

Droplet Evaporation Dynamics of Low Surface Tension Fluids Using the Steady Method

A. Alperen Günay,* Marisa Gnadt, Soumyadip Sett, Hamed Vahabi, Arun K. Kota, and Nenad Miljkovic*

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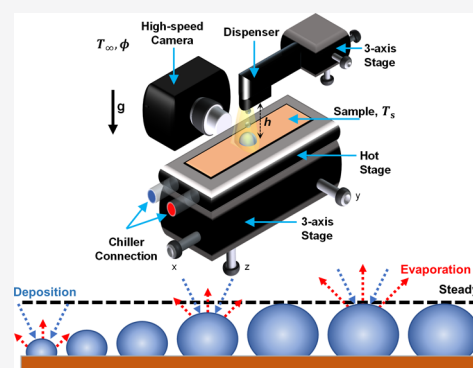
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ABSTRACT: Droplet evaporation governs many heat- and mass-transfer processes germane in nature and industry. In the past 3 centuries, transient techniques have been developed to characterize the evaporation of sessile droplets. These methods have difficulty in reconciling transient effects induced by the droplet shape and size changes during evaporation. Furthermore, investigation of evaporation of microdroplets residing on wetting substrates, or fluids having low surface tensions (<30 mN/m), is difficult to perform using established approaches. Here, we use the steady method to study the microdroplet evaporation dynamics of low surface tension liquids. We start by employing the steady method to benchmark with water droplets having base radii ($20 \leq R_b \leq 260$ μm), apparent advancing contact angle ($45^\circ \leq \theta_{a,\text{app}} \leq 162^\circ$), surface temperature ($30 < T_s < 60$ $^\circ\text{C}$), and relative humidity ($40\% < \phi < 60\%$). Following validation, evaporation of ethanol (≈ 22 mN/m), hexane (≈ 18 mN/m), and dodecane (≈ 25 mN/m) were studied for $90 \leq R_b \leq 400$ μm and $10 < T_s < 25$ $^\circ\text{C}$. We elucidate the mechanisms governing the observed behavior using heat and mass transport scaling analysis during evaporation, demonstrating our steady technique to be particularly advantageous for microdroplets, where Marangoni and buoyant forces are negligible. Our work not only elucidates the droplet evaporation mechanisms of low surface tension liquids but also demonstrates the steady method as a means to study phase change processes.



INTRODUCTION

Droplet evaporation governs several industrial processes such as liquid hydrocarbon combustion^{1–4} and phase change heat transfer.^{5–10} Because of its wide industrial implementation, researchers have studied the evaporation of droplets of different fluids including water,^{11–21} ethanol,^{22–27} hexane,^{10,28,29} and dodecane^{27,30} for more than a century. Droplet evaporation is typically characterized by the rate at which liquid is transformed into vapor. Many studies have been performed to investigate the evaporation rate of droplets residing on surfaces.^{7,17,31–36} These studies typically depend on measuring the temporal size changes of a droplet and are limited by the transient effects occurring outside and/or inside the droplet such as interfacial dynamics at the liquid–vapor interface and contact line motion.^{37–39} Furthermore, microscale droplet evaporation dynamics ($R < 500$ μm , where R is the droplet radius of curvature) are difficult to characterize because of the changing shape of the droplet as the contact line shrinks and the droplet approaches the size of wettability heterogeneity on the surface.^{40–42} In addition, most low surface tension liquids (<30 mN/m) exhibit low apparent receding contact angles ($\theta_R < 90^\circ$) on substrates. Studying evaporation of low surface tension droplets, which are typically volatile in ambient conditions,^{43,44} remains a challenge.

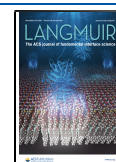
Recently, we developed a steady method to investigate droplet evaporation of water by feeding microscale droplets (≈ 20 μm in diameter) to a steady larger evaporating droplet.⁴⁵ By tuning the frequency of the dispensing microdroplets, the rate of evaporation was balanced with the rate of liquid addition, thereby maintaining a constant shape and size of the evaporating droplet. The evaporation rate was calculated from the volumetric flow rate of added liquid, eliminating spurious transient effects, and enabling the study of droplets having different sizes and shapes.

In this study, we employ this steady method to overcome the challenges facing low surface tension fluids by studying the evaporation of ethanol, hexane, and dodecane droplets having base radii $90 \leq R_b \leq 400$ μm and substrate temperatures $10 < T_s < 25$ $^\circ\text{C}$. We focus our work on a droplet size range where Marangoni and buoyant flows can be neglected, with droplet conduction and vapor-side mass-transfer governing evapora-

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tion. We first validated our method by studying water droplet evaporation at different substrate temperatures, substrate wettabilities, and droplet sizes to ensure that the results and trends are consistent with previous well-validated works. Following validation, we utilized the steady method to study the evaporation of low surface tension fluid droplets. Our results show that the rate of droplet evaporation in the presence of noncondensable gases (NCGs) increases linearly with increasing R_b because of the linear dependence of contact line length. Furthermore, we demonstrate that surface functionality (*i.e.*, nonwetting or wetting) becomes invariant during the evaporation of water droplets at elevated substrate temperatures ($T_s > 45\text{ }^\circ\text{C}$) because of the delicate balance formed between mass transfer at the droplet liquid–vapor interface and conduction heat transfer within the droplet. The outcomes of this work demonstrate the steady method as a powerful experimental platform for evaporation characterization of both microscale droplets and a variety of relevant working fluids.

EXPERIMENTAL METHODS

Surface Fabrication, Functionalization, and Characterization. For all evaporation experiments, we used functional surfaces having distinct wetting characteristics. Samples included polished silicon (Si) wafers and superhydrophobic microstructured copper oxide (CuO) surfaces functionalized with a hydrophobic self-assembled monolayer (SAM). For surface fabrication, functionalization, and characterization, please refer to Section S1 of the [Supporting Information](#) as well as previous work.⁴⁵

To enable the study of the effect of vanishing contact angle hysteresis, we used lubricant-infused surfaces (LISs) as well as hierarchically structured surfaces. Recent studies have shown fluorinated lubricants to be ideal for creating nonwetting surfaces applicable for low surface tension fluids.^{46,47} To fabricate the LIS surfaces, the fabricated superhydrophobic microstructured CuO surfaces^{48,49} functionalized with a hydrophobic SAM⁵⁰ were infused with a fluorinated lubricant Fomblin Y14/6 (Section S1, [Supporting Information](#)). Superhydrophobic hierarchical surfaces were fabricated through spray coating of a stainless steel substrate with fluorinated silica (F–SiO₂) particles.⁵¹ Fluorinated silica (F–SiO₂) particles were suspended in *n*-hexane solution and spray-coated on a polyurethane-coated stainless-steel surface. The surface was then allowed to dry at room temperature for a day. Subsequently, the substrate was rinsed in hexane and then deionized (DI) water to remove excess F–SiO₂ particles.

Experimental Procedure. The working fluids studied were DI water (CAS 7732-18-5, Sigma-Aldrich), ethanol (CAS 64-17-5, Sigma-Aldrich), hexane (CAS 110-54-3, Sigma-Aldrich), and dodecane (CAS 112-40-3, Sigma-Aldrich). [Table 1](#) summarizes the properties of the working fluids.

