Frost Damage in Unsaturated Porous Media

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Frost damage in porous materials is a weathering mechanism that can cause dangerous rockfalls or damage to built cultural heritage. The volume expansion of 9% when water freezes is usually seen as the cause of frost damage. This does not, however, explain why partially saturated porous stones also show damage despite the fact that ice should have room to grow. By performing experiments both at the scale of a single pore and in a real stone, we propose an explanation for the mechanism of frost damage at low water saturations: the meniscus at an air-water interface confines the water in the pores. Because of this confinement, ice that forms will exert a pressure on the pore walls rather than growing into the pore. The amplitude of stress is found to be larger in small pores and when the meniscus has a larger contact angle with the walls. The contact angle is also observed to increase in the case of multiple freeze-thaw cycles, which increases the likelihood of damage. We find that cracks start first in the ice (being weaker than the confining material), followed by damage in the material itself. Remarkably, when multiple air-water interfaces are induced within limestone samples through a hydrophobic surface treatment, the stones are much more susceptible to frost damage than are uncoated stones, with cracks appearing preferentially at the hydrophilic-hydrophobic interface. This shows that indeed the meniscus confining the water during freezing and consequently the wetting properties are the relevant factors for frost damage in partially saturated porous stones.

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I. INTRODUCTION

The freezing of water during winter is responsible for the destruction of road surfaces by frost heave, delamination and cracks in building materials, and damage to outdoor artworks such as sculptures made of porous materials (stones, concrete, etc.) [1,2]. Because of their porous structure, these materials can soak up water (rainwater, groundwater, or just water from the air), and during winter when the temperature drops below 0°C this water can freeze and transform to ice. With subsequent environmental fluctuations and after multiple freeze-thaw cycles, damage such as fracture and delamination can be observed in these materials [3–5]. Frost weathering is also a fundamental geomorphic process in earth science as freeze-thaw cycles promote disintegration of rock and release rock debris. This can cause dangerous rockfalls in mountain ranges [6,7] and controls the long-term evolution of cold mountains as frost weathering is currently assumed to be the major agent of erosion in periglacial environments [8].

The most-obvious explanation for this phenomenon comes from the fact that water expands by about 9% when it turns into ice. If the water completely fills the porous material and starts to freeze, the ice will subsequently apply a pressure on the material. This explanation falls short however, as stones have also been reported to break when they are not fully saturated [4]. One would then expect the ice to be able to grow where there is room for it to expand in the pores instead of exerting pressure on the pore walls [9]. Even if the stone were fully saturated, the ice should still be able to grow out of the stone. So looking at the expansion of ice alone is not enough to explain frost damage in porous materials.

A few other mechanisms have been proposed to explain frost damage, such as ice segregation or the hydraulic pressure caused by a freeze front progressing through the stone. However, these explanations usually require specific circumstances or pore geometries [10,11]. The theory of ice segregation (or ice-lens formation) is one of the most-popular explanations [2,12]. According to this theory, water freezes in larger pores first and sucks in water from the surrounding smaller pores, effectively increasing the local saturation. However, this requires that stones are very heterogeneous in their pore size distribution and a continuous liquid film is present to direct the water to the ice [13].

Although these different processes have been described and studied at the scale of porous media, there is very little work at the scale of a single pore connecting it to
the damage observed at large scales. Here, by performing multiscale experiments both at the pore scale and in porous materials, we report on a generic explanation for stones breaking due to the freezing of water in partially saturated porous media. Microcapillaries are commonly used as model systems for a single pore in a porous medium [14,15], and we use them here to study the water-ice transition in confinement. Subsequently, the fractures induced by freezing in porous materials (stones) are investigated and connected to the behavior of ice at the microscale.

Our results show that at the microscale, the liquid meniscus is capable of confining the water in the pores. Consequently, the wetting properties of the liquid on the wall play an important role in the development of the pressure: high contact angles prevent the water from expanding into the unconfined space of the pores and direct most of the ice crystallization pressure onto the pore walls. We also show that the results from the microcapillary experiments can be extrapolated to the macroscale system. Partially saturated stones break more readily if there are, because of, for example, hydrophobic treatments, multiple air-water interfaces with high contact angles inside the porous matrix than an untreated material. Hydrophobic treatments are common in civil-engineering or cultural-heritage applications; it was reported that more fractures due to ice crystallization occur in partially hydrophobic stones [16] but no explanation was given. The impact of such hydrophobic treatments in porous media has been studied in terms of drying and salt crystallization but hardly any attention has been given to ice crystallization damage.

