Micro Pirani, MKS) was attached to monitor pressure within the chamber. The thermocouple bundles and the pressure transducer were both electrically connected to an analog input source (RAQ DAQ, National Instruments), which was interfaced to a computer for data recording. A second bellows valve (Kurt J. Lesker) was integrated onto the chamber for the vacuum pump, which brought down the chamber to vacuum conditions prior to vapor filling. A liquid nitrogen cold trap was incorporated along the line from the chamber to the vacuum which served to remove any moisture from the pump-down process and ultimately assist in yielding higher quality vacuum conditions. A tertiary bellows valve (Kurt J. Lesker) was integrated on a T fitting between the vacuum pump and liquid nitrogen reservoir to connect the vacuum line to the ambient to release the vacuum line to ambient conditions once pump down was achieved. In order to visually record data, a high speed camera (Phantom v7.1, Vision Research) was placed in line with the 5" viewing windows on the chamber. The schematic of the exterior of the environmental setup is depicted in Figure 7. Images of the front and rear of the experimental setup are shown in Figure 8 and Figure 9, respectively.
3.2 JUMPING DROPLET CONDENSATION HEAT TRANSFER ENHANCEMENT

Accurate measurements of condensation heat transfer need care to minimize non-condensible gas content and to prevent build-up of the gas-rich diffusion boundary layer [21, 90]. Air concentrations as low as 3 ppm can result in significant error. Buildup of non-condensible gas near the surface, as the vapor constituent of the mixture is removed by condensation, can result in significantly reduced vapor temperature (saturation temperature corresponding to the partial pressure of the vapor) adjacent to the condensing surface. Coupled with the potential added interfacial resistance, i.e. thermal grease, between sample substrate and test rig, makes experimental data for superhydrophobic surfaces difficult to find in the literature.
Valve
Liquid nitrogen reservoir
Vacuum pump
Pressure transducer
Valve
Thermocouple bundles
Camera view window
Stainless steel bellows tube
Voltage regulator
Valve
Environmental chamber
Chamber supports

Figure 8. Image of the experimental setup shown from the front (high speed camera and data acquisition system not shown).

Figure 9. Image of the experimental setup from the rear of the chamber showing the cooling water inlet and outlet and water vapor reservoir.
Accurate surface temperature and heat flux measurements are best achieved using flat plate geometry with surface temperature and heat flux obtained from intercept and slope given by temperatures measured by accurately-located thermocouples at different depths below the condensing surface. This geometry is recommended for fundamental condensation measurements and results should be benchmarked against well-documented data sets [90-94]. An alternate method to measure condensation heat flux involves measurement of the change in specific energy of a cooling fluid flowing through a tube which undergoes condensation on the outside [17, 18, 73, 95]. Although the tube geometry makes accurate surface temperature measurement more difficult compared to the flat condensing plate, it remains a good approach for measuring the overall heat transfer rate (from the coolant side to the vapor side). Recently, the feasibility of superhydrophobic nanostructures to enhance dropwise condensation has been experimentally demonstrated on such a setup, shown in operation in Figure 10 [73]. The tube condenser is inside of the vacuum chamber described in the previous section, surrounded by pure water vapor and cooled by an internal flow of chiller water. Jumping droplet condensation is observed on the superhydrophobic copper oxide (CuO) nanoblades which had been grown on the surface of a copper tube and subsequently functionalized with trichloro(1H,1H,2H,2H-perfluoroctyl)silane (TFTS) (see Appendix for details of the CuO growth and hydrophobic functionalization). The resulting heat flux through the tube surface versus temperature difference is plotted in Figure 11.

Figure 10. (a) Jumping-droplet condensation on a superhydrophobic nanostructured copper oxide (CuO) tube (inset: magnified view of the jumping phenomena). (b) Field emission scanning electron micrograph of a CuO surface. The sharp, knife-like CuO structures have characteristic heights, \( h \approx 1 \mu m \), solid fraction \( \varphi \approx 0.023 \) and roughness factor, \( r \approx 10 \). (inset: water droplet contact advancing angle on the nanostructured superhydrophobic surface, \( \theta_a = 169^\circ \pm 3^\circ \)).
Figure 11. Heat flux ($q''$) versus log mean temperature difference ($\Delta T_{\text{LMTD}}$) through tube condensers tested in the experimental vacuum chamber setup for filmwise, dropwise, jumping, and flooded condensation.

The heat flux versus log mean temperature difference data can be used to calculate the condensation heat transfer coefficient. This heat transfer coefficient is obtained from the experimental data by subtracting out the contributions to thermal resistance for heat transfer from the chiller water to the surrounding water vapor due to the chiller water flow and the copper pipe. This is performed as shown in Equation 5.

$$h_c = \left[ \frac{1}{U} - \frac{A}{A_{\text{inner}} h_{\text{inner}}} - \frac{A \ln \left( \frac{r_{\text{outer}}}{r_{\text{inner}}} \right)}{2\pi L k_{\text{Cu}}} \right]^{-1}$$

(5)

where $U$ is the total heat transfer coefficient, interpreted as the slope of the plot of $q''$ versus $\Delta T_{\text{LMTD}}$ in Figure 11 above, $A$ is the outer tube surface area ($A = 2\pi r_{\text{outer}} L$), $A_{\text{inner}}$ is the inner tube surface area ($A_{\text{inner}} = 2\pi r_{\text{inner}} L$), $h_{\text{inner}}$ is the heat transfer coefficient of the chiller water flow between the bulk chiller water temperature and the inner copper tube wall temperature as determined from the Gnielinski correlation, $r_{\text{outer}}$ and $r_{\text{inner}}$ are the tube outer and inner radii, respectively, $L$ is the tube length, and $k_{\text{cu}}$ is the tube thermal conductivity. The results of this calculation are plotted in Figure 12 along with their associated errors found by propagation through Equation 5.
Heat transfer enhancements of approximately 30% were achieved on the TFTS SAM-functionalized copper oxide-based nanostructured surface relative to a smooth TFTS SAM-functionalized copper surface when the nanostructured surface was operating in a jumping droplet regime (Figure 10). This reason for heat transfer enhancement during jumping droplet condensation is further elucidated by considering distribution of droplet sizes on the surface, where the vast majority of droplets are less than 10 μm as shown in Figure 13. However, increasing supersaturation led to nucleation-density-mediated flooding of the surface, which resulted in stable W droplet formation and degraded the condensation heat transfer performance. This key limitation for jumping condensation occurs when the nucleation density becomes too high and the spacing between droplets is reduced, at which point the surface is “flooded” and droplet jumping cannot be sustained, as understood from Equation 4 since the nucleation density increases with increasing supersaturation. In this case, discrete droplets form which are highly adhered to the surface, and heat transfer performance is worse than for dropwise condensation due to the added thermal resistance through these large pinned droplets. The onset of flooding is quantified by the supersaturation, $S$, which is the ratio of the vapor pressure to the saturation pressure at the surface temperature, $S = \frac{P_{\text{vap}}}{P_{\text{sat}}(T_{\text{wall}})}$. For the CuO surfaces studied here, flooded condensation occurs at supersaturations $S > 1.12$. The large droplets that form degrade heat transfer performance for flooded condensation to \( \approx 40\% \) of jumping condensation over time.
3.3 SUMMARY

In this chapter, the experimental setup used throughout the thesis to observe condensation and measure heat transfer is presented. This setup consists of a vacuum chamber which can be pumped down to less than 1 Pa to remove noncondensible gases, a degassed, deionized water supply which is used to introduce pure water vapor into the chamber, and a chiller flow loop which is capable of cooling the condenser test sections by internal chilled water flow. Instrumentation includes a chamber vapor pressure gauge, a chiller water flow rate meter, and thermocouples used throughout the system to determine relevant temperatures, all connected to a data acquisition system. This experimental setup was used in past work to determine condensation heat transfer coefficients for filmwise, dropwise, and jumping droplet condensation. Jumping droplet condensation was shown to display 30% higher heat transfer than state-of-the-art dropwise condensation but was limited by the flooded mode of condensation, which occurs at elevated supersaturations. This work demonstrated that jumping droplet condensation has the potential to realize improvements in condenser efficiency and required further study.
Chapter 4

