On Localized Vapor Pressure Gradients Governing Condensation and Frost Phenomena

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Supporting Information

ABSTRACT: Interdroplet vapor pressure gradients are the driving mechanism for several phase-change phenomena such as condensation dry zones, interdroplet ice bridging, dry zones around ice, and frost halos. Despite the fundamental nature of the underlying pressure gradients, the majority of studies on these emerging phenomena have been primarily empirical. Using classical nucleation theory and Becker–Döring embryo formation kinetics, here we calculate the pressure field for all possible modes of condensation and sublimation in order to gain fundamental insight into how pressure gradients govern the behavior of dry zones, condensation frosting, and frost halos. Our findings reveal that in a variety of phase-change systems the thermodynamically favorable mode of nucleation can switch between condensation and sublimation depending upon the temperature and wettability of the surface. The calculated pressure field is used to model the length of a dry zone around liquid or ice droplets over a broad parameter space. The long-standing question of whether the vapor pressure at the interface of growing frost is saturated or supersaturated is resolved by considering the kinetics of interdroplet ice bridging. Finally, on the basis of theoretical calculations, we propose that there exists a new mode of frost halo that is yet to be experimentally observed; a bimodal phase map is developed, demonstrating its dependence on the temperature and wettability of the underlying substrate. We hope that the model and predictions contained herein will assist future efforts to exploit localized vapor pressure gradients for the design of spatially controlled or antifrosting phase-change systems.

INTRODUCTION

Anyone who has put a lid on a coffee cup and looked at the droplets condensing underneath has observed an annular dry zone around each droplet where no new droplets appear. One possible mechanism for these apparent dry zones surrounding condensing droplets is the cooperative diffusion governing dropwise condensation, in which the out-of-plane diffusion of vapor toward the substrate is coupled with an in-plane exchange of vapor between droplets.1 The in-plane pressure gradients are due to the diversity of droplet sizes on the condensing surface, as nanometric droplets exhibit highly supersaturated vapor pressures resulting from their curvature whereas micrometric droplets are approximately saturated. Therefore, when smaller droplets are proximal to a larger droplet, the in-plane pressure gradient driving the evaporation of these smaller droplets can dominate the out-of-plane differential driving their growth, creating a dry zone around the large droplet.2 Another mechanism for dry zones is that nucleation itself can be suppressed around pre-existing droplets because the critical vapor pressure to form an embryo is larger than the (nearly saturated) equilibrium pressure over large droplets.3,4

While the case of all-liquid droplets requires disparities in droplet size to produce interdroplet pressure gradients, an ice droplet exhibits a lower pressure than a supercooled liquid droplet even when both droplets are the same size. This inherent pressure differential between frozen droplets and liquid droplets is because ice has a lower saturation vapor pressure than supercooled water at the same temperature.3 Ice is therefore a humidity sink for both nanometric (super-saturated) liquid droplets and larger (saturated) liquid droplets. As an ice droplet siphons water vapor from neighboring liquid droplets, this harvest of water molecules manifests itself as ice bridges growing from the frozen droplet toward the evaporating liquid droplets.6–8 The liquid droplets being harvested will freeze as soon as the ice bridges connect; these newly frozen droplets will in turn grow ice bridges to the next row of supercooled condensate, thus propagating frost across the surface. Interdroplet ice bridging is now thought to be the dominant mechanism for condensation frosting on hydrophobic7–9 and superhydrophobic7,10–14 surfaces chilled beneath the dew point because only a single droplet needs to freeze due to heterogeneous nucleation for the chain reaction of ice bridges to occur.

Very recently, we showed that a stable dry zone can exist around a frozen droplet when the nucleation sites for supercooled condensation are sufficiently sparse and/or the

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freezing event occurs during the early growth of the condensate. Under these conditions, the droplets are small and sparse such that the liquid droplets being harvested by a frozen droplet will completely evaporate before the ice bridges can connect. Therefore, it is evident that the pressure gradient between ice and water can be used for the dual purposes of spreading frost and creating dry zones, depending upon the conditions of the system. In addition to using ice, it is also possible to create dry zones around humidity sinks by utilizing hygroscopic liquids such as salty water, nectar, and glycols in conjunction with the growth of condensation and/or frost. However, in these cases the depression in vapor pressure of the hygroscopic droplet(s) with respect to condensation/frost decays to zero as the hygroscopic droplets become increasingly diluted with the harvested water vapor.

Though the saturation vapor pressure of ice is always lower than water under isothermal conditions, interestingly this pressure gradient can flip when considering the initial freezing of a supercooled liquid droplet. During the first stage of freezing, known as recrystallization, the rapid (~10 ms) formation of an ice crystal scaffold causes the droplet to quickly heat up to approximately 0 °C as a result of the sudden input of latent heat. Until this latent heat is dumped into the ambient atmosphere via evaporation and into the substrate by conduction, the freezing droplet is warmer than its supercooled liquid neighbors. This can be sufficient to elevate its vapor pressure above that of the water droplets. Indeed, the pressure increase induced by recrystallization can cause vapor to emanate from the frozen droplet such that satellite droplets nucleate on the substrate around the droplet, which subsequently freeze over via interdroplet ice bridging to form what is known as a frost halo.

It should now be clear that localized, interdroplet vapor pressure gradients are responsible for a variety of emerging phase-change phenomena such as dry zones, condensation frosting, and frost halos. However, to date most reports on these topics have been primarily experimental, and much remains to be understood regarding the thermodynamics of the pressure gradients driving these phenomena. For example, to model the pressure difference between nucleating droplets and pre-existing droplets, one must calculate the critical vapor pressure required for embryo nucleation. Yet reports that have quantified the supersaturation required for nucleating liquid or ice embryos have produced contradictory results that do not agree with each other (Supporting Information Figures S1 and S2). To complicate matters even further, these previous studies estimating nucleation pressures used single values for the kinetic constant of nucleation ($I_0 \sim 10^{29}$ m$^{-2}$s$^{-1}$) and the critical embryo formation rate for nucleation to occur ($I_{c} \sim 10^{4}$ m$^{-2}$s$^{-1}$), despite their exact values being uncertain with $I_0/I_c$ spanning at least 3 orders of magnitude. In addition to estimating the supersaturation required to grow an embryo on pre-existing ice (i.e., frost growth), the study by Na and Webb applied the same value of $I_0/I_c \sim 10^{28}$ used for nucleation on a dry surface, but this assumption that the ratio is the same for an ice substrate is highly questionable. Indeed, there is a sharp disagreement in the literature regarding whether the vapor pressure required for frost growth is to be considered saturated or supersaturated. Considering that the emerging phenomena discussed above are typically driven by highly sensitive in-plane pressure gradients (i.e., extremely small relative to the out-of-plane pressure gradients), an improved understanding of the pressure field around nucleating and pre-existing water and ice droplets on the substrate is required to accurately model these systems.

Here, we utilize a synergistic blend of classical nucleation theory, quasi-steady diffusive growth models, and experimental results to develop a comprehensive model of the contrasting vapor pressures around nucleating and pre-existing water/ice droplets and how they govern various condensation and frost phenomena. First, we calculate the critical pressure for embryo formation on a dry substrate as a function of temperature, surface wettability, and embryo formation rate. In contrast to Na and Webb’s assertion that condensation is always thermodynamically favorable compared to desublimation, here we show that the preferred mode of embryo nucleation can switch between condensation and desublimation, depending upon the temperature and wettability of the surface. By varying the value of the $I_0/I_c$ ratio by 3 orders of magnitude for all calculations, it is concluded that the uncertainty in this ratio can appreciably affect the nucleation pressures for some of the parameter space. Using recent measurements of the kinetics of interdroplet ice bridging in conjunction with the bimodal curves of saturated water and ice, we demonstrate that the vapor pressure at the interface of growing frost must be (approximately) saturated, in contrast to recent models positing supersaturation. We then contextualize our model to emerging phase-change phenomena to show how the calculated pressure field can be used to predict and control the behavior of dry zones, interdroplet frost growth, and frost halos. It is our hope that this theoretical framework can guide the design and analysis of future experiments seeking to control the growth of condensation and frost on surfaces.