To study the effects of droplet size, surface temperature, relative humidity, and fluid volatility, we used six different substrates including Au-coated Si wafer (Si–Au), smooth Si wafer coated with a hydrophobic SAM (Si-HTMS), superhydrophobic CuO (CuO-HTMS), CuO LIS (F14/6), polished Cu (Cu), and a superhydrophobic hierarchical stainless-steel surface spray coated with fluorinated SiO₂ (FS) nanoparticles. The wetting characteristics of the substrates are summarized in [Table 2](#). All the samples were square slabs having 25 mm side lengths with 0.5 mm thickness. Droplets having low apparent advancing contact angles approaching complete wetting ($<10^\circ$) were not studied here because of the requirement for wide angle imaging techniques.

The experimental setup is described in detail in previous work.⁴⁵ Briefly, the experiment consists of a high-speed camera (FASTCAM SA2, Photron) integrated with a piezoelectric micro-goniometer (MCA-3, Kyowa Interface Science, [Figure 1](#)).⁴⁵ The rate of microdroplet addition (f) from the piezoelectric dispenser is governed

Table 1. Physical Properties of the Working Fluids at STP ($T = 297\text{ K}$, $\phi = 50\%$, $P = 1\text{ atm}$)

variable	symbol	water	ethanol	hexane	dodecane
liquid density [kg/m ³]	ρ_l	998	789	655	750
vapor density [kg/m ³]	ρ_v	0.76	1.91	3.564	7.11
liquid dynamic viscosity [mPa·s]	μ_l	0.9	1.1	0.3	1.34
vapor dynamic viscosity [mPa·s]	μ_v	0.009	0.009	0.006	0.005
molecular weight [kg/kmol]	M	18.015	46.07	86.177	170.33
liquid–vapor surface tension [mN/m]	Γ	72	22	18.43	25.35
boiling point [°C]	T_b	100	78.4	68.7	216
vapor pressure [kPa]	P_∞	2.99	7.39	19.31	0.014
latent heat of vaporization [kJ/kg]	h_{fg}	2540	913.61	367	362.83
liquid thermal conductivity [W/(m·K)]	k_l	0.61	0.167	0.13	0.14
liquid specific heat [J/(kg·K)]	$C_{p,l}$	4184	2460	2260	2210
vapor specific heat [J/(kg·K)]	$C_{p,v}$	1996	1602	1655	1750
diffusion coefficient of vapor in air [mm ² /s]	D_{va}	25.3	12	8	4.8
Lewis number	Le	1.15	1.9	1.5	3.5

Table 2. Wetting Characteristics of the Studied Fluids^a

sample	θ_a [°]	θ_r [°]	$\Delta\theta$ [°]
Water			
Si–Au	45.1 ± 5.2	0	45.1 ± 5.2
Cu ^X	85.0 ± 1.9	35.1 ± 15.2	49.9 ± 15.7
Si-HTMS	110.6 ± 2.8	101.3 ± 6.8	9.3 ± 7.2
F14/6 ^X	117.2 ± 1.7	115.1 ± 2.1	2.1 ± 2.2
CuO-HTMS	162.0 ± 2.9	150.3 ± 4.4	11.7 ± 4.9
FS ^X	159.0 ± 2.3	144.0 ± 2.4	15.0 ± 2.7
Ethanol			
Cu	32.0 ± 3.9	23.1 ± 3.2	8.9 ± 4.2
F14/6	70.0 ± 2.6	67.1 ± 3.2	2.9 ± 3.4
FS	93.0 ± 2.7	68.1 ± 5.6	24.9 ± 6.2
Hexane			
F14/6	43.4 ± 2.4	40.1 ± 3.2	3.3 ± 3.4
Dodecane			
F14/6	63.0 ± 1.1	60.3 ± 2.2	2.7 ± 2.4

^aThe superscript X denotes not reported for evaporation for the corresponding working fluids.

by the frequency controller. The experiments were performed at a potential of 6–7 V, $f = 5\text{--}500\text{ Hz}$, and sample-dispenser spacing of $h \approx 6\text{ mm}$. Imaging was carried out at 7–24× magnification depending on the droplet size, and image acquisition was done at 200 frames per second. To control the sample surface temperature ($10\text{ }^\circ\text{C} < T_s < 60\text{ }^\circ\text{C}$), we interfaced a temperature-controlled bath (PolyScience AD20R-30-V11BR, $-30\text{ }^\circ\text{C} < T < 200\text{ }^\circ\text{C}$) with the stage. A handheld thermocouple device (4015, Traceable Products) was used to measure the sample surface temperatures, which differed from the set point chiller temperatures because of the contact resistance between the sample and stage. Similarly, the ambient temperature and relative humidity were measured and recorded using a handheld device (HX93BD, Omega). A mist humidifier (TaoTronics TT-

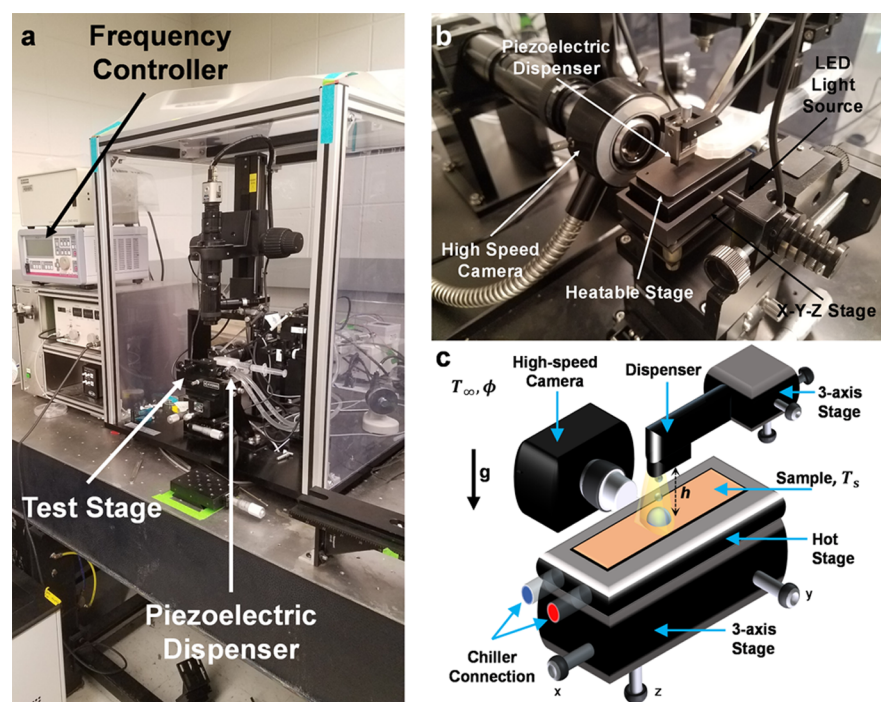


Figure 1. Photograph (a,b) and schematic (c) of the experimental setup. The temperature-controlled stage is connected to a chiller to control the surface temperature. The stage and the dispenser are connected to two independent 3-axis stages to maintain spatial control. A high-speed camera is integrated with the system to perform image analysis.

AH001) was connected to the system to control the relative humidity ($20\% < \phi < 60\%$).

