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Self-Lifting NaCl Crystals
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ABSTRACT: We show that macroscopic crystals of NaCl that form from evaporating drops of aqueous salt solutions can spontaneously lift themselves up and away from a hydrophobic surface. At the end of the evaporation process, tiny crystals of NaCl grow onto larger ones and form "legs" that push the large crystals away from the surface. The temperature dependence of the lifting speed is found to exhibit Arrhenius behavior with an activation energy similar to that of crystals growing in solution: the crystal growth itself determines the lifting speed that can be up to half a centimeter per minute. We show that surface hydrophobicity is a necessary but not a sufficient condition to obtain this "self-lifting" behavior.

Crystal nucleation and adhesion on surfaces is a major issue in a wide range of applications. It can cause problems in the built environment, the conservation of cultural heritage and is responsible for the corrosion of many types of surfaces, a major problem in outdoor electronics. In the field of cultural heritage, salts that are naturally present in stones or mortar, or salts from the environment, can be mobilized by rain and precipitate at the surface when the materials dry again; for buildings this leads to the ugly white residues seen on many old and new buildings. Also for cultural heritage, crystallization of soaps can damage oil paintings and salt crystallization can damage mural paintings and frescoes. Especially for sodium chloride, being the most ubiquitous salt on earth, its crystallization has been the subject of numerous studies.

To avoid such deterioration, surface treatments are often employed, mostly to change the affinity of the surfaces to water, using, for instance, water-repellent products. The reasoning behind this is that if aqueous salt solutions do not wet the surface, they cannot evaporate there and deposit the salt. The link between specific surface treatments and the crystallization dynamics remains elusive. Especially in the building sector, surface treatments have been much employed, sometimes with disastrous consequences: if the salt is not able to exit the porous stones, it may crystallize in the interior of the stone and cause severe damage there due to crystal growth in confined spaces.

Here we show that crystals can show antiadhesive behavior by lifting themselves up from the surface; we find that this happens only on silanized surfaces. The properties of the surface on which crystallization happens is therefore an additional factor that needs to be taken into account, and hydrophobicity alone is not sufficient to generate a "self-cleaning" effect. If salt crystals show a strong preference for avoiding contact with the surface, this leads to the spontaneous lift-off of crystals away from the surface. Since NaCl crystals usually strongly adhere to (mostly hydrophilic) surfaces, the self-lifting is a potential solution to the salt deposits forming at surfaces. This could provide a solution for numerous problems encountered not only in building and art conservation but also in (outdoor) electronics.

We study crystallization from evaporating drops of NaCl solutions on different types of hydrophobic surfaces. Homogeneous NaCl solutions are prepared slightly below the saturation concentration \( S = c_s/\Omega_{\text{NaCl}} = 0.95 \) with \( c_s = 6.16 \text{ mol/kg} \) with NaCl (Sigma-Aldrich purity \( \geq 99.9\% \)) and deionized water (Millipore, \( \rho \sim 18.2 \text{ M}\Omega \text{cm} \)). The solutions are stirred for 24 h at ambient temperature \( (21 \pm 1 \degree C) \) and left to rest after stirring for 1 h before use to ensure a homogeneous solution. Different types of hydrophobic surfaces were prepared: silanized smooth and roughened glass, PDMS coated glass, and superhydrophobic surfaces. For the silanized surfaces, microscopy slides from Corning are washed with water and ethanol, dried, and then cleaned by a plasma treatment (30 s) before submerging them into the solution of toluene and trichloroethylsilane (from Tokyo Chemical Industry) (1% vol) for 15 min. The silanization leads to a very hydrophobic surface having a contact angle (for our salt water) of \( \theta = 110 \pm 4\degree \). For the rough silanized surfaces, the slides were sandblasted before undergoing an identical silanization treatment (contact angle \( \theta = 122 \pm 6\degree \)). The PDMS surface is prepared by spin-coating a silicone oil onto the same glass slides (contact angle \( \theta = 110 \pm 6\degree \)). The superhydrophobic surface is prepared also on a glass slide...
according to the procedure described in ref 17 (contact angle $\theta = 151 \pm 8^\circ$).

The experiments of salt water drop evaporation are done by placing the glass slides on a 2 mm thick conducting copper plate that is mounted on top of a heating plate with controllable temperature. The temperature is measured by drilling a hole on the side of the copper plate and placing a thermocouple probe inside. After the heating plate is set to the desired temperature, we wait until the copper plate has reached the temperature that is set on the heating plate and wait 15 min to be sure the copper plate and the glass slide on top of it are in thermal equilibrium. Drops with a volume of $V_i = 15 \pm 1 \mu$L of salt solution are then deposited on the silanized glass using a microsyringe.