### MODEL FORMULATION

**Saturation Vapor Pressure.** The primary mechanism for local vapor pressure gradients in a vapor—water—ice system is the difference in the saturation vapor pressures of water versus ice. The Clausius—Clapeyron equation shows how the saturation pressure ($p_i$) between two phases $i$ and $j$ relates to the absolute temperature ($T$) and the change in specific enthalpy associated with phase-change ($h_i(T)$). This is given by

$$\frac{d \ln p}{dT} = \frac{h_i(T)}{RT^2}$$

where $R$ is the universal gas constant. This relation can be integrated to obtain the saturated vapor pressures of water or ice at different temperatures using the vapor pressure at the triple point ($p_t = 611.657 \pm 0.01$ Pa, $T_t = 273.16$ K) as a boundary condition. Also, the latent heat in eq 1 needs to be taken as a function of temperature. In a seminal review paper, Murphy and Koop discuss how the variation of molar heat capacity with temperature affects the latent heat at subzero temperatures and in turn the saturation pressures. Incorporating these variations of $h_i$ with temperature, we have plotted the saturation pressure of vapor over water or ice in Figure 1. The saturation vapor pressure over ice is lower than that over water for all temperatures below 0 °C. By itself, this is sufficient to create a vapor pressure gradient in a vapor—water—ice system that can cause vapor to flow preferentially from water toward ice. There are, however, other factors that can significantly influence the pressure differential and in some cases even reverse its direction altogether, which we discuss in the following sections.
Supersaturation: Nucleation on a Dry Substrate. The saturation pressure of vapor over water or ice at a given temperature, by definition, is the pressure at which the water/vapor or ice/vapor phases have the same chemical potential and are therefore in thermodynamic equilibrium. However, for phase-change processes such as condensation and desublimation to occur, they often require vapor pressures that exceed the saturation pressure, known as supersaturation. The supersaturation of water vapor is thermodynamically metastable up to a certain limit because condensation and desublimation both involve nucleation, that is, the creation of new interfaces that are energetically costly. The amount of free enthalpy involved in nucleation, that is, the creation of new interfaces that are energetically costly, is the pressure at which the water/ice vapor interface. The supersaturation degree (SSD) describes the metastable supersaturation of water vapor that occurs locally at the surface to overcome the nucleation energy barrier. This is fundamentally different from another commonly used supersaturation ratio, SSD, which quantifies the diffusive growth rate and nucleation density of condensation/frost on a given surface but cannot comment on nucleation energy barriers.

Therefore, SSD, rather than $S$, is the proper context for discussing supersaturation in the present work. The specific Gibbs free energy change associated with the nucleation of the supersaturated water vapor molecules can be written as

$$\Delta G = - RT_v \ln \frac{P_{n,w}}{P_{n,v}}$$

where $\Delta G$ is the change in Gibbs free energy, $R$ is the ideal gas constant, $T_v$ is the saturation temperature corresponding to $P_v$, and $P_{n,v}$ is the partial pressure of water vapor in the ambient atmosphere.

Instead of increasing the vapor pressure at a fixed wall temperature, an alternate path to nucleation is cooling the wall instead of increasing the vapor pressure. For an initially dry surface, the wall temperature can be decreased beneath $T_{n,w}$ along the $\Delta P = 0$ path until nucleation occurs at the critical temperature $T_{n,w} < T_{c,w}$ (horizontal arrows in Figure 2b). $\Delta T = T_{n,w} - T_{c,w}$.

Figure 1. Saturation pressure of vapor with respect to supercooled water (blue line, right y axis) or ice (black line, right y axis) as a function of temperature. Note that the difference in vapor pressure between saturated water and ice (red line, left y axis) peaks at approximately $\Delta P \approx 27$ Pa at $-12^\circ$C, as denoted by the dotted lines. Analytical expressions for these curves are available in the Supporting Information (eqs S1—S4).
T_{n,w} - T_{w} may therefore be looked upon as the degree of subcooling required for nucleation. Combining eqs 1 and 3, we can relate the change in specific Gibbs free energy upon nucleation to the degree of subcooling as

$$\Delta \tilde{g} = \frac{h_{ij} \Delta T}{T_{n,w}}$$

(4)

Of course, the critical p–T curve at which nucleation first occurs is path-independent: \(p_{nw}(T_w) \equiv T_{nw}(p_w)\).

Now that the specific free enthalpy change upon nucleation is known as a function of \(p_{nw}\) and \(T_w\) (eq 3), it is possible to estimate \(p_{nw}\) as an analytical expression in \(T_w\) provided that the value of \(\Delta \tilde{g}\) could be independently solved using an additional relation. Such an expression can be obtained by equating the change in specific Gibbs energy (\(\Delta \tilde{g}\)) to the total Gibbs energy (\(\Delta G\)). For an embryo of volume \(V\), \(\Delta G\) can be expressed as a summation of the negative change in energy inherent to supersaturated vapor becoming liquid (or ice) and the positive energy barrier associated with the creation of the interfaces (liquid–solid and liquid–vapor interfaces for condensation and ice–solid and ice–vapor for desublimation)\(^{34}\)

$$\Delta G = V \Delta \tilde{g} + A_{ij} \sigma_{ij} + A_{jk} (\sigma_{jk} - \sigma_{jk})$$

(5)

where \(i, j, k\) are the three different phases (vapor, water or ice, and the solid substrate) and \(A_{ij}\) and \(\sigma_{ij}\) represent the interfacial area and surface tension between phases \(i\) and \(j\).

Assuming that the nucleating embryo exhibits a uniform spherical-cap shape, the critical radius of curvature where nucleation is stable can by found by solving for \(\partial \Delta G / \partial r = 0\):

$$r^* = -\frac{2 \sigma_{ij}}{\Delta \tilde{g}}$$

(6)

Young's relation can be used to collapse the three surface tension terms down to a single dimensionless variable,\(^{46}\) often denoted as \(m\)

$$m = \cos \theta = \frac{\sigma_{jk} - \sigma_{ij}}{\sigma_{ij}}$$

(7)

where \(\theta\) is the intrinsic contact angle of the water (or ice) with the smooth substrate. A point rarely mentioned in the nucleation literature is the chemical limit of hydrophobicity on smooth surfaces of around \(\theta_{\text{max}} \approx 120^\circ\).\(^{47}\) Though our calculations assume a smooth substrate, they should generally apply even for rough surfaces because the length scale of surface roughness tends to be larger than the size of nucleating embryos (\(r \sim 1–10\) nm). Therefore, we restrict our parameter space here to \(0^\circ \leq \theta \leq 120^\circ\).

By combining eqs 5–7, we obtain the critical change in free energy required for nucleating an embryo:

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**Figure 3.** Supersaturation degree (SSD) required for (a) condensation or (b) desublimation embryos to nucleate on a substrate as a function of surface temperature (\(T_w\)) for different surface wettabilities (\(\theta = 30, 60, 90, \text{ and } 120^\circ\)) and embryo formation rates (\(I^* = 10^{24} \text{ and } 10^{27}\)). All curves were obtained by solving for eq 2 in conjunction with eq 10. The gray region depicting the SSD corresponding to \(\theta = 30^\circ\) is not visible because of its extremely low variation with \(I^*\). (c) and (d) represent the SSD required for condensation and desublimation, respectively, as a function of wettability (\(\theta\)) for different surface temperatures (\(T_w = 0, -10, -20, \text{ and } -30 ^\circ\)C) and embryo formation rates (\(I^* = 10^{24} \text{ and } 10^{27}\)). Although qualitatively similar, note that the SSD for desublimation is roughly 3 times greater than the corresponding condensation SSD requirement over the entire parameter space.
Therefore, fi is actually a weak function of Tw, and is thought to vary from $I_0 \approx 10^{28}$ to $10^{31}$ m$^{-2}$ s$^{-1}$.22,26,34 Many works choose $I_0 \approx 10^{29}$ m$^{-2}$ s$^{-1}$ as a fixed constant for both condensation and desublimation;23,25,48 here, we use the full span of $I_0 \approx 10^{28}$ to $10^{31}$ m$^{-2}$ s$^{-1}$ to vary $I^*$ by 3 orders of magnitude: $I^* = 10^{24} - 10^{27}$.

\[ \Delta G^* = \frac{4\pi \sigma_{ij}^3}{3 \Delta \theta^2} (2 + m)(1 - m)^2 \]  

(8)

Using the Becker–Döring exponential relationship of the embryo formation kinetics,27 we can solve for $\Delta G^*$ independently of eq 8 as a function of the surface temperature and embryo formation rate

\[ I = I_0 \exp \left( \frac{-\Delta G}{kT_w} \right) \]  

(9)

where $I$ is the embryo formation rate, $I_0$ is the kinetic constant, and $k = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant. The critical change in free energy $\Delta G^*$ corresponds to the minimum value of the embryo formation rate required for nucleation to first occur, $I = I_c$. Thus, by combining eqs 3, 8, and 9, the critical supersaturation $p_{n,w}$ required for embryo formation is finally obtained:

\[ p_{n,w} = \frac{p_0}{I_c} \exp \left( \frac{\nu}{RT_w} \frac{4\pi \sigma_{ij}^3}{3 kT_w \ln \left( \frac{I_0}{I_c} \right)} (2 + m)(1 - m)^2 \right) \]  

(10)

Note that $p_{n,w}$, $\sigma_{ij}$, and $\nu$ are all purely functions of temperature; these functions are well-known for both liquid water and ice (eqs S1–S6 in the Supporting Information). Therefore, $p_{n,w}$ is now a semi-approximate expression in $m$, $I^*$, and $T_w$, where $m = \cos \theta$ and $I^* = I_0/I_c$. It is generally agreed in the literature that the value of $I_c \approx 10^4$ m$^{-2}$ s$^{-1}$ found for homogeneous nucleation is also valid for heterogeneous nucleation on dry substrates, for both the condensation and desublimation modes.20,25–27,48 The value of the kinetic constant, $I_0$, is actually a weak function of $T_w$, $p_{n,w}$, and $\sigma_{ij}$ and is thought to vary from $I_0 \approx 10^{28}$ to $10^{31}$ m$^{-2}$ s$^{-1}$.22,26,34 Many works choose $I_0 \approx 10^{29}$ m$^{-2}$ s$^{-1}$ as a fixed constant for both condensation and desublimation;23,25,48 here, we use the full span of $I_0 \approx 10^{28}$ to $10^{31}$ m$^{-2}$ s$^{-1}$ to vary $I^*$ by 3 orders of magnitude: $I^* = 10^{24} - 10^{27}$.

