Supporting Information: How droplets nucleate and grow on liquids and liquid impregnated surfaces

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Liquid	Density (ρ)	Ywa	Yoa	Ŷwo	S _{wo(a)}	S _{ow(a)}	θ_{wa} **	θ_{wo}^{**}
	g/cc	mN/m	mN/m	mN/m	mN/m	mN/m		
Tetradecane	0.76 ⁽¹⁾	72.2	26.2 ⁽¹⁾	50.1 ^(*)	-96.1	-4.1	26.25	140.4
Hexadecane	0.77 ⁽¹⁾	72.2	27.5 ⁽¹⁾	51.1 ⁽²⁾	-95.8	-6.4	32.3	131.0
Benzene (initial)	0.877 ⁽¹⁾	72.0	28.88 ⁽¹⁾	34.0 ⁽³⁾	-77	8.94		
Benzene (final)	0.877 ⁽¹⁾	60.61 ⁽⁴⁾	28.88 ⁽¹⁾	34.0 ⁽⁴⁾	-67	-3.3	17	148
Toluene	0.9 ⁽¹⁾	72.2	27.9 ⁽¹⁾	42.9 ⁽²⁾	-87.2	1.4		
Silicone Oil	0.94-0.97	72.2	20.0	47.0 ⁽⁵⁾	-99.2	5.2		
Carbon Disulfide	1.26 ⁽¹⁾	72.2	31.6 ⁽¹⁾	47.6 ⁽³⁾	-88.18	-6.94	30	130.6
Dichloromethane	1.3 ⁽¹⁾	72.2	28.3 ⁽¹⁾	26.4 ⁽⁴⁾	-70.8	16.1		
[BMIm ⁺][Tf2N ⁻] (initial)	1.43 ⁽⁶⁾	72.0	34.0	13.0 ⁽⁶⁾	-51.0	25.0		
[BMIm ⁺][Tf2N ⁻] (final)	1.43 ⁽⁶⁾	42.0 ^(*)	34.0	13.0 ⁽⁶⁾	-21.0	-5.0	15.6	119.8
1-Bromonaphthalene	1.50 ⁽¹⁾	72.2	44.4 ⁽¹⁾	41.66	-69.46	-13.86	31.8	114.0
Chloroform	1.5 ⁽¹⁾	72.2	27.15 ⁽¹⁾	38.8 ⁽²⁾	-83.9	6.3		
Krytox	1.86 ⁽⁶⁾	72.2	17.2	49.0 ⁽⁶⁾	-104.0	6.0		

* Measured ** Calculated from $\cos\theta_{wo} = \frac{\gamma_{oa}^2 + \gamma_{wo}^2 - \gamma_{wa}^2}{2\gamma_{oa}\gamma_{wo}}$ and $\cos\theta_{wa} = \frac{\gamma_{oa}^2 + \gamma_{wa}^2 - \gamma_{ow}^2}{2\gamma_{wa}\gamma_{wo}}$

Supplementary Table 1: Spreading Coefficients of some common liquids on water. The thermodynamic properties (density, surface tension) correspond to measurements at room temperature (T=20 °C)

		Interfacial Energy Comparison			SR*			
Environment	ywo / ywa	E_{III}/E_I	E_{IV}/E_I	E _{IV} /E _{III}	State I (on OTS Surface)	State II $\theta_{ws(o)}=18$ 0°	State III (on OTS Surface)	State <i>IV</i>
Air	1				1.437 $(\theta_{ws(a)}=105^{\circ})^{*}$			
Hexadecane	0.71	0.801	0.793	0.99		1.337	1.337 $(\theta_{ws(o)}=166^{\circ})^{*}$	1.333
Tetradecane	0.694	0.785	0.782	0.997		1.329	1.329 $(\theta_{ws(o)}=163^{\circ})^{*}$	1.328
1-Bromonaphthalene	0.62	0.653	0.624	0.956		1.267	1.267 $(\theta_{ws(o)}=160^{\circ})^{*}$	1.254
[BMIm ⁺][Tf2N ⁻] (final)	0.31	0.202	0.194	0.962		1.077	1.076 $(\theta_{ws(o)}=143^{\circ})^{*}$	1.073

* Measured.

Supplementary Table 2: Comparison of interfacial energy of cluster formation and critical saturation ratios $(SR^* = exp[(2\beta)/(3kTn^{*1/3})])$ for nucleation of 2 nm diameter droplets in different states on a LIS with hydrophobic solid surface for some common liquids. The hydrophobic surface here is an OTS (octadecyltrichlorosilane) coated smooth silicon surface. The contact angles (θ) of the liquids were measured within water using goniometer. From these measurements, the contact angle of water within the liquid was evaluated as $180^{\circ}-\theta$ where θ denotes value corresponding to the average of advancing and receding contact angles of droplets on the surface.

