

## Oscillatory Growth of Silica Tubes in Chemical Gardens

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**Abstract:** We report distinct growth regimes of hollow silica fibers formed by hydrodynamic injection of cupric sulfate into silicate solution. The tubes grow either steadily along a continuous jet of buoyant solution or through relaxation oscillations that are governed by chemo-mechanical processes. The dependence of the oscillation period on flow rate and copper concentration is explained in the framework of a simple model. Tailored flow patterns allow the directional control of the tubes and their use as miniature connectors. Our findings are applicable to the understanding of chemical gardens, promise a wealth of nonlinear phenomena, and offer possible applications in microfluidics.

### Introduction

Chemical gardens consist of plantlike hollow fibers that form if certain metal salt crystals are seeded into a solution containing anions such as aluminates or silicates. They have been investigated since the late 19th century when they were mistakenly thought relevant to the origin of life.<sup>1</sup> They are used as spectacular demonstration experiments and are among the few chemical phenomena described in popular literature.<sup>2,3</sup> In recent years, their scientific study has regained importance. For example, it was shown that the tubes in aluminosilicate gardens are hierarchical nanostructures and powerful Brønsted acid catalysts.<sup>4–6</sup> Beyond these and other intriguing aspects, chemical gardens are a prototype of self-organized permanent structures that include hollow fibers in Portland cement as well as tubular corrosion products of steel.<sup>7–9</sup>

Although the term chemical garden encompasses a diverse family of reaction–precipitation systems,<sup>8,10</sup> their general mechanism is based on the formation of a semipermeable, colloidal membrane between the dissolving salt crystal and the surrounding solution. Driven by osmosis, water traverses the gel membrane and induces its swelling and rupture. Subsequently, a buoyant jet of salt solution is ejected into the surrounding medium, leading to the formation of a precipitate.<sup>11</sup> Within seconds to hours, this process builds up a hollow, tubular

structure until the osmotic pump action ceases due to complete dissolution of the seed crystal. Despite the wealth of remarkable features found in chemical gardens, little is known beyond this qualitative description.

The major obstacle for quantitative investigations has been the erratic nature of tube growth. Its sources are the continuous dissolution of the crystal, the blistering of the membrane at multiple sites, the presence of air bubbles at the growth points, and the interaction between neighboring tubes. We, therefore, have devised an experimental model of the original system that allows us to analyze and control the growth dynamics reliably.