For our knowledge, we are the first to present SSD as a function of $T_w$ and $I^*$ in addition to $\theta$, other reports simply present SSD vs $\theta$ for a fixed value of $T_w$ (typically 0°C) and $I^*$ (typically $10^{25}$).23,25,48 It can be seen that the degree of supersaturation required for embryo formation is much larger for hydrophobic surfaces (for $\theta = 120^\circ$ and $T_w$ spanning 0 to $-30^\circ$C, SSD $\approx 3 - 5$ for condensation and SSD $\approx 8 - 15$ for desublimation) than for hydrophilic surfaces (SSD $\to 0$ as $\theta \to 0^\circ$). It follows that for a chemically heterogeneous surface exhibiting both hydrophobic and hydrophilic features, nucleation events will preferentially occur within the hydrophilic patterns, which can be exploited to increase condensation heat transfer,45,49,50 enhance water harvesting,51 or control icing/frosting behavior.2,34,55 Note that in reality, though, no surface is perfectly smooth and chemically homogeneous everywhere. As such, even a chemically functionalized smooth surface has intrinsic defects that expose high-surface-energy sites beneath the coating. Hence, condensation can initiate at these sites at a significantly lower SSD even for hydrophobic substrates.56,57 In Figure 3, we also see that for a fixed wettability the value of SSD decreases with increasing temperature, with the effect being more pronounced on hydrophobic surfaces. This is because at higher temperatures the specific Gibbs energy required for nucleation is lower. Consequently, the supersaturation requirement for nucleation is also lower. However, for two substrates at the same temperature, the one that is hydrophobic would have a higher energy barrier and therefore a higher SSD requirement for nucleation.

Figure 3 also demonstrates how a variance in $I^*$ by 3 orders of magnitude can moderately affect the SSD estimations of both condensation and desublimation. For instance, desublimation SSD values can vary by more than 18% at $30^\circ$C and embryo formation rates ($I^* = 10^{24}$ and $10^{27}$). This effect is more severe on hydrophobic surfaces, especially at colder temperatures. Only the condensation SSD values for hydrophilic surfaces remain

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**Figure 4.** (a) Nucleation pressure ($p_{n,w}$, eq 10) required for condensation (blue lines) and desublimation (black lines) as a function of $\theta$ for different wall temperatures ($T_w = -10, -20, and -30^\circ$C) and embryo formation rates ($I^* = 10^{24}$ and $10^{27}$). The red dotted line is the locus of the intersection points of $p_{n,w}$ for the desublimation and condensation curves for wall temperatures ranging continuously from 0 to $-30^\circ$C, where desublimation is favored to the left and condensation to the right. (b) Phase diagram for the preferred mode of nucleation for any surface temperature and wettability, where supercooled condensation is thermodynamically favorable in the phase space above the critical line and desublimation is favorable below.
fairly constant. Therefore, we suggest that it could be fruitful for future works to remeasure the embryo formation rates standardized by Volmer and Flood in 1934\textsuperscript{26} and Becker and Döring in 1935\textsuperscript{27} using modern equipment. Also, note that the value of \( I_k \) measured by Volmer and Flood was for homogeneous nucleation, so modern measurements of \( I_k \) could benefit from explicitly characterizing heterogeneous nucleation on a substrate instead of simply applying the rate obtained from homogeneous nucleation. One final observation from Figure 3 is that the desublimation mode SSD is always higher than the condensation mode SSD, in agreement with Na and Webb.\textsuperscript{25} Recall that an alternate way to conceptualize supersaturation is to quantify the subcooling degree required for nucleation; this analogous representation can be seen in Figure S3 in the Supporting Information.

Because the SSD of condensation is always less than for desublimation, it would appear tempting to assume that condensation is always the dominant mode of nucleation. Previously, Sanders\textsuperscript{23} and Na\textsuperscript{25} have argued that for vapor pressures below the condensation SSD there is no nucleation, for pressures greater than condensation SSD but less than desublimation SSD, condensation is the favored mode of nucleation, and for pressures greater than desublimation SSD, both modes of nucleation are possible. However, recall that the pressure curve for saturated water is slightly larger than the curve for saturated ice (cf. Figure 1), so the SSD being larger for desublimation does not necessarily mean that \( p_{\infty} \) itself is always larger. Indeed, here we show for the first time that the pressure required for desublimation can be less than that for condensation if the substrate is hydrophilic enough. Figure 4a shows \( p_{\infty} \) versus \( \theta \) for several different temperatures, and it can be seen that \( p_{\infty} \) is actually lower for desublimation compared to condensation when \( \theta \) is beneath a critical value that depends upon \( T_w \) (red line). This can also be shown by plotting \( p_{\infty} \) versus \( T_w \) instead, which is depicted in Figure S4 (Supporting Information). By solving for the intersection point of the condensation and desublimation curves for any given surface temperature and wettability, a \( \theta \sim T_w \) phase map is created in Figure 4b whereas complementary \( p_{\infty} \sim T_w \) and \( p_{\infty} \sim \theta \) phase maps are provided in Supporting Information Figure SS. It can be concluded that the preferred mode of nucleation for chilled substrates is liquid condensation for hydrophobic or moderately hydrophilic substrates. However, desublimation becomes thermodynamically favorable for sufficiently hydrophilic surfaces, especially at colder temperatures. Note that for a given surface a direct comparison of the SSD for condensation versus desublimation becomes complicated by the fact that the contact angle of ice is slightly larger than that for water.\textsuperscript{25} Therefore, the \( T_w \sim \theta \) phase diagram in Figure 4 serves as a conservative limit, and in reality the red line will be shifted lower by a small amount.

**Supersaturation: Pre-existing Water Droplet.** The vapor pressure about the interface of a pre-existing water droplet is also supersaturated. However, the extent of supersaturation depends on the curvature of the droplet and its temperature at its liquid–vapor interface (\( T_d \)). In the previous section, we assumed that conductive losses across the droplet were negligible such that \( T_d \approx T_w \). However, this is not always true for pre-existing droplets, which at sufficiently large sizes and/or heat fluxes can exhibit \( \Delta T_{\text{cond}} = T_d - T_w = Q \theta / (4 \pi r^2 \kappa_w) \) across the bulk of the droplet, where \( Q \) is the rate of heat transfer (in watts) and \( \kappa_w \) is the thermal conductivity of water (in W/m-K).\textsuperscript{57,58} Thus, for a given droplet size, \( T_d \) can be calculated if the wall temperature, wettability, and heat transfer rate are all known.

Once the temperature at the interface of the droplet is calculated, the supersaturated vapor pressure can be found using the Kelvin–Laplace equation

\[
\Delta \pi = -\frac{2 \sigma}{r} = -\frac{RT}{v} \ln \frac{P_{\infty}}{P_{d,i}}
\]

where \( \sigma \) is the surface tension of the water/vapor interface, \( P_{d,i} \) is the saturated vapor pressure corresponding to \( T_d \) and \( P_{d,i} \) is the actual (supersaturated) vapor pressure around the droplet. Note that \( P_{d,i} \) represents the droplet’s vapor pressure regardless of whether the droplet is growing (\( P_{\infty} > P_{d,i} \)) or shrinking (\( P_{\infty} < P_{d,i} \)). Figure 5 gives the variation of SSD with \( T_d \) for different droplet sizes, where SSD = \( (P_{d,i} - P_{d})/P_{d,i} \). It can be seen that the supersaturation is quite significant for nanometric droplets (for example, SSD > 1 when \( r \sim 1 \text{ nm} \)) but becomes insignificant (<0.1% supersaturation) for micrometric droplets whose vapor pressure can be approximated as saturated. Note that in order to obtain better estimates of SSD, curvature-induced changes in surface tension\textsuperscript{40–42} should be considered when the droplet curvature becomes comparable to the thickness of the liquid–vapor interface.

**Supersaturation: Nucleation on Ice.** Nucleation on pre-existing ice (i.e., frost growth) is different from nucleation on other substrates because ice is perfectly hydrophilic. The contact angle of water on ice at \( T_w = 0 \text{ °C} \) is \( \theta \approx 1\text{ °} \).\textsuperscript{59} Therefore, ice, in some sense, the hydrophilic limit \( \theta \rightarrow 0\text{ °} \) of the heterogeneous nucleation curves in Figure 3c. Historically, models of frost growth typically assumed saturated vapor pressure at the interface of the growing ice,\textsuperscript{23,29–32} but more recently many works have vigorously argued that the ice interface is supersaturated\textsuperscript{25,54–56} The proponents of supersaturation give an argument that is perfectly analogous to embryo formation on a dry substrate: to nucleate more water or ice onto pre-existing ice requires the creation of new interfaces, which creates an energy barrier for the phase change. Therefore, we will begin by considering the supersaturation required to nucleate a fresh embryo onto a pre-existing body of ice. Note that because water completely wets the surface of ice,
it would be appropriate to adopt a 2D nucleation model in this case.

