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Lepinay, S.E.G.; Deblais, A.; Habibi, M.; Bonn, D.; Shahidzadeh, N.

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Capillary Forces Lead to Pendant Crystals at the Liquid–Air Interface of Evaporating Salt Solutions

Simon E. G. Lepinay, Antoine Deblais, Mehdi Habibi, Daniel Bonn, and Noushine Shahidzadeh*

ABSTRACT: We investigated the nucleation and growth processes of individual NaCl crystals from an evaporating salt solution that is supersaturated. We find that crystals nucleate at the liquid/vapor interface, resulting in distinct “pendant” crystals, which reach millimeter dimensions. The substantial size of the crystals induces deformation of the interface. This process and the evaporation rate, in turn, determine the final crystal shape, which features a deep central cavity. Our findings reveal that a delicate balance exists between gravity, buoyancy, and the surface tension of the liquid/vapor interface that allows the crystal to remain pendant. When the contact angle of the crystal with the meniscus reaches 90°, the crystal disconnects from the interface and falls into the solution. We quantitatively predict the critical mass at which this occurs.

INTRODUCTION

The flotation of objects on the surface of water holds significant importance in aquatic life, water treatment, and separation technology for extracting precious metals from ore. Recently, it has also gained attention due to the self-organization of structures at the water’s surface caused by curvature of the meniscus, known as the Cheerios effect for self-assembling microscale and mesoscale particles at liquid interfaces, with the aim of making materials with different optical and electronic properties. Generally, small or lightweight objects can float either due to buoyancy or because the surface tension of water prevents excessive surface deformations. Experiments focusing on capillary-driven self-assembly have predominantly concentrated on the spontaneous formation of intricate patterns utilizing small chemically treated plates that float at a liquid-fluid interface. Given the small size of these objects, gravity is typically insignificant and is often neglected. In the latter scenario, an additional prerequisite is that the objects possess sufficient hydrophobicity to maintain their stability at the air–liquid interface, which serves as the fundamental principle behind ore flotation. In spite of its importance for a number of applications, several aspects of the problem remain poorly understood. These include determining the size and density of objects capable of floating at an interface and their relationship with the interfacial properties. Furthermore, it is essential to explore how particles such as crystals evolve and grow in size compared to crystal growth phenomena. Whether a precipitating crystal forms in the bulk or at the surface has been shown to depend on the wetting properties of the emerging salt crystals for the liquid–vapor interface. Recently it was also shown that the preferential rearrangement of anions and cations near the surface modifies the free energy for crystal nucleation from solution.

Despite sporadic photographic observations of floating salts in experiments as well as in locations such as the Dead Sea and salt mines, this phenomenon has predominantly received little attention. Few studies have been dedicated to investigating the formation of “fleur de sel” (Flower of Salt), characterized by hollow pyramidal crystals that float and grow on the surface of ponds during hot summer days. Notably, these occurrences have been reported in coastal areas of Brittany (France) and the Algarve region of Portugal.

In this study, we investigate the floating behavior of growing salt crystals of Halite (NaCl) that form at the free surface of saturated salt solution during evaporation similarly to the study of Davies et al. (2021) who studied the interactions between a solid cube under gravity and a horizontal soap film. NaCl crystals generally can grow by three morphologies dictated by its FCC lattice and denoted with Miller planes as cube {100}; octahedron {111}; and rhomb-dodecahedron {110} with a strong tendency to form cubic crystals {100}. The surface energies of different crystallographic facets can vary depending on the atomic arrangement and bonding within the crystal lattice. For example, the {100} facet is typically considered to have the lowest surface energy, followed by the {110} and {111} facets.

