Microdroplet self-propulsion during dropwise condensation on lubricant-infused surfaces

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Abstract

Water vapor condensation is common in nature and widely used in industrial applications, including water harvesting, power generation, and desalination. As compared to traditional filmwise condensation, dropwise condensation on lubricant-infused surfaces (LIS) can lead to an order-of-magnitude increase in heat transfer rates. Small droplets \((D \leq 100 \ \mu m)\) account for nearly 85% of the total heat transfer and droplet sweeping plays a crucial role in clearing nucleation sites, allowing for frequent re-nucleation. Here, we focus on the dynamic interplay of microdroplets with the thin lubricant film during water vapor condensation on LIS. Coupling high-speed imaging, optical microscopy, and interferometry, we show that the initially uniform lubricant film re-distributes during condensation. Governed by lubricant height gradients, microdroplets as small as 2 \( \mu m \) in diameter undergo rigorous and gravity-independent self-propulsion, travelling distances multiples of their diameters at velocities up to 1100 \( \mu m/s \). Although macroscopically the movement appears to be random, we show that on a microscopic level capillary attraction due to asymmetrical lubricant menisci causes this gravity-independent droplet motion. Based on a lateral force balance analysis, we quantitatively find that the sliding velocity initially increases during movement, but decreases sharply at shorter inter-droplet spacing. The maximum sliding velocity is inversely proportional to the oil viscosity and is strongly dependent of the droplet size, which is in excellent agreement with the experimental observations. This novel and non-traditional droplet movement is expected to significantly enhance the sweeping efficiency during dropwise condensation, leading to higher nucleation and heat transfer rates.

Keywords: Lubricant-Infused Surface (LIS); Condensation; Microdroplet mobility; Oil meniscus; Capillary attraction
Introduction

Vapor condensation is ubiquitous in nature\textsuperscript{1,2} and at the basis of a wide range of industrial applications, such as power generation\textsuperscript{3}, air conditioning\textsuperscript{4}, water harvesting\textsuperscript{5}, and desalination\textsuperscript{6}. Filmwise condensation, in which the condensate forms a thick liquid film, is common, owing to the high wettability of most solid surfaces. This film acts as a thermal barrier to heat transfer.\textsuperscript{7} In contrast, dropwise condensation, in which the condensate forms discrete droplets that grow through direct condensation, coalescence, and gravity-assisted shedding, leads to an order-of-magnitude improvement in heat transfer performance compared to the filmwise mode.\textsuperscript{8–10} Lubricant-infused surfaces (LIS) promote dropwise condensation and, unlike nanostructured superhydrophobic surfaces, maintain stable operating conditions even at high supersaturation.\textsuperscript{11–13} Droplets on LIS have extremely low contact angle hysteresis due to the presence of a lubricating film between working fluid and substrate,\textsuperscript{14} which results in a remarkable mobility of the condensed droplets.\textsuperscript{15} When droplets rest on an oil film, a meniscus forms around the base of the droplet. Additionally, many lubricants cloak the working fluid, \textit{i.e.}, a thin (10s of nm) oil layer engulfs the droplet.\textsuperscript{16,17} The meniscus and cloak lead to increased viscous dissipation and lower droplet sliding velocities.\textsuperscript{18–24} On the other hand, overlapping menisci can also induce a net attractive force between droplets,\textsuperscript{25–28} potentially enhancing gravity-induced droplet sweeping. Frequent droplet sweeping is essential to remove condensate, to renew nucleation sites, and to maintain high heat transfer rates during condensation. It also plays a key role in coalescence-induced droplet growth and can accelerate oil drainage, causing LIS to fail. Hence, droplet movement during condensation on LIS is of great importance to ensure an efficient and long-term stable operation. As most previous studies have quantified the dynamics of millimetric droplets, there continues to be a lack of experimental characterization on the mobility of microscopic droplets on LIS, despite their importance for heat transfer; microdroplets with diameters $D \leq 100 \, \mu m$ account for nearly 85\% of the total heat transfer.\textsuperscript{8,29} Due to an increased meniscus-to-droplet volume ratio for microdroplets, we expect a strong relationship between the dynamics of the lubricating oil film and droplet movement.

In this paper, we reveal rigorous and gravity-independent self-propulsion of microscopic droplets as small as 2 $\mu m$ in diameter, which traverse distances multiples of their diameters at velocities up to 1100 $\mu m/s$. Gravity-independent droplet sliding has previously been reported only for droplets larger than 100 $\mu m$ in diameter, and no explanation on its nature has been provided.\textsuperscript{15} We hypothesize that this microdroplet mobility, which cannot be observed on solid (super)hydrophobic surfaces, stems from a dynamic redistribution of the lubricant film, and has a great potential to increase sweeping and coalescence rates
during condensation. Furthermore, we propose that this capillary-driven droplet mobility enables the operation of condensers in space or in mobile application, where droplet removal cannot rely on gravity-assisted shedding. Here, we use high-speed interferometry to unveil the transient re-distribution of the oil film during condensation caused by the development of oil wetting ridges. We distinguish two separate regions: oil-rich and oil-poor regions. We show that the lubricant film re-distribution and the associated oil regions cause two distinct condensate droplet movement regimes, where we observe the self-propulsion of microdroplets at the boundary between oil-rich and oil-poor regions. Through experiments and modeling, we further elucidate the dependence of velocity and displacement on oil viscosity, droplet size, inter-droplet spacing, and initial oil film thickness.