The piezoelectric dispenser dispensed small ($\approx 20 \mu\text{m}$), mono-disperse droplets of the studied fluids (water, ethanol, hexane, dodecane) onto the sample surface, resulting in a single, larger droplet, on which we analyzed the evaporation dynamics. The evaporating droplet was brought into steady state by modulating the frequency (f) of microdroplet deposition. The droplet attaining a fixed size at a given f indicates steady state, where the rate of evaporation is equal to the rate of liquid deposition. The volumetric rate of liquid deposition can be calculated by multiplying the known deposition frequency at steady state (f) with the measured volume of the individual dispensed microdroplets (V), which equates to fV . Droplet volume analysis was performed using the mean size of the deposited microdroplets ($R = 8.77 \pm 0.56 \mu\text{m}$ for water, $R = 16.47 \pm 1.73 \mu\text{m}$ for ethanol, $R = 12.67 \pm 0.22 \mu\text{m}$ for hexane, and $R = 5.37 \pm 0.57 \mu\text{m}$ for dodecane) obtained by strobe imaging (Figure S1, Supporting Information). Table S3 summarizes the uncertainties associated with the different measurements during the experiments.

RESULTS AND DISCUSSION

Droplet Size. Evaporation from a liquid–vapor interface greatly depends on the droplet size.^{52,53} Previous works have shown a linear dependence of water droplet mass evaporation rate ($\dot{m}$) as a function of increasing droplet base radius (R_b) at ambient temperature.⁴⁵ Here, we initiated our experiments by studying the dependency $\dot{m}$ on R_b for different substrate temperatures ($T_s \approx 30, 40, 50^\circ\text{C}$) with water, as shown in Figure 2. Though the dependence of $\dot{m}$ on R_b was linear, the apparent contact angle of the droplet played an important role. At lower substrate temperatures (closer to ambient), $\dot{m}$ increased with higher hydrophobicity of the sample for similar-sized droplets (Figure 2a,b). The higher $\dot{m}$ was due to the larger liquid–vapor surface area, which results in higher heat transfer with the gaseous environment when temperature differences between the droplet and substrate are small

(limited conduction from the substrate).²⁰ However, Figure 2c shows that $\dot{m}$ is invariant with the apparent contact angle at higher T_s , showing similar $\dot{m}$ for droplets of similar size evaporating on different surfaces. The results indicate that a balance exists between the liquid–vapor mass-transfer resistance, which is lower for nonwetting samples because of increased liquid–vapor surface area (Figure S6) and the droplet–surface conduction heat transfer resistance, which is lower for hydrophilic surfaces because of lower conduction length scales. Here, the liquid–vapor interfacial area is considered for a fixed droplet radius of curvature (Figure S6). At elevated surface temperatures, the invariance to wetting points to the increasing limitation of heat conduction through the droplet to the evaporating interface (decreasing mass-transfer resistance), making the contact line dominant in terms of evaporation dynamics because of its proximity to the substrate. It is important to note that the experiments conducted here were all done in the high thermal conductivity limit for the substrate.^{54,55} The materials of choice included Cu, Si wafers, and stainless steel (SS), with intrinsic thermal conductivities of $k_s = 400 \text{ W/(m}\cdot\text{K)}$, $150 \text{ W/(m}\cdot\text{K)}$, and $15 \text{ W/(m}\cdot\text{K)}$, respectively. Although the SS substrate (only used for ethanol experiments) had a lower thermal conductivity, it was much higher than the thermal conductivity of ethanol (Table 1). Furthermore, the added thermal resistance due to air pockets in the Cassie–Baxter state was negligible because of relatively low thermal resistance between the droplet and the substrate compared to vapor diffusion at the liquid–vapor interface and droplet conduction (Table 4, Section S4 of the Supporting Information).

In order to investigate the efficacy of the steady method on the evaporation dynamics of nonaqueous liquids, we studied the evaporation of ethanol, hexane, and dodecane droplets having $90 < R_b < 400 \mu\text{m}$ (Figure 3). In addition to differing

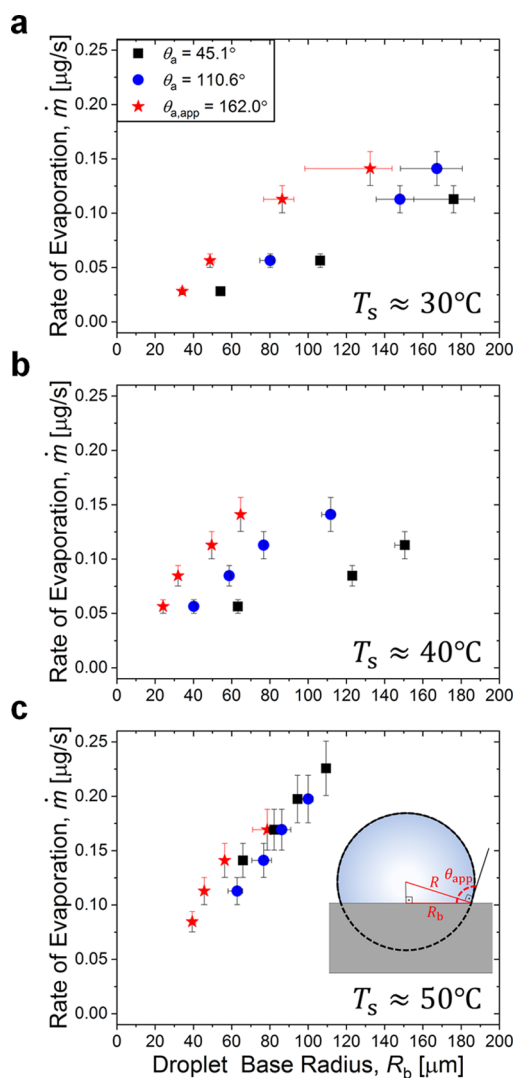


Figure 2. Droplet rate of evaporation as a function of droplet base radius for water droplets and tested samples [Si–Au ($\theta_a \approx 45^\circ$), Si-TFTS ($\theta_a \approx 111^\circ$), CuO-HTMS ($\theta_{a,app} \approx 162^\circ$)] for (a) $T_s \approx 30^\circ\text{C}$, (b) $T_s \approx 40^\circ\text{C}$, (c) $T_s \approx 50^\circ\text{C}$. The rate of evaporation varies linearly with increasing droplet size because of the linear dependence of the contact line length with the base radius. It is seen that the slopes are increasing as the substrate temperatures are increased, and the contact angle loses its importance at elevated temperatures because of the balance between conduction within the droplet and interfacial transport with the surroundings (c). Superhydrophobic droplets were in the Cassie–Baxter state through the course of the experiments. Experiments were performed at standard room conditions ($T_\infty = 25 \pm 0.5^\circ\text{C}$, $\phi = 50\% \pm 5\%$).

surface tension, alcohols and hydrocarbons have significantly higher vapor pressures and lower boiling points as compared to water (Table 1). Hence, our evaporation experiments were limited to subambient temperatures ($10 < T_s < 25^\circ\text{C}$). A close investigation of Figure 3 reveals that $\dot{m}$ follows a linear trend with R_b for ethanol, hexane, and dodecane, similar to that of water. To explore and understand the dynamics of evaporation on the studied fluids, we now investigate the driving forces for heat and mass transfer through scaling and thermal resistance analyses.

