Peristalticity-driven Banded Chemical Garden

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(Dated: 10 April 2018)

Complex structures in nature are often formed by self-assembly. Either to mimic the formation, to enhance the production, or to modify the structures, easy to use methods are sought to couple engineering and self-assembly. Chemical-garden-like precipitation reactions are frequently used to study such couplings because of the intrinsic chemical and hydrodynamic interplays. In this work we present a simple method applying periodic pressure fluctuations given by a peristaltic pump which can be used to achieve regularly banded precipitate membranes in the copper – phosphate system.

PACS numbers: 47.70.Fw Chemically reactive flows; 47.85 Dh Hydrodynamics, hydrostatics, hydraulics; 81.65 Cf Surface cleaning, etching, patterning

Keywords: periodic pressure fluctuation; flow-driven precipitation pattern.

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I. INTRODUCTION

Self-assembly plays an important role in nature to form complex spatio-temporal patterns and self-sustainable structures. Since what is formed in a natural way is always interesting, different scientific fields focus on how those patterns and structures can be made artificially and improved *via* human controlled engineering methods[1–8]. Among the numerous physical and chemical procedures, precipitation offers a tempting way to produce enduring and self-sustainable solid structures with tailored properties. One particular system known for leading to three-dimensional precipitate membranes is often referred as chemical gardens[9,10]. Such membranes can be reproducibly made by applying flow-injection techniques[11]. They are particularly interesting, since hydrodynamics and chemistry intrinsically couple during the formation of the structure giving rise to possibilities for maintaining control on the final product properties. Those systems have been thoroughly investigated, thus nowadays the wall-thickening direction[12–14], the osmotic contribution to that of active injection[15], and the effect of confinements[16,17] and varying reactants[18] together with their concentrations[19] are understood. It is also observed that, due to the growth mechanism, pressure fluctuations can be measured while the solid structures are forming and *vice versa*, fluctuation-less injection method can influence membrane connectivity [20–23].

The importance of flow chemistry in the scale of small channels and devices is obvious nowadays[24,25]. It has also been shown that flows affect not only homogeneous but also heterogeneous reactions, since flow-dependent polymorph selection[26], particle size and shape distribution[27,28], and surface modification[15] have been reached which are usually not accessible in batch. The next step on the way to achieve appropriate control on small scale self-assembled devices with tailored shape and surface properties is to enhance the macroscopic characteristics. Therefore, inhere we would like to pay more attention to the coupling of mechanical effects (i.e. periodic pressure undulation) and the evolving macroscopic membrane structure.

II. EXPERIMENTAL

To grow precipitate membranes in a reproducible way, flow-injection technique[11,29] was applied as illustrated in Fig. 1. Throughout the experiments, 0.5 M copper sulphate solution

FIG. 1. Sketch of the experimental setup. Peristaltic pump used to deliver $CuSO_4$ solution into the Na_3PO_4 solution kept in a circular container. Banded precipitate membrane captured from above.

FIG. 2. Copper phosphate precipitate membrane fingers growing radially; real color (a). Zoom of one of those fingers in black and white to illustrate the banded structure achieved (b).

($CuSO_4$, $\rho = 1.0779 \pm 5 \times 10^{-4}$ g/cm^3, pH $\approx$ 3, Scharlau) was injected into a circular pool (13.7 cm diameter and 1.5 cm depth) containing 0.25 M sodium phosphate solution (Na_3PO_4, $\rho = 1.0435 \pm 1 \times 10^{-4}$ g/cm^3, pH $\approx$ 13, Molar) at w = 0.5 mL/h (0.43 rpm) volumetric flow rate by a peristaltic pump (Gilson M312 equipped with d_{in} = 0.76 mm Tygon tube). The Na_3PO_4 solution was poured into the container to form a 1 cm deep layer open to the air. A needle in which the tubing ended penetrated 5 mm deep into the Na_3PO_4 solution, thus the injected $CuSO_4$ solution started to mix and form precipitate at the half of the layer depth. The time evolution of the precipitate structure was monitored from above by a camera (Sony DFW-x710). Further more, we highlight here that not only the low injection speed but also the unusually low pump rotation frequency is essential to achieve the pattern being described.

To investigate the pressure undulation intrinsically caused by the operating peristaltic pump, a relative pressure sensor (PASCO PS-2114, 1 Pa resolution, 20 Hz frequency) was attached via a T-junction between the pump and the inlet. In those experiments, distilled water was delivered through the pump and the pressure difference compared to the atmosphere was recorded over time.

III. RESULTS & DISCUSSION

When injection starts and thus precipitants mix at the tip of the needle, a copper phosphate precipitate membrane forms and rises towards the liquid-air interface where it splits into several fingers. Led by the contiguous inflow, those fingers grow radially right under the liquid surface as shown in Fig. 2(a). Taking a closer look, one may observe the banded membrane structure allowing to expect an oscillatory growth mechanism (see Fig. 2(b)). To investigate whether the oscillatory delivery mode of the pump (i.e. small solution parcels

FIG. 3. Gray scale distribution along the advancing precipitation front with colors corresponding to experimental images taken with 150 s time difference.

FIG. 4. Gray scale distribution of the banded precipitate tube shown in Fig. 2(b) to determine the wavelength λ.

formed between consecutive rollers) is responsible for such regularity, the following characteristics are determined stepwise: how fast the leading edge of the tube advances (linear tube growth, v_l); what is the wavelength of the oscillatory pattern (λ); and at what time periods the pump delivers fresh solution packages (T).