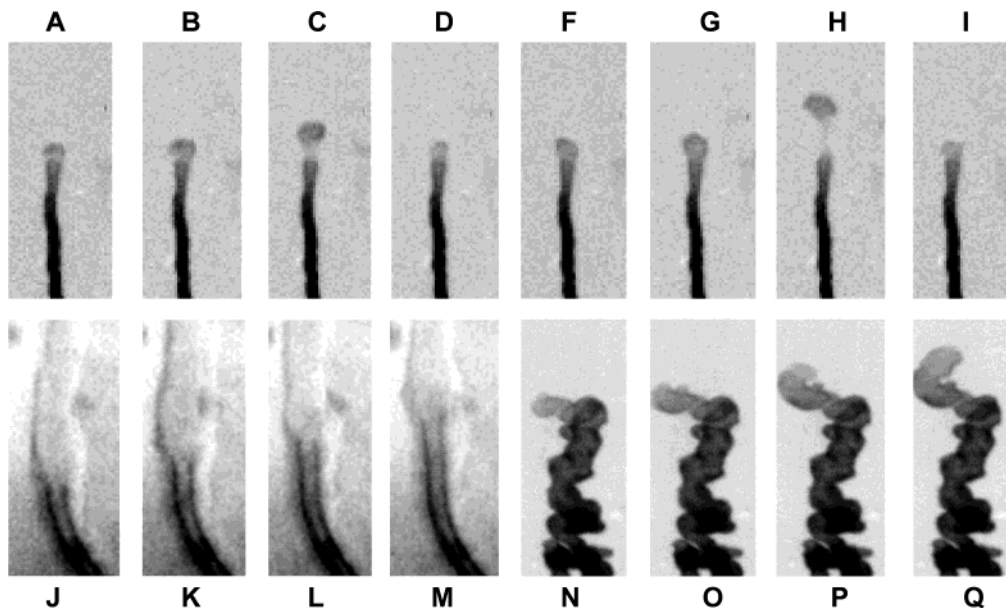
### Experimental Section

Our setup involves the hydrodynamic injection of aqueous metal salt solution (here  $\text{CuSO}_4$ ; Fisher) into a large volume of sodium silicate solution ( $\sim 1$  M; Fluka). The injection is carried out with a syringe pump (KD Scientific 200) at constant flow rate (2–15 mL/h) through a vertical glass capillary. The resulting silica tubes are monitored with a video camera connected to a PC for data analysis. Our approach typically leads to the formation of single, unbranched tubes with heights of up to 30 cm or more. Other metal salts, such as  $\text{MnCl}_2$  and  $\text{Al}(\text{NO}_3)_3$ , or mixed metal ion solutions give rise to qualitatively similar behavior. In the case of cupric sulfate, the tubes have a dark blue color because of the presence of cupric ion in the precipitate. No dependence of the tube diameter on the radius of the injection nozzle is observed, but large nozzles make the experiment susceptible to undesired backflow of the dense silicate solution. All experiments are carried out at room temperature.

### Results

We are able to distinguish three regimes of tube growth (Figure 1). At low concentration of cupric sulfate ( $< 0.1$  M), we observe thin silica tubes ( $\sim 200$   $\mu\text{m}$ ) that form along a continuous jet of buoyant copper solution (Figure 1J–M). If the concentration is increased to 0.15 M, this steady-growth behavior is replaced by oscillatory dynamics. As illustrated in Figure 1A–I, a small membrane-bound droplet forms at the tip of the fiber, inflates, pops off, and rises to the surface of the

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**Figure 1.** Image sequences of tube growth in the popping (A–I), jetting (J–M), and budding regime (N–Q). In all experiments, aqueous cupric sulfate solution is injected into sodium silicate solution (100 mL, 1 M in Si, 25 °C) at a constant flow rate (here 7.0 mL/h). The time intervals between frames and the image areas are 0.5 s,  $9.1 \times 20.4 \text{ mm}^2$  (A–I, N–Q) and 2.0 s,  $1.6 \times 3.6 \text{ mm}^2$  (J–M), respectively. The concentrations of cupric sulfate are 0.25 M (A–I), 0.05 M (J–M), and 0.50 M (N–Q).

silicate solution. The period of this cyclic process is on the order of seconds, and the resulting tubes are approximately 5 times wider than those at low concentrations. We observe a second transition in the formation of the silica tubes if the concentration is increased beyond 0.35 M. Under these conditions, the expanding droplet does not detach but rather bursts and nucleates a new droplet at the rupture site (Figure 1N–Q). The repetitive stretching and bursting creates a very wide (here 2–3 mm) bulging tube that shows signs of helicity.

To obtain quantitative clues regarding the mechanism of the oscillatory dynamics, we carried out systematic measurements of tube growth in the intermediate concentration, popping regime. Figure 2A shows an example of the sawtoothlike height evolution of a typical tube. The time interval between subsequent popping events varies around an average value of 5.6 s with a large standard deviation of 2.6 s. Short and long intervals correspond to small and large height changes, respectively. Despite the oscillatory character, we find constant average growth velocities ( $v$ ). These velocities reveal a proportional dependence on flow rate, but no significant dependence on the cupric sulfate concentration (Figure 2B). Moreover, tubes created in the low concentration, jetting mode (Figure 1J–M) have growth velocities very similar to those shown in Figure 2B, whereas the average velocities in the high concentration, budding mode are significantly higher. Our findings differ from earlier results by Coatman et al., who reported decreasing growth velocities in conventional chemical gardens.<sup>8</sup> Our experiments indicate that their observations are affected by transients such as the continuous dissolution of the seed crystal.

