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METRICS FOR QUANTIFYING SURFACE WETTING EFFECTS ON VAPORIZATION PROCESSES AT NANOSTRUCTURED HYDROPHILIC SURFACES

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ABSTRACT

A static contact angle is most often used as a means of quantifying the wetting characteristics of the liquid phase in vaporization processes at a solid surface. This metric is often convenient to measure and intuitive in its interpretation, but when a surface is superhydrophilic, the resulting low contact angles are difficult to measure accurately from photographs of sessile droplet profiles or contact line regions. For droplets at ultra low contact angles, small changes of contact angle can produce very large changes in wetted surface area, which makes small uncertainties in contact angle result in large uncertainties in wetted area. For hydrophilic nanostructured surfaces, another disadvantage is that the relationship of the macroscopic (apparent) contact angle to the nanoscale interaction of the liquid and vapor contact line with the nanostructured surface is not always clear. In this study, a new wetting metric based on spreading characteristics of sessile droplets is proposed that can be easily measured for hydrophilic surfaces. This metric also has the advantage that it is a more direct and sensitive indicator of how a droplet spreads on the surface. The spread area directly impacts heat transfer interactions between the droplet and the surface, therefore affecting evaporation time. Consequently, a metric that more directly illustrates the spread area provides an indication of how the wetting will affect these mechanisms.

Use of the proposed new metric is explored in the context of evaporation and boiling applications with superhydrophilic surfaces. Characteristics of this metric are also compared to static contact angle and other choices of wetting metrics suggested in earlier studies, such as dynamic advancing and receding contact angles, and spreading coefficients. The effects of nanoscale structure and/or roughness on the proposed wetting metric are analyzed in detail. A model is developed that predicts the dependence of the proposed wetting parameter on intrinsic material wettability for rough, nano-structured surfaces. The model results demonstrate that the proposed metric is a more sensitive indicator of macroscopic wetting behavior than apparent contact angle when the surface is superhydrophilic. This characteristic of the proposed new metric is shown to have advantages over other wetting metrics in the specific case of superhydrophilic nanostructured surfaces. Application of the proposed wetting metric is demonstrated for some example nanostructured surfaces. The results of our study indicate that this proposed new metric can be particularly useful for characterizing the effects of variable wetting on vaporization processes on highly wetted nanostructured surfaces.

NOMENCLATURE

- N_W wetting number
- θ contact angle
- t_{ce} complete evaporation time
- A_{sl} solid liquid contact area
- h_{lv} latent heat of vaporization
- k_l conductivity of water
- *r* ratio of rough surface area to plane area
- θ_{app} apparent contact angle
- θ_E Young's angle

- ϕ_S fraction of surface that is planar solid
- θ_c critical contact angle for spontaneous spreading

Greek Letters

- σ surface tension
- ρ density

Subscripts

- *lv* liquid vapor interface
- *sl* solid liquid interface
- *sv* solid vapor interface

INTRODUCTION AND BACKGROUND

In recent years, there has been significant interest in the development of hydrophilic and superhydrophilic surfaces for the purpose of enhancing boiling and evaporation. These specialized surfaces show a distinct relation between high wetting characteristics and enhanced boiling and evaporation compared to uncoated surfaces [1]. While initial hydrophilic surface coatings were studied for silicon wafers, a variety of techniques are now used to to produced these surfaces on metals (like copper) that are commonly used for effective heat conduction and dissipation. These coating techniques range from laser etching to coatings of oxides as well as nanoparticles. For hydrophilic coatings, surfaces can become so wetting that they exhibit apparent contact angles of nearly zero. These same similar contact angle surfaces often exhibit a range of boiling characteristics.

Currently, it is difficult to correlate the change in performance to a difference in contact angle because the contact angle metric does not have enough sensitivity to differentiate between small changes in surface wettability in the superhydrophilic range. It is clear that there is a correlation, since previous studies have shown enhanced boiling characteristics for a range of hydrophilic surfaces. However, these studies often avoid the most highly wetting surfaces. Forrest [2] observed an increase in the critical heat flux and the boiling heat transfer coefficient for nanoparticle thin-film coatings with contact angles as low as 11°. Similarly, Padilla [3], related contact angles to the Leidenfrost temperature, where he showed that lower angles related to higher Leidenfrost transition temperatures. Both of their data sets have a number of surfaces that exhibit a range of critical heat flux and Leidenfrost temperatures, respectively, yet have virtually the same measured contact angle. Currently, contact angles are the most commonly used metric to quantify the wettability of surfaces. Yet, as surfaces become more advanced, it is important that the metric used is sensitive enough to measure minute differences in surface wettability, especially at low contact angles.