Here, we report on the first systematic study of the nucleation and growth of NaCl face-centered cubic growth (FCC) of {100} crystals at the interface from solution. These
nucleate preferentially at liquid/air, and we study their growth until they reach a macroscopic size while floating. We show that although the NaCl crystals have a significantly larger density than the surrounding salt solution, they can float and continue to grow while deforming the interface until the capillary forces are no longer strong enough to maintain the weight of the macroscopic crystal. The crystal then falls to the bottom of the vial, and the nucleation continues with the formation of new crystals at the interface from secondary nucleation. The growth dynamics of the floating crystal at the interface is described by 2 different regimes, before and after the bending of the liquid/vapor interface. The latter results in the formation of a central cavity in the cubic crystal during the layer by layer growth of the side and bottom crystal faces submerged in the salt solution. We also show that the equilibrium between the weight of the crystal and the bending of the liquid/vapor interface gives a similar force balance as the classical equilibrium in the pendant drop system which is frequently used for the determination of surface tensions.20 Therefore, by analogy, the floating NaCl crystal allows for the determination of the surface tension of the liquid at the vicinity of a growing crystal. Finally, our results also call into question the general assumption that a salt crystal is generally wettable by its own salt solution.

■ EXPERIMENTAL SECTION

Solution Preparation. To conduct the bulk evaporation experiments, homogeneous and slightly undersaturated solutions of NaCl (BioXtra, >99.5%) with a concentration of approximately 5.9 mol/kg were prepared (the saturation being at 6.1 mol/kg). For each experiment, a mother solution was created by dissolving 34.9 g of NaCl in 100 mL of water (Millipore, ρ ≈ 18.2 MΩ cm) at a temperature of T = 21 °C. The solutions were thoroughly stirred for a period of 6 h to ensure complete dissolution and homogeneity throughout the solution.

Evaporation Setup. For the evaporation process, glass containers were made by cutting the top sections of vials. Each recipient was then assessed using a Hitachi TM3000 scanning electron microscope of the crystal the apparent bulk density was determined for each crystal.

Crystal Characterization. After nucleation, the floating crystals at the free surface were collected at different stages of growth in order to analyze their size and shape. In addition, in some other experiments, the growth was followed until the final stage of floating: when a macrocrystal becomes too large, it detaches from the interface and falls to the bottom of the recipient. The crystals were then promptly removed from the solution and rinsed with pure ethanol (purity >99%). This step effectively eliminated any remaining traces of salt solution from the crystal surfaces. The crystal sizes and shapes were then assessed using a Hitachi TM3000 scanning electron microscope (SEM) and a Keyence-VX100 3D laser profilometer with a wavelength of 404 nm. Furthermore, volume measurements were done by submerging the crystals in ethanol and recording the corresponding rise in surface level. Knowing the mass and the volume of the crystal the apparent bulk density was determined for each crystal.

■ RESULTS AND DISCUSSION

As shown in Figure 1, we typically observed the nucleation of a NaCl crystal, followed by its further growth, and eventually its fall into the solution as its weight overcomes the capillary forces, keeping it afloat. Our experimental findings reveal two distinct stages during the crystal’s growth:

(i) In the first stage, which begins right after nucleation, the crystal’s edge acts as a pinning point for the liquid/air interface. Due to the small mass of the nascent crystal, the solution surface undergoes minimal deformation (1 and 5 h in Figure 1).

(ii) In the second stage, the growth and weight increase of the crystal causes a large deformation of the liquid/air interface. The curved interface at a certain stage in the growth remains pinned near the center of the top facet.

To differentiate between these two stages, we analyzed the length L(t) of the contact line between the fluid meniscus and
the crystal. In stage 1, as the crystal grows, the contact length increases with increasing crystal size (Figure 2a). At the onset of stage 2, surprisingly, the contact line reaches a plateau, indicating that it becomes pinned at a specific size while the crystal continues to grow.

![Figure 2. (a) Evolution of the length L(t) of the contact line between the free surface and the crystal during the growth of a pendant crystal. (b) Vertical cross sections of a single crystal obtained using 3D laser profilometry at the three time points indicated by stars in (a). Heights are aligned with the bottom of the cavity and their width centered at 0. (c) Growth rates of the crystal’s height, width, and volume.](image)

The analysis of the crystals at different stages of growth shows that in stage 2, when the crystals exceed a mass of about 10 mg, they exhibit a cavity with sharp edges; cross sections of crystals’ top facets measured at a late stage of growth by laser profilometry are shown in Figure 3b.