II. CAPILLARY EXPERIMENTS

A. Setup

Borosilicate-glass capillaries of rectangular shape and different sizes are used as models for angular pores and microcracks [17]. In addition, the rectangular shape also allows imaging of the freezing-thawing process directly under a microscope. Volumes of water ranging from 2.5 to 35 \( \mu \)L are confined in capillaries of various heights ranging from 200 to 400 \( \mu \)m [Fig. 1(b) and Table I]. These capillaries are larger than the typical size of pores in stones (usually on the micrometer scale for the stones considered here). However, they still give us insight into the dynamics relevant for ice crystallization as we are still within the microfluidics scale and the chemical properties of glass are similar to those of many stones. The impact of freeze-thaw cycles and confinement parameters (volume of entrapped water and contact angle of the liquid-air meniscus) on the crystallization pressure developed during freezing and the frost damage on the scale of individual pores are investigated.

A schematic representation of the setup is shown in Fig. 1(a). The capillaries are subjected to cycles of freezing to \(-20^\circ\)C and thawing at \(20^\circ\)C by our turning a Peltier element on and off. The capillaries are cooled to at least \(-20^\circ\)C at a rate of 2.5 \(^\circ\)C/s (some experiments were also performed at \(-40^\circ\)C); the hot side of the Peltier element is cooled by running tap water. The capillaries are imaged from the top with a microscope. To prevent frost condensation on the capillaries while the freezing is being imaged, the whole setup is in a climatic chamber in which the relative humidity is kept low (approximately 10%). The freezing stage and the thawing stage both last for 2 min, and each series of measurements consists of at least five cycles. Two minutes is found to be largely sufficient to reach thermal equilibrium for both the freezing stage and the thawing stage for the sizes of our capillaries, as verified by infrared thermography.

As stated above, since water expands by about 9% when it freezes, it may exert a pressure when freezing while confined. It was established previously that for this to happen, a liquid-water film needs to remain between the ice and the pore walls [9,18]. This is because otherwise an ice crystal would form between the two surfaces, and no extra crystalline layers can be added to the crystal to create a pressure. This simple observation allows the estimation of an upper limit on the crystallization pressure that the element on and off.
growing ice can exert on a confining wall, by consideration of the chemical potential due to the undercooling [9,18]. The maximum pressure that a growing crystal can exert is then 1.2 MPa per degree of undercooling [9]. The compressive strength of bulk ice grown under atmospheric pressure is approximately 5 MPa and increases with decreasing temperature to about 25 MPa at $-30^\circ$C [19].

In our experiments, we deduce the ice crystallization pressure by measuring how much the capillary wall deforms when the entrapped water drop freezes. To measure the deformation, a cantilever is placed on top of the capillary, in the center of the entrapped water drop. The relation between the deformation and pressure is established, first, by our calibrating the cantilever experimentally by using compressed air at different pressures to deform the capillary and, second, by our numerically using a model built in COMSOL MULTIPHYSICS (see Appendix A for more details). The results obtained with both methods agree well. Moreover, as the thermal-expansion coefficient of the wall material, borosilicate glass, is much smaller than that of ice or water [20,21] it can be ignored.

B. Results

1. Freeze-thaw cycles

The deformations of the capillary measured by the cantilever during several freeze-thaw cycles are plotted in Fig. 2. Images obtained during a freeze-thaw cycle in a hydrophilic capillary partially filled with water are shown in Fig. 3: before freezing (at ambient temperature); frozen; just before thawing; and thawed (back at ambient temperature). A few features stand out.

When the Peltier element is first turned on, the temperature decreases. When the water freezes, the pressure shows a sharp peak, and subsequently relaxes (Fig. 2, peak 1). Under the pressure of this first peak the ice often cracks [see, for example, Fig. 3(b)]. While the ice is frozen, there is a sustained pressure on the walls of the capillary (between points 1 and 2 in Fig. 2). The fact that there is a sustained pressure is further indicated by the observation that the ice can continue to crack at this stage, if it did not already crack during the initial peak. After the ice cracks, fractures in the glass walls of the capillary are sometimes observed [Fig. 3(c)]. This is an important observation since the capillaries are open-ended and the ice could simply expand in the lateral direction without exerting any pressure on the walls; to the contrary, we find that the measured pressures on the capillary wall can reach 1.5 to 2.5 MPa.