Analogous to a dry substrate, nucleation occurring on pre-existing ice could occur in either the condensation mode or desublimation mode. Consider an ice droplet of temperature $T_i$ resting on a substrate of temperature $T_w$. Note that the temperature $T_i$ of the so-called ice droplet could equally apply to that of a sheet of ice; our droplet terminology here is simply due to the fact that we are often dealing with recently frozen condensate. For sufficiently large ice droplets/sheets, the temperature at the ice/vapor interface ($T_i$) is larger than the wall temperature and could be estimated in the same manner as in the previous section. Assuming that the embryo nucleating on the ice manifests itself in the shape of a monolayer-thick disk, the total Gibbs free energy change for embryo formation is

$$\Delta G = \pi r_d^2 a \Delta \tilde{\gamma} + 2 \pi a r_d \sigma_{ij}$$

(12)

where $a \approx 1 \text{ Å}$ and $r_d$ are the thickness and width of the disk and $\sigma_{ij}$ is the surface tension of the liquid-vapor (condensation) or ice-vapor (desublimation) interface. Note that because the “substrate” itself is already composed of ice, the only new interfacial area that had to be considered in eq 12 was the sides of the disk embryo. Although it is true that a condensing embryo will replace an ice-vapor interface with an ice-liquid liquid-vapor dual interface, these are energetically equivalent according to Young’s eq (eq 7) when $\theta \approx 0^\circ$, which is the case for water on ice. By setting $\partial \Delta G / \partial \sigma_j = 0$ to solve for the critical size of a stable embryo ($r_d^*$), the critical Gibbs free energy for nucleation is obtained:

$$r_d^* = \frac{\sigma_{ij}}{\Delta \tilde{\gamma}}$$

(13)

$$\Delta G^* = -\frac{\pi \sigma_{ij}^2 a}{\Delta \tilde{\gamma}}$$

(14)

Using eqs 3, 9, and 14 and replacing $T_w$ by $T_i$ and $p_{n,i}$ by $p_{n,i}$ we can write the critical supersaturation pressure for nucleation on pre-existing ice ($p_{n,i}$) as an analytical expression in $T_i$:

$$p_{n,i} = p_{n,0} \exp \left( \frac{N_v \pi \sigma_{ij}^2 a}{R^2 T_i^2 \ln I^*} \right)$$

(15)

where $N_v$ is Avogadro’s number. Note that this disk embryo model does not consider the energetics of the quasi-liquid melt layer that can exist at an ice interface when $p_{n,0}$ is sufficiently large.

Before eq 15 can be used, a value for $I^* = I_0/I_e$ needs to be chosen for the case of nucleation onto an ice substrate. Na and Webb52 used the same values of $I_0 \sim 10^{29} \text{m}^{-2} \text{s}^{-1}$ and $I_e \sim 10^4 \text{m}^{-2} \text{s}^{-1}$ as for the case of nucleation onto a dry substrate but do not provide any justification for doing so. In Figure 6, we show the implications of using the same $I^*$ values for ice as were used for dry surfaces ($I^*$ ranging from $10^{24}$ to $10^{27}$). First, this shows that even on pre-existing ice there is a change in the preferred nucleation mode between condensation and desublimation, with the inflection point denoted by the intersection of $p_{n,i}$. Also note that despite the fact that ice is perfectly hydrophilic the nucleation pressure is supersaturated for all ice temperatures. This is in sharp contrast to what we obtained from our 3D nucleation model for nucleation on a dry, smooth surface, where the nucleation pressure becomes saturated (SSD $\rightarrow 0$) as $\theta \rightarrow 0^\circ$ (cf. Figure 3). Though this may be true for the specific case of nucleation on ice, it is extremely important that the choice of $I^*$ for an ice substrate is further scrutinized before proceeding any further with this model. In the Results section below, we will probe this question with our experimental findings to reveal that the saturated curves (dotted lines in Figure 6) are in fact the most accurate representation of the nucleation pressures for frost growth. In this case, note that the desublimation is now always the favored nucleation mode on pre-existing ice.

**EXPERIMENTAL METHODS**

Four inch silicon wafers (Silicon Quest) were silanized with trichloro(1H,1H,2H,2H-perfluoroctyl) silane (Sigma-Aldrich) by vapor deposition in a covered-glass Petri dish that was placed on a hot plate set to 70 °C for 1 h. The contact angles were measured with a ramé-hart 590 goniometer using the the shrink–swell method. The receding angle was measured as $\theta_r = 89 \pm 1^\circ$, and the advancing angle was $\theta_a = 113 \pm 1^\circ$.

**Condensation Dry Zones.** A freshly prepared hydrophobic surface was thermally bonded to a Peltier stage (Linkam Scientific PE120) and placed under a top-down optical microscope (Nikon Eclipse LV150) connected to a digital camera (Phantom v711). The ambient temperature was $T_{\text{amb}} = 24.0 \text{ °C}$, and the relative humidity was $H = 26\%$, which corresponds to a dew point of $T_{\text{dp}} = 3.3 \text{ °C}$. The sample was cooled to $T_w = -10 \text{ °C}$ to observe the growth of supercooled condensation.

**Interdroplet Ice Bridging.** Under the same atmospheric conditions as for the condensation dry zone experiments ($T_{\text{amb}} = 24.0 \text{ °C}$, $H = 26\%$), the silanized sample was bonded to the Peltier...
stage under the top-down optical microscope. The sample was cooled to \( T_w = -10 \, ^\circ C \) to grow supercooled condensate. Once freezing was initiated in at least one of the condensate droplets (often at the edges of the silicon wafer), interdroplet ice bridges propagated across the population of supercooled condensate, which was recorded with a digital camera.

**Dry Zones around a Frozen Droplet.** A freshly prepared hydrophobic surface was thermally bonded to a Peltier stage enclosed inside a ramé-hart custom-made humidity chamber. The air temperature inside the chamber was \( T_{\infty} = 17.4 \, ^\circ C \), and the relative humidity was set to \( H = 21\% \), which corresponds to a dew point of \( T_{\infty,p} = -5.2 \, ^\circ C \). A 10 \( \mu L \) droplet of distilled water was deposited on the sample with the Peltier stage set to \( T_{w} = -2.5 \, ^\circ C \). The Peltier stage was then cooled to \( T_{w} = -12.5 \, ^\circ C \), at which point the deposited droplet froze by homogeneous nucleation (after about 10 min) while the surrounding condensate was still unfrozen. Immediately after the deposited droplet froze, the surrounding condensate evaporated to a certain extent and an annular dry zone was observed.

**Estimation of Thermal Losses.** The thickness of our silicon wafer samples was \( t_{silicon} \approx 550 \, \mu m \), and that of the silane monolayer was \( t_{silane} \approx 1 \, nm \). The thermal conductivities of silicon and a silane monolayer are known to be \( k_{silicon} = 150 \, W/m\cdot K \) and \( k_{silane} = 0.2 \, W/m\cdot K \), respectively.\(^{58}\) For our experimental conditions, the typical velocity of vapor was \( v \sim D(p_w - p_{\infty})/(\rho \, R \, T_w) \sim 1 \, cm/s \), where \( D \) and \( \rho \) are the diffusivity and density of water vapor, \( R \) is the water vapor gas constant, \( T_w \) is the temperature of the substrate, \( p_w \) is the vapor pressure at the boundary layer, \( p_{\infty} \) is the saturation vapor pressure corresponding to the wall temperature, and \( \zeta \) is the boundary layer thickness.\(^{29}\) For the experimental conditions described above, where \( T_{w} = -10 \, ^\circ C \) and \( p_{\infty} = 776.3 \, Pa \), we obtain \( v \approx 3.9 \, cm/s \), which corresponds to a low heat flux of \( q = \rho \, v \, h_{\infty} \approx 0.56 \, kW/m^2 \). The surface coverage of droplets in dropwise condensation typically plateaus around 65%, such that the average heat flux flowing through the condensate can be estimated as \( q_{\delta} \approx 0.87 \, kW/m^2 \). The amount of heat flux flowing through each droplet can be estimated as \( Q_{d} = q_{\delta} \pi r^2 \sin^2 \theta \) (in Watts) where \( r \) is the radius of curvature and \( \theta \) is the contact angle of the drop. The temperature drop across the silicon wafer was estimated to be \( \Delta T_{silicon} = Q_{d}\,silicon/(\pi\,r_{silicon}^2 \sin \theta) \approx 0.003 \, ^\circ C \) and the temperature drop across the silane coating was \( \Delta T_{silane} = Q_{d}\,silane/(\pi\,r_{silane}^2 \sin \theta) \approx 4.3 \times 10^{-6} \, ^\circ C \). Furthermore, the thermal loss due to conduction through a micrometric droplet \( r \approx 10 \, \mu m \) and \( \theta \approx 90^\circ \) was estimated as \( \Delta T_{cond} = Q_{d}/(4\,\pi\,r\,k_{water} \sin \theta) \approx 0.006 \, ^\circ C \). Therefore, because the thermal losses across the substrate, the coating, and the drop in our system are extremely small, we can assume the droplet temperature to be the same as the temperature at which the Peltier stage was set; that is, \( T_{d} \approx T_{w} \) for our experiments on the condensation dry zone, interdroplet ice bridging, and dry zones around a frozen droplet.