External Natural Convection. Natural convection has been shown to play an important role on droplet evaporation because of its effects on the vapor flow field.^{56,57} To explore

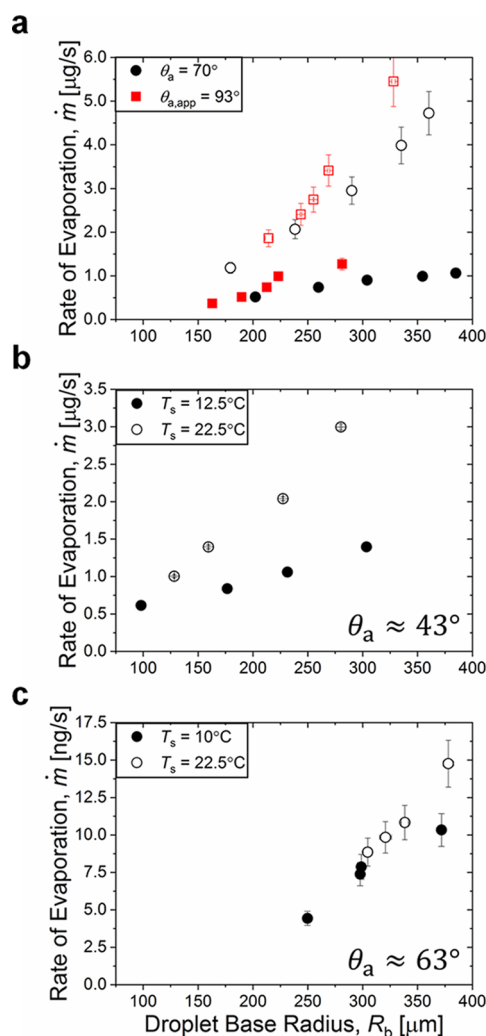


Figure 3. Droplet rate of evaporation as a function of droplet base radius for (a) ethanol on F14/6 ($\theta_a \approx 70^\circ$) and FS ($\theta_{a,app} \approx 93^\circ$, Wenzel state) for $T_s \approx 10^\circ\text{C}$ (solid symbols) and $T_s \approx 22.5^\circ\text{C}$ (hollow symbols), (b) hexane on F14/6 ($\theta_a \approx 43.4^\circ$) for $T_s \approx 12.5^\circ\text{C}$ (solid symbols) and $T_s \approx 22.5^\circ\text{C}$ (hollow symbols), and (c) dodecane on F14/6 ($\theta_a \approx 63.0^\circ$) for $T_s \approx 10^\circ\text{C}$ (solid symbols) and $T_s \approx 22.5^\circ\text{C}$ (hollow symbols). Experiments were performed at ambient conditions of (a) $T_\infty = 24.7 \pm 0.2^\circ\text{C}$, $\phi = 38\% \pm 1\%$, (b) $T_\infty = 23.7 \pm 0.5^\circ\text{C}$, $\phi = 25.1\% \pm 0.9\%$, and (c) of $T_\infty = 23.7 \pm 0.6^\circ\text{C}$, $\phi = 22.5\% \pm 0.8\%$.

the effects of natural convection with the surroundings, we calculate the Rayleigh number (Ra) of the heated sample and droplet, given by⁵⁸

$$Ra = \frac{g\beta L_c^3 \Delta T}{\alpha\nu} \quad (1)$$

where g is the gravitational constant, β is the thermal expansion coefficient of air, L_c is the characteristic length of the heated horizontal surface or droplet, ΔT is the temperature difference between the heated surface and ambient air or the ambient air and the evaporating droplet, and α and ν are the thermal diffusivity and kinematic viscosity of air, respectively. Note that two separate Rayleigh numbers were calculated. For the droplet, a temperature gradient is formed between the ambient air and droplet, in which case $Ra \approx 2$ for the largest droplets considered ($L_c = A_s/P \approx 800\ \mu\text{m}$, where A_s and P are the

surface area and perimeter of the droplet, respectively) and highest surface temperature ($T_s \approx 60^\circ\text{C}$). The calculated $Ra \approx 2$ is much smaller than the critical Rayleigh number for a heated horizontal surface ($Ra \ll Ra_{cr} = 1708$).^{59,60} For the macroscopic flow governed by the length scale of the sample (natural convection from a heated horizontal surface), $Ra \approx 850$ ($< Ra_{cr} = 1708$) for $L_c = A_s/P \approx 6.25$ mm, where A_s and P are the surface area and perimeter of the sample in which the droplet resides on and $T_s \approx 60^\circ\text{C}$. Therefore, heat transport with the surroundings was governed by heat conduction for the experiments conducted here.

Internal Droplet Natural Convection. To explore the effects of internal natural convection, we calculated the Grashof number (Gr) of the evaporating droplet ($Gr = Ra/Pr$, where Pr is the liquid Prandtl number and Ra is defined by eq 1). Here, L_c is affected by the shape of the droplet ($L_c = V/A_w$, where $A_w = \pi R_b^2$ is the liquid/solid wetted area). Hence, Gr was calculated separately for wetting and nonwetting droplets for each working fluid.⁶¹ Table 3 shows that the

Table 3. Grashof (Gr), Marangoni (Ma), and Bond (Bo) Numbers of the Working Fluids

working fluid	θ [$^\circ$]	D [μm]	Gr	Ma	Bo
DI water	45	50	1.7×10^{-4}	280	4.5×10^{-7}
		500	0.17	2800	4.5×10^{-5}
	135	50	0.03	16400	1.5×10^{-5}
ethanol	45	50	34.6	1640	1.5×10^{-3}
		500	5.8×10^{-3}	310	4.3×10^{-4}
	135	50	5.8	3130	4.3×10^{-2}
hexane	45	50	0.1	570	1.4×10^{-3}
		500	99.8	5720	0.14
	135	50	4.3×10^{-3}	470	2.8×10^{-4}
dodecane	45	50	4.3	4750	2.8×10^{-2}
		500			

calculated Gr values are much smaller than the critical Gr for internal natural convection ($Gr \ll Gr_{cr} \approx 2400$).^{61,62} Hence, internal droplet natural convection effects were not present in our experiments.

Marangoni Effects. Given the presence of temperature gradients across the droplet, the presence of Marangoni forces and flows could affect the internal and external flow fields. To investigate how temperature or concentration gradients inside the evaporating droplet affect the overall evaporation dynamics, Marangoni convection inside the droplet was analyzed.^{61,63} In order to quantify the effects of Marangoni flows, the thermal Marangoni number (eq 2) and Bond number (eq 3) need to be calculated for representative contact angle values ($\theta = 45^\circ$ for wetting and $\theta = 135^\circ$ for nonwetting) for the smallest and largest droplets of interest ($R = 50$ and $500 \mu\text{m}$) and for the highest surface temperature ($T_s \approx 60^\circ\text{C}$)⁶¹

$$Ma = \frac{L_c \Delta T \left| \frac{d\sigma}{dT} \right|}{\alpha \mu} \quad (2)$$

$$Bo = \frac{gL_c^2(\rho_l - \rho_g)}{\sigma} \quad (3)$$

where $|d\sigma/dT|$ is the rate of change of liquid–vapor surface tension with respect to temperature and $L_c = V/A_w$ is the characteristic length.

