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Pressure oscillations in a chemical garden

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When soluble metal salts are placed in a silicate solution, chemical gardens grow. These gardens are treelike structures formed of long thin hollow tubes. The growth is driven by the increase in internal pressure from osmosis. One particular case is examined here, calcium chloride in a solution of sodium trisilicate. We directly measure the internal pressure of a silicate garden as it grows via a series of relaxation oscillations. From these observations we deduce the stresses in the membrane and discuss how they influence the growth of tubes. Also we estimate the critical stress and the average Young's modulus for the silicate garden's membrane.

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I. INTRODUCTION

When soluble metal salts are placed in solutions containing silicates, hollow treelike structures grow. These three-dimensional precipitation structures have many names: silicate gardens, chemical gardens, or crystal gardens. They have been known about for centuries [1], and these days are a common science education activity [2]. Similar tubular precipitation structures abound in nature: speleothems such as helicities and "soda straws" [3,4], chimneylike structures deep in the ocean at hydrothermal vents [5], and the hollow silicate tubes observed in the formation of Portland cement [6]. Despite their common occurrence in nature, there are still many unknowns concerning how these tubular precipitation structures grow.

When the metal salt is first placed in the silicate solution, it dissolves and a permeable precipitation membrane forms instantaneously between the salt and silicate solutions, provided the concentrations are sufficiently high. The micrometer wide membrane is not a uniform material [7,8] since it separates two entirely different chemical environments: an acidic metal salt inside and a basic silicate solution outside. Osmosis causes liquid to flow through the membrane, inward, and toward the concentrated salt solution. This increases the internal pressure, driving the growth of the structure. The type of structure that grows can vary considerably, depending on which metal salt is used and the concentration of the silicate solution [9]. One common pattern produced under many conditions is a long thin tube. Tubes can form which are either open on the end [10,11], closed on the end, or with a gas bubble on the end [12].

The closed tubes are a particularly interesting case [13–17]. For these tubes, as the internal pressure increases, the stress at the tube end increases until it reaches a critical value and the membrane there ruptures. Then fluid is extruded through the rupture, and new membrane forms around the extruded liquid. This cycle can repeat itself several hundred times to produce long twisting tubes. The tubes so produced typically grow vertically, but horizontal and downward growing tubes have also been observed under different conditions. In some cases the relaxation oscillation is particularly violent, causing the entire structure to "twitch" [17], i.e., to move a few millimeters through the silicate solution in about a tenth of a second, once for each cycle.

There are many interesting and poorly understood dynamical features concerning the growth of tubes via relaxation oscillations. For example, tubes are not the only possible pattern that can be produced. Sometimes the ruptures occur at different spots on the membrane instead of always at the end of the tube. It is not well known exactly what makes tube growth stable. Similarly, it is still unknown what determines the tube radius or the oscillation period. For open tube growth, systematic studies have shown that the tube radius can be calculated from the flow rate via Poiseuille flow [15], however that description is not appropriate for the noncontinuous flow that occurs in closed tubes. A model for tube growth via relaxation oscillations has been proposed [17] but has not been systematically tested.

Here we report the results of an experiment to directly measure the pressure changes within a silicate garden as it grows. In Sec. II we describe our experimental procedure. In Sec. III we qualitatively describe our observation. In Sec. IV we quantitatively describe our observations and estimate what membrane parameters we can use from the observations: the elastic constant of the membrane and the critical stress of the membrane. In Sec. V we summarize the model previously proposed to describe tube growth from relaxation oscillations and discuss how our observations correspond with this model. We also discuss there possible future experiments.

II. EXPERIMENTAL PROCEDURE

We constructed an apparatus that pumped $CaCl_2$ solution into a silicate solution and then allowed the pressure of the $CaCl_2$ solution, relative to the atmosphere, to be measured. A sketch of the apparatus is shown in Fig. 1. The pump used was a peristaltic pump, a Gilson MiniPuls 3. The relative pressure sensor is a PASCO PS-2114 with a resolution of 1 Pa and a sampling rate of 20 times per second. The devices were connected with silicone tubing of inner diameter 2.28 mm. The silicate solution was composed of the following: 120 ml of 2.0 M stock sodium silicate solution, 5.0 ml of 0.6 M HCl, and 125 ml of distilled water. The 1.7 M calcium

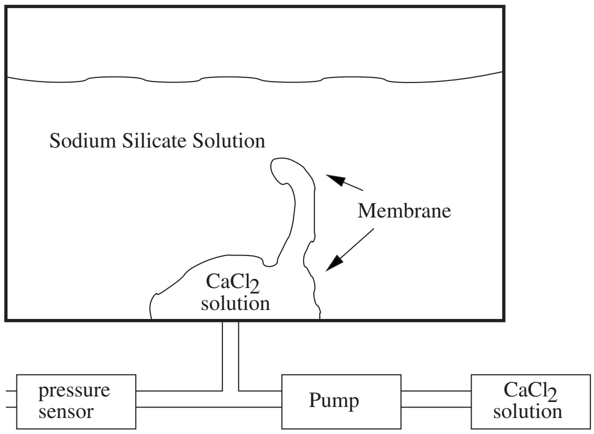

FIG. 1. Sketch of the apparatus used to measure the pressure fluctuations in the precipitation structure.

chloride solution was made from calcium chloride dihydrate and distilled water. The experiments were performed at a temperature of 20 ± 1 °C.