The setup was placed inside a sealed humidity chamber to ensure a constant relative humidity (RH) of 40 ± 1% and temperature of (21 ± 1 °C). We used a Nikon D850 DSLR camera with a Laowa 25 mm f/2.8 (2.5–5X Ultra Macro) objective to obtain movies and images of the process. The image analysis was done with image analysis software (ImageJ).

When a drop of unsaturated NaCl solution is deposited on the hot surface, the water starts evaporating and the droplet will reach the saturation concentration. Subsequently, the NaCl will start to precipitate and a large assembly of NaCl crystals is left when almost all the water has evaporated. The higher the temperature of the substrate, the faster the evaporation and the larger the number of crystals that form at the liquid–air interface. Surprisingly, at the end of the process when the salt has almost completely dried out, a number of narrow legs are observed to form and grow at the bottom of the crystal, causing it to lift up above the surface. A time sequence of this process can be seen in Figure 1.

In the first stage of evaporation, the salt solution becomes saturated and small crystallites start forming only at the liquid–air interface. As shown in the second frame in Figure 1 and the illustration in Figure 2, the crystals prefer to minimize their contact area with the solid surface, leading to their corners pointing downward. As the evaporation continues, the crystals that had already formed grow larger and in addition more crystals can precipitate depending on the evaporation rate. This results in the formation of a crystalline network, first as a skin on the droplet surface and subsequently inside the

Figure 1. Time sequence of an aqueous NaCl droplet evaporating on a heated silanized surface of 70 ± 2 °C. In the final stage, when a thin film of solution is remaining, narrow legs form on the bottom of the crystal, raising it above the surface.

Figure 2. An illustration showing the final stages of the evaporation and the start of the legs growing at the tip of the precipitated crystals. (A) Precipitation stage: The first crystals nucleate at the liquid/air interface. (B) Network stage: As more water evaporates, more crystals precipitate and form a crystal network with the salt solution surrounding it. (C) Dewetting stage: The salt solution dewets the substrate. This creates a thin film of solution under and around the crystal contact points. (D) Lift-up: The crystal network now guides the solution down where new crystals can form. The buildup of nucleated crystals under the contact points lifts the crystal network up.
remaining solution. When almost all the water has evaporated, we observe the salt solution to dewet from the hydrophobic surface, leaving a capillary bridge close to the pointy ends or edges of crystals in the vicinity of the surface. The remaining solution is then between the crystals and the substrate where new crystallites can form. The newly formed crystallites will form a bridge between the macroscopic assembly of crystals and the substrate. This process continues, causing the crystal to lift up until the water is evaporated completely. Because at higher temperature more crystals are formed, this leads to a larger number of "legs" and a faster rise of the crystal.

The physical mechanism of the formation of legs is likely to be similar to the growth in very thin films at high evaporation rates, as seen in microgravity\(^{18}\) and in porous media.\(^{19}\) In our experiments, at the last stages of evaporation, when cubic hollow crystals point toward the surface, tiny capillary bridges form, and it is only in this thin liquid film around the points of the macrocrystals that there is still salt solution from which salt can precipitate; see the Supporting Information for more details.

To quantify the dynamics of the rise, we measure the height difference between the crystal and the substrate \((\Delta h)\) as a function of the time from the onset of the rise until the end when the crystallization is finished. A sequence of the lift-up is illustrated in Figure 3. We find that the growth rate depends very strongly on temperature; for room temperature the lifting speed is \(0.34 \mu \text{m/s}\) whereas for the highest temperature we find \(60 \mu \text{m/s}\), roughly half a centimeter per minute. The very strong temperature dependence is reminiscent of an activated process, for which the growth rate varies exponentially with the inverse temperature. To see whether this can account for our observations, we start with the crystal growth rate, which can be described by\(^{20,21}\)

\[
\frac{\Delta h}{\Delta t} = K(S - 1)^g
\]

where \(K\) is the overall growth coefficient, \(S = m/m_s\) the supersaturation \((m\) being the NaCl concentration and \(m_s\) the saturation concentration), and \(g\) is the growth rate order. Previous experimental work has shown\(^{22}\) that the growth rate order \(g\), which is a function of the supersaturation, is unity for supersaturations \(S > 1.45\). In our case, we can take \(g = 1\), as the mechanism of leg formation consists of secondary nucleation and consequently the supersaturation is low.\(^{5,23}\)