## RESULTS AND DISCUSSION

In the previous section, a model was developed to calculate the vapor pressure field surrounding nucleating or pre-existing water/ice droplets on a substrate. For a surface containing condensate droplets of varying sizes or for mixed-mode phase change systems where supercooled condensate and ice droplets coexist on a surface, this pressure field will contain localized (interdroplet) pressure gradients that can generate a variety of interesting phase-change phenomena. In this section, we contextualize our model to analyze how these pressure gradients control the behavior of various phenomena such as dry zones, ice bridging, and frost halos.

**Condensation Dry Zones.** As condensation grows on a substrate cooled beneath the dew point, vacant spaces form around nucleating droplets that remain dry (Figure 7a). In an all-liquid condensing system, these dry zones are driven solely by the difference in supersaturation degree (SSD) between droplets of disparate sizes. There exist some rigorous computational studies that have solved for the heat transfer coefficients and droplet growth by numerically solving the transport equations.\(^{40,41}\) Here, we show by simple scaling
arguments how we can estimate the dry zone length between droplets over a wide parameter space. Consider a mother droplet exhibiting a radius of curvature \( r_m = 10 \, \mu m \) and a temperature \( T_d \) at its liquid–vapor interface. Recall from the previous section that for low heat fluxes this temperature could be approximated by the wall temperature, \( T_d \approx T_w \), whereas for high heat fluxes the conductive losses would have to be considered. Because of its large radius of curvature, the vapor pressure over this mother droplet would be approximately saturated, \( p_d \approx p_{d,0} \) because the SSD is negligible for micrometer-sized droplets (eq 11 and Figure 5). Now consider a daughter droplet adjacent to the mother droplet that exhibits a smaller radius of curvature, \( r < r_m \), and therefore exhibits a larger vapor pressure, \( p_{d,0} > p_{a,0} \).

This in-plane pressure gradient between the daughter and mother droplet will facilitate the evaporation of the daughter droplet (Figure 7b).

\[
m_{12} \sim \frac{I_{12}}{A} \sim \frac{D}{RT_d} \frac{p_{a,0} - p_{d,0}}{\delta} A_{12} \tag{16}
\]

where \( m_{12} \) and \( I_{12} \) are the mass flow rate and mass flux of the evaporative vapor emanating from the daughter droplet, \( A_{12} \) is the in-plane projected area of the daughter droplet, \( D \) is the diffusivity of water vapor in air, \( R = 461.5 \, J/kgK \) is the gas constant of water vapor, and \( \delta \) is the edge-to-edge separation between the mother droplet and the daughter droplet.

However, such a daughter droplet in general is surrounded by multiple mother droplets and the total evaporative flux is a summation of all of the individual in-plane mass fluxes. Let \( n \) be the number of closest neighbors where \( \delta_1, \delta_2, \delta_3, ..., \delta_n \) represent the edge-to-edge distances of the mother droplets from the daughter droplet:

\[
\sum m_{12} \sim \frac{D}{RT_d} \frac{p_{a,0} - p_{d,0}}{\delta} \left( \frac{1}{\delta_1} + \frac{1}{\delta_2} + \frac{1}{\delta_3} + ... + \frac{1}{\delta_n} \right) A_{12}
\]

\[
= \frac{D}{RT_d} \frac{p_{a,0} - p_{d,0}}{\delta} \frac{n}{\delta} A_{12} \tag{17}
\]

where

\[
\frac{n}{\delta} = \left( \frac{1}{\delta_1} + \frac{1}{\delta_2} + \frac{1}{\delta_3} + ... + \frac{1}{\delta_n} \right)
\]

such that \( \delta \) is the harmonic mean of \( \delta_1, \delta_2, \delta_3, ..., \delta_n \). Note that we need to consider only those mother droplets that are the closest neighbors. Droplets that have a significantly larger value of \( \delta \) have negligible effect on the evaporative flux because the pressure gradient scales as \( \delta^{-1} \).

For a condensing surface such as this one, the ambient vapor pressure exceeds the saturated pressure of the daughter droplet (\( p_{a,0} > p_{d,0} \)), so the daughter droplet will also be growing as a result of the out-of-plane diffusion of water vapor toward the substrate.

\[
m_{12} \sim \frac{I_{12}}{A} \sim \frac{D}{RT_d} \frac{p_{a,0} - p_{d,0}}{\zeta} A_{12} \tag{18}
\]

where \( m_{12} \) and \( I_{12} \) now represent the influx of vapor into the condensing daughter droplet, \( A_{12} \) is the out-of-plane projected area of the daughter droplet, and \( \zeta \) is the thickness of the concentration boundary layer (Figure 7b).

How should we estimate the length of a dry zone around a mother droplet? By definition, any droplet that can nucleate within the dry zone must exhibit a net outflux of vapor (\( \sum m_{12} > m_{01} \)) such that the region would appear to remain dry from a microscopic point of view. Also by definition, droplets nucleating outside of the dry zone must be free to grow (\( \sum m_{12} < m_{01} \)). Therefore, the periphery of the dry zone must be defined as the critical distance (\( \delta_{\text{cr}} \)) from the mother droplets where the net in-plane outflux and out-of-plane influx are perfectly balanced (\( \sum m_{12} \sim m_{01} \)).

\[
\delta_{\text{cr}} = \frac{\delta_{\text{cr}}}{\zeta} \sim n \beta \frac{p_{a,0} - p_{d,0}}{p_{d,0} - p_{a,0}} \tag{19}
\]

where \( \beta = A_0/A_L \) is a geometric prefactor that takes into account the ratio of the in-plane and out-of-plane projected areas. Following a spherical cap approximation for a droplet,

\[
\beta = \left\{ \begin{array}{ll}
\sec^2 \theta \left( \frac{\theta}{\pi} - \frac{\sin 2\theta}{2\pi} \right), & \text{if } \theta < \frac{\pi}{2} \\
\theta + \frac{\sin 2\theta}{2\pi}, & \text{if } \theta > \frac{\pi}{2}
\end{array} \right. \tag{20}
\]

Note that this flux balance approach was first developed by Guadarrama-Cetina et al. to calculate the dry zone around a salty water droplet\(^\text{16}\) and very recently has been employed by Boreyko et al. to estimate the dry zone around liquid droplets and ice droplets for a narrow parameter space.\(^2\) However, the previous works had not accounted for the multidroplet effect (\( n \)) or the geometric factor (\( \beta \)). The value of \( \beta \) lies between 0 and 1, and for \( \theta = \pi/2, \beta = 1/2 \). Because \( \beta \) decreases as \( \theta \) decreases, this means that the dry zone length on a hydrophilic substrate should be substantially smaller than that on a hydrophobic substrate at the same temperature under ambient conditions. Also we see that as \( \theta \to 0, \beta \to 0 \), which implies a dry zone length of zero corresponding to filmwise condensation in the hydrophilic limit. The dry zone length increases if there are multiple nearest neighbors, which is expected because increasing the number of mother droplets is equivalent to increasing the number of humidity sinks in the system, which would increase the net evaporative flux.

We now apply eq 19 to a systematic variation of wall temperatures and sizes of daughter droplets to gain a breadth of understanding of dry zone behavior. Keeping \( \zeta \) on the left-hand side of eq 19 serves the dual purposes of nondimensionalizing the equation while also rendering the calculation valid for any possible value of \( \zeta \). For a purely diffusive system where convective effects are negligible, the concentration boundary layer thickness \( \zeta \) can be estimated to within an order of magnitude as

\[
\zeta \sim \left[ \frac{D_{\text{ch}}^{3/2}}{4 \pi \alpha g (T_\infty - T_w)} \right]^{1/3} \tag{21}
\]

where \( \zeta \sim L_s \alpha (T_\infty - T_w) \nu^2 \) is the hydrodynamic boundary layer, \( \alpha \) and \( \nu \) are the volumetric thermal expansion coefficient and kinematic viscosity of air, and \( L_s \) is the characteristic length scale of the condensing surface.\(^3\) For a typical surface of \( L_s \approx 8 \, \text{cm} \) (also as used in our experiment) and for \( (T_\infty - T_w) \) as high as \( 50 \, \text{°C} \), the concentration boundary layer thickness scales as \( \zeta \sim 1 \, \text{mm} \). Note that \( \zeta \) is independent of the externally imposed supersaturations and thus a constant in purely diffusive systems.
This analysis assumed that embryos are able to nucleate near the mother droplet in the first place such that a flux balance defines the dry zone. Immediately after nucleation, condensing droplets will quickly grow to exhibit a larger radius of curvature compared to freshly nucleating droplets; therefore, a dry zone should exist around every droplet growing on the surface. An interesting observation here is that immediately after a coalescence event occurs on a condensing surface, the interdroplet distance between the merged droplet and its neighbors tends to increase. Therefore, if the dry zones around neighboring droplets were initially overlapping to a small extent, a coalescence event is often capable of triggering fresh nucleation/growth events on the surface. In the first frame of Figure 7a, no droplets grow in the intermediate space between adjacent mother droplets, which means that the edge-to-edge separation between the mother droplets must be smaller than 2δ_co to promote overlapping dry zones. In the second frame, several pairs of mother droplets have coalesced, increasing their edge-to-edge separation beyond 2δ_co and promoting the nucleation and growth of fresh condensate.