One alternative method of categorizing surfaces is with

receding and advancing contact angles, as discussed by Gao [4]. Gao explains contact angle hysteresis as the difference between receding and advancing contact angles as liquid is either removed or added from a droplet. This hysteresis affects water molecules at the three-phase contact line, which is of particular interest for hydrophilic surfaces that exhibit adhesion forces as fluid droplets are drawn into the nanoscale roughness at this contact line. The contact line and the dynamics associated with it are discussed in length in Gao, but a different thermodynamic approach can also be used.

A sessile droplet reaches equilibrium on a surface when its free surface energy is at a minimum. For this reason, researchers have developed methods to relate the relative roughness of a surface coating, to the dynamics of the contact line, and thus the formation of a droplet on a hydrophilic surface [5-11]. This thermodynamic metric, as well as advancing and receding contact angle analysis, run into the same issue as apparent contact angle measurement when surfaces are superhydrophilic. That is, the three phase contact line is difficult to image and accurately measure for surfaces that have angles below 1°. Another alternative method is quantifying wettability with spreading coefficients. The spreading coefficient calculates wetting based on a relation between surface energies, employing equations developed by Young and Dupré. However, the classical model for this metric still relies on an apparent contact angle measurement, which leads to the same occurring issue of calculating wetting for superhydrophilic surfaces without the ability to accurately measure contact angle.



FIGURE 1. Droplet on a surface with a pattern of small scale roughness, where droplet exhibits a Wenzel state of liquid fully penetrating the interstitial space between roughness elements [12].

Additional ways of studying the dynamics of a droplet on a hydrophilic surface involve an understanding of two key droplet formations known as the Wenzel and Cassie-Baxter states. These two formations, shown in Fig. 1 and Fig. 2, will be discussed in further detail as they relate to a fundamental thermodynamic model to predict the arrangement of droplets on an enhanced surface. This model goes beyond previous analysis with Young's model to derive the relationship between surface roughness and Young's contact angle.

In our study we will explore the advantages of an additional way of understanding the spread of sessile droplets on advanced



FIGURE 2. Droplet on a surface with a pattern of roughness, where the droplet exhibits a Cassie-Baxter state, where the interstitial space between the roughness elements is occupied by trapped vapor [13].

hydrophilic surfaces. By introducing a new wetting metric to accurately measure minute differences in surface wettability, we will set the stage for two analysis models. In the first model, we will develop a thermodynamic approach to determining evaporation time for droplets on a heated surface, taking into account droplet spreading on hydrophilic surfaces and applying this new wetting metric to see clear trends. This model will be compared to experimental droplet data collected by Padilla [3] using zinc oxide coated copper surfaces.

For the second model, we will advance upon an already developed thermodynamic approach to determining the droplet morphology on a solid hydrophilic surface. We explore different previously discussed droplet geometries [5–11] and relate them to the roughness of the substrate surface. By applying our proposed wetting metric to these different geometry models, we can effectively eliminate the need for contact angle measurements, a clear advantage of using this highly sensitive metric for understanding of the underlying forces of droplet formation for hydrophilic surfaces.

These two models expand the understanding of droplet spreading and evaporation, which can be further exploited for designing hydrophilic enhanced surfaces with specific heat transfer goals.

A PROPOSED WETTING METRIC

While previous wettability measurements have certain desirable characteristics, such as ease of measurement, most do not allow for complete departure from apparent contact angle measurements for superhydrophilic surfaces. So rather than developing another metric based on contact angle, we propose one that uses the wetted footprint area of a droplet on a surface to quantify wettability. The wetting number, N_W , that we propose in Eq. 1 is a dimensionless ratio relating the wetted footprint area of a fixed volume droplet to that of an equal volume droplet with 90° contact angle:

$$N_W = \frac{A_{sl}}{A_{sl,90}} \tag{1}$$

If the droplet of interest is a spherical cap, it can easily be shown that geometry dictates that this ratio is the following Eq. 2, relating the droplets contact angle:

$$N_{\rm W} = \frac{2^{2/3}(1 - \cos^2\theta)}{(2 - 3\cos\theta + \cos^3\theta)^{2/3}}$$
(2)

Simply by taking aerial photographs of the sessile droplet normal to the surface on which it rests, the wetting number can be directly calculated. These projected area images can be analyzed to determine contact footprint area, and from that the value of the wetting number can be determined. For hydrophilic surfaces, N_W will always be greater than one, while for hydrophobic it will be less than one. The angle form of Eq. 2 makes an assumption of the spherical cap model. This is an idealization for a liquid droplet on a solid surface, which can be used to calculate the contact angle based on a known spread area and vice-versa. This method is widely accepted and was used by Padilla [3] for the contact angle calculations later discussed in Fig. 4. To better visualize the unique benefit of the wetting number for low contact angles, a range of contact angles from 0° to 180° were plotted in Fig. 3 with their corresponding wetting numbers.