Liquid	Density ($ ho_o$)	Solubility of Water in Liquid		
	g/cc	(ppm by weight)	(mol/m ³ of Liquid)	
1,2- dibromotetrafluoroethane	2.162	3 ⁽⁷⁾	0.36	
Krytox	1.86 ⁽⁶⁾	17 ⁽⁸⁾	~1.8	
Octadecane	0.765 ⁽¹⁾	50.33 ⁽⁷⁾	2.14	
Hexadecane	0.77 ⁽¹⁾	53.97 ⁽⁷⁾	2.31	
Tetradecane	0.76 ⁽¹⁾	57.92 ⁽⁷⁾	2.45	
Toluene	0.9 ⁽¹⁾	541.78 ⁽⁷⁾	27.1	
Silicone Oil	0.94-0.97	700 ⁽⁹⁾	36	
Chloroform	1.5 ⁽¹⁾	871 ⁽⁷⁾	72.6	
Dichloromethane	1.3(1)	1761.6 ⁽⁷⁾	127.3	

* $C(mol/m^3)=10^{-3} * [\rho (g/cc)*1000] / [M_{water}(g/mol)] * C(ppm)$ where $M_{water}=18$

* These solubilities correspond to STP conditions.

Supplementary Table 3: Water solubilities in some liquids



Supplementary Figure S1: Schematic of Experiments. (a) Setup for condensation experiments (b) Setup

for generating vapor saturated oil



Supplementary Figure S2: Energy Barrier between State I and State III. Critical saturation ratio for nucleation at 20 °C of 2 nm diameter droplets for variable contact angles of water on the solid surface in presence of air (State *I*, blue curve) and oil (State *III*, orange curves) as a function of surface wettability in air ($\theta_{ws(a)}$), in oil ($\theta_{ws(o)}$), and γ_{wo}/γ_{wa} . Also shown on the plot are critical saturation ratios for nucleation of water on a OTS coated surface in air, and on OTS coated surface immersed in different oils. It can be seen SR^* for nucleation on OTS is highest in air environment.



Supplementary Figure S3: Energy Barrier between State I and State IV. Critical saturation ratio for nucleation at 20 °C of 2 nm diameter droplets on the solid surface in presence of air (State *I*, blue curve) and at oil-air interface (State *IV*, orange curves) as a function of contact angle of droplet in air ($\theta_{ws(a)}$), lens angles of droplet (θ_{wo} , θ_{wa}). Here solid orange lines represent oils with $\gamma_{wo} \leq \gamma_{wa}$ and dashed orange lines represent oils with $\gamma_{wo} \geq \gamma_{wa}$. Also shown on the plot are SR^* for nucleation of water on a OTS coated surface in air, and SR^* for nucleation at oil-air interface for some liquids. It can be seen SR^* for nucleation is highest on the OTS coated solid surface.



Supplementary Figure S4: Energy Barrier between State III and State IV. Critical supersaturation for nucleation at 20 °C of 2 nm diameter droplets within the oil (State *III*, blue curve) and at oil air interface (State *IV*, orange curves). However instead of SR^* , we plotted $(SR^*)^{1/\gamma_w}$ to obtain the graph independent of the oil-droplet interfacial tension. Here solid orange lines represent oils with $\gamma_{wo} \leq \gamma_{wa}$ and dashed orange lines represent oils with $\gamma_{wo} \geq \gamma_{wa}$. Also shown on the plot are SR^* for nucleation of water on OTS coated surface in liquids (red markers), and SR^* for nucleation at oil-air interface for some liquids (black markers).



Supplementary Figure S5: Cryo-FIB section of 1000 cSt Silicon Oil Surface



Supplementary Figure S6: Cryo-FIB section of 1000 cSt Silicon Oil Surface



Supplementary Figure S7: Polyhedral droplet profiles of condensing droplets. The image represents

Frame 298/300 of the movie S3 accompanying this work. The droplets have been overlaid with polygons

to represent the boundaries between condensing droplets.

Supplementary Note 1: Nucleation States and associated Free Energy of Nucleation

In state I, for a nuclei to form on a solid surface in presence of air environment, the total surface energy of the system is given by $E_{drop a} = \gamma_{ws} A_{ws}^d + \gamma_{wa} A_{wa}^d - \gamma_{sa} A_{sa}^d$. The superscript 'd' signifies droplet. The droplet volume is given by $V = \pi \psi_1 R^3 / 3$ where R=Radius of curvature of droplet, $\psi_1 = (2 + \cos \theta_{ws(a)})(1 - \cos \theta_{ws(a)})^2$ and $\theta_{ws(a)}$ is the contact angle of the condensate on the solid surface. Since $\gamma_{ws} = \gamma_{sa} - \gamma_{wa} \cos \theta_{ws(a)}$, $A_{ws}^d = \pi R^2 \sin^2 \theta_{ws(a)}$ and $A_{wa}^d = 2\pi R^2 (1 - \cos \theta_{ws(a)})$ and $A_{sa}^d = A_{ws}^d$ $\therefore E_{drop a} = \gamma_{sa} A_{ws}^d - \gamma_{wa} A_{ws}^d \cos \theta_{ws(a)} + \gamma_{wa} A_{wa}^d - \gamma_{sa} A_{ws}^d = \gamma_{wa} (A_{wa}^d - A_{ws}^d \cos \theta_{ws(a)})$ $\Rightarrow E_t = E_{drop a} = \psi_1 \pi R^2 \gamma_{wa} = \psi_1 \pi \left(\frac{3V}{\pi \psi_1}\right)^{2/3} \gamma_{wa}$ (1)