On a multidroplet condensing surface, a daughter droplet can successfully grow only at a location where δ_{exp} ≥ δ_co. The daughter droplet in Figure 7a is successfully growing at a location that is δ_A = 12.3 μm, δ_B = 25.4 μm, δ_co = 26 μm, δ_P = 21.7 μm, and δ_E = 39.1 μm away from its nearest-neighbor mother droplets labeled A−E, respectively. This yields δ_{exp} = 21.7 μm. By using eq 19 with ζ ≈ 1 mm and considering an r = 100 nm daughter droplet, we obtain a theoretical dry zone length δ_v = 18.9 μm that explains why the daughter droplet is successfully growing just outside of this length scale. Note that even if we choose to exclude the farthest neighbor E from our calculations, because δ_E is more than three times the nearest-neighbor distance δ_P, we see that δ_{exp} ≥ δ_co holds. This is because for four droplets, δ_{exp} = 19.5 μm and the theoretical δ_co = 15.1 μm. This shows the robustness of our proposed model, which captures the effect of interacting pressure fields in a multidroplet system on dry zone lengths. However, the model is based on simple scaling arguments and more importantly on the continuum limit where fluxes are governed by eqs 16 and 18. A computational model in this regard could help shed more light on the noncontinuum transport effects on dry zones in the very early stages of nucleation when r ≈ 1−10 nm.

In Figure 7c, the length of the nondimensionalized dry zone, δ_{ff} = δ_co/ζ, exhibits a power-law slope of −1 as the daughter droplet increases in size beyond 100 nm. This reveals that droplets within the dry zone will evaporate at an accelerating rate as they disappear. In Figure 7d, δ_{ff} is plotted as a function of the substrate temperature when the radius of the daughter drop is fixed at r = 100 nm. For a given p_{sat}, the magnitude of δ_{ff} increases with wall temperature, which is logical given the exponential increase in vapor pressure with temperature, which serves to increase the interdroplet pressure gradient with respect to the out-of-plane gradient. It follows that δ_{ff} → ∞ as p_{sat} approaches the supersaturated vapor pressure at the interface of the daughter drop. Figure 7d also illustrates how for a fixed radius of the daughter drop, δ_{ff} decreases with increasing p_{sat} because of the out-of-plane pressure gradient becoming more dominant over the in-plane gradient.

Finally, we should mention that a second type of dry zone is also possible, in which nucleation itself is not possible as a result of the elevated pressure required for nucleation (p_{nuc}) relative to the saturation pressure of the large mother droplet (p_{sat}). Here, we focused on the flux dry zone because it has often been ignored in recent works that have exclusively considered the nucleation dry zone. Both dry zones are of course possible, with the outer perimeter of the absolute dry zone being defined by whichever is larger. A detailed analysis of the competition between nucleation dry zones and flux dry zones, particularly for r ≈ 1−10 nm droplets, is outside the scope of the present work and will be the primary focus of a future investigation.

Also note that in the present discussion as well as in the subsequent sections we do not consider the effects of noncondensable gases in the system. It is well known that noncondensable gas concentrates at the condensing surface, thereby increasing the vapor diffusion resistance and the condensation heat transfer coefficient. However, how exactly
that would influence dry zone lengths is a nontrivial problem and requires further investigation.

**Interdroplet Ice Bridging.** From this point onward, we analyze the more complex case of multiphase systems where supercooled liquid droplets and frozen ice droplets coexist on a subfreezing substrate. Recall that interdroplet ice bridging from frozen droplets to neighboring liquid droplets is the dominant mechanism for the condensation frosting of surfaces chilled beneath the dew point.7,8 Because of the depressed vapor pressure of ice relative to water, the water molecules growing an ice bridge are being harvested from the liquid droplet that the bridge is growing toward.

Whether an individual ice bridge is able to freeze its targeted droplet can be predicted by considering the limiting case of the bridge connecting to the liquid droplet just before it has completely evaporated.7 At this critical limit, the mass of the completed ice bridge, $m_{\text{bridge}}$, equals the mass of the liquid droplet being harvested, $m_{\text{l}}$. Also, under this limiting condition, the length of the ice bridge $L$ attains its maximum possible value $L_{\text{max}}$ which is equal to the distance between the edge of the frozen droplet and the center of the liquid droplet. We consider the case of a pair of identical droplets, one frozen and the other un frozen. The mass of the liquid droplet being harvested scales as $m_{\text{l}} \sim \rho d^3$, where $d$ is the initial (projected) diameter of the liquid droplet prior to harvesting. The mass of the ice bridge scales as $m_{\text{bridge}} \sim \rho L_{\text{max}} d^2$. Equating the required mass for a completed ice bridge with the mass of the liquid droplet being harvested therefore predicts that if $L_{\text{max}} < d$ then an ice bridge can connect to the liquid droplet being harvested and if $L_{\text{max}} > d$ then it cannot and the droplet completely evaporates (Figure 8a). This mass scaling is only a good approximation for a single-pair interaction of droplets that are approximately equal in size. Also, this model is valid only for droplets with large contact angles, but this restriction is appropriate given that interdroplet frost growth typically occurs on hydrophobic and superhydrophobic surfaces. On sufficiently hydrophobic surfaces, the supercooled condensate tends to grow as a uniform film of water, which freezes over all at once.62

Here, we focus on the former case of interdroplet frost growth where $L_{\text{max}} < d$.

How can the interdroplet pressure gradient be related to the growth rate of an ice bridge? Consider a liquid droplet adjacent to another droplet that has frozen over at some initial time $t_0 = 0$; the in-plane mass flux of the evaporating liquid droplet scales as

$$m_{\text{l},\parallel} \sim \frac{f_{\text{c},\parallel} A_{\parallel}}{D} \frac{p_{\text{l},\parallel} - p_{\text{eq},\parallel}}{\delta}$$

where $p_{\text{l},\parallel}$ is the saturation pressure of the (presumably micrometric) liquid droplet, $p_{\text{eq},\parallel}$ is the unknown vapor pressure adjacent to the interface of the ice droplet and growing ice bridge, $\delta$ is the edge-to-edge interdroplet separation, and $A_{\parallel}$ is the in-plane projected area of the liquid droplet, and it is presumed that the droplet temperatures are approximately equal to the wall temperature. The in-plane mass flux of vapor growing the ice bridge is

$$m_{\text{v,\parallel}} \sim \rho v_{\parallel} A_{\parallel}$$

where $v_{\parallel}$ is the in-plane growth rate of the bridge and $A_{\parallel}$ is the in-plane projected area of the frozen droplet. By conservation of mass, $m_{\text{v,\parallel}} \sim m_{\text{l,\parallel}}$. When the frozen droplet and (initial) liquid droplet are approximately the same size, equating eqs 22 and 23 yields the following characteristic velocity of ice bridge growth:

$$v_{\parallel} \sim \frac{D (p_{\text{l},\parallel} - p_{\text{eq},\parallel})}{\rho RT_{\text{w}} \delta}$$

(24)

Recall that the pressure differential $p_{\text{l},\parallel} - p_{\text{eq},\parallel}$ is a function of temperature, so eq 24 reveals that $v_{\parallel}$ should simply scale inversely with $\delta$ while also exhibiting a more analytically complex dependence on $T_{\text{w}}$. An interesting observation regarding eq 24 is that the partial pressure of water vapor in the ambient atmosphere ($p_{\text{eq},\parallel}$) does not appear to have any effect on the propagation speed of the ice bridge, which is logical given that the bridge is entirely fueled by the liquid droplet.7 However, note that extremely large values of $p_{\text{eq}}$ would serve to reduce the net evaporation rate of the liquid droplet being harvested by an ice droplet/bridge such that the rule in which bridging fails for $L_{\text{max}} > d$ may eventually break down.

The choice of time-independent $\delta$ as the length scale over which the pressure gradient acts during bridging merits a brief discussion. Although it is true that the absolute distance between the liquid and ice decreases over time during bridging, conservation of mass mandates that the vapor harvested from the liquid droplet is flowing toward the ice through a projected area of $d^2$. Consequently, the vast majority of vapor flows beyond the tapered tip of the ice bridge before depositing somewhere further down the ice bridge. Because this model is restricted to the scenario of short interdroplet distances where bridges are always successful ($L_{\text{max}} < d$), the majority of the vapor will therefore deposit somewhere very close to the base of the bridge near the original perimeter of the ice droplet such that the pressure gradient can be held as constant to within an order of magnitude. By extension, the constant pressure gradient in eq 24 necessitates that $v_{\parallel}$ is approximately constant over time for bridging between a given pair of isothermal droplets (i.e., for a fixed choice of $\delta$ and $T_{\text{w}}$). This can be represented as $v_{\parallel} = dx/dt$, where $v_{\parallel}$ is time-independent, $x(t)$ is the evolving length of the growing ice bridge with boundary condition $x(0) = 0$, and $x(t) = L$ at the point of connection at time $t = t$. The final length of a completed ice bridge relative to the interdroplet spacing can vary slightly, ranging from $L \rightarrow \delta$ for $L_{\text{max}} < d$ (where evaporation is negligible) up to $L \rightarrow L_{\text{max}}$ at the critical limit of $L_{\text{max}} \rightarrow d$.