After roughly 2 min the Peltier element is turned off and the temperature starts to increase. The rising temperature causes a smaller second peak, as the ice expands thermally (Fig. 2, peak 2). This thermal expansion can cause the glass capillary to crack on rare occasions (for example, in Fig. 3) and could be a factor in the rockfalls observed in mountains in spring [22,23]. When the ice melts at above 0 $^\circ$C [Fig. 3(d)], the pressure drops again to zero before a new cycle is started.

2. Water volume and size of the capillary

The first noticeable result is that the pressure exerted on the capillary depends strongly on the water volume, as shown in Fig. 4.

For a given capillary size, our results show that there is an “optimal” volume that causes a maximum pressure inside the capillary. We also see that the smaller the size of the capillary, the higher the maximum pressure. One possible explanation is that the confinement of the water is more important in small pores. Indeed, the entrapped water in the hydrophilic capillaries has a concave meniscus, with a Young-Laplace pressure difference across the air-water interface (see Fig. 3). The Young-Laplace pressure depends on the size of the pore, i.e., the effects of the
meniscus are more relevant at smaller pore sizes. The higher the capillary pressure at the meniscus (i.e., smaller pores), the more difficult it will be for the curved surface to change shape and expand in the unconfined direction. In addition, the freezing dynamics that we observe are likely to be strongly influenced by the fact that the freezing starts in the corners of the liquid-air meniscus in the capillary, and subsequently the contact line can no longer move. If the confinement effect is sufficiently strong, the water is confined by the meniscus while it freezes and the crystallization pressure will be directed to the pore walls instead of making the ice grow along the pore. This is indeed what is observed in the experiment. In addition, for a small volume of water, the meniscus effect is more important than the bulk expansion effect; taken together, these considerations explain the higher observed pressures in the smaller capillaries and at smaller water volumes.

In what follows, we investigate in a more-systematic way which parameters influence the pressure exerted by the ice on the capillary during freezing. The aim is to be able to anticipate in which situation the freezing will likely lead to irreversible damage, i.e., cracks in the capillary.

### 3. Contact-angle evolution

When measuring the initial contact angles of the two menisci, we observe that with subsequent freeze-thaw cycles the contact angles evolve to higher values since the water expansion when water freezes generates the deformation and the movement of the meniscus. This is clearly visible in Fig. 3, where the shape change of the meniscus due to freezing in Figs. 3(b) and 3(c) leads to a change in the contact angles of the liquid meniscus after thawing (see also Supplemental Material [24] for a movie of a freeze-thaw cycle). Multiple measurements in different capillaries show that although the fluctuations are important, it is clear that, on average, the contact angle increases with increasing number of freeze-thaw cycles (see Fig. 5). As the temperature range in the experiments here is quite small, the change in the contact angle cannot be explained by the temperature dependence of the contact angle: according to Ref. [25], the surface-tension increase of water and supercooled water is 1 or 2 mN/m per 10°C, corresponding to a change of contact angle of less than 1° over the temperature range probed.

It has nonetheless already been shown [26] that when water droplets freeze on a flat surface, the apparent contact angle of the ice drop is far from constant and the apparent macroscopic contact angle increases towards a plateau at around 90°. A similar behavior is observed here at the curved water-air meniscus: the contact line is always (slightly) pinned on defects on the glass surface. When water is freezing, the contact angle of the curved meniscus of water increases and because of the lateral expansion of the ice, the meniscus advances and it changes shape [see Fig. 5(b) for a schematic of the contact-angle evolution during one freeze-thaw cycle]. At the thawing stage, the latter stays pinned and relaxes by returning to the concave shape, as visible in Fig. 3 and drawn in Fig. 5(b). Therefore the reason for evolving towards higher values is the contact-angle hysteresis between the ice-air meniscus and the water-air meniscus.
Interestingly, our results show that capillaries for which the contact angles of the entrapped water are higher break more frequently. We therefore investigate whether there is a correlation between the contact angle and the ice breaking the capillaries. Since the occurrence of fracture is stochastic and might also depend on inhomogeneities in the glass, we quantify the maximum pressure inside the capillary for different contact angles with the cantilever setup. Figure 6 shows that although the data are noisy, there is indeed a significant increase of the pressure for higher contact angles. The large fluctuation in these measurements is mainly related to the fact that each point in the graph is an average over the four corners and all four contact angles are not the same, leading to large variations in the observed pressures.