In state *II*, the surface energy required for creating a cluster through homogeneous nucleation within an oil environment is given as $E_{II} = \gamma_{wo} A_{wo} = 4\pi (3V/4\pi)^{2/3} \gamma_{wo}$.

In state *III*, we consider heterogeneous nucleation within oil. Oils for which the spreading coefficient of oil on surface in presence of water is positive i.e. $S_{os(w)} = \gamma_{sw} - \gamma_{wo} - \gamma_{os} > 0$, heterogeneous nucleation of oil on solid surface is improbable because any molecule reaching the surface will be replaced by the surrounding oil molecules. Here, γ_{sw} and γ_{os} are the specific surface energy of solid in presence of condensate (water), and in presence of oil respectively. If the oil does not spread on the solid surface in presence of water (i.e. $S_{os(w)} < 0$), the surface energy term is given by $E_{drop o} = \gamma_{ws} A_{ws}^d + \gamma_{wo} A_{wo}^d - \gamma_{so} A_{so}^d$. Similar to derivation of State I, the surface energy can be written as

$$E_{III} = E_{drop,o} = \psi_2 \pi \left(\frac{3V}{\pi \psi_2}\right)^{2/3} \gamma_{wo}$$
⁽²⁾

where $\psi_2 = (2 + \cos \theta_{ws(o)})(1 - \cos \theta_{ws(o)})^2$ and $\theta_{ws(o)}$ is the contact angle of the condensate on the solid surface in presence of oil.

Finally we consider heterogeneous nucleation on oil-air interface (State *IV*). If the condensate itself does not wet the oil i.e. $S_{wo(a)} = \gamma_{oa} - \gamma_{wa} - \gamma_{wo} < 0$, and the oil does not cloak the condensate i.e. $S_{ow(a)} < 0$ then the nuclei will form a lens without any adsorbed monolayer on the condensate.¹⁰ Since the gravity effects are negligible for droplets that are much smaller than the capillary length (~ mm), the oil surface is effectively planar up to the three phase contact line for non-cloaking oil¹⁰ and the total surface energy of the system is given by $E_{lens} = \gamma_{wo}A_{wo}^{l} + \gamma_{wa}A_{wa}^{l} - \gamma_{oa}A_{wa}^{l}$. The superscript '*I*' signifies lens. By balance of forces at the three-phase contact line, we have $\gamma_{wo} \sin \theta_{wo} = \gamma_{wa} \sin \theta_{wa}$, $\gamma_{wa} \cos \theta_{wa} + \gamma_{wo} \cos \theta_{wo} = \gamma_{oa}$, $R_l = R_{wo} \sin \theta_{wo} = R_{wa} \sin \theta_{wa}$. Here: R_l is the base radius of the lens, R_{wo} is the radius of curvature of the

lower section of lens, and R_{wa} is the radius of curvature of upper section of lens.

Also,
$$\cos\theta_{wo} = \frac{\gamma_{oa}^2 + \gamma_{wo}^2 - \gamma_{wa}^2}{2\gamma_{oa}\gamma_{wo}}$$
 and $\cos\theta_{wa} = \frac{\gamma_{oa}^2 + \gamma_{wa}^2 - \gamma_{ow}^2}{2\gamma_{wa}\gamma_{oa}}$

Volume of lens,
$$V = \frac{\pi}{3} \lambda R_l^3$$
 where $\lambda = \frac{\sin \theta_{wo} (2 + \cos \theta_{wo})}{(1 + \cos \theta_{wo})^2} + \frac{\sin \theta_{wa} (2 + \cos \theta_{wa})}{(1 + \cos \theta_{wa})^2}$ (3)