Recall that it remains an open question as to whether the vapor pressure at the interface of growing frost is saturated or supersaturated. This issue is difficult to settle for the more conventional case of a macroscopic sheet of ice growing out of plane on a substrate because matching the experimentally measured growth rates with a theoretical model can be simultaneously accomplished by assigning a supersaturated vapor pressure to the model or by modifying the diffusion resistance factor, which is a function of the porosity/density of the ice sheet used in the model.63 Here, we will demonstrate that the phenomenon of interdroplet ice bridging can resolve this long-standing question of the vapor pressure required to grow ice.

Over the past several years, it has been repeatedly observed that ice droplets are able to grow ice bridges by siphoning water vapor from neighboring liquid droplets over a wide range of subfreezing surface temperatures, surface wettabilities, and ambient vapor pressures.27-11 It should be emphasized that the ambient water vapor is not contributing appreciably to the
growth of these interdroplet ice bridges because bridge growth is in-plane and exactly in the direction of the liquid droplet being harvested. Therefore, it can be asserted with extreme confidence that the vapor pressure around the ice droplets (and bridges) must be lower than the vapor pressure around the liquid droplets; otherwise, this source-sink behavior would be impossible. Previous reports have observed interdroplet ice bridging across populations of microscopic or even macroscopic condensate droplets, recall from Figure 5 that liquid droplets of this size exhibit a saturated vapor pressure. However, when using Na’s assumption of $I^* = 10^{25}$ to estimate the vapor pressure around growing frost, $p_{f,d} - p_{s,i}$ is negative for all temperatures $T_w > -15 \degree C$ (Figure 8b, solid line), which implies that interdroplet ice bridging is impossible above $-15 \degree C$. This is in contrast to the findings of Boreyko and Collier, where interdroplet ice bridging was readily observed at $T_w = -10 \degree C$.\textsuperscript{7}

Therefore, we now have experimental evidence that $I^* \sim 10^{25}$ is not a good assumption when considering nucleation on ice. To satisfy the criteria $p_{f,d} - p_{s,i} > 0$ at $T_w = -10 \degree C$, the lowest possible value of the embryo kinetics is $I_{s,0}^* \sim 10^{25}$ (dotted line in Figure 8b). This corresponds to a maximum possible SSD over ice of $SSD_{f,i} \approx 0.1$ at $T_w = -10 \degree C$. By referring to experimentally measured bridge growth rates ($v_{exp} = \frac{I^*}{\delta_{exp}}$), interdroplet spacings ($\delta_{exp}$), and wall temperatures ($T_{w,exp}$) previously obtained from Boreyko and Collier,\textsuperscript{7} the vapor pressure difference driving the growth of interdroplet frost growth can be estimated as

$$p_{f,d} - p_{s,i} = \frac{\delta_{exp}}{\rho R T_{w,exp}} v_{exp}$$  \hspace{1cm} (25)

At $T_w = -10 \degree C$, experimental measurements used in eq 25 predict a pressure differential of $p_{f,d} - p_{s,i} = 21.8$ Pa, corresponding to the experimentally obtained minimum bridge growth rate of $v = 0.4 \mu m/s$ for an average $\delta_{exp} = 9.8 \mu m$. This corresponds to $I^* \sim 10^{27}$ (Figure 8b, dashed and dotted line) and SSD $= 0.018$. For $I^* = 10^{29} m^{-2} s^{-1}$, it follows that $I_{s,0} = 10^{-190} m^{-2} s^{-1}$. Such a small value of $I_{s,0}$ means that the threshold rate at which embryos spontaneously nucleate is essentially zero. Correspondingly, for $I_{s,0} \rightarrow 0$, we have $p_{f,d} \rightarrow p_{s,i}$ such that the vapor pressure at the interface of the growing ice can be considered to be saturated for all intents and purposes (dashed line in Figure 8b). This is also consistent with our observation that for heterogeneous nucleation on a substrate, SSD $\rightarrow 0$ in the hydrophilic limit $\theta \rightarrow 0$ (Figure 3). Thus, we propose that the vapor pressure adjacent to growing frost is approximately saturated, in agreement with an extremely recent work that used laser confocal microscopy and differential interference contrast microscopy to observe that the equilibrium pressure of ice is indeed aligned with the saturation curve.\textsuperscript{33}

**Dry Zone around Frozen Droplets.** During condensation frosting, where ice bridges grow across a population of supercooled condensate, it is possible to observe individual ice bridges failing to connect for interdroplet distances beyond the threshold value ($L_{max} > d$). These local incidents of complete evaporation of the condensate serve to slightly retard the velocity of the global freeze front. However, it has been reported that bridging is typically successful for nearly all of the droplets on a hydrophobic surface.\textsuperscript{19,30} Even for a jumping-droplet superhydrophobic surface exhibiting maximal interdroplet separations,\textsuperscript{34} ice bridges are still able to propagate across roughly one-third of the droplets. Very recently, we demonstrated that interdroplet ice bridging can be completely suppressed when the freezing event occurs at an early point in the growth of condensation, particularly when using chemical patterns that maximize the interdroplet separations.\textsuperscript{35} In this scenario, all water droplets neighboring the piece of ice completely evaporate, leaving a stable dry zone around the ice analogous to the dry zone around liquid droplets.

Figure 9a shows an example of such a dry zone. Instead of using the chemical micropatterns and triggered freezing techniques from before,\textsuperscript{7} here a Peltier stage enclosed in a humidity chamber was employed. A dry zone around a single ice droplet is easily obtained by depositing a water droplet onto a smooth hydrophobic surface bonded to a Peltier stage, freezing the droplet by bringing the Peltier stage to a chilled temperature while keeping the chamber dry, and then increasing the humidity to allow supercooled condensation to form on the surface.

The plateau dry zone length around a frozen droplet, $\delta_{cr}$, can be predicted by balancing the fluxes of a liquid droplet at the border of the dry zone. This is analogous to the model used...
above for liquid dry zones. A daughter drop at the periphery of the dry zone is surrounded on one side by water drops and on the other side by a single frozen drop. With this configuration, the in-plane evaporative flux is caused by the difference in saturation pressures between water and ice (cf. Figure 1). For a growing ice droplet with vapor pressure \( p_{ad} \) and a liquid droplet of pressure \( p_{ad,l} \) the nondimensionalized dry zone length can be obtained:

\[
\delta^*_C = \frac{\delta_C}{\zeta} \sim \frac{p_{ad,l} - p_{ad,i}}{p_{ad,l} - p_{ad,d}}
\]

(26)

As always, note that \( p_{ad} \) will be supersaturated for nanometric droplets and saturated (\( p_{ad} \approx p_{ad,l} \)) for larger droplets (Figure 5). Inspired by the interdroplet ice bridging analysis performed in the previous section, we suggest that the vapor pressure around the ice droplet is approximately saturated, \( p_{ad,i} \approx p_{ad,l} (I^* \rightarrow \infty) \). However, here too we can test the validity of the assumption of supersaturated frost growth based on \( I^* \) values ranging from \( 10^{-24} \) to \( 10^{-27} \) (as used in heterogeneous nucleation) by comparing their predicted dry zone lengths with experiments.

In Figure 9a, the dry zone between the ice droplet and visible microscopic condensate is measured to be \( \delta_C = 354 \mu m \) for the experimental conditions of \( T_w = -12.5 \, ^\circ C \) and \( p_{ad} = 417.5 \, Pa \). Using eq 26 for \( \beta = 0.5 \) and saturated conditions about the ice droplet at \( T_w = -12.5 \, ^\circ C \), the experimentally observed dry zone length corresponds to a boundary layer thickness of \( \zeta = 4.3 \, mm \). This agrees with our theoretical estimation of \( \zeta \sim 1 \, mm \) (eq 21) to within its order of magnitude.\(^{2,6} \) For \( I^* = 10^{24} \), there should be no dry zone at all because \( p_{ad,i} > p_{ad,d} \). For \( I^* = 10^{27} \), the experimentally observed dry zone length of \( \delta_C = 354 \mu m \) corresponds to a boundary layer thickness of \( \zeta = 171.9 \, mm \), which is an implausible 2 orders of magnitude higher than the predicted \( \zeta \sim 1 \, mm \). This further supports our hypothesis that the vapor pressure at the interface of growing ice is not supersaturated to any appreciable extent.

Figure 9b depicts the dimensionless dry zone length as a function of wall temperature for a fixed value of \( p_{ad} \). The vapor pressure of the daughter droplet corresponds to \( r \sim 100 \, nm \) (Condensation Dry Zones section). The \( \delta^*_C \) variation with temperature shows a trend similar to that of the saturation pressure difference between water and ice as observed in Figure 1. This is because the low degree of supersaturation on the liquid droplet of \( r \sim 100 \, nm \) is not sufficient to change the nature of the inherent difference in the saturation pressures, though it does shift the peak closer to \( 0 \, ^\circ C \). In addition to depicting the dry zone lengths, Figure 9b can also be considered to be a phase map describing the behavior of the surface on either side of the dry zone calculated on the basis of the saturation vapor pressure of ice (red line). Condensate droplets located at some value \( \delta < \delta_C \) will evaporate, but droplets located at \( \delta > \delta_C \) will be free to grow. When \( I^* = 10^{27} \) or \( I^* = 10^{24} \) is chosen (black lines), the graph reveals that there should be no dry zone for \( T_w > -13.5 \, ^\circ C \) or \( T_w > -12 \, ^\circ C \), respectively. This is obviously incorrect, given the large dry zone experimentally observed at \( T_w = -12.5 \, ^\circ C \), providing more evidence for the saturated ice hypothesis.