4. Electrostatic Charging of Jumping Droplets

One century ago in 1913, Millikan analyzed the motion of droplets electrified by a cathode ray tube in a uniform electric field to quantify the fundamental charge of an electron [96]. Researchers have since studied the nature and mechanism of charge accumulation on atomized droplets [97], sessile droplets [98-100], and the hydrophobic coatings beneath them [101-104] extensively, sometimes using a modification of Millikan's approach [99]. These studies arrived at conflicting results between positive [105, 106] and negative [107, 108] charging in what remains a topic of significant debate [102, 109]. Recently, with the broad interest and development of superhydrophobic surfaces, more detailed insights on droplet interactions on these surfaces have emerged. Specifically, jumping droplet research has been promising for heat transfer, anti-icing, and self-cleaning, and research has focused on the role of surface structure on the jumping mechanism [39], viscous dissipation during coalescence [34], and modeling of the jumping process [80, 110], while assuming no electrostatic interactions and charge neutrality of the coalescing and departing droplets.

Here, we show that jumping droplets gain a net positive charge that causes them to repel each other mid-flight. In a modified experiment inspired by that of Millikan [96], we used a uniform transverse electric field to quantify the charge on the droplets and showed that the charge is dependent on the surface area of the departing droplet and independent of the structure beneath the coating. Accordingly, we explained the mechanism for the charge accumulation, which is associated with the formation of the electric double layer at the droplet-coating interface, and subsequent charge separation during droplet jumping governed by the fast time scales of droplet coalescence. Our results demonstrate the important role of surface charge interactions on jumping droplet dynamics and also provide insight into jumping droplet physics, in addition to sessile droplet charging on hydrophobic surfaces.

4.1 DROPLET-DROPLET INTERACTION

To characterize droplet-droplet interactions on a well-defined surface, we investigated jumping droplet behavior on copper tubes coated with functionalized CuO nanostructures (Figure 10 and Figure 14) by condensing water vapor on the surface and observing droplet jumping. Hydrophobic functionalization was obtained by depositing TFTS from the vapor phase (see Appendix). This SAM coating had a typical
advancing angle of $\theta_a \approx 120^\circ$ when measured on a smooth reference surface and typical advancing/receding angles of $\theta_a/\theta_r \approx 171/167 \pm 3^\circ$ when measured on the nanostructured CuO surface. To observe droplet jumping, the CuO tubes were tested in the vacuum chamber. Prior to performing the experiments, the water for the vapor supply was vigorously boiled and the test chamber was evacuated to a pressure $P < 0.5 \pm 0.025$ Pa to eliminate non-condensible gases. Throughout the experiments, the chamber pressure and temperature were continuously monitored to ensure saturated conditions. The temperature of the tube was independently controlled via the water chiller loop.

Figure 15 shows long exposure images (50 ms) taken during steady-state condensation on the CuO tube, where the white streaks are the trajectories of the jumping droplets. The CuO surface showed efficient droplet removal via the jumping mechanism as expected, with numerous microscale droplets departing from the surface. Figure 15 shows significant droplet-droplet interactions after droplets departed from the surface, as seen by the rapid directional changes in the droplet trajectories. This is highlighted by the false-colored trajectories where, when droplets approach one another, they tend to repel each other and do not coalesce, an unexpected observation if the droplets were neutral [111]. Instead, the mid-flight repulsion indicates that droplets may carry electric charge. Furthermore, the uniform repulsive interaction of droplets shows that the charge polarity, i.e., positive or negative, should be identical for all jumping droplets since attraction events were not observed.
4.2 DEMONSTRATION OF ELECTROSTATIC CHARGING

To validate the charging hypothesis and determine the charge polarity, we modified the experimental setup by adding an electrode beneath the condenser tube (Figure 16). The electrode was a 350 \( \mu \)m diameter copper wire, and was connected to a 600 V DC power supply (N5752A, Agilent Technologies) with the opposite terminal connected to the grounded tube sample. The electrode was placed beneath the superhydrophobic surface to allow interactions between the electrode and jumping droplets passing as

\[
\Delta V \rightarrow E
\]

Figure 16. (a) Schematic and (b) photograph showing experimental setup. A copper wire electrode was placed \( \approx 5 \) mm beneath the tube and voltage biased relative to the tube sample (\( \Delta V \)). The voltage potential difference created an electrostatic field (\( E \)) allowing for the charged droplet interactions with the field to be observed.
they fell under the influence of gravity. With an applied constant electrical bias ($\Delta V$), an electric field between the electrode and grounded tube was established, creating droplet motion toward or away from the electrode depending on the polarity of the bias (negative or positive).

When a negative bias was applied to the electrode ($\Delta V = -100$, -300V), significant droplet-electrode attraction was observed (Figure 17, top frames). To eliminate the possibility of induced electrical effects, i.e., droplet motion due to dielectrophoresis, we reversed the polarity of the electrode ($\Delta V = +100$, 

![Images showing droplet motion under different voltage conditions](image)

**Figure 17.** Long exposure time images (50 ms) of jumping-droplet condensation with negative electric field (electrode is negative, tube is grounded) and positive electric field (electrode is positive, tube is grounded). When the electrode was biased with a negative voltage ($\Delta V = -100$ and -300V), attraction between the departing droplets and electrode was observed. When the electrode was biased with a positive voltage ($\Delta V = +100$ and +300V), repulsion between the droplets and electrode was observed. The results are consistent with the droplets being positively charged (chamber vapor pressure $P_v = 2,700 \pm 68$ Pa, $S \approx 1.04$).
+300V) and saw a significant droplet-electrode repulsion (Figure 17, bottom frames). The repulsion and attraction observed under positive and negative electrode bias, respectively, indicates that dielectrophoresis was not the cause of droplet-electrode interaction and that all of the droplets were positively charged after jumping from the surface. Although the magnitude of the droplet charge could be calculated from these electrode experiments, the complex geometry introduces error, and potential charging of the hydrophobic surface coating may arise [102, 103], altering the voltage bias so that the magnitude of the electric field is difficult to determine. Also, it is important to note that although charging may occur from the tube substrate beneath the nanostructure via flow electrification [112], droplet charging was found to be independent of the cooling water flow rate, thus eliminating this possibility.

4.3 QUANTIFICATION OF DROPLET CHARGE

To better control the electric field, we adapted an approach similar to that of Millikan [96] whereby external parallel plates were used to create a uniform field. Figure 18(a) shows a schematic of the modified experimental setup. Two polished copper plates (10 x 20 cm, Alloy 110, McMaster-Carr) were placed \( L = 10 \pm 0.05 \) mm beneath the tube and spaced \( d = 19 \pm 0.05 \) mm apart (Figure 18(b)). One plate was grounded while the other plate was connected to the power supply. Control of the voltage bias and plate spacing allowed for accurate calculation of the magnitude and direction of the electric field \( E = \Delta V/d \). A high speed camera was mounted outside of the chamber facing the parallel plates to record the droplet motion between the plates. The camera was mounted \( \approx 20 \) mm below the top of the plates to avoid non-parallel field edge effects and to allow droplets to reach terminal velocity prior to entering the field of view of the camera. Analysis of long exposure images (33 ms) of the droplet trajectory under applied electric fields of \( E = \Delta V/d = 1.31, 2.63 \) and 5.26 kV/m show that 1) the droplet deflection \( \theta \) was dependent on the electric field, and 2) for each applied field, the deflection angle \( \theta \) was constant, indicating that terminal velocity was reached. Droplets traveling at terminal velocity were analyzed in terms of the forces in the x (horizontal) and y (vertical) directions. A charged droplet at terminal velocity experiences a force in the x-direction of \( \Sigma F_x = 0 = -F_D \cdot \cos \theta + q \cdot E \), and in the y-direction of \( \Sigma F_y = 0 = F_D \cdot \sin \theta + (\rho_v - \rho_w) \cdot V \cdot g \), where \( F_D \) is the drag force, \( \theta \) is the angle between the droplet trajectory and the vertical, \( q \) is the charge on the droplet, \( \rho_v \) and \( \rho_w \) are the water vapor and liquid water densities, respectively, \( V \) is the droplet volume \( (V = (4/3) \cdot \pi R^3) \), and \( g \) is the gravitational constant. The ratio of the two force components yields the trajectory equation \( q/[(\rho_v - \rho_w) \cdot V \cdot g] = (g/E) \cdot \tan \theta \).
Figure 18. (a) Schematic and (b) photograph showing the parallel plate experimental setup used to quantify electric charge on the jumping droplets. Two copper plates insulated from the chamber were biased relative to each other ($\Delta V$). The potential difference created a uniform electrostatic field ($E$) between the parallel plates away from the edges, resulting in linear droplet trajectories at terminal velocity.