Our procedure consisted of pumping the calcium chloride solution into the silicate solution at a relative high rate for a short period of time, e.g., 2 ml/min for a couple of minutes. This was done to create an initial structure in the silicate solution consisting of a few milliliters of calcium chloride solution surrounded by a precipitation membrane. Then the pump was turned off and the subsequent pressure fluctuations were observed. At the same time the structure was videotaped for later analysis. The pump was turned off during our observations because pressure fluctuations associated with the pump were clearly observable even at pumping rates significantly less than the flow rate from osmosis. These pressure fluctuations from the pump were large enough to cause noticeable effects on the relaxation oscillations. Thus the pump was off for all of our observations, unless explicitly stated otherwise.

III. QUALITATIVE OBSERVATIONS

We observed changes in pressure, which tends to be of two types: a "fast" mode with a period of 1–2 s and a "slow" mode with a period that was an order of magnitude larger. The slow relaxation oscillations corresponded to ruptures at different locations on the membrane. The locations, when they could be identified, appeared to be relatively randomly distributed across the surface of the initial structure. The long periods allowed a relatively large amount of fluid to accumulate in the structure so that the amount of fluid extruded at the rupture site was large enough to produce long narrow filaments of varying length. After many of these slow relaxation oscillations the structures somewhat resembled the form of a porcupine or sea urchin. In contrast, the fast mode corresponded to tube growth. In this mode the ruptures always occurred at the tube end. This was a stable mode that, once started, could go on for hundreds of relaxation oscillations to produce tubes with a length of several centimeters and a diameter of about 2.5 mm.

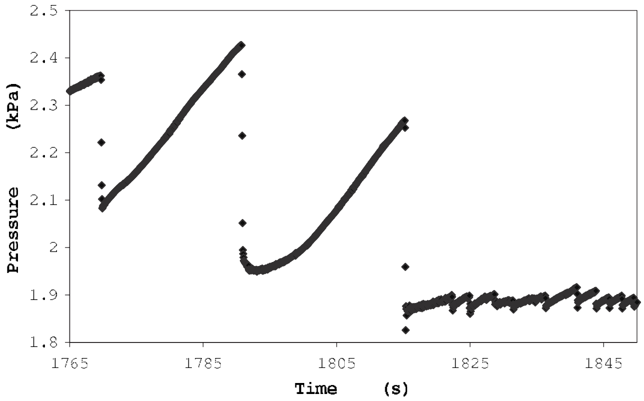

FIG. 2. Typical plot of pressure versus time observed in our experiment. A couple of slow mode oscillations are shown, followed by the fast mode, which corresponds to tube growth. Pumping started at $t = 0$ and lasted about 130 s.

Figure 2 is a plot of some of our data. It shows a couple of slow mode relaxation oscillations, changing to fast mode relaxation oscillations. In our experiments the slow mode oscillations had an average amplitude typically around 0.3 kPa, while for the fast mode it was about 0.02 kPa. To put these numbers in a physical perspective, the pressure change, δP, from a change in depth of water of δz is given by

$$\delta P = \rho g \delta z. \tag{1}$$

Using the standard density of water this gives that 0.1 kPa corresponds to the pressure from a column of water 1 cm high.

The existence of the two modes tells us something about the conditions necessary for tube growth. In tube growth, the membrane preferentially ruptures at or near where it ruptured previously. This implies that "young" membrane is much more fragile than "old" membrane [17]. One effect that might contribute to this is an expected continual decrease in concentration of membrane forming solute inside the tube at the tube end. However this effect cannot explain the observation that sometimes a tube will stop growing and the membrane will instead rupture at some other location, with the first tube never to grow again. Thus a large factor in explaining the stability of tube growth must be that the membrane strength or thickness grows on a time scale of order the fast mode period (1–2 s). However in slow mode, these effects do not dominate and instead the rupture site is not at the same location. Our observations suggest a possible reason for this. In slow mode the rupture sites have a relatively small radius, and so long thin filaments are emitted. Since the stress in a membrane is proportional to the curvature, the small filaments tend to have much smaller stresses in their membranes. Thus the smaller radii of the protrusion in slow mode are enough to compensate for the time it takes the membrane to strengthen. It thus appears that it takes a relatively large rupture to initiate stable tube growth.