**Materials and methods**

**Preparation of lubricant-infused surfaces (LIS)**

To fabricate the substrates, a plain microscope glass slide (Thermo Scientific) was first cleaned with acetone, isopropanol, and deionized (DI) water, and dried with compressed N₂. Subsequently, the glass slide was treated with a layer of commercially available superhydrophobic agent (Glaco Mirror Coat, soft 99 Co.), which is an alcohol-based suspension of silica nanoparticles. Then, the sample was placed in the fume hood for one hour to ensure complete solvent evaporation. To obtain the lubricant-infused surface, the nanostructured surface was impregnated with Krytox oils via spin coating at 1000 – 3000 rpm, depending on the oil viscosity. The initial oil thickness ranged from 4 to 15 μm, as determined by interferometry (see Fig. S1 in the Supplement Information (SI)). The oils used in this work are listed in Table 1. Krytox GPL series oils completely spread on the superhydrophobic sample and also cloak water, i.e. spread on the condensed water droplets, due to positive spreading coefficients, i.e., $S_{os(w)} = \gamma_{sw} - \gamma_{os} - \gamma_{wo} > 0$ and $S_{wo(a)} = \gamma_{wa} - \gamma_{oa} - \gamma_{wo} > 0$, where $\gamma_{wa}$, $\gamma_{oa}$, $\gamma_{wo}$, and $\gamma_{sw}$ denote the interfacial energies between water-air, oil-air, water-oil, oil-solid, and solid-water, respectively.

**Experimental setup**

To observe the dynamics of the lubricant oil and droplets during condensation, the sample was mounted on a Linkam PE120 cold stage using double-sided thermally conductive tape (Marian Inc., Chicago) and placed under an upright microscope (Nikon Eclipse LV100). The thermo-electric cold stage was set to 2 ± 0.2 °C during all experiments. A well-sealed Erlenmeyer flask containing de-ionized (DI) water was heated on a hot plate to approximately 50 °C, as measured by a digital thermocouple meter (Digi-Sense). Compressed N₂ was supplied to the bottom of the container at ≈ 10 liter per minute (LPM) using a flexible
PVC tube. The vapor-saturated N₂ was then guided through a second PVC tube to the sample to achieve 100 % relative humidity near the sample surface. The experiments were performed in an open environment (room temperature ≈ 20 °C at 30 – 40 % relative humidity). The condensation experiments were conducted on horizontally placed samples. Between individual experimental runs, dry N₂ was gently blown over the sample to prevent flooding. The experimental setup, as shown in Fig. 1, was placed on an optical table (TMC) to isolate the setup from environmental vibrations. Two brightfield objectives (50× L Plan SLWD, Nikon, and 100× T Plan Fluor EPI SLWD, Nikon) were used to visualize droplet sliding. Two interferometry objective lenses (10× and 50× CF IC Epi Plan DI Interferometry Objectives, Nikon) were used to visualize transient oil thickness gradients. Videos were recorded using either an AmScope microscope color camera or a Photron FASTCAM Mini AX200 high-speed camera at 30 to 10,000 frames per second (fps).

![Experimental Setup Diagram](image)

**Fig. 1** Schematic of the experimental setup. (Insert) Scanning electron microscope (SEM) images of the nanoparticle coating

| Lubricant          | Viscosity $\mu_o$ [cP] | Surface Tension $\gamma_{oa}$ [mN/m] |
|--------------------|------------------------|-------------------------------------|
| Krytox GPL 102     | 73                     | 17                                  |
| Krytox GPL 104     | 350                    | 17                                  |
| Krytox GPL 105     | 1034                   | 17                                  |
| Krytox GPL 106     | 1627                   | 18                                  |
| Vacuum pump oil    | 500                    | 22                                  |
Interferometry

Interference microscopy allows for non-contact profiling of the dynamic re-distribution of the oil film on LIS. We used monochromatic light sources (SOLIS-623C Red LED and Green LED M530L3, Thorlabs) to measure the oil meniscus shape surrounding the droplets and a white light halogen lamp to qualitatively visualize the dynamic change in oil film thickness during condensation. Since the resolution of the Photron high-speed camera is limited to 370 nm/pixel at 50× magnification, the maximum meniscus slope $\varphi$ that could be discerned with the green LED ($\lambda = 530$ nm) was approximately $35^\circ$. The change in oil meniscus height $\Delta h$ between two neighboring interference fringes (bright and dark) of distance $\Delta x$ is then given by\textsuperscript{32}:

$$\Delta h = \frac{\lambda}{2} = \Delta x \tan \varphi .$$

(1)