Table 3 shows that the Marangoni numbers are higher than the critical value ($Ma > 80$ – 100),⁶⁴ and Bond numbers are

sufficiently small ($Bo \ll 1$), suggesting that the internal flow is Marangoni convection dominated for each case. However, previous studies have shown that for sufficiently small droplets, Marangoni convection cannot initiate because of rolling caused by the instabilities of the mass center because of heating from below and cooling from above.⁶³ Scaling the characteristic velocities of Marangoni flows obtained from the Marangoni number Ma ($U_{Ma} \sim |d\sigma/dT| \Delta T / \mu$) and body rotation because of the deviation of the mass center of the droplet, which is obtained by a balance of viscous dissipation and the gained potential energy because of rolling ($U_R \sim 2\Delta\rho g(\sigma/\rho g)^{3/2}/\mu D$) with $\Delta\rho \sim \rho\beta\Delta T$, we find the critical droplet diameter for each working fluid at which Marangoni convection will become dominant⁶³

$$D \sim \frac{\sigma\beta\sqrt{\frac{\sigma}{\rho g}}}{\left| \frac{d\sigma}{dT} \right|} \quad (4)$$

Utilization of eq 4 yields $D \sim 0.7$ mm for water, $D \sim 1.3$ mm for ethanol, $D \sim 3.5$ mm for hexane, and $D \sim 1$ mm for dodecane, much larger than the droplets studied here ($D = 2R < 0.5$ mm). Furthermore, it has been experimentally demonstrated that for water droplets, which are prone to contamination, Marangoni flows are suppressed by 100 times even for very low surface contamination levels (~ 300 molecules/ μm^2).^{65,66} Considering contamination effects and the fact that our droplets are smaller than the critical diameter, Marangoni effects were negligible for the conditions used in this study.

Concentration Effects. The effects of the temperature gradient in the vapor flow surrounding the evaporating droplet are characterized by analyzing the Ludwig–Soret effect and Dufour effect for the mixtures (i.e., air–water vapor, air–ethanol vapor, air–hexane vapor, and air–dodecane vapor). The Soret [$S_T = -\nabla c/(c(1-c)\nabla T)$] and the Dufour ($D_T = (T_0 a^2/c_p \beta^2)(\partial\mu/\partial c)$) numbers were calculated for each case and found to be negligible ($S_T \approx 0.05$, $D_T \approx 0$).^{67,68} Hence, secondary effects due to the concentration gradients were negligible for our experiments.

Evaporative Cooling. Self-cooling of evaporating droplets can play an important role in the dynamics of evaporation.^{8,9} The conversion of liquid to vapor from the liquid–vapor interface of an evaporating droplet absorbs latent heat of vaporization (h_{fg}) from the remaining liquid in the droplet, which cools the droplet interface and in turn reduces the local liquid temperature, vapor pressure, and hence the evaporation rate. Self-cooling becomes especially important for nonwetting substrates because of the larger liquid–vapor interfacial area and droplet conduction resistance from the base, leading to increased resistance to evaporation as the droplet self-cools.

A number of previous studies have analytically captured the effect of self-cooling of droplets because of evaporation, focusing on isothermal interfaces.^{69,70} For droplets evaporating in quiescent air, the liquid–vapor interfacial temperature can be calculated by a balance of the instantaneous rate of sensible heat transfer to the droplet and the instantaneous rate of heat absorption by the droplet in the absence of radiation as⁶⁹

$$T_{int} = T_\infty - \frac{h_{fg} D_{va} M P_{v,int}}{k_f \bar{R} T_\infty} \quad (5)$$

where D_{va} is the diffusion coefficient of the vapor (subscript v) in air (subscript a), M is the molecular mass of the evaporating

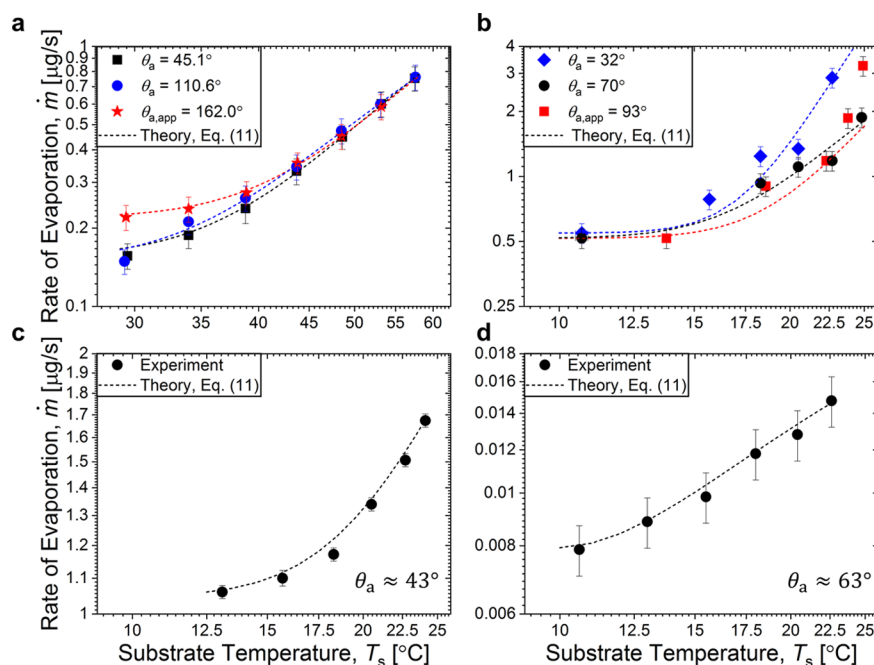


Figure 4. Droplet rate of evaporation as a function of the substrate temperature for fixed radii. (a) Rate of evaporation as a function of the substrate temperature for water droplets evaporating with $R \approx 250 \mu\text{m}$ ($T_\infty = 24.0 \pm 0.7^\circ\text{C}$, $\phi = 35.1\% \pm 1.3\%$), (b) rate of evaporation as a function of the substrate temperature for ethanol droplets evaporating with $R \approx 200 \mu\text{m}$ ($T_\infty = 24.7 \pm 0.2^\circ\text{C}$, $\phi = 38\% \pm 1\%$), (c) rate of evaporation as a function of the substrate temperature for hexane droplets evaporating with $R \approx 300 \mu\text{m}$ ($T_\infty = 23.7 \pm 0.5^\circ\text{C}$, $\phi = 25.1\% \pm 0.9\%$), (d) rate of evaporation as a function of the substrate temperature for dodecane droplets evaporating with $R \approx 350 \mu\text{m}$ ($T_\infty = 23.7 \pm 0.6^\circ\text{C}$, $\phi = 22.5\% \pm 0.8\%$). The same exponential trends were observed in all cases because of the dependence of evaporation on the vapor pressure and concentration. Fits were obtained by fitting eq 11 to the rate of evaporation data using the respective physical constants for each working fluid. The coefficients of determination (R -square) were >0.99 for water, hexane, and dodecane and >0.90 for ethanol. All experiments were performed on the same day for each working fluid to minimize the effects of the variations in ambient conditions.