IV. QUANTITATIVE OBSERVATIONS OF TUBE GROWTH

In this section we focus on the fast relaxation oscillations associated with tube growth. Several quantitative measurements can be extracted from our observations. From the

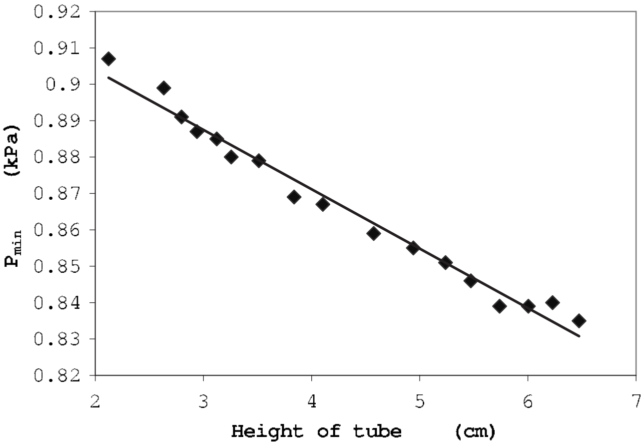

FIG. 3. Plot of the minimum pressure during the cycle versus the height of the tube as measured from the bottom of the container. The data is from one continuous measurement.

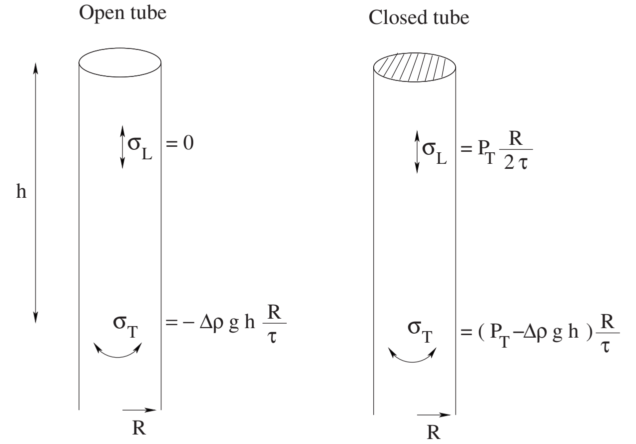

FIG. 4. Schematic showing the stresses in the tube just after rupture (open tube) and while the internal pressure is increasing from osmosis (closed tube). At the top of the closed tube, the internal pressure is larger than the external pressure by P_T, $\Delta\rho = \rho_{ex} - \rho_{in}$ is the density difference between the external and internal solutions [see Eq. (3) for measured value], R is the radius of the tube, τ is the thickness of the tube membrane, and h is the vertical distance below the tube tip to where the transverse stress is calculated.

video tape of the structure, we can extract the radius of the tube and the position of the tube end. From the pressure measurements, it is observed that each relaxation oscillation is basically a linear rise followed by a quick drop. The drop is usually too fast to fully resolve with our pressure detector. Thus the description of each relaxation oscillation cycle can be reduced to three independent quantities: dP/dt, the rate of pressure build up during the cycle, $\Delta P = P_{max} - P_{min}$, the pressure change occurring at the drop in pressure, and P_{min}, the minimum pressure during the cycle (which occurs after the quick drop in pressure).

A. Observations of P_{min}

The tubes in this experiment are observed to grow predominantly in the vertical direction. This is presumably because the interior solution is less dense than the exterior solution; so an upward buoyant force acts on the tubes, producing vertical growth. The density difference can also be seen directly in the pressure measurements. We have observed that the average pressure usually decreases, while a vertical tube is growing. Taking P_{min} for the reference pressure during a cycle, we plot it versus the height of the tube (as measured from the bottom of the container) in Fig. 3 for one continuous observation. The relationship between P_{min} and the height is approximately linear. This behavior can be easily understood.

When a tube ruptures and fluid emerges out the tube end, the internal pressure drops until it approximately equals the external pressures at the rupture site (there can be the occasional, small amount of "overshoot" beyond equal pressure at the pressure drop, as seen from Fig. 2 at 1815 s, which presumably occurs because of the inertia of the fluid moving along the tube). Then there is no contribution to the internal pressure from stresses in the membrane, the pressure detector just gives the pressure from the weight of the liquid above it. If the detector is at a depth L below the surface of the liquid and the tube extends a height h above the detector, then the recorded pressure is just the sum of that from the column heights $(L-h)$ of external fluid and h of internal fluid,

$$P_{min} = \rho_{ex} g (L - h) + \rho_{in} g h, \tag{2}$$

where ρ_{ex} and ρ_{in} are the densities of the external and internal solutions. The slope of the data in Fig. 3, divided by the acceleration of gravity, g, thus gives us the average density difference between the internal and external liquids for this particular tube's growth,

$$(\rho_{ex} - \rho_{in}) = 0.16 \frac{\mathrm{g}}{\mathrm{cm}^3}. \tag{3}$$

The measured initial densities of the solutions are $\rho_{ex}^0 = 1.21\ \mathrm{g/cm^3}$ and $\rho_{in}^0 = 1.13\ \mathrm{g/cm^3}$. Thus the average density difference between the liquid in the tube and the external liquid is much larger than that of the initial solutions.