Important conclusions can be drawn from the flow rate dependence of the period of popping events (Figure 2C). The average period  $T$  changes with the flow rate  $Q$  in a nearly inverse relation, yielding constant products  $vT$  and  $QT$  for a given concentration of cupric sulfate (Figure 2D,E). The product  $vT$  is the average growth per period, which ranges between 250 and 750  $\mu\text{m}$ . The product  $QT$  specifies the volume of solution delivered

per oscillation period and, hence, measures the volume of the detaching droplets. This critical volume increases with the concentration of the metal salt, but does not depend on flow rate. The existence of a critical volume is the key feature of the cyclic growth mechanism because it controls the switching between slow volume expansion of the buoyant droplet and rapid formation of a new membrane at the temporarily uncapped tube. This finding reveals that silica tubes growing in the popping mode are relaxation oscillators which are intensively studied in a broad range of disciplines such as optics, hydrodynamics, and biology.<sup>12–14</sup>

The relaxation oscillator that is most reminiscent of our system is the “dripping faucet” in which a transition from jetting to dripping occurs via a Savart–Plateau–Rayleigh capillary instability.<sup>15–17</sup> Tate’s law for the dripping faucet predicts the critical mass of the drop by equating the corresponding weight to the surface tension force at the point of detachment.<sup>18</sup> Silica tubes in the oscillatory popping mode can be discussed in an analogous way. We equate the buoyant force of the detaching droplet with a critical force  $F_{\text{crit}}$ . The latter force does not depend on the flow rate, but reflects the physical properties of the droplet’s membrane. Accordingly, we obtain the equation  $gQT\Delta\rho = F_{\text{crit}}$ , where  $g$  denotes the acceleration of gravity ( $9.8 \text{ m/s}^2$ ), and  $\Delta\rho$  is the density difference between the sodium silicate solution,  $\rho_2 = 1124 \text{ kg/m}^3$ , and the effective density  $\rho_1$  of the droplet. Because the concentration range for popping tube growth is small (0.2 M), we express the concentration dependence of the density  $\rho_1$  as  $\rho_0 + \xi[\text{CuSO}_4]$ , where  $\xi$  is an experimental constant. Thus, we find that  $QT = F_{\text{crit}}/\{g(\rho_2 - \rho_0 - \xi[\text{CuSO}_4])\}$ .