Table 4. Thermal Resistance Analysis for Water, Ethanol, Hexane, and Dodecane at Different Surface Temperatures^a

Water									
$T_s \approx 30^\circ\text{C}$					$T_s \approx 60^\circ\text{C}$				
$\theta [^\circ]$	$R [\mu\text{m}]$	$R_{\text{th,base}}^*$	$R_{\text{th,drop}}^*$	$R_{\text{th,int}}^*$	$R_{\text{tot}} [\text{K/W}]$	$R_{\text{th,base}}^*$	$R_{\text{th,drop}}^*$	$R_{\text{th,int}}^*$	$R_{\text{tot}} [\text{K/W}]$
45	275	$\ll 1$	0.132	0.868	4058	$\ll 1$	0.222	0.778	2410
110	225	$\ll 1$	0.266	0.734	4570	$\ll 1$	0.438	0.562	2775
162	250	0.004	0.613	0.384	7750	0.004	0.740	0.255	6420
Ethanol									
$T_s \approx 12.5^\circ\text{C}$					$T_s \approx 22.5^\circ\text{C}$				
$\theta [^\circ]$	$R [\mu\text{m}]$	$R_{\text{th,base}}^*$	$R_{\text{th,drop}}^*$	$R_{\text{th,int}}^*$	$R_{\text{tot}} [\text{K/W}]$	$R_{\text{th,base}}^*$	$R_{\text{th,drop}}^*$	$R_{\text{th,int}}^*$	$R_{\text{tot}} [\text{K/W}]$
70	200	$\ll 1$	0.483	0.516	7140	$\ll 1$	0.560	0.439	6160
93	200	$\ll 1$	0.229	0.771	4620	$\ll 1$	0.251	0.749	4210
Hexane									
$T_s \approx 12.5^\circ\text{C}$					$T_s \approx 22.5^\circ\text{C}$				
$\theta [^\circ]$	$R [\mu\text{m}]$	$R_{\text{th,base}}^*$	$R_{\text{th,drop}}^*$	$R_{\text{th,int}}^*$	$R_{\text{tot}} [\text{K/W}]$	$R_{\text{th,base}}^*$	$R_{\text{th,drop}}^*$	$R_{\text{th,int}}^*$	$R_{\text{tot}} [\text{K/W}]$
43.4	350	$\ll 1$	0.461	0.538	4180	$\ll 1$	0.462	0.537	4170
Dodecane									
$T_s \approx 12.5^\circ\text{C}$					$T_s \approx 22.5^\circ\text{C}$				
$\theta [^\circ]$	$R [\mu\text{m}]$	$R_{\text{th,base}}^*$	$R_{\text{th,drop}}^*$	$R_{\text{th,int}}^*$	$R_{\text{tot}} [\text{K/W}]$	$R_{\text{th,base}}^*$	$R_{\text{th,drop}}^*$	$R_{\text{th,int}}^*$	$R_{\text{tot}} [\text{K/W}]$
63	400	$\ll 1$	0.826	0.173	2120	$\ll 1$	0.809	0.190	2170

^aThe * denotes normalization by the total resistance value (R_{tot}).

liquid, $P_{\text{v,int}}$ is the vapor pressure at the liquid–vapor interface temperature, k_f is the thermal conductivity of the evaporating liquid, $\bar{R}$ is the universal gas constant, and T_∞ is the ambient air temperature. Equation 5 reveals that for given fluid and ambient conditions, the only unknown parameter is the

liquid–vapor interfacial temperature T_{int} , which is solved iteratively. Here, it should be noted that the effects of the substrate on temperature have been neglected, which may not always hold true depending on the evaporation conditions. The effect of the substrate has already been extensively studied

for evaporating quasisteady droplets in the conduction dominated regime.^{71,72} For such droplets, the nondimensional temperature distribution at the solid–liquid interface can be obtained by a balance of the energy conducted into the droplet from the substrate and energy transferred to the cooler liquid–vapor interface by conduction within the droplet⁷¹

$$\frac{T_s - T_{s,0}}{T_s - T_\infty} \approx \sqrt{\frac{2k_f}{k_s}} \quad (6)$$

where T_s represents the bulk substrate temperature far from the liquid–solid interface, $T_{s,0}$ represents the temperature at the center of the droplet solid–liquid interface, and k_s represents the thermal conductivity of the solid. Utilizing eq 6 for the working fluids and the substrates of interest ($k_f \sim 0.1$ W/(m·K), $k_s \sim 100$ W/(m·K), $k_f/k_s \ll 1$), we observe $(T_s - T_{s,0})/T_s - T_\infty \approx 0$ and $T_s \approx T_{s,0}$. Hence, the scaling argument shows that the solid–liquid interface is isothermal and eq 5 is valid.

Using eq 5, for water at room temperature ($T_\infty = 24$ °C), $\phi = 50\%$ relative humidity, and atmospheric pressure (101 kPa), we calculated $T_{\text{int}} = 22.8$ °C, showing a 1.2 °C decrease in ambient conditions. More importantly, under the same environmental conditions, we calculated $T_{\text{int}} = 17.5$ °C for ethanol, $T_{\text{int}} = 14$ °C for hexane, and $T_{\text{int}} = 23.8$ °C for dodecane (Section S4, Supporting Information). The results indicate that self-cooling is important for hexane and ethanol and negligible for water and dodecane. The observed trend is expected because of the higher vapor pressures of hexane and ethanol, which enhances liquid-to-vapor mass transfer.

Effects of Surface Temperature and Droplet Morphology. To study the effect of surface temperature (T_s), the rate of evaporation ($\dot{m}$) of similar-sized (<10% variation in droplet diameter) water droplets on varying samples was analyzed (Figure 4a). The results show an exponential dependence of $\dot{m}$ on T_s . Furthermore, droplets evaporating at lower T_s are more sensitive to droplet shape (apparent contact angle) because of the relative imbalance between the thermal resistances associated with conduction within the droplet and mass transfer at the liquid–vapor interface. To quantify the effect of different mechanisms of heat and mass transfer, we use a thermal resistance analogy. Assuming spherical-cap droplet shapes ($Bo \ll 1$, Figure S2), we calculate the thermal resistance to heat transfer from the substrate to the droplet base ($R_{\text{th,base}}$, Section S4, Supporting Information), thermal resistance to heat conduction within the droplet ($R_{\text{th,drop}} \approx \theta/4\pi R k_f \sin \theta$),⁷³ and thermal resistance at the liquid–vapor interface ($R_{\text{th,int}}$, Section S4, Supporting Information). The results of the analysis are given in Table 4 for all working fluids at the two temperature extremes. From Table 4, it can be concluded that droplet evaporation is governed by interfacial effects (vapor diffusion and conduction with the surroundings) and conduction within the droplet when Marangoni and natural convection effects are negligible. In addition, because the substrate has very low thermal resistance when compared to other thermal resistances ($R_{\text{th,base}}^* \ll 1$, see Table 4 and Section S4 of the Supporting Information), we assume that the droplet base is at the same temperature as the substrate underneath it. Furthermore, droplet conduction resistance increases while interfacial resistance decreases as the surface becomes nonwetting (hydrophobic) because of morphological effects. As the contact angle increases, for similar radii droplets, overall

height of the droplet goes up, increasing the distance that the heat from the substrate must travel to reach the evaporating interface, effectively reflected as an increase in the droplet conduction resistance. In parallel, as the contact angle increases, the liquid–vapor interfacial area also increases, effectively increasing the total heat and mass transfer with the surroundings (reflected as decreased interfacial resistance). This, together with the higher conduction resistance, implies that the average temperature of the droplets will decrease as the surface becomes nonwetting because of lower heat conduction from the higher temperature substrate to the evaporating interface undergoing self-cooling. Our experimental observations here are in-line with results from previous numerical studies.¹⁹ However, the average temperature of droplets on wetting (hydrophilic) surfaces will be higher because self-cooling effects are negligible because of effective conduction within the droplet. Hence, while the superhydrophobic droplet will have an almost constant temperature difference with the surroundings ($T_{\text{avg}} \approx T_{\text{int}}$, $\Delta T = T_{\text{avg}} - T_\infty$, where T_{int} is limited by the wet-bulb temperature T_{wb}), the hydrophilic droplet will have higher temperature difference with the surroundings ($T_{\text{avg}} \approx 0.5(T_{\text{int}} + T_s)$, $\Delta T = T_{\text{avg}} - T_\infty$, where T_{int} is limited by the wet-bulb temperature T_{wb}). At higher temperature differences between the sample surface and the droplet ($\Delta T = T_s - T_{\text{avg}}$), higher temperature gradients within the droplet are formed, resulting in increased heat conduction through the droplet, effectively increasing its average temperature. Although this results in better diffusion because of decreased interfacial resistance, self-cooling effects become negligible for the superhydrophobic droplet because more heat is transferred through conduction. Simultaneously, mass transport through the interface becomes easier for the wetting droplet because of decreased interfacial resistance at elevated temperatures ($T_s > 45$ °C). Hence, surface functionality and droplet morphology lose importance at elevated temperatures ($T_s > 45$ °C) because of the formed balance between droplet conduction and interfacial effects for all studied water droplets (Figures 2c and 4a).