The volume of the external silicate solution is very large compared to the amount of calcium chloride solution used, so the density of the silicate solution does not change significantly during the growth of a structure. However the density of the internal calcium chloride solution is expected to decrease as the structure grows because of dilution from osmosis and also because internal solute is used to construct the tube. Note that both of these effects will be largest toward the top of the tube, near the tip. That is where the depletion of internal solute is largest from the reasons just mentioned, and also that is where buoyant forces will drive the least dense fluid. Thus it is understandable that the observed density difference between the liquid in the tube and the external liquid is much larger than the initial fluid densities.

These observations have important consequences for the stresses in the membrane. Considering a vertical tube, we shall divide the stress up into its vertical (longitudinal) and horizontal (transverse) components, see Fig. 4 for a schematic. For a perfectly vertical rigid tube, open at the end (as occurs at rupture), there is no vertical force on the tube end from the difference in densities. Then the vertical stress in the tube's membrane will be zero. Vertical stresses in the membrane will only be produced by (1) buoyant forces on nonvertical parts of the tube and by (2) the increase in internal pressure when the tube is closed. The situation is very different for the stresses in the horizontal direction. There the density difference will give rise to a net inward force on the tube membrane that increases with depth. This force causes a compressive horizontal stress. In summary, for an open vertical tube the density difference tends to give no vertical stresses in the membrane but it does produce horizontal compressive stresses which grow larger as one moves away from the tip of the tube.

When the tube end is closed, the internal pressure increases from osmosis. This creates a positive longitudinal stress all along the tube and a positive transverse stress near the tip of the tube (see Fig. 4). In particular, assuming an osmotic driven internal pressure increase of 20 Pa (typical for fast mode oscillations), and using Eqs. (1) and (3), we find that below 1.2 cm from the tube tip the horizontal membrane stresses are purely compressive throughout a cycle. In the 1.2 cm near the tip, the horizontal stresses alternate in sign during a cycle. The total tensile stress will clearly be largest at the tube tip. Since a tensile stress is needed to rupture the membrane and grow a tube, *the density difference helps to stabilize tube growth*. However this cannot be the only factor in producing stable tube growth since horizontal tube growth has also been observed for a different metal salt [17].

For tubes with a height of several centimeters, the compressive horizontal stresses at the base may be large. In particular, if the membrane thickness was uniform, then the compressive stress at the base would be several times larger than the tensile stresses at the tube tip that produce rupture. The fact that tubes grow this high (see Fig. 3 for an example) shows that the membrane is not failing at the base. Thus either the membrane material has a larger compressive strength than it does tensile strength or the thickness at the base is several times larger than the thickness at the tip. In general, a finite compressive strength would give rise to a maximum height that tubes could grow. We have not systematically searched for this effect, and in fact our typical observation was that the tubes grew until they reached the surface of the silicate solution.

B. Observations of dP/dt

The rise in the pressure during an oscillation cycle, dP/dt, depends on the rate of liquid flow through the membrane, dV/dt, and on how the system responds to this increase in volume. We define a parameter B

$$\frac{dP}{dt} = \frac{B}{V}\frac{dV}{dt}, \tag{4}$$

where V is the volume contained in the membrane and B parametrizes how the system responds to pressure changes. The more easily the membrane stretches, the smaller B will be.

Treating the structure as a pressure vessel [18], B can be calculated for simple structure geometries. Making the simplistic approximation that the structure is a uniform tube of radius R, we have that [17]

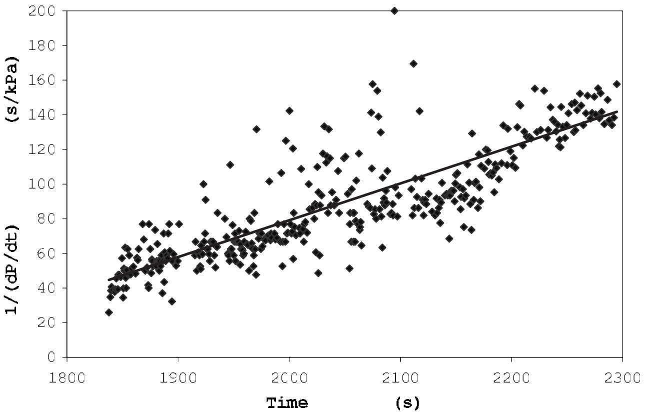

FIG. 5. Plot of the inverse of the measured pressure increase during a cycle, dt/dP, versus time. The data is from the growth of one tube. Pumping started at $t=0$ and lasted for a total of 220 s. The line shown is a fit to the data.

$$B = \left[\frac{2}{5-3\nu}\right]\frac{E\tau}{R}, \tag{5}$$

where E is the Young's modulus, ν is Poisson's ratio, and τ is the membrane thickness. This formula makes the simplistic assumption that the stretching is uniform and linear. When using this formula to estimate E, we shall take $\nu \approx 0.5$, the value for a perfectly incompressible material that deforms elastically. Note that while B does depend on the curvature of the structure it is independent of the length of the tube. Thus we naively expect B to be a constant as a tube grows.