Results and discussion

Oil meniscus shape surrounding a microdroplet on LIS

The oil meniscus surrounding a droplet becomes increasingly important as the droplet size decreases, as it plays a key role in droplet dynamics on LIS.\textsuperscript{33} The wetting state of a millimetric droplet placed on LIS has been extensively studied.\textsuperscript{17,19,20,23} As shown in Fig. 2a, an annular oil ridge (i.e., meniscus) surrounds the base of the droplet and a thin oil film separates the droplet from the substrate. Microdroplets have a similar wetting state, however, the meniscus-to-droplet size ratio is significantly increased, as illustrated in Fig. 2b. To quantify the relationship between the meniscus shape and the droplet size at the microscale, we experimentally observe the shape change of the oil meniscus as a water droplet slowly evaporates on LIS (the evaporation of Krytox oil is negligible). Figure 2c shows the evolution of the profiles of the microdroplets and corresponding oil menisci during evaporation (for comparison, see Figs. 2a,b). Interestingly, the maximum meniscus height remains nearly constant when the droplet diameter is greater than $D \geq 130$ $\mu$m, likely caused by the limited oil supply on LIS. For droplets $D < 130$ $\mu$m, the maximum meniscus height decreases with decreasing droplet size.
To allow for mathematical modeling (see modeling section below), we are interested in obtaining an analytical expression describing the meniscus shape. For an isolated object placed at the liquid-air interface of a bulk liquid, the interface will deform to form a well-developed meniscus whose shape is governed by the Laplace equation:\(^\text{23}\)

\[
\gamma a \left\{ \frac{d^2 h}{dx^2} + \frac{dh}{dx} \frac{dh}{dx} \right\} + g \left( \rho_l - \rho_a \right) h = 0 ,
\]

(2)

\(\gamma\): interfacial tension, \(a\): radius of curvature, \(g\): gravitational acceleration, \(\rho_l\): density of the liquid, \(\rho_a\): density of the air.
where $x$ denotes the distance from the center of the object; $h = h(x)$ is the height of the meniscus above the equilibrium liquid level, and $\rho_l$ and $\rho_a$ are the liquid and air densities, respectively. For eq. (2), a general analytical solution is not available. However, for the special case of a symmetrical object and unlimited liquid supply, eq. (2) can be approximated by two asymptotic regimes at $x \ll l_c$ (‘inner’ regime) and $x >> l_c$ (‘outer’ regime), where $l_c = (\gamma_{oa}/\rho_o g)^{1/2}$ is the capillary length.\textsuperscript{23,34} For Krytox oil, the capillary length is approximately $l_c = 1$ mm. Unfortunately, both of the ‘inner’ and ‘outer’ solutions are not a good fit to represent the meniscus around a microdroplet on LIS, as shown in Fig. 2c. However, we found that the meniscus profile can be well described by an exponential expression: $h(x) = a \exp(-bx) + c$,\textsuperscript{35} where the fitting parameters $a$, $b$ and $c$ are determined empirically. This exponential approximation will be used for the remainder of this study.

**Transient oil re-distribution and formation of oil menisci**

The surface of a pristine sample is covered with an oil film of uniform thickness. During condensation, droplets nucleate at the oil-air interface and submerge into the oil due to capillary forces and cloaking.\textsuperscript{16} When the condensed droplets are still sufficiently small, we observe dense microscopic droplets ($D \approx 3$ $\mu$m $<$ oil film thickness) submerged within the oil, having a relatively smooth oil-air interface. As droplets continue to grow via direct condensation, the oil between submerged droplets drains, allowing for droplet coalescence. The characteristic time for droplet coalescence is directly proportional to the oil viscosity.\textsuperscript{24,37} Hence, immersed droplets grow faster for the low viscosity oil (GPL 102, 73 cP) and the droplet size distribution becomes less uniform, as shown in Fig. 3a. After protruding the oil-air interface, droplets move around on the sample and coalesce with neighboring droplets. For the high viscosity oil (GPL 106, 1627 cP), the coalescence resistance is higher and the densely packed pattern of uniformly sized microdroplets persists for longer periods of time, as shown in Fig. 3b. Eventually, coalescence is promoted due to a higher squeezing pressure as droplets grow bigger. Immediately following coalescence, droplet-vacant regions appear. As condensation continues, larger droplets with smaller ones trapped in their oil menisci form clusters due to capillary interactions. Relatively larger droplets ($D > 90$ $\mu$m) of comparable size typically remain in this cluster without coalescing for a period on the order of 10s of seconds. In the brightfield-videos, darkened regions appear surrounding these droplet clusters, as seen in Figs. 3a, b. We attribute this darkened region to the existence of menisci, i.e., oil-rich regions surrounding large droplets or droplet clusters. The total area of such oil-rich regions depends strongly on the sizes of the droplets and the initial lubricant layer thickness. Due to conservation of mass, oil drains from the peripheral areas as it accumulates near the droplet clusters, and oil-poor regions form. The location and area-ratio of oil-
rich and oil-poor regions change dynamically due to droplet growth and movement during condensation. For example, oil-rich regions can re-develop within oil-poor regions due to the same re-distribution mechanism after droplet nucleation and growth. Over time, the oil thickness in the oil-rich and oil-poor regions decreases because of continuous lubricant depletion.\textsuperscript{21} Only once the lubricant is severely depleted, this dynamic re-distribution no longer occurs. Fig. 4 visualizes the uneven distribution of lubricant after the oil re-distribution process using interferometry. Using 3D confocal fluorescence microscopy, we measured the oil film thickness of the oil-poor regions after two condensation sweeping cycles to \( \approx 3 \ \mu\text{m} \). In the oil-rich region surrounding a droplet with \( D \approx 37 \ \mu\text{m} \), the meniscus is up to 12 \( \mu\text{m} \) tall. Due to the incompatibility of Krytox oils with common fluorescent dyes, we used vacuum pump oil (500 cp) dyed with Lumogen F Red 305 (BASF Colors & Effects) for these confocal microscopy measurements (see Fig. S2).