To further validate our hypothesis that droplet evaporation is governed by mass diffusion at the interface and droplet conduction, we expanded our studies to the evaporation of ethanol, hexane, and dodecane droplets (Figure 4b,d). Similar to water, $\dot{m}$ increased exponentially as a function of T_s for each fluid even though the studied temperatures and the temperature ranges were much smaller (10 °C $< T_s < 25$ °C). The effects of apparent advancing contact angle could not be studied because of the difficulty in obtaining nonwetting droplet morphologies for low-surface tension working fluids. The quantitative results for ethanol, hexane, and dodecane matched with the water droplet results, lending credence for the need of a more rigorous scaling analysis examining the driving forces for evaporation.

Considering liquid and gas thermal conductivities and droplet morphology to be temperature independent for small-temperature variations, the droplet conduction heat-transfer resistance can be assumed to be independent of T_s or T_∞ . Hence, the change in droplet evaporation behavior with changing T_s is governed by vapor diffusion in the vicinity of the liquid–vapor interface (wetting droplet limit), which is governed by Fick's law of diffusion in the ambient air adjacent to the interface.⁷⁴

$$J = D_{va} \frac{dc}{dx} \sim \left(\frac{D_{va}}{t} \right) (c - c_{\infty}) \quad (7)$$

where D_{va} is the diffusion coefficient of vapor (subscript v) in air (subscript a) (Table 1), t is the thickness of the diffusion boundary layer, c is the vapor concentration at the liquid–vapor interface, and c_{∞} is the concentration of vapor in the ambient air far from the droplet at the mass-transfer boundary layer edge. Note that although interfacial transport at the liquid–vapor interface is a key resistance to mass transfer from liquid to vapor, it is negligible compared to diffusional resistances encountered in NCG-laden environments and not considered here.^{45,75} Assuming that water vapor at ambient conditions behaves as an ideal gas⁷⁶

$$J(T_{int}) = D_{va} \frac{dc}{dx} \sim \frac{D_{va}(P_v - P_{v,\infty})}{R_v t T_{int}} \sim \frac{P_v(T_{int})}{T_{int}} \quad (8)$$

where R_v is the specific gas constant for the evaporating liquid, P_v is the vapor pressure of the evaporating fluid at the liquid–vapor interface, and $P_{v,\infty}$ is the vapor pressure of the evaporating fluid in ambient air far from the droplet. Using the Clausius–Clapeyron solution for an ideal gas, we obtain⁷⁷

$$\ln \left(\frac{P_v}{P_{v,\infty}} \right) = \frac{h_{fg}}{R_v} \left(\frac{1}{T_{\infty}} - \frac{1}{T_{int}} \right) \quad (9)$$

$$P_v(T) = P_{v,\infty} \exp \left(\frac{h_{fg}}{R_v T_{\infty}} \right) \exp \left(- \frac{h_{fg}}{R_v T_{int}} \right) \sim \exp \left(- \frac{h_{fg}}{R_v T_{int}} \right) \quad (10)$$

Substituting eqs 10 into 8, we obtain an analytical relation for J as a function of T_{int}

$$J(T_{int}) \sim \frac{P_v(T_{int})}{T_{int}} \sim \frac{1}{T_{int}} \exp \left(- \frac{h_{fg}}{R_v T_{int}} \right) \quad (11)$$

Note that because T_{int} is related to T_s , we use T_s on our experimental trend lines (Figure 4). Although high fidelity models incorporating contact angle and droplet shape effects have been developed for water droplet evaporation in gas diffusion-limited settings,⁷ few models exist that can accurately predict the evaporation of arbitrary low surface tension fluids. Hence, we have limited our analysis to the results of the scaling analysis as given by eq 11. Our experimental results (Figure 4) follow the trend obtained by eq 11 closely for higher temperatures, indicating the validity of the scaling analysis used to predict evaporation behavior by the steady method for different temperatures as well as elucidating the dynamics of liquid–vapor transport at the interface for droplets on different functional surfaces.

It is important to note that the surface temperature may also play a role in rate of evaporation by affecting the apparent contact angles of the formed droplets on surfaces. Careful analysis of the experimental results indicated no significant changes for droplets of any liquid used because of the negligible changes in the surface tension values over the studied temperature range (Figure S3, Supporting Information). A summary of the governing phenomena for water droplet evaporation for different temperatures and droplet morphologies is given in Table 5.

Saturation State. Another important phenomenon governing mass transport is the relative humidity, which represents the saturation state of a vapor in the ambient

Table 5. Phenomena Governing Water Droplet Evaporation^a

θ [°]	$T_s < \approx 45$ °C	$T_s > \approx 45$ °C
$\ll 90^\circ$	vapor diffusion	balanced
$\approx 90^\circ$	vapor diffusion	balanced
$\gg 90^\circ$	droplet conduction	balanced

^aFor low-to-intermediate temperatures, droplet evaporation is governed by vapor diffusion effects at the liquid–vapor interface for wetting droplets and by droplet conduction for nonwetting droplets. At intermediate-to-high temperatures, a balance between effective vapor diffusion and droplet conduction is formed because of higher average droplet temperatures, yielding more heat to conduct from the base and negligible self-cooling effects for all droplet morphologies.

environment. Relative humidity is physically represented by a ratio of vapor pressures, which can be described by concentrations considering ideal gas behavior⁷⁶

$$\phi = \frac{P_{v,\infty}}{P_{v,\infty}^*} \sim \frac{c_{\infty}}{c_{\infty}^*} \quad (12)$$

where the superscript * represents the equilibrium states at a given temperature. Revisiting Fick's Law (eq 7)

$$J \sim \frac{D_{va}}{t} (c - c_{\infty}) \sim -c_{\infty}^* \phi \quad (13)$$

Our experiments show a linear decrease in the rate of evaporation with increasing ϕ (Figure S4, Supporting Information). As ϕ increases, the surrounding air approaches saturation and the equilibrium state, diminishing mass transport. Because of the negligible concentration of vapors of the low surface tension fluids in air, the evaporation dynamics of ethanol, hexane, and dodecane were independent on the air relative humidity, as shown in Figure S5, Supporting Information.