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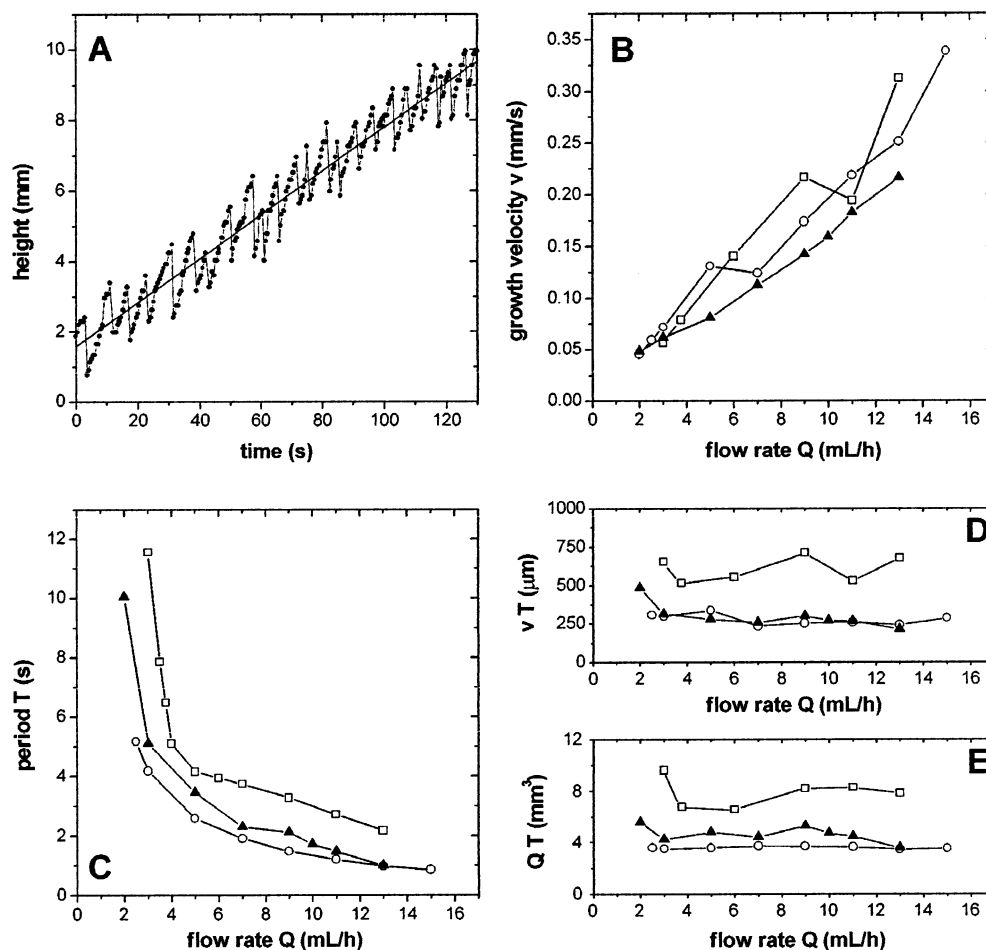
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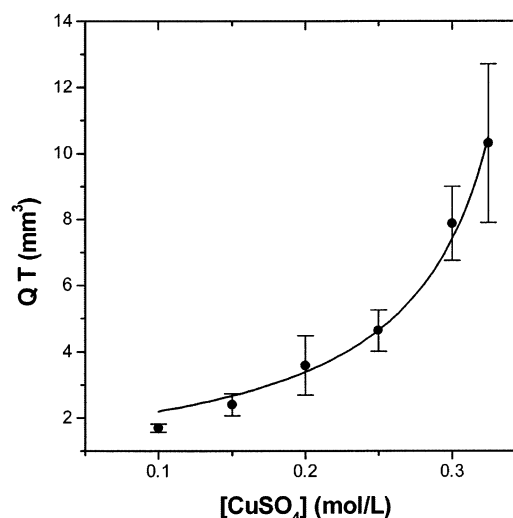
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**Figure 2.** Data obtained from silica tubes in the popping mode. (A) Example of the oscillatory height evolution at  $[\text{CuSO}_4] = 0.25 \text{ M}$  and a flow rate of  $Q = 3.0 \text{ mL/h}$ . The average growth velocity is  $62 \mu\text{m/s}$  (solid line). In general, this velocity shows a nearly proportional dependence on the flow rate (B). The average oscillation period decreases with increasing flow rates (C), yielding constant values for the growth per period  $vT$  (D) and the volume delivered per period  $QT$  (E). In parts B–E,  $\circ$ ,  $\blacktriangle$ , and  $\square$  indicate data obtained for  $[\text{CuSO}_4] = 0.20, 0.25,$  and  $0.30 \text{ M}$ , respectively.

As shown by the least-squares fit in Figure 3, our experimental data are in good agreement with this equation. Assuming that the membrane makes only a small contribution to the effective droplet density and that  $\rho_0$  is the density of pure water ( $999 \text{ kg/m}^3$ ), we found that these values yield  $F_{\text{crit}} = 2 \mu\text{N}$  and  $\xi = 0.3 \text{ kg/mol}$ . The latter parameter is remarkably close to the known value  $\xi' = 0.16 \text{ kg/mol}$  for the concentration dependence of the density of pure cupric sulfate solutions.<sup>19</sup> We suggest that the critical force  $F_{\text{crit}}$  is related to the tensile strength of the colloidal membrane surrounding the droplet. Although the membrane thickness is unknown, one can expect it to have extremely low tensile strength, which is in agreement with the low critical force obtained. Our results emphasize the importance of buoyant forces and the characteristics of the repetitively forming membrane. These factors also dominate the transition from popping to budding behavior (see Figure 1). Here, the buoyant forces are not strong enough to induce detachment, and the droplets expand beyond their elastic limit, leading to small ruptures without release of material. This interpretation predicts that under microgravity<sup>20,21</sup> popping oscillations should be