![Fig. 3 Time sequence showing the re-distribution of the lubricant layer for (a) Krytox GPL 102 and (b) Krytox GPL 106 during early stages of water vapor condensation. Examples of oil-rich and oil-poor regions are outlined by dashed yellow circles and red rectangles, respectively.](image1)

![Fig. 4 Visualization of the uneven lubricant layer after the initial oil re-distribution in the same region on a sample using (a) brightfield and (b) interferometry imaging.](image2)
Movement of microdroplets induced by asymmetrical oil menisci

The coexistence of oil-rich and oil-poor regions, which prevail at varying length scales after the initial redistribution, strongly influences the mobility of microdroplets (see Movie S1). As shown in Fig. 5a, nucleation is predominantly found in the oil-poor regions (dashed red rectangle), since the oil film is thin and poses a low conduction resistance (i.e., the oil-air interfacial temperature is lowest).\textsuperscript{16,22,29} The microdroplets are generally pinned before growing large enough through direct condensation, at which point they suddenly coalesce with nearby droplets. Their growth and mobility are similar to those of droplets condensing on (super)hydrophobic surfaces, but will not jump out of plane because of strong adhesion and viscous dissipation.\textsuperscript{38,39} Conversely, microdroplets display high mobility in the oil-rich and transition regions surrounding larger pinned droplets or droplet clusters. After nucleation and growth via direct condensation in the oil-poor region, a microdroplet protrudes the oil film and becomes visible at the periphery of an oil-rich region. Then, the microdroplet starts to move towards the big droplet along the center-to-center line and finally comes to a halt at a certain distance $r_c$ from the big droplet. This distance depends on the sizes of the microdroplet, the big droplet, and the meniscus. Droplets of all sizes are highly mobile on substrates infused with the low viscosity oil (Krytox GPL 102), so the overall displacement distance is short due to frequent random coalescences. For high viscosity oils (Krytox GPL 104, 105,106), the movement of microdroplets is not random: microdroplets located in the transition regions spontaneously move long distances (multiples of their diameters) towards the big central droplet, sometime regardless of the existence of other neighboring droplets close-by, as shown by the colored tracks representing droplet motion in Fig. 5b. In Fig. 5c, we plot the displacement - velocity profiles of the moving droplets from Fig. 5b. Initially, the microdroplet accelerates and the velocity increases. After reaching a size-dependent maximum velocity $v_{\text{max}}$ at the critical distance $r_c$ from the big droplet, microdroplets decelerate. Their movement seizes as either a) the two droplets coalesce, or b) the microdroplet becomes almost fully submerged in the oil meniscus (see Fig. S3). The velocity profiles for different droplet sizes are self-similar, which implies that a common physical mechanism underlies the movement. The same kind of movement is also observed on vertical samples during vapor condensation (see Movie S2 and Fig. S4). Side view images in Figs. 5d-g exemplify a typical sequence of microdroplet mobility. We hypothesize that capillary attraction causes the observed droplet movement on LIS. When the menisci of two neighboring droplets overlap, the non-symmetry on opposing sides of a droplet induces an attractive force.\textsuperscript{26–28} Consequently, in oil-poor regions where menisci do not extend far enough to interact with neighboring wetting ridges, microdroplets display no or little movement.
Fig. 5 Gravity-independent microdroplet movement. (a) Time sequence of a condensation process on LIS. (b) Microdroplets move toward one big pseudo-stationary droplet sitting in the center of the oil-rich region. (c) Relationship of the velocity of the small moving droplets in (b) and their displacement. (d) – (g) A typical movement in side view.

To test our hypothesis on the influence of oil menisci on the self-propulsion of droplets in oil-rich regions, we use high-speed interferometry to visualize the interplay of oil menisci and droplet movement. Fig. 6a shows typical interference fringe patterns surrounding the droplets. Following eq. (1), the change in oil thickness along the red line is plotted in Fig. 6b. We define $\phi_L$ and $\phi_R$ as the effective angles of attack on the left and right side of the moving microdroplet, respectively (see Fig. 6b). Due to the overlapping menisci of the two droplets, the meniscus slope $\phi$ along the apparent fluid contact line of the microdroplet will change as the two droplets approach each other. The meniscus facing the big droplet is elevated and the slope $\phi$ becomes smaller, i.e., $\phi_L < \phi_R$. The horizontal component of the surface tension force along the apparent contact line becomes unbalanced and induces a lateral capillary attractive force. In most
cases, the direction of movement is coincident with the maximum gradient in lubricant layer thickness, which is along the center-to-center line between droplets.