FIGURE 3. Semi-log plot of the wetting number as a function of apparent contact angle for spherical cap droplet.

As the contact angle approaches zero, a spherical cap model predicts that the footprint of a droplet on the surface will become increasingly large. So, as the contact angle approaches zero, a small change in contact angle produces an increasingly large change in droplet footprint area. Changes in the wetting number, defined here, thus reflect more accurately the changes in wetted area for a droplet on a highly wetted surface. This increases sensitivity for surface types that consistently produce nearzero contact angles. Unlike small contact angle measurements, which require a high performance camera, enhanced lighting, and careful calibration, and still can have a high degree of inaccuracy, the wetted area for a droplet on a surface can be easily measured to a great degree of accuracy with a camera and simple, accessible imaging software. For this study, a free image processing program called ImageJ was used to process the projected wetted area of droplets on nanostructured surfaces. The accuracy of this method depends on the quality of the photo, but even basic cameras have a high enough pixel count for ImageJ to effectively eliminate any measurement uncertainty and calculate wetted area out to the 4th decimal place. In a similar vein, our experiments measurement show that technique is repeatable under circumstances where the droplet is being deposited on a fully desorbed surface. With any advanced hydrophilic surfaces it is very easy for small particles to adsorb to the surface even when using deionized water and careful experimental environment. We have seen that these particles as well as residual water within the nanostructured surface will lead to inconsistent area measurements. However, when each droplet spread area measurement is taken after a heated desorption of the surface, the wetted area measurement is consistent.

With the area measurements that are taken, the wetting number can be calculated and this can be applied to heat transfer tests. The integration of a wetted area, rather than a contact angle, takes into account the physical contact between the liquid and solid and this has advantages when working with evaporation and heat transfer, it is key to take into account this contact area, so it is logical that a wetting metric be based on this footprint. As droplets spread out very thin on heated surfaces, evaporation is enhanced by increased surface contact as well as the potential development of thin film evaporation, which leads to effective cooling and can be important in field of electronics cooling. This correlation between contact surface area and enhanced heat transfer is at the heart of this new wetting number, and therefore allows for particular application in boiling and evaporation. Especially for superhydrophilic surfaces, Fig. 3 shows how a small contact angle change can lead to dramatic changes in wetting number.

In Fig. 4 and Fig. 5, data was taken from sources that were previously summarized by Padilla [3]. Padilla's Leidenfrost data summary includes a review of ZnO hydrophilic surfaces, silicon dioxide enhanced surfaces, and stainless steel enhanced surfaces, all of which have contact angles below 20°. In Fig. 4, the Leidenfrost transition temperature is plotted against the individual surface contact angles. Leidenfrost points range from 270 to 450°C, and most of this range is for contact angles reported to be well below 3°. As previously discussed, achieving accuracy for contact angle measurements for such highly wetting surfaces is difficult and there is no clear trend from the bundle of points on the left-most part of Fig. 4. However, in Fig. 5, when the same data is plotted against the wetting number, the lower contact angles are more sensitively represented with wetting numbers spreading the points out.



FIGURE 4. Leidenfrost temperature variation for a range of surfaces and contact angles. Data shown are from multiple sources summarized by Padilla [3].



FIGURE 5. Leidenfrost temperature variation with N_W . Data shown are from multiple sources summarized by Padilla [3]. Error bars represent a contact angle measurement error of $+/-0.05^{\circ}$

For Fig. 5, the lowest contact angle surfaces are shown on the right hand side. Although five of the data points in Fig. 5 reported measured contact angles of zero, they were calculated as 0.1 when plugged into Eq. 2. The error bars on these five data points show how a very small error of only 0.05° could result in dramatic change in the wetting number. This shift would change the shape of the graph and emphasizes the importance in measuring the wetting number directly through area measurements, which remove the risk of a small error having a large effect on the wetting number. Another clear change from Fig. 4 to Fig. 5 can be seen by looking specifically at the square data points in Fig. 5. They are much more spread out in Fig. 5 than they were in Fig. 4. The application of this wetting number allows the trends in the change of Leidenfrost temperature with changing surface wetting to be seen more clearly, despite some scatter in the data.

If the experiments for the data shown in Fig. 5 were collected as areas rather than contact angles (allowing direct use of Eq. 1 rather than Eq. 2) it is possible that there would be a more robust, visible trend. Right now, the five contact angle measurements of zero have a wide range of Leidenfrost temperatures, but perhaps with a more accurate measure of the wettability, the wetting number could reveal a difference in wettability between those data points.