Figure 9c depicts \( \delta^*_C \) as a function of \( p_{ad} \) for various values of \( T_w \). It is still assumed that the liquid droplet is of size \( r \sim 100 \, nm \) and the ice is assumed to be saturated, \( p_{ad,i} \approx p_{ad} \). As expected, drier ambient environments correspond to larger dry zones as the in-plane pressure gradient becomes more dominant. As mandated by eq 26, it can be seen that \( \delta^*_C \) exhibits asymptotic behavior as \( p_{ad} \rightarrow p_{ad,i} \). This asymptotic behavior of \( \delta^*_C \) occurs at higher values of \( p_{ad} \) for higher substrate temperatures as \( p_{ad} \) increases exponentially with temperature. In Figure 9b, we saw that for a given \( p_{ad} \) the same dry zone length can be observed for two different temperatures before and after the peak (around \( T_w \approx -7.5 \, ^\circ C \)). This is why we see the \( 0 \, ^\circ C \) curve in Figure 9c intersecting with the curves corresponding to \( -10, -20, \) and \( -30 \, ^\circ C \) at ambient pressures where the \( 0 \, ^\circ C \) curve exhibits the same dry zone lengths that they exhibit.

**Frost Halos.** For the isothermal case of all droplets exhibiting the same approximate temperature as the chilled substrate, it seems nearly universal that the vapor pressure of the ice droplets is lower than that of the supercooled liquid droplets. This leads to the ice bridging and dry zone behaviors that have already been discussed here. But is it possible to invert this pressure gradient? A keen observation by Jung et al. has revealed that \( p_i > p_l \) is indeed possible during the initial freezing of a supercooled droplet, causing vapor to be rapidly expelled from the freezing droplet and condense on the substrate around the droplet.\(^{20} \) Once the droplet has finished freezing, it grows bridges to freeze the surrounding ring of satellite condensation, hence the term frost halo.\(^{20,21} \) Here, we apply our vapor pressure model to the context of frost halos to
gain some fundamental insights regarding the phase space where the phenomenon can occur.

Inspired by the observations of the frost halo, Figure 10a depicts a droplet that has just finished the initial recalcitrant stage of freezing where a thin shell of ice surrounds the droplet. Because of the latent heat deposited during first-stage freezing, the temperature of the droplet rapidly increases from \( T_D \approx T_w \) up to \( T_c \approx 0 °C \). Note that the duration of time where \( T_c \approx 0 °C \) can range from fractions of a second to tens of seconds, depending on the thermal conductivity of the underlying substrate. This heat transfer time scale must be larger than the vapor diffusion time scale in order for the halo effect to be possible.20,65 As justifi ed above, let us assume that the vapor pressure around this recalcitrant droplet corresponds to the saturation pressure of ice: \( p_{i,o} \approx (p_{v,i})_{T=0 °C} = 611.2 \text{ Pa} \). Therefore, the nucleation of embryos on the substrate around the freezing droplet should be possible when

\[
p_{i,o} > p_{w,o} \exp \left[ \frac{\nu}{RT_w^2} \frac{4 \pi}{3 k T_w \ln \left( \frac{L}{T} \right)} (2 + m)(1 - m)^2 \right] \tag{27}
\]

where the right-hand side of the equation corresponds to the critical pressure \( p_{w,o} \) required for nucleation (cf. eq 10).

In Figure 10b, we show where \( p_{i,o} > p_{w,o} \) attains a positive value (thus fulfilling the criteria for nucleation) as a function of \( \theta \) for multiple values of \( T_w \). Both the condensation (blue lines) and desublimation (black lines) modes of nucleation are considered, where the preferred mode corresponds to whichever curve exhibits a lower value of \( p_{i,o} - p_{w,o} \) (and hence a larger value of \( p_{i,o} \)) for given values of \( \theta \) and \( T_w \). Figure 10b reveals that for a given surface temperature there exists a critical contact angle above which nucleation cannot occur; this critical \( \theta \) corresponds to where each curve intercepts the x axis. These findings suggest that the halo effect should be suppressed for sufficiently hydrophobic surfaces (aside from surface defects), particularly for wall temperatures approaching \( T_w \rightarrow 0 °C \). As a validation of our theoretical predictions, we compare our fi ndings with the experimental conditions where Jung et al. observed frost halos.20 In their experiments, \( T_w = -14.5 °C \) and \( \theta \approx 72° \). For a surface temperature of \( T_w = -14.5 °C \), our model predicts that the largest contact angle surface where the halo effect can be observed should correspond to \( 86° < \theta_{max} < 90° \) for \( 10^4 < I^* < 10^7 \). Therefore, their observation of halos forming for a surface wettability of \( \theta = 72° \) is in agreement with our model.

By calculating the critical wettability for every possible wall temperature, a complete phase map was constructed as shown in Figure 10c. The blue and black lines represent the critical \( T_w - \theta \) curves beneath which condensation and desublimation can occur, respectively. In other words, beneath these critical curves the \( p_{i,o} > p_{w,o} \) condition for nucleation is fulfi lled. To determine which mode of nucleation is favorable, the critical \( T_w - \theta \) curve from Figure 4b is added to the phase map (red lines), where the condensation mode is favored above the curve and desublimation is favored below. By considering these critical curves in conjunction with each other, the phase map can theoretically predict whether no halo, a condensation halo, or a desublimation halo should occur upon the freezing of a supercooled droplet. It should be noted that the experiments of Jung et al. were over a narrow parameter space that demonstrated only a condensation halo,20 so the prediction of a desublimation halo has yet to be experimentally validated.

## CONCLUSIONS

We have developed a comprehensive model to calculate the pressure field of water vapor over a substrate exhibiting condensation, ice, and/or frost, which has been used to make predictions and phase maps for phenomena including dry zones, interdroplet frost growth, and frost halos. Key fi ndings can be summarized as follows.

1. The supersaturation degree (SSD) required for nucleation on a substrate was calculated as a function of surface temperature and wettability. Although we agree with a previous report that SSD is always higher for desublimation than for condensation,25 by considering the SSD in conjunction with the difference in saturation pressure between water and ice we showed that desublimation can actually be the thermodynamically favorable mode of nucleation at sufficiently low surface temperatures and wettabilities. This is in contrast to previous reports that stated that condensation is always the favored mode of nucleation.

2. The SSD around pre-existing droplets can be calculated for liquid droplets using the Kelvin–Laplace equation and for frost by considering the free energy required to nucleate a disk-shaped embryo on top of the ice. Unlike with a dry substrate, the kinetics of embryo formation on ice are not known and therefore the extent of supersaturation required to grow frost has been a long-standing debate. Here, we used experimental measurements of interdroplet ice bridging, which are highly sensitive to vapor pressure, to demonstrate that the vapor pressure at the ice-vapor interface must be approximately saturated. This also suggests that desublimation on ice should always be the thermodynamically favorable mode of nucleation. Although the growing frost considered here was in the context of ice bridges, we expect that our fi nding of saturated vapor conditions should extend to more general cases such as macroscopic frost sheets.

3. Annular dry zones around droplets can materialize even for surfaces cooled well beneath the dew point. For condensation, these dry zones are due to the depressed (i.e., saturated) vapor pressure of larger pre-existing droplets with respect to the supersaturated pressure of smaller, recently nucleated droplets. Dry zones can also form between an ice droplet and the surrounding supercooled condensation as a result of the decreased saturation pressure of ice with respect to liquid water at the same temperature. The steady-state length of a dry zone was estimated by considering droplets at the perimeter of the dry zone, where the out-of-plane in fl ux of vapor from the ambient atmosphere matches the in-plane outfl ux of vapor toward the droplet acting as a humidity sink.

4. Interdroplet ice bridging between a frozen condensate and a neighboring liquid condensate has been known to be the primary mechanism of in-plane frost growth on nonwetting surfaces for several years,26 but a fundamental understanding of the bridging kinetics is lacking. Here, by using our pressure field model in conjunction with diffusive scaling arguments, we obtained an analytical expression for the effective growth velocity of ice bridging.

5. A phase map was created to model the recently reported frost halo effect,27 where the rapid increase in temperature and vapor pressure of a freezing droplet can illicit a ring of nucleation on the surrounding substrate. We fi nd that three regimes are possible depending on the temperature and
wettability of the substrate: no halo, a condensation halo, or a desublimation halo. To our knowledge, this is the first mention of a desublimation halo being possible, which we hope will inspire experimental validation.

It is now clear that dry zones, ice bridges, and frost halos are all governed by localized in-plane pressure gradients, such that these phenomena need to be simultaneously examined from both fundamental and experimental perspectives. Indeed, just as this fundamental study was inspired by recent experiments demonstrating these emerging phase-change phenomena, we hope that this model in turn will inspire the design of future experiments that can fully exploit these vapor pressure gradients to gain an unprecedented level of control over condensation and frost formation on surfaces.

ASSOCIATED CONTENT

Supporting Information

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Overview of the article’s nomenclature and eqs S1–S6 and Figures S1–S6 as mentioned in the text (PDF)

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