Figure 19 shows droplet charge as a function of droplet diameter on the CuO superhydrophobic surface for the three different field strengths applied ($E = 1.31$, 2.63 and 5.26 kV/m). The results show that droplet charging was independent of the electric field strength, indicating that induced electrification or dielectrophoretic effects were not factors in the experiment. Furthermore, there are two distinct regimes: 1) for smaller radii ($R \leq 7 \mu$m), the droplet charge was independent of the surface area ($\sim R^2$). This behavior can be explained by examining the droplet growth prior to coalescence. Droplets growing on the superhydrophobic surface first nucleate within a structure unit cell, i.e., area between the structures, eventually emerging from the unit cell to grow up and above the structures with a constant basal area [73, 113]. Throughout this growth, the interfacial area between the structured surface and liquid droplet remains relatively constant since the droplet grows primarily by increasing its contact angle and forming a more spherical shape [113], resulting in a constant electrostatic charge. 2) For large radii ($R \geq 7 \mu$m) the charge is droplet surface area dependent ($\sim R^2$) and is equal to $q'' = 7.8 \pm 3.6 \mu$C/m$^2$. These two regimes are illustrated schematically in Figure 20. This dependency on surface area indicates that the charging mechanism of droplets is potentially associated with the interfacial area between the condensing droplets and the hydrophobic surface beneath them when the growth phase enters a period on constant contact angle with increasing basal area expanding over the tops of the surface structures [73].
Figure 19. Experimental individual droplet charge ($q$) plotted as a function of departing droplet radius ($R$). Points are shown from three different uniform electric fields, $E=\Delta V/d=1.31, 2.63$ and $5.26$ kV-m$^{-1}$. Droplet charging was independent of the applied electric field, which indicates that induced charging effects are not responsible for the charging phenomenon. Dashed lines represent fits to the data for both regimes ($R \leq 7 \mu m$ and $R \geq 7 \mu m$). Error bars denote the propagation of error associated with the high-speed camera resolution and the calculation of droplet size from terminal velocity obtained from image processing. The spread in the experimental data is expected because droplet coalescence can occur between two different size droplets or between more than two droplets ($P_c = 2.70 \pm 0.07$ kPa, $S = 1.04$).

4.4 CHARGING MECHANISM

Based on our results, we propose a charge separation mechanism governed by the critical time scale associated with the droplet coalescence. Most hydrophobic coatings have a negative zeta potential [100]. In the presence of liquid water, these surfaces tend to adsorb negative charge and form an electric double layer in the fluid. Although the water used in these experiments is deionized, the dissociation of water molecules into their HO$^-$ and H$^+$ constituents continues in equilibrium [100]. As water droplets nucleate and grow on the superhydrophobic surface, OH$^-$ ions transport to the coating and preferentially adsorb to the surface, forming a diffuse double layer at the coating surface inside the nanostructure unit cell [102].
Figure 20. Experimental individual droplet charge ($q$) plotted as a function of departing droplet radius ($R$) with schematic illustrations for the different regimes of growth by changing contact angle and by advancing contact line ($R \leq 7 \mu m$ and $R \geq 7 \mu m$). For this case, $E=\Delta V/d=1.31 \text{kV-m}^{-1}$ ($P_e=2.70 \pm 0.07 \text{kPa}, S\approx 1.04$).

If the droplet is removed fast enough (via coalescence and jumping), charge separation can occur, resulting in $H^+$ accumulation inside the jumping droplet. However, if the droplet is removed slowly, the motion of the contact line and subsequent accumulation of $H^+$ in the droplet will create a counter electric field, accelerating the desorption of the $OH^-$ ions and ensuring net neutrality of the removed droplet.

To gain a better understanding of these dynamic processes, the time scales associated with each (coalescence, diffusion, and electrophoresis) are considered. For the droplet radii $\geq 2 \mu m$, the coalescence time scale is governed by a capillary-inertial scaling [114-116], $\tau_c \sim (\rho_w \cdot R^2/\sigma)^{1/2}$. The time scales for charge transport from the hydrophobic coating to the droplet bulk can be characterized by two separate mechanisms, diffusion of the desorbed ion through the liquid residing in the structure [117] $\tau_d \sim h/[2 \cdot (D_{H^+})^{1/2}]$ and electrophoresis of the desorbed ion due to the formation of the counter electric field [118] $\tau_e \sim h/(E \cdot \mu_{e,H^+})$, where $h$ is the characteristic structure height, $D_{H^+}$ is the diffusivity of the $H^+$ ion, $\mu_{e,H^+}$ is the combined electrophoretic and electroosmotic mobility of the $H^+$ ion, and $E$ is the magnitude of
the counter electric field. H\(^+\) was chosen as the ion for analysis due to its higher diffusivity and mobility compared to OH\(^-\), thus providing a conservative estimate of the critical time scales. If the time scale of the coalescence process is too fast, insufficient time is allotted for OH\(^-\) desorption and subsequent transport to the droplet bulk before it jumps. Comparing the characteristic time scales shows that \(\tau_c/\tau_d \ll 1\) and \(\tau_e/\tau_s \ll 1\) for the entire range of measured droplet charge (2 \(\mu\)m < \(R\) < 40 \(\mu\)m), demonstrating that, although a counter electric field develops at the rapidly moving contact line during coalescence, the time needed for OH\(^-\) desorption and transport to the droplet bulk is not sufficient, leaving OH\(^-\) adsorbed to the surface while resulting in a positively charged jumping droplet.

4.5 SUMMARY

Repulsive interactions between jumping droplets were observed, suggesting that the droplets may carry electrostatic charge. Experimental quantification of the charge via observation of droplet motion in a uniform electric field was performed. The mechanism for the charge accumulation is due to the much faster timescale for coalescence and jumping as compared to the timescales for diffusion of the desorbed ion and electrophoresis of the desorbed ion due to the formation of the counter electric field for droplets in the range of sizes commonly observed during jumping. This work offers insights into a wide variety of possible applications such as the use of external electric fields to control the jumping frequency from the surface to increase condensation heat transfer or the implementation of charged droplet jumping to harvest energy from a temperature gradient, as will be discussed in the following sections. Furthermore, by providing a relative measure of the charge adsorption, the droplet charge measurement offers exciting future opportunities to characterize the electrokinetic properties, such as the zeta-potential, of hydrophobic materials and coatings on large scale surfaces [119].
Chapter 5

5. Electric-Field-Enhanced Jumping Droplet Condensation

After droplets jump away from the condenser surface, the existence of a vapor flow towards the surface imparts a drag force on the jumping droplets in the direction of the surface, which can lead to complete droplet reversal and return to the surface (Figure 21). This effect, termed progressive flooding, limits the possible heat transfer enhancement because larger droplets form upon droplet return to the surface that impede heat transfer until they can be either removed by jumping again or finally shedding via gravity. By modeling and experimentally observing individual droplet trajectories during condensation on superhydrophobic nanostructured copper oxide surfaces, we show that this vapor flow entrainment dominates droplet motion for droplets smaller than $R \approx 30 \mu m$ at moderate heat fluxes ($q' > 2 W/cm^2$). Subsequently, we demonstrate electric-field-enhanced (EFE) condensation, whereby an externally applied electric field prevents jumping droplet return. This concept leverages the phenomenon discussed in the previous section whereby these droplets gain a net positive charge due to charge separation of the electric double layer at the hydrophobic coating. As a result, with scalable superhydrophobic CuO surfaces, we experimentally demonstrated a 50% higher overall condensation heat transfer coefficient compared to that on a jumping-droplet surface with no applied electric field for low supersaturations ($<1.12$). This work not only shows significant condensation heat transfer enhancement, but also offers new avenues for improving the performance of self-cleaning and anti-icing surfaces as well as thermal diodes.