One way to obtain the parameter, B, is to evaluate Eq. (4) at a fixed time. The slope of the rise in pressure during a cycle is dP/dt, and this is easily obtainable from the pressure measurements. The videotape data gives us dL/dt, the change in length of the tube, and during those short time intervals when the tube is growing straight dV/dt can be calculated directly using

$$\frac{dV}{dt} = \pi R^2 \frac{dL}{dt}, \tag{6}$$

where R is the radius of the tube. The structure volume V can be calculated from the pumping rate times the time pumped or estimated from the volume observed in the videotape. Using the values for these quantities measured at the start of tube growth and Eq. (4), we get

$$B = 40 \pm 20 \text{ kPa}. \tag{7}$$

This is our estimate for the pressure response parameter from the base of the structure, without any significant tube growing from it.

Our observations show that, as a tube grows, dP/dt decreases significantly in time. For example, Fig. 5 contains observations of dP/dt for the growth of one tube. For the data plotted in the figure, dP/dt decreases by a factor of more than 3. Such a large change is quite surprising because (1) direct observations of dV/dt, in this experiment and in previous experiments [17], find that it is approximately constant as a tube grows and (2) the volume of the tube is small compared to that of the total structure. Thus the pressure response parameter, B, must change considerably as the tube grows. In particular, the tube membrane must stretch more easily than the base membrane.

There are a couple of possible explanations for why the base membrane is less stretchy than the tube membrane. One possibility is a difference in membrane thickness between the initial structure and the growing tube. The measurements of P_{min} versus height showed that the interior liquid in the tube was significantly less concentrated than the initial pumping fluid. Thus it is to be expected that the membrane produced by the less concentrated solution would have a smaller thickness and thus would stretch more easily. Visually, the tube membrane does appear to be more transparent than the base membrane. However another possibility is that the membrane is very uneven and has nonlinear elastic properties. Since, throughout a relaxation oscillation cycle, the bottom of the structure has large horizontal compressive stresses while the top of the tube has smaller expansive stresses, nonlinear elasticity would give rise to a variation in B with the height of the tube. Both effects could be occurring together.

The change in dP/dt with time provides a way to estimate an effective B for the tube. Assuming constant dV/dt, then $V=V_0+t(dV/dt)$. As argued in the previous paragraph, the evidence indicates that, as the tube grows, the base of the structure becomes less important for the pressure response of the system, so V_0 is effectively small and the change in the pressure response can be attributed to a change in the effective volume. Then Eq. (4) can be rewritten as

$$\frac{1}{dP/dt} = \left[\frac{V_0}{dV/dt} + t\right]\frac{1}{B}. \tag{8}$$

The slope of dt/dP versus time, as plotted in Fig. 5, then yields $1/B$ directly. Combining the results of several tubes, we get

$$B = 4 \pm 1 \ \text{kPa}. \tag{9}$$

This is our estimate for the effective pressure response parameter of a tube.

For the base structure produced by the initial pumping, it is typically a lumpy, twisting tube with a value for the average diameter of about $2R=0.5\pm0.2$ cm. Using Eq. (5), we get

$$E\tau \approx 200 \pm 100 \ \frac{\text{N}}{\text{m}} \tag{10}$$

for the initial structure produced by pumping. For the growing tube, we take the average diameter to be $2R = 0.24-0.30$ cm and get

$$E\tau \approx 10 \pm 3 \ \frac{\text{N}}{\text{m}}. \tag{11}$$

To estimate the Young's modulus, E, one needs to know the membrane thickness, τ. We have not directly measured τ in this experiment, but we did observe that, for the growing tube, it was less than or equal to the resolution of our video camera observations, approximately 100 μm. Others [8], working at lower concentrations, have examined dried membranes from silicate gardens using scanning electron microscopy and found τ values of order 10 μm. Using our values from Eqs. (10) and (11) and taking $\tau \approx 10-100$ μm gives

$$E \approx 0.1-10 \ \text{MPa} \tag{12}$$

for our estimate of the elastic modulus of the membrane.