The area terms are then given as $A_{wo}^{l} = \frac{2\pi R_{l}^{2}}{1 + \cos\theta_{wo}} = 2\pi R_{wo}^{2} \left(1 - \cos\theta_{wo}\right)$, $A_{oa}^{l} = \pi R_{l}^{2} = \pi R_{wo}^{2} \sin^{2}\theta_{wo}$

$$A_{wa}^{l} = \frac{2\pi R_{l}^{2}}{1+\cos\theta_{wa}} = 2\pi R_{wa}^{2} (1-\cos\theta_{wa}) = 2\pi R_{wo}^{2} (1-\cos\theta_{wa}) \frac{\sin^{2}\theta_{wo}}{\sin^{2}\theta_{wa}}$$

$$\therefore E_{lens} = \gamma_{wo} 2\pi R_{wo}^{2} (1-\cos\theta_{wo}) + \gamma_{wa} 2\pi R_{wo}^{2} (1-\cos\theta_{wa}) \frac{\sin^{2}\theta_{wo}}{\sin^{2}\theta_{wa}} - \gamma_{od} \pi R_{wo}^{2} \sin^{2}\theta_{wo}$$

$$\Rightarrow E_{IV} = \pi \left(\frac{3V}{\pi\lambda}\right)^{2/3} \xi \gamma_{wo} \qquad (4)$$

where $\xi = \left(\frac{2}{1+\cos\theta_{wo}} - \cos\theta_{wo}\right) + \frac{\sin\theta_{wo}}{\sin\theta_{wa}} \left(\frac{2}{1+\cos\theta_{wa}} - \cos\theta_{wa}\right)$ and
 $\lambda = \frac{\sin\theta_{wo}(2+\cos\theta_{wo})^{2}}{(1+\cos\theta_{wo})^{2}} + \frac{\sin\theta_{wa}(2+\cos\theta_{wa})}{(1+\cos\theta_{wa})^{2}}.$

Using $\gamma_{wo} \sin \theta_{wo} = \gamma_{wa} \sin \theta_{wa}$, the surface energy can also be written in terms of oil-air surface tension as

$$\Rightarrow E_{IV} = \pi \left(\frac{3V}{\pi\lambda}\right)^{2/3} \xi \frac{\sin\theta_{wa}}{\sin\theta_{wo}} \gamma_{wa}$$
(5)

Supplementary Note 2: Nucleation Rates in immiscible liquids

To understand the role of environment and miscibility of vapor molecules with the oil on nucleation rate, we consider the simpler case of homogeneous nucleation.

From nucleation theorem, the nucleation rate $J(m^{-3}s^{-1})$ for homogeneous nucleation is given by¹¹

$$J = Zf^*C_0 \exp\left(-W^*/kT\right)$$
(6)

where Z is the Zeldovich non-equilibrium factor, f^* is the collision rate of monomers with the critical cluster or the attachment frequency, C_0 is the concentration of nucleation sites that is equal to total number of molecules present in an environment, W^* is the work of formation $(W^*=4\beta^3/27\alpha^2)$ of critical cluster size $n^*(\text{where } n^*=(2\beta/3\alpha)^3)$. Here, $\alpha = kT \ln(SR)$ and $\beta = \psi \pi [(3\nu_m)/(\pi\psi)]^{2/3} \gamma$. ¹¹ The Zeldovich factor Z is given by

$$Z = \sqrt{\frac{\left(-d^2 W/dn^2\right)_{n=n^*}}{2\pi kT}} = \frac{3\alpha^2}{4\beta^2} \sqrt{\frac{\beta}{\pi kT}}$$
(7)

The attachment frequency f^* is dependent upon the saturation dynamics of condensing molecules with its environment that can be understood in terms of solute-solvent interactions. The transport of vapor molecules (solute) in a gaseous environment (solvent) occurs through diffusion and is given through Fick's law. The transport of vapor molecules across the oil can also be expressed in terms of Fickean Diffusion if the passage of such molecules does not lead to anomalous effects such as swelling of the oil.¹² With these assumptions, the attachment frequency f^* in a solvent (oil or gas) is given by¹¹

$$f^* = \left(48\pi^2 v_m\right)^{1/3} \alpha_m D_{ab} SR \cdot C_s n^{*1/3}$$
(8)

where D_{ab} is the mutual diffusion coefficient of the vapor in the solvent medium, and *SR* is the saturation ratio defined as $SR=C_c/C_s$ where C_c is the solute concentration and C_s is the solubility of the solute molecule in the solvent, and a_m is the monomer sticking coefficient (accommodation coefficient).^{11,}

When the solvent environment is a gas phase, then $C_c = P_v N_A / \overline{R}T$ and $C_s = P_i N_A / \overline{R}T$ from ideal gas law and the saturation ratio $SR = C_c / C_s$ reduces to $SR = P_v / P_i$. Here P_i is the saturation pressure at temperature T, P_v is partial pressure of condensing species, N_A is the Avogadro's number and \overline{R} is universal gas constant.

From Eqn. to , we can estimate nucleation rates of a condensate in different oils as a function of their properties such as solubility, diffusion coefficient of vapor molecules in oils etc. For comparison, we also evaluate nucleation rates of homogeneous nucleation in air. For water vapor diffusing in air the diffusion coefficient is $\sim 10^{-5} m^2/s$ and from ideal gas law, the typical molar concentration of water vapor molecules is $\sim 1 \text{ moles/m}^3$ at room temperatures. In ambient conditions, the molar concentration of gas molecules is $\sim P_a/\overline{R}T = 40 \text{ moles/m}^3$ where P_a is atmospheric pressure, from which the concentration of nucleation sites/volume is $C_0 \sim 40N_A$.