Determination of the droplet footprint area from a digital photograph can be easily done with high precision, whereas measurement of a very low ($< 5^{\circ}$) contact angle is more difficult to do accurately. The increased precision in the footprint area allows for more than just creating relations between key boiling points like Leidenfrost transition and critical heat flux. It can also be a metric to establish a link between evaporation heat transfer and wetting in a droplet evaporation model.

DROPLET EVAPORATION MODEL

A simplistic model is proposed here to calculate the time for complete evaporation of a droplet on heated surface as a function of the wetting number. An energy balance was developed equating the rate of latent heat consumed as the droplet evaporates and shrinks, to the heat conducted from the solid surface to the droplet liquid-vapor interface. This was used to derive Eq. 3, where δ_h is the mean thickness of the droplet during the evaporation process.

$$\rho_l h_{l\nu} \frac{d}{dt} (V_l) = -\frac{k_l A_{sl} \Delta T}{\bar{\delta}_h} \tag{3}$$

Here, we postulate that the average, or mean, thickness for computing conduction heat transfer will be proportional to droplet volume, and inversely proportional to droplet footprint area, at any point in time. Assuming this, we modify the relation in Eq. 3 by replacing δ_h with $\gamma V_l / A_{sl}$. Where γ is an first order constant. This volume over contact area modification is consistent with shape factor treatment for conduction in bodies with complex geometries. Rearranging the resulting equation after substitution, we arrive at Eq. 4 which can be integrated from initial wetted area to time dependent wetted area.

$$\frac{dA_{sl}}{dt} = -\frac{2k_l\Delta T}{3\gamma\Gamma^2\rho_l h_{l\nu}} \qquad \Gamma = \frac{2-3\cos\theta + \cos^3\theta}{2\pi^{1/2}sin^3\theta} \quad (4)$$

When the value of A_{sl} (the final wetting area), is set to zero, then evaporation is complete. Taking this into account, we rearrange the equations and obtain the following relation for evaporation time as a function of the wetting number, shown in Eq. 5.

$$t_{ce} = \gamma \frac{A_{sl,0}}{N_w^3} \left[\left(\frac{2}{3\pi} \right) \left(\frac{\rho_l h_{lv}}{k_l \Delta T} \right) \right]$$
(5)

The benefit of a model like this is that we show how an accurate understanding of the wetting number, and thus surface morphology and wetting characteristics, allows one to predict quite accurately the evaporation time of a single droplet on a surface. We do make an assumption for this model by idealizing that the droplet's geometry is always a spherical cap, and that the contact angle (and thus the wetting number) remain constant throughout evaporation. For conditions at which the droplet geometry is close to a spherical cap, we expect a value of $\gamma \cong 1$ would apply. If the geometry deviates from the spherical cap model, due to distortion by gravity forces, for example, a value of $\gamma = 1$ may no longer match experiments and can be adjusted accordingly to develop stronger models for a specific system. Additionally, bubble nucleation is not active in this model, so the wall superheats to be used in this should be low enough that there is no nucleation. Based on the droplet evaporation data collected by Padilla [3], with ZnO surfaces, an evaporation model, with $\gamma = 1$, was used to create the data comparison shown in Fig. 6, with experimental evaporation times on the vertical and calculated times using the model on the horizontal axis.

A dashed linear trend line with a slope of approximately one can be observed in Fig. 6. Droplets on a surface with a 20° superheat on the lower left side of Fig. 6 are very close to the trend line, while droplets with a lower superheat of 10° are somewhat linear, but have longer experimental evaporation times than the model predicts. This could be fixed with an adjustment of γ to accommodate a better model for different superheats. In general, though, this graph provides confirmation of this model and the possibility of applying it to other types of hydrophilic surfaces and possibly different droplet liquids, as well as droplet size. It is noteworthy that the model predicts a very strong dependence between evaporation time and this wetting parameter, making it a very sensitive indicator of the impact that surface wetting will have on the droplet evaporation rate. This is particularly apparent when the surface is highly wetting and the wetting number value is large (see Fig. 3).