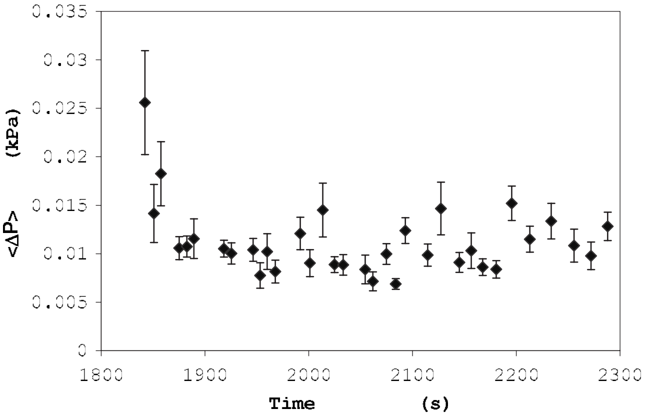

FIG. 6. Plot of the average pressure drop during a cycle, ΔP, versus time. The data is from the growth of one tube, the same growth as shown in Fig. 5.

C. Observations of ΔP

The drop in pressure during a relaxation oscillation is denoted as ΔP. During tube growth, ΔP is observed to have large fluctuations from cycle to cycle with the spread in values comparable in size to the average. Note that this is different than the observations of dP/dt, where the fluctuations are much smaller. Given the large fluctuations, we divide the observation of ΔP's into three categories: the average value of the pressure drops, $\langle \Delta P \rangle$, the frequency distribution, $dN/d(\Delta P)$, and the autocorrelation of the ΔP's. We shall discuss each in turn.

The average value of the pressure drops, $\langle \Delta P \rangle$, versus time is plotted in Fig. 6. The data is for the same tube observations used for Fig. 5. This data was chosen to illustrate our observations because it is one of our longest observations of tube growth. Here, several hundred cycles were observed during the growth of a single tube. The ΔP for each cycle was measured, the data was then broken down into groups of ten, the mean and the standard deviation of the mean were computed for each group, and the result is shown in the figure. Note that, aside from the initial few points, the general trend in Fig. 6 is that the average value of the pressure drops is approximately constant in time.

The average value in Fig. 6 (0.01 kPa) is rather small compared to our other observations of the pressure change during tube growth. While we observed the pressure change to be roughly constant for a particular tube's growth, the constant value was different for different tubes. Averaging over all of our observations of tube growth gives $\langle \Delta P \rangle \approx 0.019 \pm 0.005$ kPa. We can relate this to the critical stress at the tube end. Treating the tube end as approximately a hemisphere, the stress in the membrane is given as [17]

$$\sigma = \frac{PR}{2\tau}, \tag{13}$$

where P is the pressure difference across the membrane, R is the radius, and τ is the membrane thickness. Evaluating this at rupture time, we have

$$\sigma_c \tau_r = 0.013 \pm 0.004 \ \text{N/m} \tag{14}$$

for the critical stress, σ_c, times the membrane thickness at rupture time, τ_r. Taking the ratio of the tube elasticity to the tube critical stress, Eqs. (11) and (14), the tube thickness approximately cancels out. The value so obtained is comparable to that for many materials. Assuming a membrane thickness of 10–100 μm, as discussed previously, gives

$$\sigma_c \approx 0.1 - 1 \ \text{kN/m}^2 \tag{15}$$

for our estimate of the critical stress of the membrane.

The qualitative behavior of approximately constant $\langle \Delta P \rangle$, shown in Fig. 6, is quite typical of our observations. While sometimes there were slow decreases or increases in $\langle \Delta P \rangle$ over time, the changes were rather small, much smaller than the corresponding changes in dP/dt. Note that the period of the relaxation oscillation is $T = \Delta P/(dP/dt)$. Thus for the data shown in Figs. 5 and 6, the period increases by a factor of more than 3 from the start to the finish of the shown data. Given the large changes in some quantities, it is quite surprising that $\langle \Delta P \rangle$ remains so constant.

Qualitatively, there are two effects that would be expected to cause $\langle \Delta P \rangle$ to evolve over time. First, $\langle \Delta P \rangle$ should increase as dP/dt decreases (and T increases) since then the membrane will have more time to grow thicker. Second, the concentration of tube building materials at the tube end will decrease as the tube grows longer (from being used to build the walls and from osmosis), decreasing the rate at which new membrane can form and so decreasing $\langle \Delta P \rangle$. Since $\langle \Delta P \rangle$ is observed to be constant, the two effects appear to approximately cancel each other out. The concentration change at the tube end is difficult to model accurately because it is sensitive to how the fluid inside the tube mixes, which is unknown. This makes it difficult to compare the observed behavior of $\langle \Delta P \rangle$ over long times with the predictions of models [17] for the tube building process.