The concentration of nucleation sites per unit volume in oils can be calculated from $C_0 = (\rho_o/M_o + SR^* C_s)^* N_A$. Here ρ_o and M_o are the density and molecular weight of the oil respectively. As test oils for our

theoretical analysis, we consider Silicone oil with viscosity 10 cSt ($\rho_o = 935 \text{ kg/m}^3$, $M_o = 1250$) and Krytox ($\rho_o = 1860 \text{ kg/m}^3$, $M_o = 2400$) since both polymers are considered very immiscible with water and also cloak the water drops. The diffusion coefficient of small molecules like water in polymers can be obtained using the Free-Volume theory, and is strongly a function of the solute concentration within the polymer.^{14, 15} However, for simplification, we use diffusion coefficients of water vapor obtained by experimental data. The diffusion coefficient of water vapor in Silicone oil (PDMS)¹⁶ and Krytox like perfluoropolyether oil⁸ has been determined as ~10⁻⁹ m²/s and ~10⁻¹⁰ m²/s respectively. Although considered immiscible, the solubility of water in PDMS is ~40 (mol of water)/(m³ of polymer)⁹, while the solubility of water in Krytox is ~1.8 (mol of water)/(m³ of polymer)⁸.

Based on the above-mentioned data, we calculated the effect of saturation ratio on nucleation rate of water in environment of Silicone oil, Krytox and air (Fig. S4). In our calculations, we assumed that the accommodation coefficient is one in different environments. Surprisingly, we find that despite very low solubilities of water in Krytox and Silicone oil, these solubilities are still large enough so that large nucleation rates can be initiated at smaller saturation ratios within these oils as compared to supersaturation required to observe similar nucleation rates in air. This is attributed predominantly to the presence of large number of nucleation sites (C_0) within the oils, and lowering of the interfacial tension of condensing vapor in these oils because of which lesser work is required to form the cluster. However as saturation ratio is increased, the nucleation rate in air can eventually surpass the nucleation rate in the oils.



Supplementary Figure S8: Nucleation rate versus saturation ratio for homogeneous nucleation within Silicone oil, Krytox and air.

The nucleation rate as shown in Fig. S8, was calculated under the assumption that the monomer sticking coefficient (accommodation coefficient) is one. Depending upon the accommodation coefficient, the supersaturation for obtaining large nucleation rates may vary considerably. Fig. S9(a) shows the variation of supersaturation with the accommodation coefficient to obtain large nucleation rate (10³⁰ drops/m³/s). Studies on determining the sticking coefficient of vapor molecules on aerosols covered with films of organic liquids have shown that the sticking coefficient can be substantially lower than one for long chain organic liquids.^{17, 18} Although, the accommodation coefficient of vapor molecules in polymers like Silicone Oils or Krytox are not available, the behavior of water molecules in these oils can be

expected to be similar to long chain organic liquids. In such situation, it is quite possible that very high supersaturations may be required to form large number of nuclei in these oils.

It should also be noted that with respect to nucleation of water, miscibility matters greatly in initiating large nucleation rates. As an example, we show in Fig. S9(b) the Saturation Ratio required to cause homogeneous nucleation rate of 10³⁰ drops/m³/s. We observe that below solubility of 1 mol/m³, the requirements for saturation ratio undergo sharp transitions and very large supersaturations are required.



Supplementary Figure S9(a): SR versus accommodation coefficient to obtain nucleation rate of $J=10^{30}$ drops/m³/s for 2 nm diameter sized droplets. The orange line corresponds to oils with same properties as Krytox. The blue line corresponds to oils with same properties as Silicone Oil.

Supplementary Figure S9(b): SR versus solubility of water in different oils to obtain nucleation rate of $J=10^{30}$ drops/m³/s for 2 nm diameter sized droplets. The violet line corresponds to oils with same molecular weight as Krytox. The blue line corresponds to oils with same molecular weight as Silicone Oil.

Supplementary Note 3: Permeation through thin films

The permeability (P) through an oil film is related with the diffusion coefficient (D) and solubility of solute species (S) as P=DS.¹⁹⁻²¹ To examine the transport across submicroscopic thin oil films, we choose a system comprising of droplet on a LIS, taking advantage of the fact that such thin films (~O(100 nm and less)) can form spontaneously on droplets if the impregnating oil spreads on the droplet (Fig. 4). Studying permeation through thin films during condensation is challenging since, nucleation at the oil-air interface is unavoidable. Instead of condensation, studying the evaporation of cloaked droplets in low humidity environment is advantageous since a concentration gradient automatically exists across the cloaked film, and the droplet acts as constant source of solute species to transfer across the cloak. As test liquids for cloaking the droplets, silicone oils of different viscosities (10, 100 and 1000 cSt viscosity) were chosen. For polymers with different viscosities, the diffusion coefficient of a solute has a negligible dependence on the polymer molecular weight (i.e. viscosity) at low mass fractions of the solute.^{14, 22} However, the solubility of solute molecules is dependent upon the size of the solute and solvent molecule size²³, and hence expected to differ in different viscosity oils with identical chemical nature. A difference in evaporation behavior of a droplet on LIS with different viscosity polymer liquids is thus an indicator that the transport (permeation) of solute molecules is limited by the solute content within the oil film i.e. the solubility of the solute in the polymer oil.

