Partial Wetting of Water on Ice

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Supplemental Material

Non-sessile droplet measurements

Fig. S1 shows the receding and advancing contact angles. Here we used another technique; varying the planar angle of an ice surface before conducting sessile drop experiments.

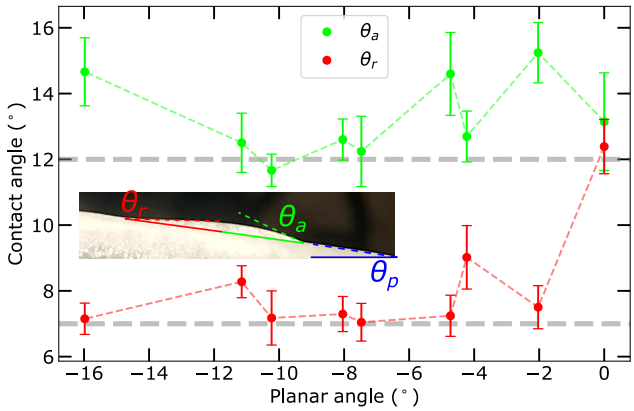

Figure S1: Advancing (green) and receding (red) contact angles of deposited sessile droplets on planar ice surfaces with varying inclinations. θ_a and θ_r yield again 12° and 7°, respectively. Inset is showing one of the measurements with a planar angle of (θ_p) in blue of approximately $-10°$.

Model as a function of final diameter D_{end}

Fig. S2 shows the measured and predicted final diameter of 5 μL sessile droplets as a function of ice temperature. Above $T_c = 259$ K, the model fails to accurately represent the experimental values as it diverges to infinity. The blue curve corresponds to Eq. 4 of the manuscript, and thus to the blue curve of Fig. 4 with $h_{crit} = 10$ μm.

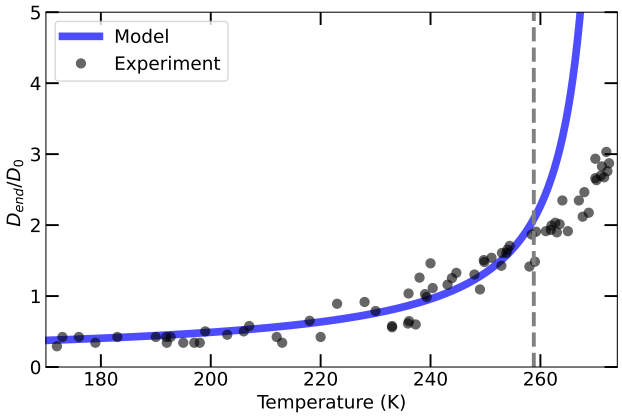

Figure S2: Experimental values for the final diameter of 5 μL sessile droplets as a function of ice temperature (black dots) compared to our model (blue line). The model is based on Eq. 4 of the manuscript, with h_{crit} = 10 μm. The vertical dashed gray line represents T_c.

Glass surfaces

Fig. S3 shows the measured apparent contact angle of 5 μL sessile droplets deposited on borosilicate glass, as a function of the glass temperature. The green line shows the same model, as being described in the manuscript, with thermodynamic properties of glass instead of ice. Fitting parameters yield $h_{crit} = 12$ μm + Young's contact angle of $\sim 28^\circ$ (dotted green line).

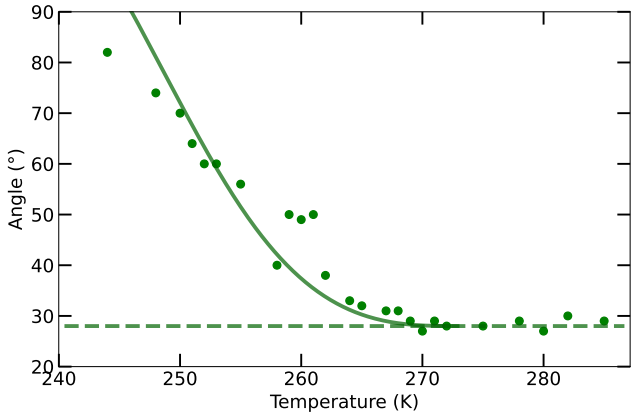

Figure S3: Measured contact angle of 5 μL sessile water droplets on glass as a function of glass temperature. The green line depicts the fit for our model with $h_{crit} = 12$ μm + Young's contact angle of $\sim 28^\circ$ (dotted green line).