Fig. 6 Theoretical analysis of the gravity-independent droplet movement. (a) Interference patterns around microdroplets during condensation. (b) Oil film thickness change along the red line in (a). Note that the absolute oil film thickness is unknown. (c) Schematic of the proposed mechanism for capillary-induced droplet movement for a condensed droplet located in the meniscus region of a pseudo-stationary (static) larger droplet. (d) Transformation of the surface tension force from the x-y-z to the x'-y-z' coordinate system by rotation of angle α, where the apparent contact angle θ_app remains constant. (e) Balance of the components of the capillary force in the x'-y coordinate system. (f) Capillary force analysis in the x-z coordinate system. A net driving force acts in the negative x-direction.

Mathematical model of the gravity-independent droplet movement

To further reveal the underlying physical mechanism of this gravity-independent droplet movement, we developed a theoretical model based on a lateral force balance on the microdroplet. We made several simplifying assumptions: A) The model only includes a pair of droplets, a microdroplet droplet with radius \( R_1 \) moving towards a pseudo-stationary larger droplet with radius \( R_2 \), surrounded by an oil-rich region. Several concurring microdroplet movements would be considered independently of each other. B) We restrict the size ratio of the droplets to \( R_1/R_2 << 1 \) in the analysis, so that we can exclude the displacement...
of the bigger droplet. We assume that the larger droplet is nearly immobile unless size-comparable droplets are involved, or it approaches the capillary length of water \((l_c = (\gamma_w/\rho_w g)^{1/2} \approx 2.7 \text{ mm})\), at which point gravity would dominate its movement. C) The droplet shape resembles a spherical cap with a base radius of \(R\). We approximate the droplets as a hemisphere and with the mass \(m_i = 2\pi\rho R^3/3\). The mass of the two droplets is treated as constant during the studied process, as the static droplet has an initial large volume and the microdroplet is partially immersed in the oil, limiting direct condensation. D) The interface between the droplet, the oil cloak, and the air is represented by an effective interfacial tension \(\gamma_{\text{eff}} = \gamma_{wo} + \gamma_{oa}\), which then satisfies an adapted Neumann triangle assumption in which the angles remain constant and rotate as the meniscus slope changes (see Fig. S5).

To determine the net force acting on the microdroplet, we set up a force balance taking into account capillary and viscous forces. The Bond number of microdroplets, \(Bo = \Delta \rho g D^2/\gamma_{wo} \approx 0.00138 << 1\), so that the gravitational force is negligible. In our experiments, the oil viscosity \(\mu_o\) is much larger than that of water \(\mu_w\). For an isolated millimetric/sub-millimetric droplet moving on LIS, viscous friction generally has three sources: viscous dissipation in the droplet, in the oil film underneath the droplet, and in the oil ridge surrounding the droplet. The viscous forces in the drop and oil film scale as \(\mu_o \pi v R\), independent of oil viscosity. The resistance force from the meniscus, which scales as \(\mu_o \pi v R\), typically dominates viscous dissipation for droplets moving on LIS.\(^{18,19,40}\) As a microdroplet approaches the pseudo-stationary droplet, the moving droplet will gradually immerse into the larger static oil ridge. Viscous dissipation is no longer confined to the microdroplet’s own meniscus. Instead, we approximate this case with Stokes flow, \(i.e.,\) the small droplet has to overcome a hydrodynamic drag force \(F_s = 6\pi \mu_o v R_1\). Furthermore, as the small droplet approaches the big one, oil has to squeeze out of the closing gap. We add this distance-dependent hydrodynamic interaction resistance to the Stokes force equation, generalizing \(F = 6\pi \mu_o v (1 + R^2/(r - R_1 - R_2))\), with \(R^* = R_1 R_2/(R_1 + R_2)\).\(^{25}\) Overall, the total viscous resistance force can be approximately as:

\[
F_{r,\text{net}} = (6\mu_o + 2\mu_w)\pi R_1 + 6\pi \mu_o v R^2/(r - R_1 - R_2),
\]