Figure 21. Jumping droplets (highlighted here in green) reverse direction after jumping away from the surface due to drag from the vapor flow towards the surface.
5.1 DROPLET RETURN: PROGRESSIVE SURFACE FLOODING

When a pair of equal-sized droplets coalesce and jump on a superhydrophobic nanostructured surface, they travel away from the surface in a trajectory perpendicular to the surface [34]. However, if the surface is oriented in such a manner as to allow jumping to occur against gravity (i.e., horizontally facing upwards), the returning droplet may either 1) coalesce and undergo another jump, or 2) pin to the surface and form a stationary droplet until coalescence occurs again. To eliminate gravitational return, these condensing surfaces can be oriented such that the gravitational force does not act opposite to the droplet motion; rather, it can act transverse (i.e., vertical plate) or parallel (horizontally facing downwards) to the plate. However, other mechanisms such as vapor flow towards to surface dictate droplet return, and returning droplets result in progressive flooding, which manifests as an increased droplet size distribution on the surface over time (Figure 22) that degrades heat transfer performance.

![Figure 22. Progressive flooding as jumping droplets return to the condenser surface due to vapor flow and the effect of this phenomenon on droplet size on the surface over time.](image)

We first characterized droplet jumping away from the surface in the direction opposite to the gravitational force. We condensed water vapor on copper tubes coated with functionalized copper oxide (CuO) nanostructures (see Appendix) and observed droplet jumping. The radial geometry of the tubes allowed for simultaneous high speed imaging of the top (against gravity) and bottom (with gravity) surfaces. To visualize the behavior, the CuO tubes were tested in the vacuum chamber visualized with the Phantom high speed camera.

Figure 23 shows a long exposure time image (50 ms) obtained during steady-state condensation on the CuO tube, where the streak lines show the trajectories of the droplets. Droplets leaving the tube bottom
(with gravity) were observed returning to the bottom surface. This return of droplets against gravity implies that either a bulk vapor flow was present which traveled upwards (i.e., due to buoyancy), or that a local mass-conserving radial vapor flow moving towards the tube entrained droplets and caused them to return to the surface. To study the potential effect of a buoyant flow, we modified the experiment to include a flow blockage beneath the tube. Return of droplets from the bottom surface was as frequent as before indicating that buoyancy-induced bulk vapor flow was not the mechanism of droplet return.

The second possible mechanism capable of causing droplet return is from entrainment of droplets in the local vapor flow towards the tube due to condensate mass conservation (i.e., water vapor supplied to the condensing surface) [120]. To examine this hypothesis, we first modeled the radial vapor flow towards the tube to obtain the drag on departing droplets. The model was simplified from the general case presented in Figure 23 by assuming that a jumping droplet departs normal to the surface directly downward in the direction of gravity. It is also assumed that, due to the relatively small size of departing droplets (~10 μm), the shape of droplets remained spherical during flight. This assumption is justified given that the vapor density is small compared to the density of the liquid droplets (ρ_v << ρ_w) and Bo = ρ_w g R^2/γ << 1, where Bo and R are the droplet Bond number and radius (~10 μm), respectively, ρ_w and γ are the water density (~1000 kg/m^3) and surface tension (~72 mN/m), respectively, and g is the gravitational constant. In addition, We = (ρ_v U_v^2 R)/γ << 1 and Ca = μ_v U_v/γ << 1, where We and Ca are the Weber and Capillary numbers, respectively, U_v is the characteristic vapor velocity (~1 m/s), and ρ_v is
the vapor density (≈0.03 kg/m³), and \( \mu_v \) is the vapor dynamic viscosity (≈130 μPa·s) [121]. Figure 24 shows a cross-sectional schematic of the developed model with a magnified view showing the force balance on a departing droplet. The equation of motion for the departing droplet, which includes inertia (first term), the gravitational force \( F_g \) (second term), and the drag force due to vapor flowing in the reverse direction \( F_D \) (third term) is:

\[
\frac{4}{3} \pi R^3 \rho_w \frac{dv}{dt} = \frac{4}{3} \pi R^3 g \rho_w - \frac{1}{2} \rho_v \pi R^2 C_D (v + u_v(x))^2
\]  

(6)

where \( R \) is the droplet radius, \( \rho_w \) is the droplet density, \( v \) is the droplet velocity, \( t \) is time, \( g \) is the gravitational constant, \( \rho_v \) is the vapor velocity, \( C_D \) is the Reynolds number dependent drag coefficient on a sphere [122], and \( u_v \) is the velocity of the vapor flow past the spherical jumping droplet. To determine the vapor velocity, mass conservation is applied to the condensing vapor. The tube heat transfer rate, \( q \) (measurable quantity), is then balanced by the energy released via vapor-to-liquid phase change:

\[
\dot{m} h_{fg} = q
\]  

(7)

where \( h_{fg} \) and \( \dot{m} \) are the latent heat of vaporization and the mass flow rate towards the tube of the condensing vapor, respectively. Therefore, relating the mass flow rate to the vapor velocity gives an expression for the vapor velocity as:

48
\[ u_v(x) = \frac{R_t q''}{\rho_v (R_t + x) h_f g} \]  

(8)

where \( R_t \) and \( L \) are the condensing tube outer radius and length, respectively, \( x \) is the distance from the tube surface, and \( q'' \) is the heat flux.

In order to obtain the droplet trajectory, the initial condition relating the jumping velocity \( (U) \) of the droplet leaving the tube surface to the droplet radius \( (R) \) is needed. Although a previous study experimentally determined the initial droplet velocity as a function of radius [34], a carbon nanotube surface with droplets condensing at atmospheric pressure was studied, which is distinct from our experiments carried out at low vapor pressures (< 4 kPa). To minimize uncertainties associated with the different experimental conditions, we experimentally determined the initial droplet velocity as a function of departing droplet radius. For water droplets of radii \( R \geq 2 \mu m \), coalescence is governed by an inertially-limited viscous regime at low neck radii \( (R_{min}/R) \leq Oh \), where \( R_{min} \) is the radius of the neck connecting the two coalescing droplets, and \( Oh \) is the characteristic droplet Ohnesorge number defined by \( Oh = \mu/\rho_v \sigma R_{m}^{1/2} \) and by an inertial regime at larger neck radii \( (R_{min}/R > Oh) \) [123]. Due to the relatively low Ohnesorge number, \( Oh \approx 0.02 \) to 0.1, the majority of droplet coalescence (> 90% for \( R = 2 \mu m \)) occurs in the inertial regime [123] where the time scale is governed by a capillary inertial scaling [114, 124, 125]. Balancing the excess surface energy and kinetic energy of the jumping droplet [34], we obtain the characteristic scaling for the droplet velocity:

\[ U \sim \sqrt{\gamma/\rho R}. \]  

(9)

This characteristic velocity corresponds to a value of unity for the droplet Weber number, \( We = (\rho_v \cdot U^2 \cdot R)/\gamma = 1 \). To account for the incomplete conversion of excess surface energy to kinetic energy not captured by the scaling, we introduce a proportionality constant \( C \), on the right hand side of Equation 9 [126]. For our experiments on CuO at low vapor pressure \( (P_v < 4000 \text{ Pa}) \), Equation 9 best fits the experimental data with \( C \approx 0.23 \) (see Figure 25).
Combining the initial condition (Equation 9 with proportionality constant $C$) and the vapor flow velocity (Equation 8) with the droplet equation of motion (Equation 6) (using a numerical discretization with a Runge-Kutta method), the droplet position beneath the tube ($x$) was determined as a function of time ($t$) for varying droplet radius ($R$) and condensing tube heat flux ($q''$). Figure 26(b) shows that for a heat flux of $q'' = 1$ W/cm$^2$, droplet entrainment in the condensing vapor flow becomes significant, with droplets smaller than $R \approx 19$ μm returning to the surface against gravity. In contrast, droplets larger than $R \approx 19$ μm have enough gravitational body force acting on them to depart from the surface such that they do not return from entrainment in the vapor flow, even as time extends past the limit of the plot.