1D model of ice front growth

To describe how the freezing front grows inside the droplet, we assume that the system can be simplified as a semi infinite liquid in contact with a semi infinite solid maintained at temperature $T_s < T_m$ with a solid phase nucleating at the interface (see Fig. S4).

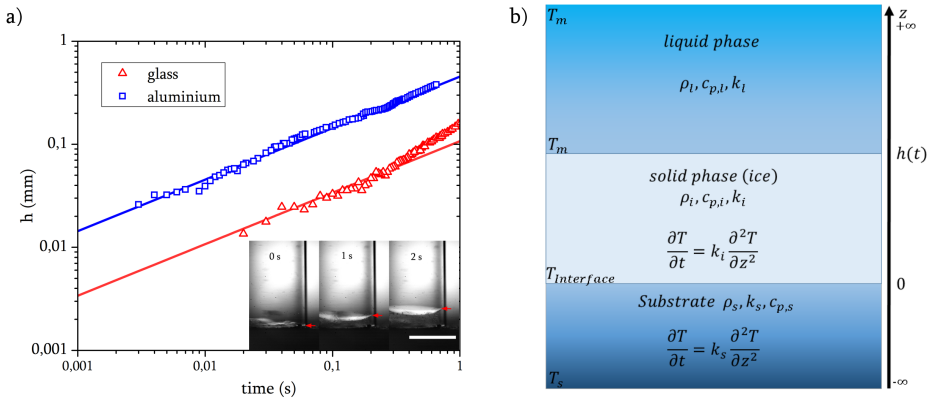

Figure S4: (a) Freezing front growing inside a pipette which is placed on the cold microscope glass slide or an aluminum block maintained at $T_s = -20°C$. Water is at $T_l = +23°C$ before entering in contact with the substrate. Numerical solutions of freezing model are reported for both substrates as solid lines (aluminum in blue and glass in red). Inset: Snapshots of water freezing inside the pipette in contact with a glass substrate kept at $T_s = -20°C$. Scale bar: 1 mm. (b) Schematic overview of the freezing model used. Parameters explained in the text.

This is known as the Stefan problem and has been solved with different boundary conditions.[1–4] As can be seen in Fig. S4, we choose the same model as in[2] by assuming that our liquid droplet is at T_m right after impact.

The thermal diffusion coefficient and the effusivity are given by $D_n = k_n/\rho_n c_{p,n}$ and $e_n = \sqrt{k_n \rho_n c_{p,n}}$. respectively. Here, k_n, ρ_n, and $c_{p,n}$ denote the thermal conductivity, density, and heat capacity, respectively, of the phase of index n, with $n = s$ for the substrate, $n = i$ for the newly crystallized ice, and $n = l$ for the liquid phase. For experiments conducted on ice, we used $e_i = e_s$. The problem is governed by the heat diffusion equations (see Fig. S4b) inside the three media, and the Stefan condition (see Eq. 1) which states that from conservation of energy, the latent heat L released at the interface is dissipated through the solid and liquid phase. As we fix the liquid

temperature to $T_l = T_m$, heat is only dissipated through the solid phase:

$$\rho_i L \frac{dz}{dt} = k_i \frac{dT}{dz} \tag{1}$$

The heat diffusion equations inside the two media (solid phase and substrate) are written as:

$$\frac{\partial T}{\partial t} = k_n \frac{\partial^2 T}{\partial z^2}, \tag{2}$$

for $t > 0$. For the substrate, we have $z(t) < 0$, while for the solid phase $0 < z(t) < h(t)$. As the nucleating solid phase is ice, we should use $n = i$ in the above equation.

The initial and boundary conditions for $h(z,t)$, $T_s(z,t)$, and $T_l(z,t)$ are the following :

$$h(0,0) = 0 \tag{3a}$$

$$T_s(0,0) = T_s \tag{3b}$$

$$T_l(0,t) = T_m \tag{3c}$$

$$\lim_{z\to\infty} T_l(z,t) = T_m \tag{3d}$$

An analytical solution of these equations can be written using a similarity variable η:

$$h(t) = 2\eta\sqrt{D_i t}, \tag{4}$$

with η a parameter obtained by solving the transcendental equation resulting from the Stefan condition (Eq. 1):

$$Ste = \sqrt{\pi}\eta \exp\left(\eta^2\right)\left(\frac{e_i}{e_s} + \mathrm{erf}(\eta)\right) \tag{5}$$

with the Stefan number defined as $Ste = c_{p,i}(T_m - T_s)/L$. Solving Eq. 5 and replacing the solution for η in Eq. 4 gives the freezing front dynamics $h(t)$.