The transition between the two regimes and the formation of a cavity can be explained as follows. Immediately after nucleation at the free surface of the salt solution, the crystal is so small that its weight has a negligible effect on surface deformation (Figure 4a). Only facets exposed to the solution are capable of growth, allowing for horizontal and downward growth only. As the crystal continues to grow, its increasing weight starts to deform the salt solution/air interface. It has been demonstrated that particles with sharp edges are more likely to float compared to particles with smooth surfaces,\(^1\) for our case of cubic crystals, the capillary attachment force is greater than that of a spherical particle with the same wet perimeter and contact angle\(^2,3\) (Figure 4a). The pinned bent meniscus then acts as a reservoir of salt solution for the upper edges of the crystals, enabling horizontal growth (diagonally) in these regions as well (Figure 4b). Consequently, the crystal continues to grow upward, sideways, and downward as water evaporates (Figure 4c–e). With the deposition of new layers of salt on the crystal surfaces, the crystal expands in size, while the contact line remains fixed to the original edge. The gradual increase of the contact angle of the meniscus, caused by the bending due to the increased weight of the crystal, allows for perfectly vertical growth, ultimately resulting in the formation of the cavity until the contact angle approaches 90°. While the weight of the crystal increases continuously, the three-phase contact line makes discontinuous jumps as a consequence of the stochastic nature of the contact line anchoring and hysteresis, resulting in the observed steps (Figure 3a). The steps correspond to a discontinuous motion of the three-phase contact line between the crystal, the fluid, and the vapor.

To examine the growth process in more detail, we write the condition for the crystal’s flotation in terms of interfacial tensions; as illustrated in Figure 5, the system has the lowest surface energy for a crystal forming at the liquid/vapor interface when

\[
\gamma_{sv} < \gamma_{lv} + \gamma_{dl}
\]

where subscripts l = liquid, v = vapor, and s = solid. For salt solutions, the liquid/vapor surface tension is higher than pure water and increases with the concentration of ions in the solution; for a saturated NaCl solution (6.1 mol/kg), we measured \(\gamma_{lv} \approx 81\) mN/m using the pendant drop method. The crystal/vapor surface tension is notoriously difficult to measure, and literature values differ by almost an order of magnitude.\(^2,3\) To nonetheless obtain an estimate, we use the approximation proposed by Israelachvili:\(^2,4\)

\[
\gamma_{12} \approx \frac{A}{24\pi D_o^2}
\]

where \(\gamma_{12}\) is the interfacial tension between the media 1 and 2 (in mN/m), \(D_o\) is the intermolecular cutoff (0.165 nm), and \(A\) is the Hamaker constant:

\[
A \approx \frac{(3\hbar\nu_{uv})}{(8\sqrt{2})} \frac{2(\epsilon_2 - \epsilon_1)}{((\epsilon_1 + \epsilon_2)3/2)}
\]

where \(\epsilon_1\) denotes the dielectric constant of the solid (80), the solution \(\epsilon_2 = 1\), the vapor \(\epsilon_2 = 4.9\), the Planck constant \(\hbar = 6.63 \times 10^{-34}\) J s, and the plasma frequency of the free electron gas \(\nu_{uv} = 5 \times 10^{13}/s\). We find \(\gamma_{sv} \approx 30.9\) mN/m and \(\gamma_{dl} \approx 4.5\) mN/m by considering media 1 to be the NaCl crystal phase (solid) and media 2 is either the liquid (salt solution) or vapor phase (air). These estimates underlying the lower surface tension of the solid phase agree with eq 1, explaining why the crystal forms at the liquid/air interface. This could, in principle, be due to the fact that the salt concentration is higher there because the evaporation concentrates the ions.
near the interface. However, we do not anticipate significant heterogeneity in the solution as the evaporation at $T \approx 21 ^\circ C$, RH $= 50\%$ is slow (several days for 10 mL of solution), so the Peclet number will be very low as well. In addition, the corresponding experiment with an evaporating droplet of NaCl solution also shows that even if the concentration gradients are stronger at the contact line, crystals form near the apex of the drop. For cubic crystals such as the ones formed here, the 6 facets are equivalent, and since these crystals form at the solution–air interface, the Young equation tells us that the solution does not wet the crystal-air interface. In agreement with this, measurement of the contact angle that a saturated salt solution makes on a high quality single NaCl crystal (IR window) gives a contact angle of $8 \pm 2^\circ$ (see Figure S1). This confirms again that the salt solution does not fully wet the surface.