As discussed above, overlapping menisci and different slopes attacking the droplet act as the driving force for microdroplet motion. To compute the driving force, we follow an analysis procedure as outlined in Figs. 6 d-f. First, we approximate the larger meniscus with a constant slope \(\alpha(r)\), which can be obtained from the derivative of the meniscus profile \(h(x) = a \exp(-bx) + c\) at \(x = r\). Then, we rotate the \(x-z\) coordinate system (\(y\) axis is fixed) of the smaller droplet by the angle \(\alpha\), such that the apparent contact angle \(\theta_{\text{app}}\) remains constant. In the \(x'-y-z'\) coordinate system, the capillary force can be computed by integrating the surface tension exerted by the meniscus over the (apparent) lubricant-droplet-air contact line and then
separately projected onto the $x'$-$y$ plane and the $z'$ axis. Forces in the $x'$-$y$ plane are balanced, since $h_{n,d} = \text{const}$., but there will be a net force in the negative $z'$ direction, $F_z = 2\pi r_m y_0 \sin(\varphi')$, where $r_m$ is the projected radius of the meniscus at the (apparent) lubricant-droplet-air contact line. For a droplet subject to a sloped meniscus, the net lateral driving force can be approximated by projecting the force $F_z$ onto the $x$ axis:

$$F_{c,\text{net}} \approx 2\pi r_m y_0 \sin(\varphi') \sin(\alpha).$$

(4)

Note that there is also a vertical force component $F_z = F_z' \cos(\alpha)$, which causes the droplet to immerse into the meniscus.

After adding all relevant forces, Newton’s second law for the moving droplet is then:

$$\ddot{r} + \left(6 \mu_0 + 2 \mu_w \right) \pi R_1 + \frac{6\pi \mu_0 R_1^2}{r - R_1 - R_2} \cdot \ddot{r} - k \cdot \frac{2r m y_0}{m} \cdot \sin(\varphi') \sin(\alpha) = 0,$$

(5)

where $r$ is the center-to-center distance of the two droplets and $m$ is the mass of the moving droplet. We use $k$ as a fitting parameter to account for errors from the approximations made above and set it as $k = 0.9$ to achieve a good agreement between numerical results and experimental data. To solve eq. (5), the parameters $\varphi'$ and $r_m$ need to be computed from geometrical considerations. We correlate the hemispherical expression for the moving droplet, $y = \sqrt{R_1^2 - x^2}$, and the meniscus profile of the static droplet, $h(x) = a \exp(-b(x+r)) + c$, to obtain two intersection points $(x_i, y_i)$ and $(x_n, y_n)$ in the $x$-$z$ coordinate systems of the moving droplet. We can then write: $r_m \approx (x_i + x_n) \sin(\alpha)$. The angle in the air phase $\Theta_a$ is experimentally found to be nearly constant at 150° (see Fig. S5). Based on geometry, the relationship $\varphi' = \Theta_{\text{app}} - (\pi - \Theta_a)$ is obtained and the angle $\Theta_{\text{app}}$ can be computed by differentiating the hemispherical approximation of the moving droplet. Finally, we solve the resulting differential equation using Matlab.

**Dependence of droplet velocity on droplet size and oil viscosity**

From Eq. (5), we know the sliding velocity is directly related to the droplet size, the meniscus shape, and the oil viscosity. Here, we first experimentally determine the fitting parameters for the meniscus shape of oil surrounding a static droplet with radius $R_2 = 35 \, \mu m$. In the following analysis, the size of the pseudo-stationary droplet is considered to be constant to exclude a change of meniscus size. We compare the velocity obtained numerically by solving eq. (5) to droplets of similar size (i.e., varying $R_1$ with $R_2 = 35 \, \mu m$ fixed) from the vapor condensation experiments on LIS with different oil viscosities. Fig. 7a shows the relationship between the maximum velocity and the size of moving droplets. Interestingly, we find that the velocity achieves maximum values for $R_1 \approx 7$-$8 \, \mu m$ (excluding peak values from sudden coalescence.
events) for all viscosities. The velocity approaches zero when the moving droplet size becomes smaller than $R_1 \approx 1.5 \, \mu m$. For these small droplet sizes, the angle difference $(\phi_L - \phi_R)$ around the moving droplet becomes negligible due to its small radius and the gentle slope of the meniscus. When the size of moving droplet becomes comparable to that of the static droplet (i.e., $R_1 \approx R_2$), the velocity also rapidly decreases, as the assumption of $R_1/R_2 << 1$ fails and the two droplets equally contribute to the movement.

We also examine the relationship of maximum velocity and oil viscosity, as presented in Fig. 7b. Our numerical results are in good agreement with the experimental results, and show the expected decrease in sliding velocity with increasing lubricant viscosity. The numerical results indicate that microdroplets could achieve much higher sliding velocities than those obtained experimentally in this study at even lower lubricant viscosity due to vanishing viscous dissipation.

![Fig. 7 Experimental and numerical results on the influence of (a) droplet size and (b) lubricant viscosity on the maximum sliding velocity.](image)
Conclusion, significance, and outlook

In this paper, we investigated the gravity-independent movement of microdroplets (focusing on \( D \leq 40 \mu m \)) during water vapor condensation on lubricant-infused surfaces. We experimentally reported a dynamic re-distribution process of the lubricant layer on LIS during vapor condensation, which results in a novel sliding mechanism for condensate microdroplets. In oil-rich regions, the gravity-independent self-propulsion of microdroplets follows a self-similar movement pattern, which is independent of initial lubricant thickness, lubricant viscosity, or droplet size. We successfully modeled this movement based on a lateral force balance. Overlapping lubricant menisci between droplets create an anisotropic oil profile, resulting in unbalanced lateral components of the surface tension force along the droplet – lubricant contact line. We reported that the sliding velocity initially increases due to a relatively big difference of the angle of attack on the two sides of the microdroplet. Then, the velocity sharply decreases as the small droplet approaches the bigger one and submerges into the oil meniscus or the larger droplet. Faster sliding velocities are achieved by decreasing the lubricant viscosity, but the distance and occurrence of sliding events generally decrease due to frequent droplet coalescence and a higher mobility of the larger microdroplets.