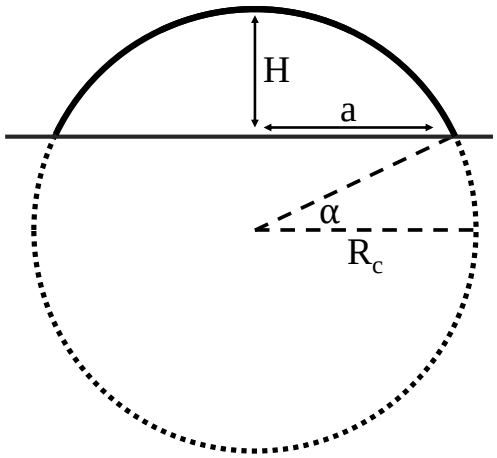

Figure S5: Sketch of a spherical cap, showing the sphere radius R_c, droplet height H, contact radius $a = D_{end}/2$ and contact angle $\theta = \frac{\pi}{2} - \alpha$

Contact angle of a spherical cap

A sketch of the spherical cap is shown in Fig S5.

The volume of the spherical cap is $V_c = \frac{\pi}{6} H \left(3a^2 + H^2\right)$. Using the volume conservation between the spherical cap and the spherical droplet of radius R_0 prior to impact with the surface, we obtain the following equation:

$$H^3 + 3a^2 H - 8{R_0}^3 = 0 \tag{6}$$

Eq. 6 is a third-order polynomial equation of the form $x^3 + cx + d = 0$ with $c = 3a^2$ and $d = -8{R_0}^3$, which can be solved using the Cardan method. We therefore define U and V as:

$$U = \frac{-d - 2\sqrt{\Delta}}{2} \tag{7a}$$

$$V = \frac{-d + 2\sqrt{\Delta}}{2} \tag{7b}$$

$$\Delta = \frac{d^2}{4} + \frac{c^3}{27} \tag{7c}$$

The solution of Eq. 6 is then:

$$H = U^{1/3} + V^{1/3} \tag{8}$$

The relation between the contact radius a, the cap height H and the radius of the spherical cap R_c is:

$$a^2 + (R_c - H)^2 = {R_c}^2 \tag{9}$$

From Eq. 9, we found $R_c = \frac{a^2+H^2}{2H}$. The angle α is found from R_c, and a and is given by:

$$\alpha = \arccos\left(\frac{a}{R_c}\right) \tag{10}$$

The contact angle of the drop with the surface θ is related to α by:

$$\theta = \frac{\pi}{2} - \alpha \tag{11}$$

Replacing α and using $a = D_{end}/2$ in Eq. 11, we express the final contact angle of a drop on a cold surface:

$$\theta_{end} = \frac{\pi}{2} - \arccos\left(\frac{HD_{end}}{H^2 + \frac{1}{4}D_{end}^2}\right) \tag{12}$$

References

References

(1) Nauenberg, M. Theory and experiments on the ice–water front propagation in droplets freezing on a subzero surface. *European Journal of Physics* **2016**, *37*, 045102, Publisher: IOP Publishing.

(2) Thiévenaz, V.; Séon, T.; Josserand, C. Solidification dynamics of an impacted drop. *Journal of Fluid Mechanics* **2019**, *874*, 756–773.

(3) Stiti, M.; Castanet, G.; Labergue, A.; Lemoine, F. Icing of a droplet deposited onto a subcooled surface. *International Journal of Heat and Mass Transfer* **2020**, *159*, 120116.

(4) Kant, P.; Koldeweij, R. B. J.; Harth, K.; van Limbeek, M. A. J.; Lohse, D. Fast-freezing kinetics inside a droplet impacting on a cold surface. *Proceedings of the National Academy of Sciences* **2020**, *117*, 2788–2794.