To experimentally validate the model, droplet trajectories directly below the condensing tube (Figure 26(a)) at a heat flux of $q'' \approx 0.8 \pm 0.2$ W/cm$^2$ were analyzed using high speed imaging. For each departing droplet which returned to the surface against gravity, the maximum vertical distance traveled beneath the tube prior to droplet return was measured ($L_{\text{max}}$, interaction length). The histogram in Figure 26(a) presents droplet interaction lengths measured during the experiment. The maximum distance a droplet traveled away from the tube before returning to the surface was $L_{\text{max,exp}} \approx 2.4$ mm, which is in good agreement with the model solution shown in Figure 26(b), which predicted $L_{\text{max}} \approx 2.7$ mm at a heat flux of $q'' = 1.0$ W/cm$^2$. The agreement between experiments and theory indicates that droplet return (Figure 1c) is due to vapor flow entrainment.
Figure 26. (a) A histogram of experimentally measured droplet interaction lengths for a condensation heat flux of $q'' = 0.8 \pm 0.2 \text{ W/cm}^2$, where the interaction length is defined as the maximum distance a droplet travels before being returned to the condensing surface due to vapor flow entrainment. The experimentally measured maximum travel distance $L_{\text{max, exp}} \approx 2.4 \text{ mm}$, which is in good agreement with the model result (b) for droplet position $x$ beneath the tube as a function of time $t$ for a condensing heat flux of $q'' = 1 \text{ W/cm}^2$, where $L_{\text{max, model}} \approx 2.7 \text{ mm}$.

To further characterize the effects of condensate vapor flow on droplet departure, we calculated the maximum distance that the largest entrained droplets travel downward away from the tube prior to being returned to the surface ($L_{\text{max}}$) as a function of condensation heat flux (Figure 27(a)). As the condensation heat flux increased, the maximum returning radius also increased due to the entrainment of progressively larger departing droplets (Figure 27(b)).

The experimental and model results indicate a fundamental limit to jumping-droplet condensation. Due to the entrainment of departing droplets, the maximum attainable heat flux is limited since larger heat fluxes result in faster vapor flow and more droplet return. As a result, this limitation presents an opportunity to utilize external body or surface forces to further aid droplet removal from the surface at high fluxes, whether from forced convection [127-129], Marangoni stresses [130], or electrostatic fields [131]. Here, electrostatic fields are used to take advantage of the recent discovery discussed in the previous chapter that jumping droplets gain a positive electrostatic charge as they depart from the condensing surface [131]. Exploiting this electrostatic charge using external electric fields provides a unique and easily implementable approach to enhance droplet removal from superhydrophobic nanostructured condensing surfaces by overcoming vapor drag.
5.2 MANIPULATION OF CHARGED DROPLETS

With this understanding of the limitations for droplet removal due to vapor flow entrainment in mind, electric-field-enhanced (EFE) condensation was developed. To overcome entrainment and attract droplets, an external electrode biased to attract positively charged departing droplets was used in the previous chapter [131]. Here, we modified our experimental setup to include a copper wire cage electrode surrounding the condensing superhydrophobic CuO tube (Figure 28). By applying a voltage between the grounded tube and wire cage, droplets jumping from the surface were attracted towards the cage and away from the surface, limiting droplet return due to entrainment.

Figure 29 shows long exposure (40 ms) time-lapse images of no-field and EFE condensation, respectively. It is observed that as the condensation time approached 8 minutes, the no-field jumping-droplet condensation mode (upper frames) had a larger population of pinned liquid droplets on the surface. Although droplet jumping was still present at later times, progressive flooding of the surface due to return of departing droplets created a larger average droplet size. In contrast to no-field droplet jumping, the EFE condensing mode (lower frames) displayed little increase in average droplet size on the surface through the experiment. This observation implies that EFE condensation provides a means to further increase jumping-droplet heat transfer by minimizing the average droplet size and increasing the
Figure 28. Schematic of EFE condensation and accompanying photo of experimental setup. The outer copper grid is biased negative relative to the condensing tube, creating an electric field and attracting jumping droplets away from the surface and preventing droplet return due to vapor flow entrainment.

It is important to note that although charged jumping droplets feel an attractive Coulomb force \( F_c \) towards the tube at all times (due to opposite charge left on the hydrophobic coating), the magnitude of the force is negligible at the length scales of droplet deceleration and reversal. The characteristic Coulomb force can be estimated by \( F_c = qE \approx q\zeta/L \), where \( q \) is the individual charge on a droplet (~10 fC),

Figure 29. Progressive flooding as jumping droplets return to the condenser surface due to vapor flow is shown in the top frames, while EFE condensation is shown below at the same times after the onset of condensation. The surface droplet size is plotted versus time to the left.
$E$ is the magnitude of the electric field between the droplet and charged surface which is approximated as the zeta potential of the surface, $\zeta$ (\approx 100 mV), divided by the distance between the droplet and surface, $L$ (\approx 1 mm). The characteristic drag force on a jumping droplet at its maximum distance from the tube (immediately prior to reversing direction) can be approximated by Stokes drag as $F_d = 6 \cdot \pi \mu \cdot U \cdot R$. Substituting and solving for the characteristic forces, the result is that the Coulomb force $F_C$ (\approx 1 pN) $\ll F_d$ (\approx 10 nN), the drag force, showing that the magnitude of the Coulomb force is negligible compared to the drag force on jumping droplets at these length scales.

### 5.3 Experimental Heat Transfer Results

To experimentally quantify the effect that elimination of droplet return and progressive flooding has on condensation heat transfer, the overall heat transfer coefficient ($\overline{U}$) was measured for varying electric fields. Figure 30 shows the overall surface heat flux as a function of the log-mean-temperature-difference ($\Delta T_{LMTD}$) between the saturated vapor and cooling water. Relatively low cooling water flow rates of 0.5 \pm 0.025 L/min were used in the experiments to increase the temperature difference from inlet to outlet and obtain a greater signal to noise ratio. However, reducing the flow rate led to relatively low overall heat transfer coefficients due to the larger convective resistance on the coolant side.