SURFACE ROUGHNESS MODEL

Another application of the wetting number is in creating a better relation of surface roughness to the droplet distribution on a given surface. This could allow for more precisely engineered



FIGURE 6. Droplet evaporation times for droplet sizes of 2.5, 3.0, and 3.9mm, and superheats of $\Delta T = 10$ and 20°C. Experimental evaporation times compared to model evaporation times.

surface designs; adjusting particle density, height, surface area, and materials in order to focus in on key characteristics that can be exploited to develop a high performance surface. One of the key ways of apply the wetting number to surface morphology is through a surface roughness metric that has already been discussed and developed for Wenzel [12] and Cassie-Baxter [13] surfaces, like those shown in Fig. 1 and Fig. 2. This metric, briefly outlined and expanded upon in [5–11], allows for a better understanding of the correlation between the roughness of a surface and the contact angle and thus, the wetting number. This requires a differentiation between apparent contact angles which can be measured using imaging software and inherent or equilibrium contact angles, which are calculated using Young's formula, Eq. 6. Young's formula for the equilibrium contact angle in Eq. 6 relates the surface tension of the fluid with that of the surrounding vapor and solid surface to determine an inherent contact angle.

$$\cos\theta_E = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \tag{6}$$

The apparent contact angle, θ_{app} , which is the measured angle, can be related to Eq. 6 using a Gibb's free energy calculation that relates contact line displacement to a differential change in total free energy for a liquid completely wetting a surface, a Wenzel state. Since equilibrium for a droplet on a hard surface corresponds to a minimum free energy, the contact line for a droplet on a surface at equilibrium will correspond to a differential energy change of zero for Eq. 7.

$$dG = 0 = r(\sigma_{sv} - \sigma_{sl})dz + \sigma_{lv}dz\cos\theta_{app}$$
(7)

When simplified, in Eq. 8, the cosine of the apparent contact angle, θ_{app} , is related to the effective contact angle through a factor of *r*, which is a ratio of the rough surface area of a specialized coating to the plane (or footprint) area of the surface on a macro scale (Eq. 9).

$$\cos\theta_{app} = r\cos\theta_E \tag{8}$$

$$r = \frac{\text{actual surface area}}{\text{apparent (footprint) area}}$$
(9)

This value for r can be measured or approximated for a wide variety of rough surfaces and will change depending on the density and size of roughness elements for a given surface.

This relation of the apparent to the intrinsic surface contact angle is applicable to the Wenzel droplet model where all the interstitial spaces between roughness elements are filled with the liquid, as shown in Fig. 1. As such, we can say that for hydrophilic situations, in which $\theta_E < 90^\circ$ and $\theta_{app} < \theta_E$, increasing roughness (increasing r) will cause the surface to be more wetting. The opposite is true for when $\theta_E > 90^\circ$ and $\theta_{app} >$ θ_E . This model assumes that the intrinsic contact angle, θ_E , for a surface is consistent throughout and can be applied readily to surfaces of a consistent material. However, the enhanced surface coatings found to exhibit hydrophilic characteristics are often non-homogeneous (with a different material for both substrate and coating) and therefore must be evaluated slightly differently. The previous equations must be modified to accommodate both a substrate material's intrinsic angle, θ_E , as well as that of the surface coating.



FIGURE 7. A penetrating liquid film that spreads and fills the interstitial spaces between roughness elements, representing a non-homogeneous surface.

Here we can modify Eq. 8 to represent a sort of composite surface, where the droplet is in contact with both the solid planar region as well as planar regions of liquid, which are fully wetting. This is shown in Fig. 7, where the liquid film fully penetrates the rough non-homogeneous surface, while the top planar surface is a solid. Thus, a droplet on top is in contact with a non-homogeneous planar surface with areas of water and areas of solid. For this, we define ϕ_S as the fraction of the overall surface which is the planar solid, with an intrinsic contact angle of θ_E . The fraction of the surface that is liquid is $1 - \phi_S$, where the contact angle of water to water is effectively zero. Thus, we develop an equation similar to analysis published by Ishino [8–10], where $\cos \theta_E = 1$ for the region of water to water contact.

$$\cos \theta_{app} = \phi_S \cos \theta_E + (1 - \phi_S) \tag{10}$$

It has been shown [5–11], that Eq. 10 can be used to develop a model for spontaneous spreading within the surface matrix. This phenomenon is observable in Fig. 8 and Fig. 9 as both a cross sectional view as well as an experimental photograph of a water droplet deposited on an unheated nanostructured ZnO coating copper surface (from Padilla [14]).



FIGURE 8. A cross sectional view of a sessile droplet on a solid surface where certain intrinsic conditions lead to spontaneous spreading.