To determine the conditions for crystal flotation, we consider the force balance between gravity, $F_g$, buoyancy force, $F_b$, and capillary forces, $F_{cap}$, for a crystal of volume $V$ and contact perimeter $L$. Here, the capillary force depends only on the surface tension between salt solution and air $\gamma_v$ because it is the only interface that can deform.

$$F_g = F_b + F_{cap}$$  \hspace{1cm} (4)

where the capillary force $F_{cap}$ can be written as the surface tension times the perimeter length of the contact line $L$, leading to the force balance in the $z$-direction:

$$(\rho_{crystal} - \rho_{solution})gV \equiv \Delta \rho g V = \gamma_v L \sin(\theta)$$  \hspace{1cm} (5)

so that $\sin(\theta) \sim \Delta \rho g / \gamma_v L$. The density of the crystal has been obtained from two different experimental techniques (Figure 6); profilometry allows us to get an accurate volume for the smaller crystal’s size, while the immersion method (ethanol) allows us to determine density for larger crystal mass ($m > 50$ mg).

We plot $\sin(\theta)$ against $V \Delta \rho g / L$ in Figure 7. From a linear fit, we find that $\gamma_v = 79 \pm 3 \text{ mN/m}$, which is consistent with the value of 81.5 mN/m for saturated salt solution.\textsuperscript{25} The force has a component parallel and perpendicular to the interface; the latter increases when the angle becomes larger and is maximum at an angle of $90^\circ$. This, in turn, determines the maximum weight of the crystal that can remain suspended. From this we can also deduce the maximal mass for a crystal attached to the surface from the maximum capillary upward force; we find $\sim 300 \text{ mg}$, consistent with the maximum weight of the crystal (310 mg) measured experimentally after sinking in our series of experiments. In the hypothesis of a full cubic crystal, we can substitute the contact line length with the full perimeter of the crystal in eq 5, and in the limit where $\sin(\theta) = 1$, the maximum weight more than doubles.

From this data, we can compute a critical Bond number, $B_{0,c}$:

$$B_{0,c} = \frac{\Delta \rho g L^2}{\gamma_v}$$  \hspace{1cm} (6)

that we found in our case $B_{0,c} \sim 0.5$, consistent with values reported from simulation and experiment for a cubic crystal.\textsuperscript{17} Density and shape of objects floating at an interface are crucial ingredients that determine the critical number at which they will detach from the interface.\textsuperscript{8} Here, in this situation, the nucleation process gives rise to a specific $\{100\}$ crystal; this shape could be changed through nucleation of other type of salt (e.g., calcite or potassium alum) at the air/liquid interface, that may lead to another type of crystal shape such as rhombic or hexagonal.\textsuperscript{17} For such a shape, one could check if the critical Bond number at which the crystal falls is universal.
Finally, it should be noted that the evaporation rate is an important factor determining the geometry of the cavity during the growth of the crystal at the liquid/vapor interface. Recently, it has been shown that high evaporation rate can increase the total volume of inclusions in growing crystals in a solution, affecting their density. In the case of pendant crystals, a series of experiments done at different temperatures up to 90 °C show clearly that the higher the temperature, the deeper the cavity becomes (Figure 8). Although high evaporation rates lead to high nucleation rates, making the observation of single pendant crystals scarce. In our experiment, the measured evaporation rate at 90 °C (0.03 mm/s) allows for the evaluation of Peclet number, Pe, denoting the relative importance of ion advection and ion diffusion.