We have also examined the frequency distribution of pressure amplitudes, $dN/d(\Delta P)$. Figure 7 shows the distribution for the same tube growth as plotted in Figs. 5 and 6. The shape is similar to that observed in other bursting phenomena, such as popcorn [19]. The shape of the observed distributions are very similar to those reported previously [17] for the period, T. This is not surprising since $\Delta P = (dP/dt)T$, and the spread in dP/dt is typically small. The distribution is asymmetric, with a longer tail in the direction of larger amplitudes. We note that one possible explanation for this asymmetry is the growth of the membrane during the oscillation cycle. That is, the longer the pressure increases the thicker or stronger the membrane grows, and consequently it will rupture at an even larger value of the amplitude. While this may qualitatively explain some of the skewness of the distribution, it is difficult to quantify this explanation. This is because the main source of the spread of the distribution could be due to several factors, such as fluctuations in radius due to the rupture geometry, fluctuations in solute concentration at the tube end, and/or fluctuations in membrane defects [20]. Because of the many unknowns, we have not tried to model the distribution.

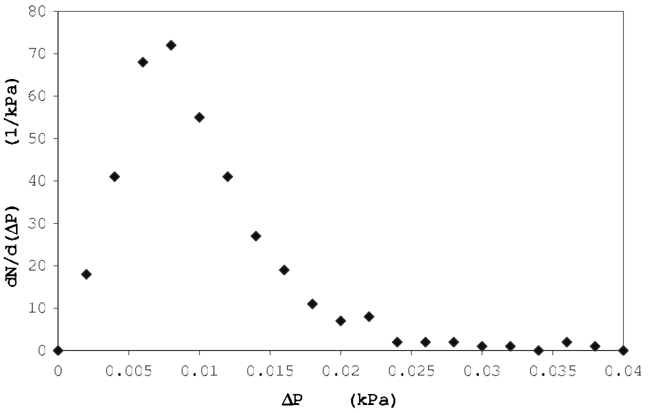

FIG. 7. Frequency distribution of ΔP's observed during the growth of one tube. The data is for the same growth as shown in Figs. 5 and 6.

The distribution of ΔP values definitely has a large stochastic contribution. However there does appear to also be a small tendency for a large or long cycle to be followed by another large or long cycle. To quantify this the autocorrelation of the data

$$A_k = \frac{1}{(n-k)\sigma^2} \sum_{i=1}^{n-k} (\Delta P_i - \langle \Delta P \rangle)(\Delta P_{(i+k)} - \langle \Delta P \rangle) \tag{16}$$

was calculated. The data was broken up into groups of $n = 30$ cycles, and the autocorrelation was calculated for each group. In general, a small positive correlation was found for one time step, but for larger differences the correlations were generally consistent with zero. The size of the autocorrelation at 1 time step varied considerably from group to group but was about $A_1 = 0.2 \pm 0.1$. This is consistent with a previous analysis [17] looking at the autocorrelation of the periods.

V. DISCUSSION

A model for the relaxation oscillations that produce tube growth was proposed in Ref. [17]. The model used a difference equation to relate one cycle to the next cycle. The fixed point of the difference equation describes the average properties of the tube. Here we will briefly summarize the model's assumptions that are necessary to describe the fixed point. We shall drop the $\langle\ \rangle$ notation that we previously used to denote an average. Instead, in this section, the period, T, the tube radius, R, and the rupture pressure difference, ΔP, are all average quantities. We shall examine how pressure measurements can constrain the model.

The stress at the tube end is described by Eq. (13). As osmosis drives fluid into the structure, the pressure difference across the membrane increases and the stress increases until it reaches a critical value and rupture occurs. To model how the stress evolves in time, it is assumed that the radius at the tube end is constant, but this cannot be assumed about the thickness of the membrane. Tube growth occurs because ruptures happen at the site of previous ruptures. Since this is true for vertical and horizontal growing tubes, it tells us that membranes thickness or strength evolves on a time scale comparable to or larger than the period of the relaxation oscillations. Thus the rate at which the membrane grows thicker or stronger is crucial to understanding why tube growth is stable. To model this over the short time of a fast relaxation oscillation, a simple form based on a power law is assumed;

$$\frac{d\tau}{dt} = \frac{\alpha}{\tau^{\gamma}}, \tag{17}$$

where τ is the membrane thickness, γ is the scaling exponent, and α is a parameter that depends on the concentration of the interior and exterior solutions. This equation can be integrated to give the thickness as a function of time and, with Eq. (13), the stress as a function of time.