This hierarchical contact line, often described as a fried egg effect, can be explained through a similar free energy thermodynamic analysis developed from Eq. 7. In Eq. 11, when dG < 0, it is thermodynamically favorable to have spontaneous spreading, as seen in Fig. 8.

$$dG = (r - \phi_S)(\sigma_{sl} - \sigma_{sv})dz + (1 - \phi_S)\sigma_{lv}dz \qquad (11)$$

In Eq. 11, we define *r* as the ratio of rough surface area to footprint area of the surface in the plane corresponding to the mean surface position. For ϕ_S we define a ratio of dry surface area to the footprint area. The first term on the right side represents the energy to convert solid-vapor interface to a solidliquid interface, while the second term is the energy to create the liquid-vapor free surface at the top of the film between locations where a dry solid surface existed prior to spreading. This is directly related to the fully wetted surface and the dry surface in Fig. 7



FIGURE 9. The spontaneous spreading (fried egg) effect seen from a top down view photograph from experiments on a ZnO hydrophilic surface (Note: the white region in the photograph is reflected light and not some surface effect).

Spontaneous spreading is thermodynamically favored when dG < 0, so by applying this condition for spontaneous spreading, we can rearrange Eq. 11 to the form Eq. 12

$$\frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} > \frac{1 - \phi_S}{r - \phi_S} \tag{12}$$

Which can be translated into Eq. 13 using Young's angle equation.

$$\cos\theta_c = \frac{1 - \phi_S}{r - \phi_S} \tag{13}$$

Here, we define a critical angle, θ_C as the condition for spontaneous spreading. When

$$\cos \theta_E > \cos \theta_c$$

or, equivalently when

 $\theta_E < \theta_C$,

the droplet will spread out through the matrix. From this, we can consider when the intrinsic angle of θ_E is below the critical value of θ_C . The liquid will penetrate the rough surface matrix and give rise to the hydrophilic spreading behavior shown in Fig. 8. Since θ_C is a function of *r*, then when a surface is more rough and *r* is higher, there is more flexibility in the value of θ_E for spontaneous spreading. Because if this, we can control the type of spreading that occurs through choice of the roughness as well as the base



FIGURE 10. Regimes of apparent contact angle θ_{app} variation with intrinsic contact angle θ_E .

materials that define θ_E . One way of depicting this relationship between $\cos \theta_{app}$ and $\cos \theta_E$ is through a plot, shown in Fig. 10.

Figure 10 depicts the relation for two hydrophilic regimes of droplet liquid distribution on a coated surface. Note that the critical angle creates a knee in the graph showing a definitive change in the relationship between roughness and contact angle for a hydrophilic surface that has an intrinsic equilibrium contact angle that is either higher or lower than the critical angle defined in Eq. 13. Figure 10 represents hydrophilic surfaces for which $\cos \theta_{app}$ and $\cos \theta_E$ are greater than zero. For the region with $\cos \theta_E < \cos \theta_c$ there is no spontaneous spreading, and we can apply the relation from Eq. 8 for a Wenzel state droplet. For $\cos \theta_E > \cos \theta_c$ or when the intrinsic contact angle, θ_E , is less than the critical contact angle, θ_C , spontaneous spreading arises and we apply Eq. 10. For changes in roughness, the location of the critical angle changes, thus changing the graph and adjusting the range of θ_E values in which spontaneous spreading is observed. Therefore, by changing the roughness value of r, we can adjust the spontaneous spreading, and change the types of materials that can be used in a system to cause rise in spontaneous spreading.

At some point, though, as critical angles get higher and apparent contact angles get low, we encounter similar issues to the plots seen in earlier analysis of superhydrophilic surfaces in Fig. 4, where highly wetting angles will all bunch together in one part of the graph. In this case, superhydrophilic surfaces will fall on the very upper right regions of Fig. 10, and will ultimately be crowded and difficult to determine trends from. For this reason, it is optimal to again apply the wetting number to this developed method of analyzing surfaces and provide a more accurate picture of the spread of surface types and the effects of surface roughness on these droplet regimes.

Applying Thermodynamic Analysis to Experimental Data

Previously collected data from sessile droplets on three different ZnO hydrophilic surfaces is shown in Table 1. These three nanoparticle coated surfaces were grown using hydrothermal synthesis on a copper substrate. Different characteristics of nanostructured surfaces that were grown for 4, 10, and 24 hours were averaged and shown in the Table 1. The information for surface area was taken from SEM images of surfaces after growth and desorption.

Surface Type	Average Pillar Height [μm]	Footprint Area [µ ²]	Total Pillar Surface Area [μ^2]	r	φs
4 hour	1.7	102.66	113.46	1.1	0.074
10 hour	2.66	38.15	138.18	3.62	0.14
24 hour	3.25	115.58	523.85	4.53	0.29

TABLE 1.
 ZnO hydrophilic surface morphology.

The average apparent contact angle associated with each surface is shown in Table 2. This table also includes whether or not the droplet had a hierarchical contact angle or "fried egg" morphology.