To test this aspect qualitatively, LIS was prepared by impregnating a microtextured surface (a=b=h=10 µm) with silicone oils of different viscosities (10, 100 and 1000 cSt viscosity). A 2 µl water droplet was gently deposited on the LIS samples and allowed to evaporate in room conditions. The room temperature and humidity were measured as 20 °C and 30% respectively. Evaporation of the droplet was observed using Zeiss AxioZoom microscope fitted with a 'Plan APO-Z 1.5x lens' and a polarizer at 260x magnification. The videos were recorded using Nikon D-800 camera (1920X1080) at 30 fps. The experiments showed that the droplet evaporation time increased on LIS as the viscosity of the impregnating liquid increased (Fig. S10, also see Supporting Movie S2). As discussed before, the delay in evaporation times on different viscosity silicone oils shows that the limiting mechanism during droplet evaporation is the solubility of water molecules in the oil.



Figure S10 | Evaporation of droplet on LIS. Evaporation of 2 μl droplet on LIS prepared by impregnating the micropost surface with Tetradecane ($S_{ow(a)}<0$), Silicon Oil ($S_{ow(a)}>0$) with viscosities of 10 and 1000 cSt. The micropost surface (similar as used for Fig. 3) was impregnated with tetradecane,

and silicone oils with 10, 100 (not shown in image) and 1000 cSt viscosities. Scale bar: 250 μ m. For complete video, see supplementary movie S2.

To understand the extent of the permeation barrier provided by the oil cloak around the droplets, we performed an experiment of droplet evaporation on a LIS impregnated with a non-cloaking liquid. For this experiment, we chose Tetradecane as the non-cloaking liquid because of its low vapor pressure and low solubility of water with this oil (see Supplementary Table 3). As before, a 2 µl droplet was deposited on the Tetradecane LIS, and the droplet was allowed to evaporate under the same thermodynamic conditions, as were used for the droplet evaporation on silicone oil LIS experiments. Comparing the time scales of evaporation, we found that indeed the droplet evaporation time was shorted on the non-cloaking case. However, the evaporation times of the droplets on cloaking LIS of different viscosities were within similar order as magnitude as evaporation times on the non-cloaking LIS. This indicates that silicone oils used in this work may not act as significant barriers against permeation. Further, the evaporation time scales between different viscosity oils, though different, are within the same order of magnitude of each other. Based on this, one may surmise that the permeation rates across these oils are similar.

Supplementary Note 4: Droplet growth modeling

In general, the volume of droplet and the principal radius of growth are related as $V = \pi \psi R^3/3$ from where $R = \sqrt[3]{(3V)/(\pi \psi)}$, Ψ is a shape factor depending upon the geometry of condensate.

For a droplet condensing in form of a lens on a oil or soft surface, the droplet growth occurs at the oilair interface and the lens-air interface is the only interfacial area that is considered in contributing to the growth by direct diffusion from the air. The volume of the upper lens with the principle radius of curvature $R=R_{wa}$, is

$$V_{wa}^{l} = \pi \psi_{wa} R_{wa}^{3} / 3, \text{ where } \psi_{wa} = (2 + \cos \theta_{wa}) (1 - \cos \theta_{wa})^{2}$$

$$\tag{9}$$

Following the method of Sokuler²⁴, the basic equation of a drop condensing on a surface is given as

$$\frac{dV_{wa}^{l}}{\left(V_{wa}^{l}\right)^{\frac{l}{3}}} = \left(\frac{3}{\pi\psi_{wa}}\right)^{\frac{l}{3}} \frac{4\pi D_{ab}}{\rho_{w}} (c_{v} - c_{i}) dt$$
(10)

Here, c_v is the concentration of vapor far away from the droplet, and c_i is the concentration of vapor at the droplet interface, ρ_w is the density of the condensate and D_{ab} is the diffusion coefficient of the vapor in the medium (air). Eqn. can be rearranged to give

$$\Rightarrow \frac{3^{\frac{1}{3}}\pi\psi R_{wa}^2 dR_{wa}}{R_{wa}(\pi\psi_{wa})^{\frac{1}{3}}} = \left(\frac{3}{\pi\psi_{wa}}\right)^{\frac{1}{3}} \frac{4\pi D_{ab}}{\rho_w}(c_v - c_i)dt \qquad \Rightarrow \psi_{wa}R_{wa}dR_{wa} = \frac{4D_{ab}}{\rho_w}(c_v - c_i)dt \tag{11}$$