![Figure 30. Experimental steady-state overall surface heat flux ($q''$) as a function of log mean water-to-vapor temperature difference ($\Delta T_{LMTD}$) for tube surfaces undergoing jumping-droplet condensation (no applied voltage) and EFE condensation ($P_v = 2.70 \pm 0.07$ kPa, $1.02 < S < 1.04$, chiller loop flow rate inside the tube $\approx 0.5 \pm 0.025$ L/min). Faster droplet removal and reduction of droplet return when an external electric field was applied resulted in the higher heat fluxes for EFE jumping than for jumping with no electric field.](image-url)
Figure 30 shows that for the case of no electric field, the overall heat transfer coefficient (the slope of the curve of $q''$ versus $\Delta T_{\text{inlet}}$) was approximately $0.51 \pm 0.14 \text{ W/cm}^2\text{K}$. However, by applying an electric field of $E = 100 \text{ V/cm}$, the heat transfer coefficient increased by approximately 50% to $0.77 \pm 0.12 \text{ W/cm}^2\text{K}$. Note that the no-field overall heat transfer coefficient is lower than the value previously reported ($U_{\text{jumping}} = 1.65 \pm 0.22 \text{ W/cm}^2\text{K}$) [73] due to the lower internal cooling water flow rate used in these experiments in order to achieve a larger inlet-to-outlet temperature difference and signal to noise ratio. It is important to note that higher condensation heat fluxes ($S > 1.04, q'' > 1 \text{ W/cm}^2$) were not studied due to the presence of progressive (droplet return mediated) flooding on the no-field jumping-droplet surface. Furthermore, at higher supersaturations ($S > 1.12, q'' > 8 \text{ W/cm}^2$) for EFE condensation, flooding of the surface due to high nucleation densities remained [113], as previously observed on superhydrophobic CuO surfaces. The flooding mechanism was found to be independent of the electric field strength for these high supersaturations which indicates that, for the voltage range explored, electric fields cannot remove more droplets than would have already departed due to jumping. This result agrees well with theory since the electric field can only act on droplets once they have attained an electrostatic charge by coalescing and leaving the surface.

This work supports the findings that vapor flow entrainment is a performance limiting phenomenon during jumping-droplet condensation and that efficient droplet removal is critical in realizing enhanced condensation heat and mass transfer over state-of-the-art dropwise condensing surfaces. Furthermore, the experimental results suggest that, although EFE condensation on superhydrophobic surfaces has the ability to enhance condensation performance, these surfaces cannot currently be used for high heat flux applications due to flooding of the surface [73, 113, 134]. In the future, an investigation of different surface geometries with uniform vapor flow velocities (i.e., flat plate heat exchangers) may be beneficial to identify optimum EFE condenser designs. Furthermore, alternate methods of creating electric fields via positively biased embedded electrodes beneath the condensing surface [135] (which would repel jumping droplets as opposed to attracting them with an external electrode) promise to be attractive and less obtrusive alternatives to using external electrodes.

5.4 SUMMARY

The vapor drag towards the condensing surface was demonstrated to act as a barrier to heat transfer performance during jumping droplets condensation on superhydrophobic surfaces. Through experiments and modeling, the entrainment and return of jumping droplets result were shown to result in progressive flooding of the condensing surface that is characterized by the gradual increase in average droplet size
and gradual deterioration of condensation heat transfer performance. To counteract the vapor drag, the jumping droplet charging phenomenon was implemented in conjunction with external electric fields to develop a new mode of condensation called electric-field-enhanced (EFE) condensation. As a result, 50% higher overall heat transfer coefficients were obtained at electric fields of 100 V/cm and greater as compared to typical (no-field) jumping droplet surfaces. At high supersaturations \( S > 1.12 \), however, flooding of the nanostructured surfaces still led to the formation of highly pinned droplets, which degraded the condensation heat transfer coefficient. These results provide guidelines for the fabrication of high performance nanostructured CuO surfaces for moderate condensation heat flux applications.
Chapter 6

6. Energy Harvesting with Charged Jumping Droplets

Energy harvesting is the conversion of ambient energy present in the environment into electrical energy [136-139]. Typically, energy harvesting involves the conversion of low-quality ambient energy to power small (~1 cm), low-power (~1 μW) electronic devices. Ambient energy sources suitable for harvesting include light, heat, motion or vibration, and even electromagnetic waves. In addition to these harvesting devices being pollution free while in operation, the harvested energy is usually derived from waste energy streams that are otherwise not harnessed for useful work. Energy harvesting has therefore attracted much interest because of its potential use as a source of power in applications such as low-power wireless sensor networks [140] and electronic systems [141]. In this work, we jumping-droplet-based energy harvesting with nanoengineered superhydrophobic surfaces is experimentally demonstrated. This concept relies on the recent observation that jumping droplets are positively charged (~10 - 100 fC per droplet), and can be manipulated with electric fields. Here, the charged droplets jump between superhydrophobic CuO and hydrophilic copper surfaces to create an electrostatic potential and generate power by direct condensation of atmospheric moisture. We experimentally demonstrated power densities of ~15 pW/cm² and describe near-term approaches to increase power densities to ~1 μW/cm².

6.1 EXPERIMENTAL SETUP

To investigate jumping-droplet energy harvesting, the vacuum chamber was modified to accommodate an energy harvesting device which was cooled over an area of 89 x 75 mm its bottom face one side. To provide cooling over this area, a custom chiller block was fabricated from copper as shown in Figure 31.

The energy harvesting device was fabricated from interdigitated nanostructured superhydrophobic CuO and hydrophilic copper (Cu) combs. The CuO nanostructures were grown on commercially purchased Cu heat sinks (comb) with overall dimensions 26 x 89 x 75 mm (height x width x depth) (E1U-NPFSS-30, Cooler Master). Each comb had 14 fins which measured 18.7 mm and 0.48 mm in height and thickness, respectively. Alternating fins were removed to increase spacing during interdigitation and avoid short circuiting. Each comb was cleaned in an ultrasonic bath with acetone for 10 min and rinsed with ethanol, isopropyl alcohol and deionized (DI) water. The combs were then dipped into a 2.0-M hydrochloric acid
solution for 10 min to remove the native oxide film on the surface, then triple-rinsed with DI water and dried with clean nitrogen gas. Nanostructured CuO was grown on one comb as described in the Appendix. To render the CuO coated comb superhydrophobic, a P2i hydrophobic coating was applied with plasma-enhanced vapor deposition. This process allowed for the development of a highly conformal (~30-nm thick) polymer layer that is covalently bonded with the CuO surface. Goniometric measurements (MCA-3, Kyowa Interface Science) of ≈ 100 nL droplets on a smooth P2i-coated silicon wafer surface showed advancing and receding contact angles of $\theta_a = 124.3^\circ \pm 3.1^\circ$ and $\theta_r = 112.6^\circ \pm 2.8^\circ$, respectively. Meanwhile, the advancing and receding contact angles on the superhydrophobic CuO surface were measured to be $\theta_a,\text{CuO} = 171^\circ \pm 3^\circ$ and $\theta_r,\text{CuO} = 164^\circ \pm 4^\circ$, respectively. A schematic of the assembled combs electrically isolated from each other and the chamber and connected to an electrometer is shown in Figure 32 (a). A photo of this setup inside the chamber and placed on the custom chiller block is shown in Figure 32 (b).
To harvest energy from the charged jumping droplets, the temperature of the CuO comb was reduced via the chiller water flow until jumping droplet condensation occurred. To visualize the behavior, the interdigitated device was imaged with the Phantom high-speed camera *in-situ* in the vacuum chamber. Due to the electric-double-layer charge separation at the liquid-hydrophobic coating interface and subsequent fast-timescale coalescence and jumping, the droplets departed the surface with a droplet-radius-dependent electrostatic charge (~10-100 fC). The jumping droplets travelled from the superhydrophobic CuO comb fins to the hydrophilic Cu comb fins, resulting in an electric potential buildup by charge accumulation, shown in time-lapse images taken from high-speed video in Figure 33. Along the droplet trajectory, the electric field between the fins and viscous drag from the surrounding vapor decelerated the jumping droplets. As the droplets moved to a location of higher potential (the hydrophilic fins), their kinetic energy was directly converted into electrical energy in the same way as electrostatic energy generation [142, 143]. Current was then drawn from the high potential hydrophilic fin to do useful work.