TABLE 2. Contact angles for ZnO surface.

Surface Type	Average Contact Angle, θ_{app}	Dual Contact Angle
4 hour	12°	No
10 hour	1.0°	Yes*
24 hour	12.4°	Yes

Of these three surfaces, the 10 hour surface only exhibited a dual contact angle for the first and second desorption, but not after experiments. One possible explanation for this is that the roughness was affected after the experiment resulting in a change in the droplet morphology.

Based on the model created, we would expect that for the 4 hour growth surface, which did not exhibit fried egg morphology, would have a $\cos \theta_E < \cos \theta_C$. From the regimes shown in Fig. 10, $\cos \theta_{app}$ should be calculated using Eq. 8 and is 0.889, while $\cos \theta_C$ is calculated using Eq. 13 and is 0.903. Thus we conclude

that, in fact, the theoretical calculation is consistent with the no fried egg morphology. This can be shown in a plot similar to Fig. 10, where Fig. 11 has a very large range of $\cos \theta_E$ and there is no fried egg morphology. Our surface, as indicated, it falls on the upper range of this limit of no spontaneous spreading.



FIGURE 11. Regimes of apparent contact angle θ_{app} variation with intrinsic contact angle θ_E for the 4 hour ZnO nanostructured surface.

A similar process can be done for the 24 hour ZnO nanostructured surface, shown in Fig. 12



FIGURE 12. Regimes of apparent contact angle θ_{app} variation with intrinsic contact angle θ_E for the 24 hour ZnO nanostructured surface.

For the 10 hour surface, the value of $\cos \theta_E = 0.276$ and $\cos \theta_C = 0.247$, which are extremely close, meaning that a small change in roughness, and therefore $\cos \theta_C$ could result in a shift from fried egg morphology to a typical Wenzel drop geometry without spreading. It makes sense, then that this 10 hour surface, with a small amount of degradation over time would have different spreading morphology, as indicated above.

SURFACE ROUGHNESS AND THE WETTING NUMBER

This droplet spreading model is a framework that can be used to develop advanced surfaces to exhibit specific droplet characteristics, however, it is flawed in that it still relies on the contact angle which is inaccurate and difficult to measure for superhydrophilic surfaces. In order to use this model to full advantage, we can apply the wetting number, N_W , as defined in Eq.1, to develop a robust guide for designing surfaces that can be fine tuned for precise droplet manipulation. Further, with the wetting number, this can be done to an incredibly high degree of accuracy, particularly for superhydrophilic surfaces. Taking the known ratio of the wetting number and applying the spherical cap assumption, we can develop equations for the apparent and intrinsic equilibrium wetting numbers, shown in Eq. 14 and Eq. 15.

$$N_{WE} = \frac{2^{2/3} (1 - \cos^2 \theta_E)}{(2 - 3\cos \theta_E + \cos^3 \theta_E)^{2/3}}$$
(14)

$$N_{W,app} = \frac{2^{2/3} (1 - \cos^2 \theta_{app})}{(2 - 3\cos \theta_{app} + \cos^3 \theta_{app})^{2/3}}$$
(15)

In a similar fashion to Fig. 10, 11 and 12, the apparent and intrinsic equilibrium wetting number can be plotted against each other to develop a better understanding of the relationship of roughness to the wetting number and droplet morphology. For Fig. 13 a range of equilibrium contact angles were plotted against the apparent wetting number for the 10 hour ZnO nanoparticle surface.



FIGURE 13. The relation of the apparent wetting number to a range of values for the cosine of the intrinsic equilibrium contact angle. The critical contact angle is labeled for the 10 hour ZnO nanoparticle surface($\phi_S = 0.14$, r = 3.62).

What is unique about Fig.13 is the clear knee in the graph where critical value of $\cos \theta$ is marked for the 10 hour ZnO hydrophilic surface. This is the definitive dividing line between spontaneous spreading and a simple Wenzel morphology. However, we are still relying on assumptions of spherical cap model and ultimately coming back to a contact angle measurement, which we've shown to be inaccurate for small angle measurements. Figure 14 shows a trend in the droplet morphology that is completely independent of contact angle measurements. This semi-log plot, which shows the data for a 4 hour ZnO surface, has the largest range of wetting number values in which there is no spontaneous spreading.



FIGURE 14. The relation of the apparent wetting number to a range of intrinsic equilibrium wetting numbers for the 4 hour nanoparticle surface ($\phi_S = 0.074$, r = 1.1).