Assuming vapor to behave as ideal gas, the concentration c can be given as $c = PM_w/\overline{R}T$. Here P is the pressure, M_w is the molecular weight of the condensate, \overline{R} is the gas constant and T is the temperature. Far away from the droplet, the vapor pressure is $P=P_v$ and the vapor temperature $T=T_v$. If the humidity far

away from the droplet (Eg. humidity of room if condensation is done in open air) is *RH*, then the vapor pressure P_v can be given as $P_v = RH * P_{saturation}(T_v)$ where $P_{saturation}(T_v)$ is the saturation vapor pressure at temperature T_v . At the droplet interface, the droplet is maintained at a subcooled temperature $T=T_i$. Because of the droplet curvature, the droplet saturation vapor pressure can be given through Kelvin Equation and expressed as $P_i = P_{i0} * Exp\left(\frac{2\gamma_{wa}V_m}{R_{wa}\overline{R}T_i}\right)$ where $P_{i0} = P_{saturation}(T_v)$ is the saturation vapor pressure at temperature T_i . For a given subcooling, supersaturation conditions are generated around the interface, and depending upon the driving force ($SR=P_v/P_{i0}$), a minimum droplet size nucleates on the surface. The

minimum droplet size is given by $R_0 = \frac{2\gamma_{wa}V_m\cos\theta}{\overline{R}T_i\ln SR} \Rightarrow \frac{2\gamma_{wa}V_m\cos\theta}{\overline{R}T_i} = R_0\ln SR$ so that

$$P_{i} = P_{i0} Exp \left[\frac{R_{0} \ln(SR)}{R_{wa}} \right] = P_{i0} * SR^{R_{0}/R_{wa}}.$$
 With abovementioned relations, Eqn. can be given as

$$\Rightarrow \psi_{wa} R_{wa} dR_{wa} = \frac{4M_{w} D_{ab}}{\rho_{w} \overline{R}} \left(\frac{P_{v}}{T_{v}} - \frac{P_{i}}{T_{i}} \right) dt$$
(12)

Eqn. is the fundamental equation that can be solved for droplet growth for all size ranges. To get a

simplified solution, we can solve Eqn. in limit of $R_{wa} >> R_0$. Under such assumption $P_i = P_{i0} * SR^{\frac{R_o}{R_{wa}}} = P_{i0}$

$$\Rightarrow R_{wa}dR_{wa} = \frac{4M_{w}D_{ab}}{\rho_{w}\psi_{wa}\overline{R}} \left(\frac{SR*P_{i0}}{T_{v}} - \frac{P_{i0}*SR^{\frac{R_{min}}{R_{wa}}}}{T_{i}} \right) dt \Rightarrow R_{da}dR_{da} = \frac{4M_{w}D_{ab}SR*P_{i0}}{\rho_{w}\psi_{wa}\overline{R}T_{i}} \left(\frac{T_{i}}{T_{v}} - \frac{1}{SR} \right) dt$$

$$\Rightarrow R_{wa}dR_{wa} = \eta dt \quad \text{where } \eta = \frac{4M_{w}D_{ab}P_{i0}SR}{\rho_{w}\psi_{wa}\overline{R}T_{i}} \left(\frac{T_{i}}{T_{v}} - \frac{1}{SR} \right)$$

$$(13)$$

Eqn. can be integrated and simplified under the assumption of $R >> R_0$ to give evolution of the curvature of the upper segment of the lens as

$$R_{da} = \sqrt{R_0^2 + 2\eta t} \tag{14}$$

Here, we note that a part of the volume addition due to condensation also increases the volume of the lower segment of the lens. As a result, the effective change in upper lens volume is decreased. If we assume that in a time dt, the droplet grows from R_{wa} to $R_{wa}+dR_{wa}$, then the volume added to the upper lens is $dV_{wa}^{l} = 3\pi\psi_{wa}R_{wa}^{2}dR_{wa}$. Assuming that this volume addition adjusts instantaneously throughout the droplet, the new effective curvature of the upper lens becomes $R_{wa}+dR_{wa,eff}$ and the curvature of the lower lens becomes $R_{wa}+dR_{wa,eff}$ and the curvature of the lower lens becomes $R_{wa}+dR_{wa,eff}$ and the curvature of the lower lens becomes $R_{wo}+dR_{wa,eff}$ find are related by $(R_{wo} + dR_{wo,eff})\sin\theta_{wo} = (R_{wa} + dR_{wa,eff})\sin\theta_{wa}$ from where we get $dR_{wo,eff}\sin\theta_{wa} = dR_{wa,eff}\sin\theta_{wa}$. The newly adjusted volumes of the upper and lower part of lens are given $dV_{wa}^{l} = 3\pi\psi_{wa}R_{wa,eff}^{2}$ and $dV_{wo,eff}^{l} = 3\pi\psi_{wa}R_{wa,eff}^{2}$ and $dV_{wo,eff}^{l} = 3\pi\psi_{wa}R_{wo,eff}^{2}$. From this we get,