To measure the electrostatic power generation of the interdigitated device, we measured the open circuit voltage ($V_{oc}$) and short circuit current ($I_{sc}$) between the two combs during condensation using a Keithley 6517B Electrometer, indicated as (V, I) in Figure 32. The high accuracy electrometer was connected to
the interdigitated combs via an electrical feed through on the chamber. The chamber and electrometer chassis were grounded to the optical table beneath them. The chamber acted as both a ground and a shield for the electrical measurements.

To replicate atmospheric water vapor content conditions, the energy harvesting process was studied at a cooling water temperature of $T_c \approx 8^\circ C$ and water vapor pressure of $P_v \approx 2$ kPa. Figure 34 and Figure 35 show the independently measured open circuit voltage, $V_{OC}$, and short circuit current $I_{SC}$, of the device, respectively. The $V_{OC}$ was obtained by connecting the positive terminal of the electrometer to the Cu comb and the negative terminal to the CuO comb, then measuring the voltage potential during condensation. The $I_{SC}$ was obtained by electrically connecting the Cu and CuO combs in series through the electrometer and measuring the current during condensation (For electrical circuit diagrams, see Appendix). Prior to condensation, $V_{OC}$ and $I_{SC}$ were $\approx 0$ ($t < 18$ minutes in Figure 34 and $t < 16$ minutes in Figure 35). To initiate the condensation process for the electrical measurements, the cooling water temperature was decreased until jumping droplet condensation was observed between the fins of the interdigitated device. During condensation, the vapor pressure ($P_v$) decreased due to the finite amount of vapor inside the chamber, and $T_c$ was maintained $\approx 7.1$ $\pm$ 0.5$^\circ C$. As the condensation process intensified due to transient cooling of the CuO fins, $V_{OC}$ and $I_{SC}$ increased and eventually reached quasi-steady values of $V_{OC} \approx 15$ V and $I_{SC} \approx 1.15$ nA, respectively ($t \approx 25$ minutes in Figure 34 and $t \approx 17.5$ minutes in Figure 35). After $\approx 30$ seconds of reaching a steady measurement, the cooling water temperature was increased ($t \approx 18$ minutes in Fig. 3b) and $V_{OC}$ and $I_{SC}$ slowly decayed with time due to the smaller
supersaturation for condensation and lower droplet jumping frequency. The maximum energy-harvesting
rate in these experiments was approximated by $P_{\text{MAX}} = 0.25I_{\text{SC}}V_{\text{OC}} \approx 15 \text{ pW/cm}^2$, where the prefactor of
0.25 accounts for a balanced resistive load being powered by the generator. The relatively low energy
density of our device was mainly due to: i) the low cooling rates ($<0.01$ W/cm$^2$), and ii) the non-optimum
fin arrangement, resulting in the coldest temperature being at the base of the superhydrophobic fins and
the inability to maximize the use of the whole comb area for droplet jumping.

![Graph showing open circuit voltage vs time]

**Figure 34.** Experimentally measured open circuit voltage ($V_{\text{OC}}$) of the interdigitated device. The experiment
was conducted by filling the controlled chamber with saturated water vapor and closing off the vapor inlet
valve. Once pressure and temperature equilibrium was reached, the cooling water temperature ($T_c$) was
gradually decreased and the water vapor began to condense. Due to the finite volume of water vapor in the
chamber, the saturation pressure decreased as well, resulting in a corresponding decrease in droplet-jumping
frequency and, accordingly, $V_{\text{OC}} (P_r = 2 \pm 0.2 \text{ kPa, } T_c = 8 \pm 0.5^\circ \text{C})$. 
Figure 35. Experimentally measured short circuit current ($I_{SC}$) of the interdigitated device. The maximum electrostatic energy harvesting rate in these experiments ($P_{MAX} = 0.25V_{oc}I_{SC}$) was $\approx 4.3$ nW or $\approx 15$ pW/cm$^2$ (based on an approximated prototype active jumping area of 278 cm$^2$). Again, due to the finite volume of water vapor in the chamber, the saturation pressure decreased during condensation, resulting in a corresponding decrease in droplet-jumping frequency and $I_{SC}$ ($P_s = 2 \pm 0.2$ kPa, $T_s = 8 \pm 0.5^\circ$C).

6.2 POWER GENERATION MODEL

To provide insight into the experimental results and also estimate the maximum potential of jumping-droplet energy harvesting, a model to determine $V_{OC}$ and $I_{SC}$ based on the heat transfer during condensation was developed. Assuming a jumping-droplet radius of $R \approx 10$ µm [73], and relating the condensation heat flux ($q''$) to the energy associated with the latent heat of phase change per droplet ($\rho V h_{fg}$), the frequency of jumping droplets leaving the superhydrophobic surface per unit area ($f$) can be determined explicitly as $f = q''/(V h_{fg} \rho)$, where $V$ and $\rho$ are the jumping-droplet volume ($\approx (4/3)\pi R^3$) and density ($\approx 1000$ kg/m$^3$), respectively. Assuming that all of the departing droplets leave the superhydrophobic surface and reach the hydrophilic surface, the short circuit current per unit area can be calculated from $I_{SC} = f Q_d$, where $Q_d$ is the individual droplet charge ($Q_d \approx 8$ fC for $R \approx 10$ µm) [144]. By considering the parallel CuO and Cu surfaces as capacitors with a separation distance $d$, the open circuit voltage can be determined by considering the case when charged jumping droplets will only be
able to reach the hydrophilic fin with the kinetic energy available. At the open circuit condition, the droplets are decelerated along their trajectory by the force exerted by the electric field $E$ on the droplet charge $Q_d$, with the force balance $ma = -Q_dE - F_{fr}$, where $F_{fr}$ is the drag force due to the surrounding gas phase. To estimate an upper limit of $V_{OC}$, we assumed the drag force to be zero. Balancing the total jumping-droplet kinetic energy ($E_d = (1/2)\rho Vu^2$) with the work required to traverse the electric field ($W_d = Q_dEd$), we obtained $V_{OC} = (\rho Vu^2)/(2Q_d)$. Therefore, the maximum theoretical device power per unit area is approximated as $P_{MAX} = 0.25I_{SC}V_{OC}$ for a balanced load. Explicitly, $P_{MAX}$ can be re-written in terms of the experimental parameters as:

$$P_{MAX} = \frac{q''u^2}{8hfg}$$  \hfill (10)

Equation (1) suggests that the most important parameter for further increasing the energy harvesting
power generation is to increase the jumping-droplet velocity \( (P_{\text{MAX}} \sim u^2) \) by minimizing the jumping-droplet radius. For the simplest case of two equally-sized inviscid spherical droplets coalescing on a surface with no adhesion, the energy-balance gives a characteristic jumping speed that follows an inertial-capillary scaling \( u \sim \sqrt{\gamma \rho R} \), where \( \gamma \) is the droplet surface tension \([34, 145]\), as seen in the previous chapter. Previous condensation experiments on these superhydrophobic CuO surfaces have shown that jumping water droplets with radii approaching \( \approx 10 \, \mu m \) had a maximum jumping velocity of \( \approx 1 \, m/s \) \([145, 146]\). However, limited approaches exist to attain further increases in jumping droplet velocity other than minimizing the surface droplet adhesion \([145]\) and droplet departure diameter. A secondary and more practical approach to increase the energy harvesting rate is to maximize the condensation heat flux \( (P_{\text{MAX}} \sim q^*) \) and jumping droplet frequency in order to attain energy harvesting values approaching \( \sim \mu W/cm^2 \) (Figure 36).

### 6.3 SUMMARY

This work demonstrates that jumping-droplet condensation can be used for electrostatic energy harvesting. In the future, it would be interesting to investigate the performance of the device under different load resistances. Variable load resistances can change the voltage build-up in the device and modify the overall device performance. In addition, the fabrication of high surface area devices holds promise for further increases in the energy density this method of energy harvesting, in addition to potentially reducing the environmental footprint. Furthermore, the theoretical calculations will provide insights to further improve device design if frictional drag and other associated energy dissipation mechanisms are included by identifying additional critical parameters (i.e., surrounding gas density and viscosity) to maximize power output.