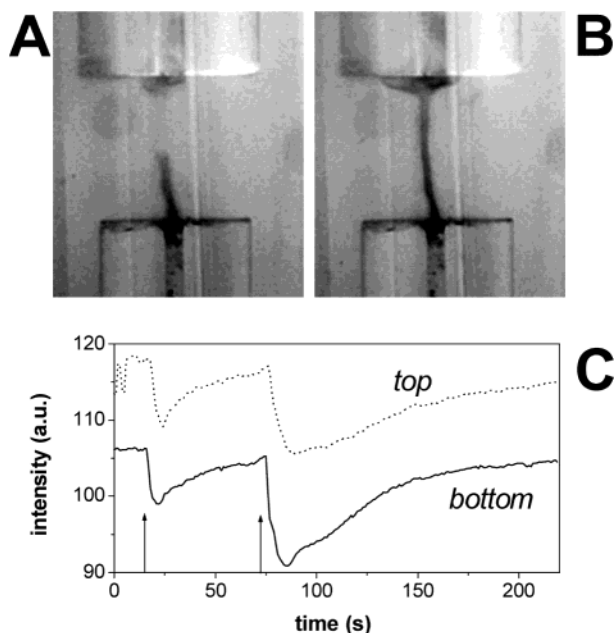


**Figure 3.** The volume of solution delivered during one period of the oscillatory popping events,  $QT$ , is shown as a function of the concentration of cupric sulfate. Each data point is the average of several experiments at different flow rates in the range of 2–15 mL/h.  $QT$  also estimates the maximal volume of the droplets forming at the top of silica tubes (e.g., Figure 1C). The solid curve represents the fit of the function  $QT = 1/(a + b [\text{Cu}^{2+}])$  to the experimental data. It yields the parameters  $a = (0.61 \pm 0.05) \text{ mm}^{-3}$  and  $b = -(1.6 \pm 0.2) \times 10^6 \text{ mol}^{-1}$  that are related to physical quantities in the framework of our model (see text).

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**Figure 4.** Silica tube growth between two glass capillaries before and after formation of a connection (A,B). The tube is grown in the jetting mode ( $[\text{CuSO}_4] = 0.05 \text{ M}$ ) by injection from the lower capillary. It is attracted to the upper capillary that withdraws liquid from the system at the same rate (5 mL/h). The resulting tube has a diameter of  $240 \mu\text{m}$  and establishes a bridge between the inflow and outflow port. Field of view  $9.3 \times 10.7 \text{ mm}^2$ . (C) Injections of rhodamine solution into the flow of cupric sulfate (see arrows) lead to temporarily decreasing intensities within the lower and upper glass capillaries, demonstrating that the silica tube forms a closed connection.

suppressed and give way to the lower frequency dynamics of budding.

While more work is needed to develop a full understanding of the involved mechanisms, our alternative experimental approach to chemical gardens also opens avenues for microfluidic applications.<sup>22</sup> For example, one can direct the growth of the silica tubes through tailored hydrodynamic flow patterns

in the sodium silicate solution. Moreover, we have succeeded in producing self-guiding connections between inflow and outflow ports of a simple model device. A typical example for this technique is shown in Figure 4. A silica tube grows between a lower glass capillary injecting cupric sulfate solution and an upper capillary withdrawing liquid from the system. The tube forms around a continuous jet attracted by the fluid-intake into the upper capillary. Once the hollow fiber reaches the orifice, it creates a footlike junction (Figure 4B) or sometimes continues to grow inside the capillary. We tested the sturdiness of the connection by injecting rhodamine solution to the flow. Figure 4C shows the intensity changes in the upper and lower capillary in response to two injections, demonstrating the mechanical integrity of our unusual microfluidic connection.

### Conclusions

From studies of conventional chemical gardens, it is known that silica tubes can undergo splitting or merge with neighboring fibers.<sup>8</sup> Our experimental approach should allow the control of these phenomena, thus providing all of the necessary components to build up three-dimensional networks for lab-on-a-chip-like applications and chemical sensors. The microtubes in these networks can consist of a variety of mixed or stratified metal/silica materials with interesting catalytic properties and tailored surface characteristics. Further studies on this system should also clarify the lack of strict periodicity in the relaxation oscillations. Such efforts are likely to reveal a wealth of nonlinear phenomena including quasi-periodic dynamics and deterministic chaos.

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