4. **Capillaries with a hydrophobic-hydrophilic interface**

The impact of the contact angle of the air-water meniscus on the fracture observed in glass capillaries is investigated further by our treating one side of the capillary with a commercially available hydrophobic coating (Nanocoat liquid). NanoCoat treatment is a one-component-nanotechnology surface treatment based on the use of silica nanoparticles in solution. The treatment does not change the appearance of the treated surface, and glass clarity remains the same after treatment. A water drop is subsequently introduced in the capillary in a way to have one of the menisci at the hydrophobic-hydrophilic interface and the drop on the hydrophilic side [Fig. 7(a)]. We observe that the contact angle of the meniscus at the hydrophobic-hydrophilic interface is close to 90°, whereas the other meniscus, on the hydrophilic part, has a curved shape with contact angles significantly smaller than 90°. Figure 7 shows a freeze-thaw cycle after which microcracks formed in the glass.

Those microcracks appear near the hydrophilic-hydrophobic region, after ten freeze-thaw cycles on average. One can also note that during freezing, the ice expands more laterally on the hydrophilic side than on the hydrophobic side, showing once again that the confinement is more important when the contact angle is high, on the other side.

When water freezes and expands in the capillary, it exerts a stress normal to the capillary wall ($\sigma_r$). In a cylindrical capillary, this radial stress causes a tangential stress in the glass, called “hoop stress” ($\sigma_h$). To simplify the situation, this is schematically represented for a cylindrical capillary in Fig. 8, where one can see vertical and horizontal cross sections of water in the capillary. When the hoop stress exceeds the tensile strength of the glass, the capillary breaks. We expect that the stress due to the expansion follows the meniscus and thus expect the hoop stress to increase with the contact angle because more of the crystallization pressure is directed along the meniscus into the glass. At low contact angles, part of the stress is directed parallel to the glass, following the contact line as indicated by the solid blue arrow in Fig. 8. At contact angles close to 90°, the crystallization stress is mainly directed normal to the glass, as indicated by the dashed light-blue arrows.

If one ignores the thermal expansion of the ice (which is significantly smaller, see Appendix B), one can calculate which fraction of the hoop stress is directed to the wall in $r = r_p$ (where $r_p$ is the inner radius of the capillary):

\[
\sigma_h = \left( 0.04 E_{\text{comp}}^{\text{ice}} \frac{\gamma_{\text{air-ice}}}{r_p} \right) \sin \theta \left( \frac{2r_p^2 + 2r_p t + r^2}{2r_p t + r^2} \right),
\]

(1)
where $E_{\text{comp}}^{\text{ice}}$ is the compressive strength of ice, measured to be 25 MPa at large undercooling [19], $\gamma_{\text{air-ice}}$ is the interfacial tension between ice and air (measured to be 0.09 N/m [27]), $\theta$ is the contact angle between the ice and the glass, and $t$ is the thickness of the glass (see Appendix B for the derivation of this equation). When trying to break the capillaries with compressed air, we find the breaking stress of the glass to be on the order of 2 MPa. This implies that the stresses generated by the ice are indeed sufficient to break the glass, and by taking the direction of the force into account, we understand why the probability of breaking is higher at higher contact angles.

One can nonetheless notice that for superhydrophobic capillaries, where contact angles are higher than 90°, the hoop stress $\sigma_h$ should decrease. However, in reality, at the hydrophilic-hydrophobic boundary, the meniscus cannot advance due to contact-line pinning, and in our experiments the angle is rarely larger than 90°. In addition, hydrophobic treatments tend to lose their hydrophobic properties over time [28,29], which could lead to a situation where $\theta \approx 90°$, even in an originally superhydrophobic capillary. Thus, even though theoretically the hoop stress $\sigma_h$ decreases for superhydrophobic capillaries, we do not think that such treatments should be used to prevent frost damage in porous media. Therefore, it can be concluded that if the local contact angle of the liquid meniscus evolves towards higher values with freeze-thaw cycles or because of the hydrophobic treatments, the capillary will be more prone to damage, as is indeed borne out by the experiments. These results directly apply to stone materials. To consolidate them, or make them water repellent, some hydrophobic treatments are often applied [28,30]. This provides motivation for the second part of our study, where we study limestone samples during freeze-thaw cycles with and without a hydrophobic coating.