Our findings have broad implications on the selection of lubricants and the use of LIS for thermal management and water harvesting systems. This reported novel gravity-independent droplet movement is promising for zero-gravity situations (e.g., in space) or portable devices, where droplet removal and droplet shedding cannot rely on gravity. Furthermore, we expect this capillary-driven droplet motion on LIS to increase sweeping and re-nucleation rates, reduce droplet sizes, and consequently lead to enhanced condensation heat transfer rates as compared to traditional surfaces. We hope this work will be helpful in the selection of a lubricant for LIS to achieve high heat transfer and water collection rates, to enhance our understanding of lubricant depletion and drainage, and to complement similar studies on microdroplet or microparticle movement at air-liquid interfaces.

Conflicts of interest

There are no conflicts of interest.
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Supplement Information (SI)

Content

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S2: 3D confocal fluorescence measurement for lubricant thickness characterization
S3: Droplet immersion into lubricant layer
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Movie 1: Droplet mobility in oil-rich and oil-poor regions
Movie 2: Droplet movement during vapor condensation on a vertical sample
S1. Determination of initial lubricant layer thickness

We use high-speed interferometry to observe the early stages of vapor condensation to estimate the initial oil film thickness. First, we focus the 50x interferometry objective on the oil-air interface. The uniform black-white interference patterns seen in Fig. S1a originate from a slightly misaligned (i.e., tilted) sample holder with respect to the objective. Next, we gently blow water vapor over the sample at very low flow rates (2 LPM). As shown in Fig. S1b, nucleated droplets appear, but do not interrupt the interference patterns, which means the droplets are still fully immersed in the lubricant layer. Anand et al. showed that submerged droplets are spherical.\(^1\) As condensation proceeds, the droplets grow mainly through coalescence. When the droplets grow large enough and protrude the oil-air interface, small circular interference fringes form (red circles in Fig. S1c). We measure the droplet diameter \(D\) at this instance and assume that it is equal to the initial oil film thickness \(h_{\text{oil}}\), based on the spherical geometry of the droplets.

Fig. S1 Determination of initial oil film thickness using high-speed interferometry imaging. (a) Smooth oil-air interface before vapor condensation. (b) Small condensed droplets are fully immersed in the oil film. (c) The condensed droplets start to protrude the oil-air interface (red circles), at which point we measure the droplet size \(D\) and set it equal to the initial oil film thickness \(h_{\text{oil}}\).
**S2. 3D confocal fluorescence measurement for lubricant thickness characterization**

To obtain the absolute thickness of the lubricant at later stages during condensation (i.e., after lubricant re-distribution), we used scanning confocal fluorescence microscopy (Zeiss LSM 880 Airyscan Confocal Microscope) to measure the film thickness in oil-rich and oil-poor regions separately. Vacuum pump oil (Cole Parmer CP500) was used for this measurement and dyed with Lumogen F Red 305 (BASF Colors & Effects). We infused a Glaco-coated glass slide with the pump oil at 2500 rpm. Then, we conducted water vapor condensation experiment under the microscope. A 561 nm laser was used and the resolution in the vertical direction (Z stack) was set at 0.2 μm/slice. Fig. S2a shows a confocal microscope image of the oil film on LIS after two sweeping cycles. The red fluorescence signals represent the vacuum pump oil. We determined the oil film thickness of the oil-rich region surrounding a droplet with \( D \approx 37 \mu m \) (Fig. S2b) to \( h_{rich} \approx 12 \mu m \) after two condensation sweeping cycles. In the oil-poor regions (Fig. S2c), we found an oil film thickness of only \( h_{poor} \approx 3 \mu m \).

Fig. S2 Characterization of the oil film thickness in the oil-rich and oil-poor regions. (a) Top-view of a confocal microscope image after two condensation sweeping cycles. Fluorescence signals (red) show the vacuum pump oil, whereas droplets appear as empty spaces (black; no dye). (b) Cross-sectional view of a condensed droplet (\( D = 37 \mu m \)) and the oil film, corresponding to the upper yellow dashed line in (a). \( h_{rich} \) is defined as the oil film thickness at the apparent lubricant-droplet contact line. (c) Cross-sectional view of the oil film in the oil-poor region along the lower line in (a). Scale bars are 10 μm.
S3. Droplet immersion into lubricant layer