\[
\text{Pe} = \frac{U \times h_{\text{sol,nuc}}}{D} \tag{7}
\]

Here, \(U\) is the characteristic fluid velocity (advection rate) or the evaporation rate of the solution. In our case, we estimated it from the change of height of the liquid in time \(\frac{dh_{\text{sol}}}{dt}\) (see Supporting Information, Figure S2); \(h_{\text{sol,nuc}}\) is the characteristic length or characteristic dimension (e.g., the size of the system or the distance over which the substance is transported); \(D\) is the diffusion coefficient of the NaCl solution, \(D = 1.6 \times 10^{-5} \text{ cm}^2/\text{s}\)). Taking the characteristic length scale of the Peclet number to be the fluid depth (in the beaker) at the moment the first crystals are observed, we find \(P \sim 500\). This is very large, much larger than unity, showing that ions are strongly advect to the evaporative surface. This in turn leads to a much faster growth of the crystal at its edges close to the liquid–vapor surface compared with the bulk growth of the submerged faces. This anisotropic growth results in the creation of larger and deeper cavities with a pyramidal morphology.

\section*{CONCLUSIONS}

We studied the evaporation of NaCl salt solutions in a hydrophilic glass recipient and found that NaCl crystals nucleate systematically at the liquid/air interface and continue to grow up to millimeter-sized while remaining suspended at the interface. The growth proceeds in two distinct stages. First, the crystal facets in contact with salt solution grow sideways layer by layer without affecting the liquid/air interface. Second, as it grows and becomes heavier, it pulls down the liquid/air interface, which will facilitate the growth of the top surface at the edges, leading to cavity formation in the cubic layered crystal. The cavity forms when the contact line remains anchored at the surface of the crystal, the part of the surface that is in contact with the solution continues to grow but the part that is in contact with the vapor not. Such growth results in a cubic crystal with a slightly lower density compared to that of the same type of cubic crystal grown from a bulk solution. Finally, when the bending angle of the meniscus reaches 90°, the crystal completely sinks into the salt solution, leaving room for another crystal to possibly form.

By considering surface and interface energy balances, we show why the crystal initially remains suspended, although its density is higher than the salt solution. The contact angle is directly related to crystal and solution parameters, revealing a critical mass below which the crystal remains floating as it grows. The continuous growth on curved liquid/air interface is also in good agreement with previous studies showing that NaCl crystallization can take easily the shape of curved liquid capillary bridges in confinement. It may therefore also be feasible to obtain the controlled growth of certain crystal shapes or size by tuning the surface properties, e.g., by using surfactants or evaporation rate. In addition, the results could also explain the pyramidal growth of “fleur de sel”, which occurs at higher temperature; higher evaporation rate induces a larger advection of ions at the evaporative surface and induces a faster growth of the top facet, leading to the creation of larger cavities and subsequently a pyramidal morphology.

Studying crystal growth at the free surface offers valuable insights into the influence of interfacial phenomena on the kinetics and mechanisms that govern crystal nucleation and growth. By carefully manipulating growth conditions, such as the temperature and evaporation rate, it becomes possible to exert control over the shape, size, and surface characteristics of the crystals. This level of control is particularly significant in various applications in which specific crystal morphologies are desired for their distinct properties or functionality. Conversely, the precise details of crystal shape and their point of formation hold paramount importance in understanding the damage caused by salt crystallization in porous materials, such as building materials and stone artworks.

\section*{ASSOCIATED CONTENT}

\subsection*{Supporting Information}

The Supporting Information is available free of charge at https://doi.org/10.1021/acs.langmuir.3c01830.

Additional details on the contact angle measurement of a saturated NaCl solution at the surface of a NaCl crystal and on the evaporation rate of the solution (PDF).
Corresponding Author
Noushine Shahidzadeh – Institute of Physics, University of Amsterdam, 1098 XH Amsterdam, Netherlands; orcid.org/0000-0003-2692-0764; Email: n.shahidzadeh@uva.nl

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