III. MACROSCALE EXPERIMENTS IN STONES

To investigate to what extent the conclusions from the experiments in single capillaries (models for a single pore) translate to real stones, we perform freeze-thaw experiments in partially saturated limestone samples. If the stone is fully saturated with water, the whole porous network is filled with water. When samples are partially saturated, there will also be air in between the grains. As shown in Fig. 9, the water can position itself between the grains in two different ways; If the grains are hydrophilic, usually the water will form a continuous film around the grains [31]; see Fig. 9(b). In this case the ice has sufficient room to grow during freezing as the contact angles between the grains and water are very low. If the substrate is treated with a hydrophobic coating, the high contact angles in the hydrophobic zone will induce the formation of pockets of water on the hydrophilic side. This is schematically presented in Fig. 9(c) and is shown in Fig. 9(d), where a limestone sample treated on its surface with a hydrophobic coating has a wet hydrophilic core (1) and the dry hydrophobic outer layer (2).

A. Setup

We perform freeze-thaw cycles on Maastricht limestones of 20.5 cm$^3$ (19.5 × 19.5 × 54.0 mm$^3$). Such stone is very brittle at a maximum compressive stress of 2 MPa [32], and has high porosity of around 49%. The pore size is homogeneous and on the order of 30 µm [33]. As the stone is brittle, and the maximum compressive stress is well within the range of pressures measured in the microscopic experiments, we expect to see frost damage in a few cycles.
To evaluate the effect of a hydrophobic interface, the hydrophobic Nanocoat treatment is applied to some samples with a brush on five of the six surfaces. The hydrophobic treatment penetrates to a certain depth [see Fig. 9(d)], making the subsurface hydrophobic. The bottom side is left uncoated, to allow water to penetrate inside the stone, which is subsequently filled with water to achieve at maximum a saturation of 60% of the pore volume. Some stone samples are left untreated and filled to the same saturation as their coated counterparts. The samples are put in a freezer \((T = -20 \, ^\circ C)\) for 3–5 h. During the thawing phase, the stones are placed in a high-humidity chamber at room temperature to avoid drying.

After five freeze-thaw cycles, the mechanical properties of the stones that do not show any visible damage are measured by our performing uniaxial compression tests using an Instron universal testing instrument. The samples are placed between two metal platforms, where the top platform is set to move at a slow constant speed of 0.5 mm/min. The force exerted on the sample and the displacement of the top platform are measured. The measurement is performed until the sample cracks, and the yield stress is reached. From the stress-strain curve, the Young’s modulus and yield stress are calculated. For this, we used the method of Malkowski and Ostrowski [34], in which the part of the stress-strain curve used to calculate the Young’s modulus is limited to the part between 30% and 70% of the yield stress.

B. Results

Figure 10 shows pictures of partially saturated, untreated, and hydrophobically treated stones after five freeze-thaw cycles. It is observed that the untreated stone does not exhibit damage [Fig. 10(a)]. In contrast, all the stones with a hydrophobic coating show fractures and cracks [Figs. 10(b) and 10(c)] and some break. Some samples broken in two show clearly that the depth of the damage (cracks) and the hole caused by granular disintegration reach the hydrophilic-hydrophobic interface.

The mechanical properties of the stones that do not break after several freeze-thaw cycles are measured. Typical experimental results for an untreated stone and a sample with a hydrophobic coating are plotted in Fig. 11(a). For the untreated hydrophilic stones subjected to freeze-thaw cycles, no changes in the Young’s modulus or the yield stress are observed compared with intact stones. However, stones with the hydrophobic coating show a decrease of the Young’s modulus and the yield stress of \(\Delta E = 100 \, MPa\) and \(\Delta P = 0.5 \, MPa\) after freeze-thaw cycles. Moreover, Fig. 11(b) shows that the hydrophobic stone breaks on its already-weak points during the compression test, i.e., following the microcracks and holes visible at the surface after the freeze-thaw cycles.