During self-propulsion of microdroplets, we observed that the majority of moving droplets fully immersed into the oil ridges of static droplets. To confirm our initial observation, we turned off the vapor supply after a period of vapor condensation to stop re-nucleation in the transition regions. Then, we focused on a static droplet surrounded by smaller droplets, which were either arrested at various distances from the larger droplet (black circles in Fig. S3a) or were still moving towards the larger droplet (yellow circles in Fig. S3a). We used high-speed interferometry to inspect the meniscus smoothness near these droplets. Fig. S3a shows the interference fringes nearby a static big droplet by lifting the focus plane of the microscope. From section S1 of the SI, we know that the interference fringes of the oil meniscus will be interrupted by the existence of partially immersed (i.e., partially protruding) droplets, as shown in Fig. S3b. When the self-propulsion of a small moving droplet ends, the fringe pattern is ordered and parallel, which indicates that the droplet is fully immersed in the oil ridge. We also note that larger droplets do not fully immerse, since their size is larger than the meniscus height surrounding the big droplet.

![Image](image.png)

Fig. S3 Visualization of microdroplets immersed into the oil ridge surrounding a large pseudo-stationary droplet. (a) Interference patterns around a static droplet surrounded by several small droplets. (b) Interference patterns of the meniscus near a moving droplet (yellow circles in (a)). (c) Interference patterns of the meniscus near a static, fully submerged droplet (black circles in (a)).

S4. Vapor condensation on vertical samples

To verify that the microdroplet movement reported in the main manuscript is independent of gravity, we conducted additional vapor condensation experiments on a vertical sample. The setup is shown in Fig. S4. We observed the same movement of microdroplets as that on horizontal substrates (see Movie S2). However, once droplet sizes approach the capillary length, gravity comes into effect and droplets slide...
down, i.e., naturally sweep the surface. We notice a decrease in the oil thickness in the trail of the sliding droplet, which enhances nucleation and the formation of more oil-rich regions.

![High-speed camera](image)
![LED light source](image)
![Microscope](image)
![Cold stage](image)

Fig. S4 Simplified schematic of the vertical setup

**S5. Adapted Neumann triangle**

For a non-cloaking oil, the water droplet (w), the oil ridge (o), and the surrounding vapor/air (a) meet at the fluid three-phase contact line. The angles between these phases are given by the Neumann triangle:

$$\cos \Theta_w = \frac{\gamma_{oa} - \gamma_{wo}^2}{2 \gamma_{wo} \gamma_{wa}}, \quad \cos \Theta_o = \frac{\gamma_{wa} - \gamma_{oa}^2}{2 \gamma_{wo} \gamma_{oa}}, \quad \cos \Theta_a = \frac{\gamma_{wo} - \gamma_{wa}^2}{2 \gamma_{oa} \gamma_{wa}}. \quad (S1)$$

Here, $\Theta_w, \Theta_o, \Theta_a$ denote the angles inside the droplet, the oil ridge, and the surrounding air phase, respectively (see inset of Fig. S5a). The Krytox GPL oils used in our experiments cloak water droplets due to a positive spreading coefficient, eliminating a direct three-phase liquid contact line.\(^3\) The thickness of the cloaking layer was experimentally and theoretically reported on the scale of tens of nanometers.\(^1,4\)

Here, we will use an effective interfacial tension, $\gamma_{eff} = \gamma_{wo} + \gamma_{oa} - \delta$, at the droplet-lubricant-air interface, where $\delta$ is a function of the thickness of the nanoscopic oil wrapping layer.\(^5\) We hypothesize that an adapted Neumann triangle is still applicable, where three surface tension vectors form a Neumann triangle, i.e., $\gamma_{eff} + \gamma_{oa} + \gamma_{wo} = 0$, and define the apparent ‘three-phase’ fluid contact line where the concave oil ridge meets the convex droplet profile, as seen in Fig. S5a. The angle $\Theta_a$ can be experimentally measured from side-view images of microdroplets placed on LIS. Fig. S5b shows that $\Theta_a$ fluctuates between 140° and 160° for a wide range of droplet sizes. For the calculations presented in the main manuscript, we assume that $\Theta_a$ is constant and at 150°, independent of droplet size. With this insight, we can also compute the effective surface tension $\gamma_{eff}$ and replace $\gamma_{w}$ in equation eq. (S1) to calculate $\Theta_w$ and
Furthermore, we assume that the Neuman triangle of a moving microdroplet will rotate with respect to the solid surface and the three angles remain constant. Based on the geometry of the droplet, the apparent contact angle $\Theta_{\text{app}}$, the meniscus angle of attack $\varphi$, and $\Theta_a$ have the relationship $\Theta_{\text{app}} = \varphi + (\pi - \Theta_a)$ at the apparent fluid contact line.

Fig. S5 Adapted Neumann triangle and measurements of the angle in the air phase $\Theta_a$. (a) Schematic of an adapted Neumann triangle (insert) for a microdroplet with an oil cloaking layer. We assume an apparent contact line where the concave oil ridge meets the convex droplet profile. (b) Relationship of the adapted Neumann angle in the air phase $\Theta_a$ with droplet size. Black squares: experimental data for $\Theta_a$. Red dash line: approximated average value from experimental data.

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