With \(g = 1\), rearranging eq 1 gives for the growth rate:

\[
\ln K = \ln C - \frac{\Delta G_a}{R} \frac{1}{T}
\]

where \(C\) is the pre-exponential factor that gives the attempt frequency of the reaction and \(\Delta G_a\) is the activation energy. The inset of Figure 4 shows the measured height over time for different temperatures. Showing a faster growth rate for higher temperature.

\[
\frac{\Delta h}{\Delta t} = K(S - 1)^8
\]

Figure 3. Sequence of images taken at different times starting from the onset of lift-up \(t = t_0\) at a temperature of \(70 \pm 2 ^\circ\text{C}\). The total time \((\Delta t)\) of the rise in this experiment was \(11 \text{s}\).

\[
\ln K = \ln C - \frac{\Delta G_a}{R} \frac{1}{T}
\]

where \(C\) is the pre-exponential factor that gives the attempt frequency of the reaction and \(\Delta G_a\) is the activation energy. The inset of Figure 4 shows the measured height over time for different temperatures. We see that the growth rate increases rapidly for increasing temperatures. Using the slope \(\frac{\Delta h}{\Delta t}\) of these measurements and eqs 2 and 3, we can plot \(\ln(K)\) over the inverse temperature, as can be seen in Figure 4, to obtain the activation energy and the attempt frequency. The slope yields an activation energy of \(\Delta G_a = 40 \text{kJ/mol}\) and the intersection with the \(y\)-axis indicates an attempt frequency of \(C = 4.9 \times 10^8 \text{s}^{-1}\). Previously reported activation energies for NaCl growth are similar, around \(20 \text{kJ/mol}\).\(^{22}\) The difference of a factor of about 2 is probably due to the fact that the process here is somewhat different. In ref \(^{22}\) the growth of single crystals was studied; here we have secondary nucleation, and because of the very specific shape of the "legs", the incorporation of molecules can occur only at specific crystalline faces which can lead to a higher activation energy. The lifting speed is then simply determined by the growth speed of the crystallites. If we perform the same experiment for KCl, we find a activation energy of \(67 \text{kJ/mol}\), which compares favorably to the value reported in the literature of \(60 \text{kJ/mol}\);\(^{25}\) see the Supporting Information.
is only observed on silanized glass (frame l). For superhydrophobic and PDMS coated surfaces, crystallization occurs at the solid–liquid interface (frames b and f). The lift-up is only observed on silanized glass (frame l).

Information for more details on the KCl experiment. The activation energies for the growth then depend on the details of the incorporation process into the crystalline lattice, which in turn depend on the crystalline face and possibly the shape of the crystals growing in bulk or small volume of liquid. It is therefore perhaps not surprising that we do not find exactly the same results in our specific experiment than in a controlled crystallization one in bulk solution.

Our observations pose the question of what force lifts up the crystals. A natural explanation is that the force generated by the crystallization pressure is large enough to overcome the gravitational force. The crystallization pressure is basically the thermodynamic driving force for crystal growth and can be described in terms of the supersaturation and the activity of the solution using26,27

$$P_{\text{crys}} = \frac{\nu RT}{V_m} \left( \ln(S) + \frac{\gamma_S}{\gamma_{S,0}} + \frac{\nu_0}{\nu} \ln \frac{a_w}{a_{w,0}} \right)$$

Here $V_m$ is the molar volume of the solution, $\nu$ is the number of different ions (2 for NaCl), $T$ is the temperature, $S$ is the supersaturation, $\gamma_S$ is the mean activity coefficient, and $a_w$ is the water activity. As discussed earlier, in secondary nucleation, which consists of nucleation when crystals of the nucleating species are already present, the reduced energy required implies that it occurs at a lower supersaturation, i.e., close to unity.28 For a low supersaturation of NaCl solutions, the second and third term can be neglected, leading to the equation26,27

$$P_{\text{crys}} \approx \frac{\nu RT}{V_m} \ln(S)$$

With $V_m = 27$ cm$^3$/mol for NaCl and a range of supersaturation $S$ of 0.5–1%, we obtain a crystallization pressure of $P_{\text{crys}} \approx 0.9–1.8$ MPa at room temperature. To compute the force generated by this pressure, we measured the surface fraction of the bottom of the crystal that is making contact with the substrate, see Figure S1. It shows a scanning electron microscopy (SEM) image of the bottom of the final crystal assembly, we find a minimum force on the order of $F_{\text{crys}} \approx 170$ mN. Comparing this with the gravitational force pulling on the crystal with a measured mass of $m = 5.2$ mg, $F_{\text{grav}} \approx 51$ $\mu$N, these results show that the crystallization pressure can exert a force that is more than large enough to overcome the gravitational force and lift the crystal.