In conclusion, jumping-droplet electrostatic energy harvesting has been successfully demonstrated. Charged droplets jump from superhydrophobic copper oxide to hydrophilic copper surfaces to create an electric potential which is used to generate power during formation of dew. Through experiments and modeling, power densities of \( \sim 15 \, pW/cm^2 \) were demonstrated; these can be improved in the near-term to \( \sim 1 \, \mu W/cm^2 \) based on the previously described model. Future devices with higher condensation rates \((>1 \, W/cm^2)\) and high-surface-area designs have the potential to achieve high energy harvesting rates, making them more attractive to power small electronic devices \((>1 \, \mu W)\) \([147, 148]\). This work demonstrates a surface engineered platform that promises to be low cost and scalable for atmospheric energy harvesting and electrostatic power generation.
7. Bibliography


Appendix

COPPER OXIDE GROWTH

To create the CuO nanostructures, commercially available oxygen-free Cu substrates were used (99.9% purity). For the tubes used as experimental test samples, the outer diameters were $D_{OD} = 6.35$ mm and the inner diameters were $D_{ID} = 3.56$ mm, and the length was $L = 131$ mm. Each Cu tube was cleaned in an ultrasonic bath with acetone for 10 min and rinsed with ethanol, isopropyl alcohol and deionized (DI) water. The tubes were then dipped into a 2.0-M hydrochloric acid solution for 10 min to remove the native oxide film on the surface, then triple-rinsed with DI water and dried with clean nitrogen gas. Nanostructured CuO films were formed by immersing the cleaned tubes (with ends capped) into a hot (96±3 °C) alkaline solution composed of NaClO₂, NaOH, Na₃PO₄·12H₂O and DI water (3.75 : 5 : 10 : 100 wt%). During the oxidation process, a thin (~300 nm) Cu₂O layer was formed that then re-oxidized to form sharp, knife-like CuO oxide structures with heights of $h \approx 1$ μm, a solid fraction $\varphi \approx 0.023$, and a roughness factor $r \approx 10$. 

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**TFTS SURFACE FUNCTIONALIZATION**

Trichloro(1H,1H,2H,2H-perfluorooctyl)silane (TFTS) was deposited from the vapor phase. Before silane deposition, each tube was oxygen plasma cleaned for 2 hr to remove organic contaminants on the surface. Once clean, the tube samples were immediately placed in a vacuum desiccator (06514-10, Cole Parmer) with a small amount of liquid silane. The desiccator was evacuated by a roughing pump for 2 min to a minimum pressure of ≈2 kPa. A valve was then closed to isolate the pump from the desiccator and the sample was held in vacuum (≈ 2 kPa) for another 7 min. The functionalized tubes were then rinsed in ethanol and DI water and dried in a clean nitrogen stream.

**P2I SURFACE FUNCTIONALIZATION**

The P2i hydrophobic coating was performed with plasma-enhanced vapor deposition. The process occurs under low pressure within a vacuum chamber at room temperature. The coating is introduced as a vapor and ionized. This process allows for the development of a highly conformal (~30 nm thick) polymer layer, which forms a covalent bond with the CuO surface, making it extremely durable. Goniometric measurements (MCA-3, Kyowa Interface Science) of ≈100 nL droplets on a smooth P2i-coated silicon wafer surface showed advancing and receding contact angles of $\theta_a = 124.3^\circ \pm 3.1^\circ$ and $\theta_r = 112.6^\circ \pm 2.8^\circ$, respectively.
JUMPING DROPLET TRAJECTORY MATLAB CODE

clc
tic
x = 3000; %Number of rows in data output matrix (Increments)
y = 9; %Number of columns in data output matrix (Result variables)
Data = ones(x, y); %Data output matrix
R = 30E-6; % Radius of departing droplet [m]
g = 9.81; % Gravitational constant [N/kg]
Sigma = 72E-3; % Water surface tension [N/m]
rho_w = 100; % Liquid water density [kg/m3]
rho_v = 0.02199; % Water vapor density at P 3000Pa
mu_w = 9.86E-6; % Water vapor viscosity at P 3000Pa
q_flux_max = 1*100*100; % Heat flux [W/m2]
h_fg = 2.453E6; %Vapor/liquid Enthalpy change (J/kg)
v_i = 0.23*sqrt(Sigma/R/rho_w); %Jumping droplet initial velocity [m/s]
v_1_c = v_i; % Droplet velocity assuming creeping flow, subscript "c"
denounced Stokes flow approximation, I've solved both
x_1_c = 0; % Droplet position assuming creeping flow, subscript "c" denounced
Stokes flow approximation, I've solved both
v_1 = v_i; % Droplet velocity making no assumption about flow
Reynolds number
x_1 = 0; % Droplet position making no assumption about flow Reynolds number
R_t = (6.35E-3)/2; % Tube radius [m]
L = 130E-3; % Tube length [m]
dt = 0.03/x; % Time increment in numerical simultaion
q_max = q_flux_max*pi();2*R_t*L; % Heat Transfer [W]

The following is a loop set up to calculate the full trajectory. I've
discretized the equations of motion before using them here.
i = 1;
while i < x
    u_v_c = q_max/(rho_v*h_fg*2*pi()*(R_t+x_1_c));
    u_v = q_max/(rho_v*h_fg*2*pi()*(R_t+x_1));
    Re_c = rho_v*(v_1_c+u_v_c)^2*R/mu_v;
    Re = rho_v*(v_1+u_v)^2*R/mu_v;
    C_d = 24/Re+2.6*(Re/5)/(1+(Re/5)^1.52)+0.411*(Re/263000)^(-7.94)/(1+(Re/263000)^(-8))+(Re^0.8/461000);
    v_2_c = v_1_c + ((g/rho_w)*(rho_w-rho_v)*
                   (9*mu_w/2*R^2*rho_w)*(v_1_c+u_v_c)))*dt;
    v_2 = v_1 + ((g/rho_w)*(rho_w-rho_v)*
                   (3/8)*rho_v*C_d*(v_1+u_v)^2/(R*rho_w))*dt;
    x_2_c = x_1_c + v_1_c*dt;
    x_2 = x_1 + v_1*dt;
    %Output of data
    Data(i,1) = i*dt*1000;
    Data(i,2) = x_1_c*1000;
    Data(i,3) = v_1_c;
    Data(i,4) = Re_c;
    Data(i,5) = Re;
    %Increment counter
    i = i+1;
    v_1_c = v_2_c;
    x_1_c = x_2_c;
\[ v_1 = v_2; \]
\[ x_1 = x_2; \]

% If the position is negative, end simulation (the droplet has already
returned to the surface)
\[ \text{if } x_1 < 0 \]
\[ i = x; \]
\[ \text{end} \]

% Output of the results is in a file called Results
name = num2str(R);
xlswrite('Results', Data, name, 'Al');
toc
ENERGY HARVESTING: ELECTROMETER WIRING DIAGRAMS

To measure the electrostatic power potential of the interdigitated device, we measured the open circuit voltage ($V_{OC}$) and short circuit current ($I_{SC}$) during condensation. A high accuracy electrometer (6517B, Keithley Instruments) was electrically connected with a triaxial cable to the interdigitated combs via an electrical feed through (Kurt J. Lesker) mounted on a vacuum chamber aperture. Inside the chamber, the combs were connected to the electrical feed through via insulated copper electrical wires. The electrometer was electrically connected (GPIB) to the vacuum chamber DAQ, which was interfaced to a computer for data recording. Figures S1(a) and S1(b) show diagrams of the electrical connections used during the experiments to measure $V_{OC}$ and $I_{SC}$, respectively. The chamber and electrometer chassis were grounded to the optical table. The chamber acted as both a ground and a shield for the electrical measurements.

Figure S1. Electrical circuit schematics of the (a) open circuit voltage, $V_{OC}$ and (b) short circuit current, $I_{SC}$, measurement.