Zhang et al. [16] suggested that a hydrophobic-hydrophilic interface in a porous material would lead to more damage by freeze-thaw cycles but did not explain why. As one can observe in Fig. 10(c), the stones with the hydrophobic coating exhibit granular disintegration over the whole depth of the coating. This strongly suggests that
the freezing starts in the hydrophilic core of the stone, where the water is, but the maximum pressure is developed at the interface region between the hydrophobic part and the hydrophilic part, where the contact angle is the highest. The cracks subsequently propagate towards the outer surface. These results can therefore be directly related to those obtained in partly hydrophobically treated capillaries and once again confirm the effect of the contact angle on the pressure developed at the hydrophobic-hydrophilic interface.

IV. CONCLUSIONS AND PERSPECTIVES

The freezing of water in confinement is known to cause damage such as fracture, delamination, or granular disintegration of asphalt on roads and in outdoor artworks. In addition, it can also cause dangerous rockfalls in mountains. By performing multiscale experiments at both the pore scale (capillaries) and the macroscale in limestone, we bring some new insights into why partially saturated porous materials can be damaged during freeze-thaw cycles despite the fact that ice has room to expand in the confinement. Our results show that the wettability properties and the volume of confined water are two important parameters for the development of cracks in porous materials during freeze-thaw cycles.

At the pore scale, the pressure exerted during the freeze-thaw cycles is measured and is found to depend on the capillary size, with higher pressures measured in small capillaries (which underlines the important role of the liquid-air meniscus and its contact angle). For high contact angles, the expansion of ice exerts a larger stress normal to the pore walls compared with the perfect-wetting situation in which water can expand into the unconfined space of the pores. We also show that with multiple freeze-thaw cycles and the successive pinning and depinning of the water meniscus, the contact angles of the water in hydrophilic capillaries evolves towards higher values. Subsequently, capillaries that show such a contact-angle increase after several freeze-thaw cycles have a larger probability of breaking. In accordance with this, we also demonstrate that when capillaries are partially treated with a hydrophobic coating, damage (cracks) appears in the hydrophilic-hydrophobic region, where the contact angle is close to 90°.

Macroscale experiments in limestone confirm the results obtained at the pore scale. After several freeze-thaw cycles, partially saturated stones with a hydrophobic coating exhibit cracks and granular disintegration, whereas untreated stones remain intact. The formation of water pockets separated from the hydrophobic region by multiple air-water interfaces with high contact angles inside the porous matrix induces large stresses normal to the matrix, causing damage in these regions and the degradation of the mechanical properties. Our results clearly show that hydrophobic treatments that are sometimes applied as conservation measures (water-repellent, consolidant, and antigraffitti products) at the surface of porous materials can induce more damage in partially saturated stones in cold regions, where the material is exposed to freezing. Hopefully, these results will guide conservation scientists to find adapted treatments for the conservation of outdoor cultural heritage and infrastructure in colder climates.

Moreover, in geophysics and civil engineering, frost damage of porous stones and building materials is a major cause of degradation. Our results show how the potential damage is related to the petrophysical properties of the porous materials and their wetting behavior. The observation that damage is less likely to occur for materials with larger pores suggests a way of tuning the material durability, which could e.g., be applied to prevent frost damage of roads by tuning the porosity and pore size distribution. The observation that the contact angle is an important parameter suggests that hydrophilic treatments may be an efficient way to prevent frost damage.

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APPENDIX A: COMSOL MULTIPHYSICS PRESSURE CALIBRATION

We use COMSOL MULTIPHYSICS version 5.5 with the solid-mechanics module to model the behavior of our capillaries and relate the deformation of the capillaries under the crystallization pressure to the internal pressure responsible for this deformation. To do so, we copy the exact dimensions of the capillaries used in the experiments, including the following material constants for borosilicate glass: density 2230 kg/m³, Young’s modulus 64 GPa, and Poisson ratio 0.2.