Vapor Pressure. Volatility of a liquid is measured by the equilibrium vapor pressure generated by the liquid at a fixed temperature (Table 1). Liquids having higher vapor pressure are more volatile, as they are closer to the boiling point, and more liquid is transferred into the vapor phase because of larger concentration gradients between the liquid–vapor interface of the droplet and the ambient air. Figure 5 shows the effect of vapor pressure on the rate of evaporation for the obtained exponential fits of the studied fluids (hexane, ethanol, water, and dodecane). The results show that the rate of evaporation significantly increases for a given surface temperature as the volatility increases.

In summary, we present a rigorous analysis of droplet evaporation of fluids having distinct properties using the developed steady method.⁴⁵ Low surface tension liquids tend to wet conventional hydrophobic surfaces because the surfaces and the low surface tension liquids usually have comparable surface energy values. The liquid droplets thus easily spread on such surfaces, causing wetting and larger liquid–surface contact area. This necessitates the need to have larger imaging apertures for studying evaporation, which can lead to higher uncertainties in the evaporation measurements. Most low surface tension fluids are also highly volatile and rapidly evaporate and are thus difficult to study because of the short evaporation timescales. Moreover, it is difficult to dispense similar-sized discrete droplets of low surface tension liquids continuously because the liquid wets the dispensing nozzle/needle, often forming a film around the tip. Using the steady

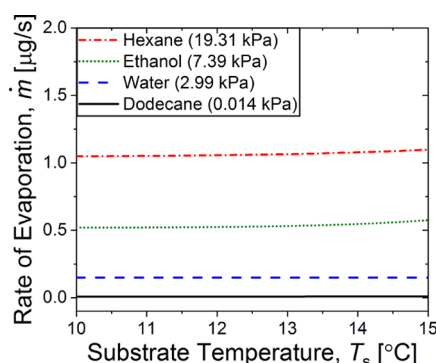


Figure 5. Rate of evaporation as a function of substrate temperature for fluids of different volatilities. At a given temperature, hexane is the most volatile (characterized by higher vapor pressure), which also shows the highest evaporation rate because of higher concentration gradients. Dodecane is the least volatile, showing the lowest evaporative behavior because of lower concentration gradients. Fits were obtained from experimental data and the exponential behavior the evaporation rate displays with surface temperature.

method, we show that it is possible to accurately characterize the evaporation dynamics of droplets of volatile fluids because of the ability to control droplet deposition timescales (*i.e.*, modulation of the frequency of deposition) to match the fast evaporation timescales. Furthermore, size control of evaporating liquids has traditionally been difficult to achieve, leading to studies with larger droplets. This issue was predominant for the volatile fluids, which may be toxic and pose health risks to the researcher. Because the steady method allows for the study of droplets having small length scales ($D \sim 100 \mu\text{m}$) because of the ability to dispense microdroplets ($D \sim 10 \mu\text{m}$), the amount of the fluid that is used is minimized. Using minimal fluid makes the method not only more advantageous because of the ability to analyze smaller droplets (fewer gravity effects) but also much safer than traditional methods where the dispensed volumes of potentially toxic fluids are much higher.

Another advantage of the steady method is its high-throughput functionality. Multiple droplet sizes and conditions can be characterized in a single experimental run without removing the liquid from the surface. This has implications for the study of a multitude of phenomena related to phase change and interfacial science, for example, binary droplet systems, where two droplets could be printed and their impact on the evaporation behavior on one another could be analyzed. In addition, similar methods with the same experimental setup have already been used to explore cloaking on LISs,⁷⁸ induced coalescence,^{79,80} droplet jumping,^{51,81,82} and fluid mechanics.⁸³

The steady method also enables the spatial control of monodisperse microdroplet deposition. For biphilic or hybrid surfaces, droplets can precisely be deposited to study evaporation dynamics.⁸⁴ Although we only considered flat surfaces here, the steady technique also enables the study of evaporation on microscale wires.

Because of the adaptability of the steady method, many interesting interfacial and phase change phenomena can be studied in the future. One interesting study would be to measure the thermal conductivity of fluids via time-domain thermoreflectance,⁸⁵ where the droplet size could be fixed by using the steady method. It would also be interesting to study other fluids that may not evaporate quickly but that can undergo phase change in the droplet after deposition such as freezing on a supercooled substrates,⁸⁶ liquid metal drop-

lets,^{87,88} and phase change of paraffins because of heat loss to the substrate.⁸⁹ Furthermore, the effects of wetting state (Cassie-Baxter, Wenzel, or during Cassie-Baxter to Wenzel transition) for droplets evaporating on textured structures can be further investigated. In addition, because of the high resolution in dispensing droplets, contact line phenomena such as droplet sliding can be accurately characterized.

CONCLUSIONS

In this study, evaporation dynamics of water droplets were investigated using the steady method for a wide range of droplet base radii (20–400 μm) on different surfaces having a wide range of wettability characteristics ($32^\circ < \theta_a < 162^\circ$). In addition, employing the steady method, microdroplets of different low surface tension fluids (ethanol, hexane, and dodecane) were also studied to characterize their evaporation rates in ambient conditions. Because the steady method enables the decoupling of physical phenomena that are simultaneously governing the droplet evaporation process such as surface temperature, relative humidity, and volatility, we individually studied each phenomenon to observe their respective contribution to evaporation dynamics. Our results showed that the rate of evaporation has a linear dependence on the droplet base radius for each tested surface temperature and working fluid. We also show that for a given surface, an exponential dependence exists between the droplet rate of evaporation and the surface temperature, and that the wettability characteristics of the surface loses its role on the evaporation dynamics at higher surface temperatures. We also noted an inverse linear trend between the rate of evaporation and relative humidity for water droplets and found no effect of relative humidity on the rate of evaporation for the droplets of low surface tension fluids. Increases in the rate of evaporation values for more volatile fluids were also observed because of elevated liquid-to-vapor mass transfer caused by higher vapor pressures. This work sheds light on the evaporation dynamics of microdroplets of diverse working fluids on different surfaces and offers insights into alternate avenues in the study of droplet evaporation of different shapes and sizes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.0c02272>.

Surface fabrication, functionalization, and characterization; strobe images for monodisperse droplets; detailed calculation of the interfacial temperatures; plots of contact angle variations; thermal resistance analyses; effects of relative humidity; variation of the interfacial surface area with droplet contact angle; and uncertainty associated with experiments (PDF)

AUTHOR INFORMATION

Corresponding Authors

A. Alperen Günay – Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States; orcid.org/0000-0002-2013-9101; Email: günay@photon.t.u-tokyo.ac.jp

Nenad Miljkovic – Department of Mechanical Science and Engineering and Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States; Materials Research

Laboratory, University of Illinois, Urbana, Illinois 61801, United States; International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan; orcid.org/0000-0002-0866-3680; Email: nmiljkov@illinois.edu

Authors

Marisa Gnad – Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

Soumyadip Sett – Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States

Hamed Vahabi – Department of Biomedical Engineering, Duke University, Durham, North Carolina 27708, United States

Arun K. Kota – Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States; orcid.org/0000-0001-9061-7896

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.langmuir.0c02272>

Author Contributions

A.A.G. and N.M. conceived the initial idea for this study. N.M. guided the work. A.A.G. and M.G. fabricated, functionalized, and characterized the functional samples and carried out the experiments. H.V. and A.K.K. fabricated and functionalized the stainless steel-based omniphobic sample. S.S. fabricated, functionalized, and characterized the LISs. A.A.G., M.G., and S.S. analyzed the data. All authors contributed to the writing of the manuscript and have given approval to the final version of this manuscript.

Notes

The authors declare no competing financial interest.

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