$$3\pi\psi_{wa}R_{wa}^{2}dR_{wa} = 3\pi\psi_{wa}R_{wa\,eff}^{2}dR_{wa\,eff} + 3\pi\psi_{wo}R_{wo\,eff}^{2}dR_{wo\,eff}$$

$$\Rightarrow R_{wa}^{2}dR_{wa} = \left[1 + \frac{\psi_{wo}}{\psi_{wa}}\left(\frac{\sin\theta_{wa}}{\sin\theta_{wo}}\right)^{3}\right]R_{wa\,eff}^{2}dR_{wa\,eff}$$

$$\Rightarrow R_{wa\,eff}^{2}dR_{wa\,eff} = \varphi R_{wa}^{2}dR_{wa} \text{ where } \varphi^{-1} = 1 + \frac{\psi_{wo}}{\psi_{wa}}\left(\frac{\sin\theta_{wa}}{\sin\theta_{wo}}\right)^{3}.$$
(15)

Here, the correction factor φ , gives the effective decrease in radius of curvature. For $\varphi = 1$, the case of condensation on hard surfaces is recovered. Integrating Eqn. between limits of R_0 and R_{wa} , we get

$$\Rightarrow R_{wa\,eff}^3 = (1 - \varphi)R_0^3 + \varphi R_{wa}^3 \tag{16}$$

Combining Eqn. and , the effective growth rate of the droplet is found as

$$\Rightarrow R_{wa\,eff}^{3} = (1 - \varphi) R_{0}^{3} + \varphi \left(R_{0}^{2} + 2\eta t \right)^{\frac{3}{2}}$$
(17)

For droplets of size $R >> R_0$, the contribution of the initial droplet size R_0 is negligible so that the droplet growth equation in terms of the upper lens curvature becomes

$$\Rightarrow R_{wa\,eff} = \varphi^{\nu_3} \sqrt{2\eta t} \tag{18}$$

For convenience, we use the symbol R instead of $R_{wa,eff}$ to denote the droplet growth.

From here, the droplet growth rate $(U_d = dR/dt)$ is given by $U_d = \varphi^{1/3} \sqrt{0.5\eta} t^{-1/2} = \varphi^{2/3} \eta / R$. Note, here the singularity in droplet growth velocity at *t*=0 can be avoided by preserving the initial term (*R*₀).

Supplementary Note 5: Drainage time estimation

For two droplets of the same size approaching each other with an applied force F_{ext} , the drainage of the intermediate fluid between them can be given through Stefan Reynolds flat plate model. The disjoining pressure $\Pi(l)$ has the non-retarded Van der Waals form: $\Pi(l) = -A/6\pi l^3$ where A is the Hamaker constant.²⁵ The drainage equation assuming that droplet surfaces are immobile is then given by²⁵

$$F_{ext} + \frac{3\pi\mu_o a^4}{2l^3} \frac{dl}{dt} + \frac{\pi a^2 A}{6\pi l^3} = 0$$
(19)

where a is the drop deformation and l is the separation between the drops.

If two droplets are located initially at distance much larger than the range at which intermolecular forces between droplets become active, then it is important to estimate the F_{ext} that pushes the droplet in proximity. If we consider the dynamics of growth of an isolated droplet in an outer fluid then a droplet growing at a rate of $U_d = dR/dt$ exerts a driving force on the surrounding oil that can be given by $F_{ext} = \mu_o R U_d$ where $R = \varphi^{1/3} \sqrt{2\eta t}$ and $U_d = \varphi^{2/3} \eta/R$. This implies that two droplets approach each other with a constant force $F_{ext} = \mu_o \eta \varphi$ irrespective of the droplet size. In addition to the force exerted by growing droplets to the surrounding medium, neighboring droplets at a oil-air interface or sitting atop a LIS can also exert additional attractive force towards each other²⁶ due to the interaction of their 'wetting ridges' that will affect the drainage time. Solving the dynamics of film drainage for condensing droplets at large separations requires further consideration and is out of the scope of this work. If the droplets are separated by a distance ($l\sim 100$ nm) where the drainage happens purely due to VdW forces, then in absence of an external force, Eqn. reduces to $dl/dt = -A/(9\pi\mu_o a^2)$. For nearly spherical droplets, the film radius or deformation *a* can be given by $a \sim \sqrt{Rl}$.²⁷ Substituting this we get $ldl/dt = -A/(9\pi\mu_o R)$ and by integrating this, the coalescence time can be estimated as $t_{c,VdW} = 9\pi\mu_o RL^2/2A$.

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