Shown in Fig. 14, the area without spontaneous spreading is to the left of the marked critical wetting number, where the apparent contact angle remains steady for $N_{W,E,C} < 3.23$. Then, for the intrinsic or equilibrium wetting numbers greater than $N_{W,E,C}$, the measured apparent wetting number, calculated in Eq. 15, increases exponentially because of the effect of spontaneous spreading. A growing wetting number means that the droplet has an increasingly large wetted footprint area, which is consistent with the spontaneous spreading prediction for $N_{W,E} > N_{W,E,C}$. This framework can now be used to manipulate droplet morphology with different surface roughness. In this case, done completely independent of contact angle.

CONCLUDING REMARKS

This paper presents a new wetting number metric that is particularly useful for quantifying wettability of highly wetting surfaces. We introduce the wetting number, N_W , a nondimensional ratio that is calculated by measuring the wetting footprint of a sessile droplet on a given solid surface. This has the advantage of being generally much easier to do with precision than measuring extremely small contact angles from a sideview. We show that this wetting number is a more sensitive metric for highly wetting surfaces, which allows for a clearer definition of the trends in Leidenfrost temperatures with changing wetting conditions on superhydrophilic surfaces. We also demonstrate that formulating a droplet evaporation model in terms of this wetting number results in a predictable relation for evaporation time that directly indicates the strong dependence of evaporation time on wetting conditions, as quantified by this parameter. This wetting number can also be used in conjunction with previously developed models that evaluate the relation of apparent contact angle to the equilibrium or Young contact angle through a roughness parameter. By eliminating contact angle measurements from this model, and instead using the wetting number, experimental data confirms the existence of a critical angle that divides hydrophilic behavior into two categories: one with a single contact line, and the second with liquid spread through the coated surface as a penetrating film. We show that the wetting number is a more sensitive indicator of macroscopic wetting behavior, providing equations that dictate how spontaneous spreading can be effectively turned on or off, using inherent material qualities or changing the roughness of a hydrophilic coating. The advantage of this new wetting metric is its extreme sensitivity to small changes in wetting characteristics, allowing researchers to fine tune and develop more advanced hydrophilic surfaces that fit precise evaporation and droplet morphology requirements.

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REFERENCES

- Carey, V., 2002. "On the role of wetting in vaporization and condensation heat transfer". *Thermal Science and Engineering*, **10**(9), pp. 3–9.
- [2] Forrest, E., Williamson, E., Buonjiorno, J., Hu, L., Rubner, M., and Cohen, R., 2010. "Augmentation of nucleate boiling heat transfer an critical heat flux using nanoparticle thin-film coatings". *International Journal of Heat and Mass Transfer*, **53**(1-3), pp. 58–67.
- [3] Padilla, J., and Carey, V., 2014. "An experimental study of the leidenfrost transition for water on nanostructured superhydrophilic surfaces". In Proceedings of 15th International Heat Transfer Conference, p. 9581.

- [4] Gao, L., and McCarthy, T., 2006. "Contact angle hysteresis explained". *Journal of American Chemical Society*, 22, pp. 6234–6237.
- [5] Bormashenko, E., 2015. "Progress in understanding wetting transitions on rough surfaces". Adv. Colloid Interface Science, 222, pp. 93–103.
- [6] Quéré, D., 2008. "Wetting and roughness". Annual Rev. Mater. Res., 38, pp. 71–99.
- [7] Bico, J., Thiele, U., and Quéré, D., 2002. "Wetting of textured surfaces". *Colloids Surf A*, **68**, pp. 41–46.
- [8] Ishino, C., Okumura, K., and Quéré, D., 2004. "Wetting transitions on rough surfaces". *EuroPhys Letters*, 68, pp. 419–425.
- [9] Ishino, C., and Okumura, K., 2008. "Wetting transitions on textured hydrophilic surfaces". *Euro Phys J.E.*, 25, pp. 415–424.
- [10] Ishino, C., Reyssat, M., reyssat, E., Okumura, K., and Quéré, D., 2007. "Wicking within forests of micropillars". *EuroPhys Letters*, **79**, p. 56005.
- [11] Corbin, L., Denieul, E., Dressair, E., Ajdari, A., Roper, M., Ajdari, A., and Stone, H., 2007. "Imbibition by polygonal spreading on microdecorated surfaces". *Nature, Materials*, 6, pp. 661–64.
- [12] Wenzel, R., 1936. "Resistance of solid surfaces to wetting by water". *Ind. Eng. Chem*, **28**, pp. 988–994.
- [13] Cassie, A., and Baxter, S., 1944. "Wettability of porous surfaces". *Trans. Faraday Soc.*, **40**, p. 546.
- [14] Padilla, J., 2014. "Experimental study of water droplet vaporization on nanostructured surfaces". University of California Berkeley, PhD Dissertation.