To understand the generality of these observations, we also conducted these experiments on a variety of hydrophobic surfaces with high contact angles, since the dewetting of the salt solution appears to be an essential ingredient in creating the "legs" locally. These experiments were performed at room temperature to have a slow controlled evaporation. Remarkably, the lifting was not observed on any other hydrophobic surface than the flat silanized one. We performed these experiments on superhydrophobic,17 roughened silanized glass, and PDMS coated glass slides. In most cases, the initial nucleation happens mostly at the solid/liquid interface; therefore the nucleation appears to be favored there. For the PDMS surfaces (Figure 5e,f), we indeed observe that the crystals form at the solid surface, implying a lower nucleation barrier for this surface; in addition the dewetting of the liquid does not take place as readily as for the silanized glass (Figure 5i–l). For the rough silanized and superhydrophobic surface (Figure 5a–d), we observe that crystals form even more preferentially at the solid surface. The key difference with the silanized flat glass is that the superhydrophobic surface and the roughened silanized glass have micro- and nanometer sized protrusions, which makes corners and asperities facilitating the nucleation.30–32 In addition, air is trapped underneath the droplets, causing a Cassie state for the superhydrophobic surface and a Wenzel state for the rough silanized surface.33,34 The air pockets for the superhydrophobic surface create numerous liquid/air interfaces underneath the droplet, where it is energetically favorable for the crystallites to nucleate.35,36 The smooth hydrophobic surface is not the only necessary condition for the formation of legs. This is mainly related to the chemistry of the surface. The interaction of the hydrophobic surface with water or salt solutions is due to van der Waals forces, dipole interactions, ionic interactions, hydrogen bonding, and proton exchange. Hydroxyl groups are

Figure 5. Time sequences for evaporation experiments of saline droplets on three different surfaces: (a)–(d) super hydrophobic surface; (e)–(h) PDMS coated glass slide; (i)–(l) silanized glass surface. The experiments here were all performed at ambient temperature (21 °C) and a relative humidity of 50%. For superhydrophobic and PDMS coated surfaces, crystallization occurs at the solid–liquid interface (frames b and f). The lift-up is only observed on silanized glass (frame l). Using $F = P_{\text{crys}}A\phi$ with $A$ the circular area of the bottom of the final crystal assembly, we find a minimum force on the order of $F_{\text{crys}} \approx 170$ mN. Comparing this with the gravitational force pulling on the crystal with a measured mass of $m = 5.2$ mg, $F_{\text{grav}} \approx 51$ $\mu$N, these results show that the crystallization pressure can exert a force that is more than large enough to overcome the gravitational force and lift the crystal.
the most common sites for hydrogen bonding. Silane interacts with hydroxyl groups at the surface, which impacts the hydrophobicity by eliminating the hydroxyls as water adsorbing sites, as well as shielding the polar substrates from further interaction with the liquid phase. Entities that present sterically closed structures that minimize van der Waals contact further interaction with the liquid phase. In our case, it also explains the difference between PDMS and the silanized surface in our experiments: the former can provide sites for NaCl growth at the solid liquid interface, whereas the silanized one prevents this.

In summary, NaCl crystals usually start to form at the liquid−air interface. Studying substrates of different hydrophobicities on which the evaporating drop is placed, we find that for most of these surfaces the NaCl crystals can also form at the solid and attach to these surfaces. However, for a flat silanized glass surface, we find that the crystals do not form at the substrate. The crystals start forming at the liquid−air interface, and to minimize contact with the surface, at the end of the evaporation the cubic crystals have their pointy ends oriented toward the substrate. At the last stages of evaporation tiny capillaries bridge form, and it is only in this thin liquid film around the points of the macrocrystals that there is still salt solution from which salt can precipitate. In this confined space, small crystallites form onto the points pushing the cubes away from the surface: the collection of crystals lifts itself away from the surfaces. In addition, step growth is also observed to occur. The lifting of the crystals is likely to be due to the crystallization pressure of the salt in contact with its supersaturated solution, and the growth of the “legs” under the macroscopic crystal assembly that push it away from the surface. This is reminiscent of salt creeping, where salt crystals can grow onto each other forming a porous structure that by capillarity sucks up the salt solution and new crystallites can grow onto each other forming a porous structure on the surface. This is reminiscent of salt creeping, where salt under the macroscopic crystal assembly that push it away from the surface.

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REFERENCES