Next, we define a rectangular area on the surfaces inside the capillary; this represents where the drop sits in the capillary. From these surfaces, we define a force normal to the surface, directed outwards. This models the crystallization pressure. The model does not include any effects from lateral expansion or the contact angle (the contact angle is effectively set to 90°), and includes only the effect of the component of the force normal to the capillary walls. Running the simulation, we obtain results such as those in Fig. 12: the capillary deforms outwards.

Now we measure the deformation at the highest point. The deformation of the capillary scales linearly with the applied pressure, so we can define a deformation constant to relate the deformation to the pressure:

\[ D = CP, \quad (A1) \]
where $D$ is the upwards deformation at the highest point, $C$ is the deformation constant, and $P$ is the internal pressure. The deformation constant varies slightly with the droplet volume, as depicted in Fig. 13.

The best value for the deformation constant is found for each capillary with use of a least-squares fit: $11.0 \text{ mm/GPa}$ for the $0.2 \times 2 \text{ mm}^2$ capillary; $16.9 \text{ mm/GPa}$ for the $0.3 \times 3 \text{ mm}^2$ capillary; $22.7 \text{ mm/GPa}$ for the $0.4 \times 4 \text{ mm}^2$ capillary.

Now Eq. (A1) with the right constants for each capillary can be used to determine the pressure inside the capillary on the basis of the measured deformation.

**APPENDIX B: HOOP-STRESS EQUATION**

When ice starts growing in a capillary, it exerts a radial stress on the capillary wall. If we assume the undercooling of the ice is sufficient for the water to freeze completely, we can define an equation for this expansion based stress, $\sigma_r$:

\[
\sigma_r = E_{\text{comp}}^{\text{ice}} \left( \frac{(r_{\text{ice}} - r_{\text{water}})}{r_{\text{water}}} \right) \\
= E_{\text{comp}}^{\text{ice}} \left( \frac{\rho_{\text{water}}}{\rho_{\text{ice}}} \right)^{1/2} - 1 \\
= 0.04E_{\text{comp}}^{\text{ice}}
\]

where $\rho_{\text{water}} = 0.9998 \text{ g/cm}^3$ is the density of the water, $\rho_{\text{ice}} = 0.917 \text{ g/cm}^3$ is the density of the ice, $r_{\text{water}}$ is the radius of the pore as defined in Fig. 8 before freezing, and $r_{\text{ice}}$ is the radius of the pore after the water has frozen. $E_{\text{comp}}^{\text{ice}}$ is the compressive strength of ice and gives a limit on the pressure ice can exert. It has been measured to be $25 \text{ MPa}$ at $-25^\circ \text{C}$ undercooling [19]. We ignore the effects of the negative thermal expansion of the ice during cooling, since this is significantly smaller (on the order of a factor of $10^{-5} \text{ K}^{-1}$ [35]).

A second cause of radial stress that should be accounted for is the surface tension. The surface tension gives a negative pressure that is given by the Young-Laplace equation. So, for the radial stress we now get

\[
\sigma_r = 0.04E_{\text{comp}}^{\text{ice}} - \frac{\gamma_{\text{air-ice}} \sin \theta}{r_p},
\]

where $\gamma_{\text{air-ice}}$ is the interfacial tension between air and ice, measured to be $0.09 \text{ N/m}$ [27]. The radial stress will cause a stress in the glass tangential to the capillary wall. For a cylindrical capillary, the hoop stress in $r = r_p$ (where $r_p$ is the inner radius of the capillary) is linked to the radial stress according to the following equation:

\[
\sigma_h = \sigma_r \left( \frac{2r_p^2 + 2r_r t + t^2}{2r_p t + t^2} \right),
\]

where $t$ is the thickness of the glass.

As a last assumption, we expect that the stress due to expansion will follow the meniscus (see Fig. 14 for a schematic of the stresses applied on the capillary).

So, at low contact angles the expansion will for a large part be parallel to the capillary wall, in the corner flow. At high contact angles, however, the expansion will be
directed into the walls, increasing the radial stress. To account for this effect, we multiply the radial stress due to expansion by the sine of the contact angle. This leaves us with a final equation for the hoop stress:

$$\sigma_h = \left( 0.04E_{\text{comp}}^{\text{ice}} \frac{\gamma_{\text{air-ice}}}{r_p} \right) \sin \theta \left( \frac{2r_p^2 + 2r_p t + t^2}{2r_p t + t^2} \right).$$

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