To describe the radius of the tube end, we need some information on how the radius is determined by the previous relaxation oscillation. This depends on the geometry of the rupture and how fluid is extruded through the rupture. In slow mode ruptures, small ruptures plus large extrusion volumes produce thin filaments which have small radii and hence small stresses so they do not rupture again. In fast mode, which corresponds to tube growth, the ruptures and radii are consistently larger. Lacking any other information on what sets the scale of the tube size, it is assumed that the scale of the tube radius is set only by the amount of fluid extruded through the rupture site

$$R = c\left(\frac{dV}{dt}T\right)^{1/3}, \tag{18}$$

where T is the oscillation period, dV/dt is the flow rate of fluid into the structure (a constant over a cycle), and c is a dimensionless geometric constant. This form clearly does not model the slow mode; however it hopefully reflects the situation for fast mode where a stable process exists. Together, Eqs. (13), (17), and (18) provide a model for the average relaxation oscillations observables: T, R, and ΔP. Fluctuations around the average values can be included in the model [17], but we do not pursue that here.

The dimensionless parameter c can be calculated by simultaneously measuring the tube radius, R, the period, T, the tube growth rate, dL/dt, and using Eq. (6). Our observations in this experiment give

$$c = \left[\frac{R}{\pi T dL/dt}\right]^{1/3} = 1.3 \pm 0.1. \tag{19}$$

A previous experiment using pellets of calcium nitrate [17] found $c = 1.1 \pm 0.1$, in agreement with the current observations.

Using the model we can calculate steady state quantities such as the period, T, the tube radius, R, or the pressure change, ΔP, in terms of the flow rate, dV/dt, the pressure response parameter, B, the critical stress, σ_c, and the membrane growth parameters α and γ. For example, the average pressure change is given as

$$\Delta P = [(\gamma+1)\alpha]^{3/(4\gamma+1)}\left[\left(\frac{2\sigma_c}{c}\right)\left(\frac{B}{V}\right)^{1/3}\right]^{3(\gamma+1)/(4\gamma+1)} \times \left(\frac{dP}{dt}\right)^{-3/(4\gamma+1)}. \tag{20}$$

Here we have chosen to express this relation in terms of a quantity that is easily observable in our experiments, dP/dt, instead of dV/dt. We would like to use our observations and this relation to determine some of the model parameters, such as γ. However there is a problem. While a tube grows, many of these parameters evolve in time. While the evolution of dP/dt is observable, and the evolution of B/V may be deduced, the evolution of α, which depends on the solution concentration at the tube end, is not directly observable. Thus it is difficult to test the model from long terms observations of the growth of a tube.

It should be possible to test the model by inducing variations over a short period of time. For example, we tried turning on the pump during tube growth and thus changing dV/dt and dP/dt. By keeping the period of observation short, the other parameters (B and α) should not change much. However there are also problems with this method. Most importantly, our observations showed that our pump induced pressure fluctuations larger than those associated with tube growth. These fluctuations occurred on longer time scales, and we tried to minimize their effects; but given their presence we shall only report our observations as suggestive of what may be possible with this method. For example, in one observation we found the average values $\Delta P = 20.5 \pm 1.3$ kPa and $dP/dt = 21.3 \pm 0.5$ kPa/s for the 40 s before turning the pump off and $\Delta P = 26.8 \pm 2.7$ kPa and $dP/dt = 11.9 \pm 0.2$ kPa/s for the 40 s after turning the pump off. Using these observations and Eq. (20), we find

$$\gamma = 1.4 \begin{matrix} -0.5 \\ +0.9. \end{matrix} \tag{21}$$

This value is consistent with the naive expectation of gamma=O(1), from diffusion through the membrane. We plan on trying different pumping techniques to see if it possible to find one that does not induce fluctuations in the pressure. We note that several previous experiments by other groups have been published where pumping was used to quantify tube formation in silicate gardens. These experiments used a different pumping technique which we have not examined. However these groups did not measure the pressure fluctuation from their pumps.

We intend to repeat our experiments using other metal salt solutions. In particular, with calcium nitrate pellets it was observed that the tubes grew horizontally [17]. Thus there must have been only a small density difference between the interior and exterior solutions. In that case, the pressure difference across the membrane at the base will not differ significantly than that for the tube end. Thus the large stresses on the lower parts of the structure that were present in the current experiment would not be present when the internal and external solutions have similar density. This would probably affect how the structure responds to pressure, the B parameter. Thus observing how dP/dt evolves with time with similar density solutions would give insight into how the membrane responds to volume changes when large stresses are not present.

In future experiments we may try repeating these experiments using different solution concentrations. However our observations here suggest that the concentration at the tube end inside the structure differs considerably from the solution we pumped into the structure. This is not surprising given that dilution of solute from osmosis and from loss of material due to tube formation are most pronounced at the tip. But it may be possible to understand these process better by varying the concentration of the pumping solution.

Finally, one experiment we intend to pursue is to try and synchronize the pressure fluctuation to imposed pressure pulses from a transducer. Indeed, we have already inadvertently observed some synchronization in this experiment where pressure fluctuation produced by the pump influenced those produced by tube growth. Synchronizing the relaxation oscillations to induced pressure pulses may provide a method for controlling tube growth.

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