As an example case, we illustrate here the results obtained for the tube seen in Fig. 2(b) but in overall, 19 tube growths were compared to ensure reliability. To determine v_l, first the gray scale distribution is followed in time along the advancing precipitation front (x) as depicted in Fig. 3. We see that high intensity (I) belongs to the bright tip of the membrane which clearly differs from that of the black background. The minimum of the first derivative of $I(x)$ is sought and then its trend recovered through the different instances thus leading to $v_l = 30 \pm 4$ μm/s linear tube growth, which agrees well with the average value determined for the set of experiments ($\bar{v}_l = 30 \pm 6$ μm/s). From the small experimental error of v_l and the regularly succeeding curves seen in Fig. 3 we can conclude that the precipitate membrane grows with a constant and well-defined rate.

As a next step, the wavelength λ of the banded pattern is determined. To do so, the gray scale intensity along the already formed membrane is plotted as a function of the spatial extension. Fig. 4 shows one such plot for which $\lambda = 0.34 \pm 0.01$ mm is found. This value fits within the experimental error to the average wavelength determined on the basis of 19 tubes ($\bar{\lambda} = 0.41 \pm 0.07$ mm). Combining $\bar{v}_l$ and $\bar{\lambda}$ values together with their errors, taking the error spreading into account as well, we obtain that in average $T_{\mathrm{band}} = 13.7 \pm 3.6$ s is required for one band to evolve under the experimental conditions maintained. Therefore, to investigate whether this time period can be comparable to that given by the oscillatory liquid delivery of the peristaltic pump, we have determined the expected period from the parameters of the pump as $T = 1/(N\omega) = 1/(10 \times 0.43 \text{ rpm}) = 13.9$ s, where N is the number of rollers in the pump and ω is the angular velocity of the pump. Since the predicted period is in excellent agreement with the experimentally determined one, in separate

FIG. 5. Pressure oscillations detected when water is delivered through the peristaltic pump.

experiments we recorded the pressure change over time while water was injected through to ascertain the industrial parameter values. The result of one such experiment is shown in Fig. 5, where the period is found to be $T = 13.84 \pm 0.01$ s. The small experimental error clearly highlights the precision of the pump. We also see by comparing T_{band} to T, that the time elapsed while one band formed is in the time range in which one solution parcel between two rollers leaves the pump. We highlight here that such T is realistic considering the very slow injection rate (w = 0.5 mL/h) and the very slow rotation frequency (0.43 rpm).

One can put together all those results to complete the physical picture if the operation mode of the peristaltic pump is taken into account. The injected solution is delivered in small parcels between the rollers of the pump. When one such parcel is between two rollers, interior pressure increases compared to the outer one ($\approx$ 26 Pa operational pressure increase for the case shown in Fig. 5). When the parcel leaves the last roller, this operational pressure decreases due to the opening up of the previously compressed elastic tube section. That pressure drop slightly withdraws the contiguous solution filament from the channel which causes a tiny backward flow and thus a better mixing, and a longer reaction time at the tip of the evolving membrane. This leads to the formation of a more compact (denser) precipitate layer where less liquid is trapped inside the tubular structure, which manifests as a brighter segment in Fig. 2(b) and higher intensity values in Fig. 4 (for more experimental evidence, see parts D – G in Fig. 4 in Ref[29]). In the succeeding phase when flow in the membrane becomes faster again, the time for the reaction decreases and a less compact segment containing more liquid inside evolves. The outer tube diameter in Fig. 2(b) generally does not show periodicity, most probably the inner diameter does so. In some cases porous precipitate membranes inside the tube may form during the phases of small backward flow which also appear as lighter bands in the precipitate tube. It is important to point out that segmented tubular structures have also been observed in classical chemical gardens [30]. The periodic nature of osmotic growth is inherent due to the alternation of membrane formation and rupture in the mechanism, which can lead to a visible periodic pattern in the precipitate structure, depending on the properties of the membrane. The pressure modulation introduced by the pump in this work, however, represents a tunable control on the structure formation.

This could be interesting from a small scale device engineering point of view. For example, one may imagine a situation where such a tube with periodic inner diameter and catalytically active inner surface is used as a small flow-through reactor. The mixing of the delivered liquid will be more effective due to the Hagen-Poisseuille-flow[31] which can enhance the productivity.

IV. CONCLUSION

Being able to modify self-assembly is a promising tool to engineer small scale devices and obtain complex structures. One particularly interesting field is the coupling of chemical reactions and hydrodynamics since small scale flow chemistry bears with increasing relevance nowadays. We have shown that a simple mechanical effect (inhere an oscillatory pressure change) can be used to shape the evolving structure. It is seen that multiple, oscillatory banded copper phosphate membranes can be yielded by injecting one solution into the other one *via* a sufficiently slowly rotating peristaltic pump just because the solution is delivered in oscillatory manner with well-defined pressure variations leading to pulsating flow. Changing the reaction for an other one providing more cohesive (i.e. sustaining larger pressure drop) and faster precipitation (e.g. silicates) may allow the investigation of how the length, diameter, and periodicity of the bands can be tuned by adjusting the peristalticity of the pump.

V. ACKNOWLEDGEMENT

This work was supported by the National Research, Development and Innovation Office (K119795 and PD121010) and GINOP-2.3.2-15-2016-00013.

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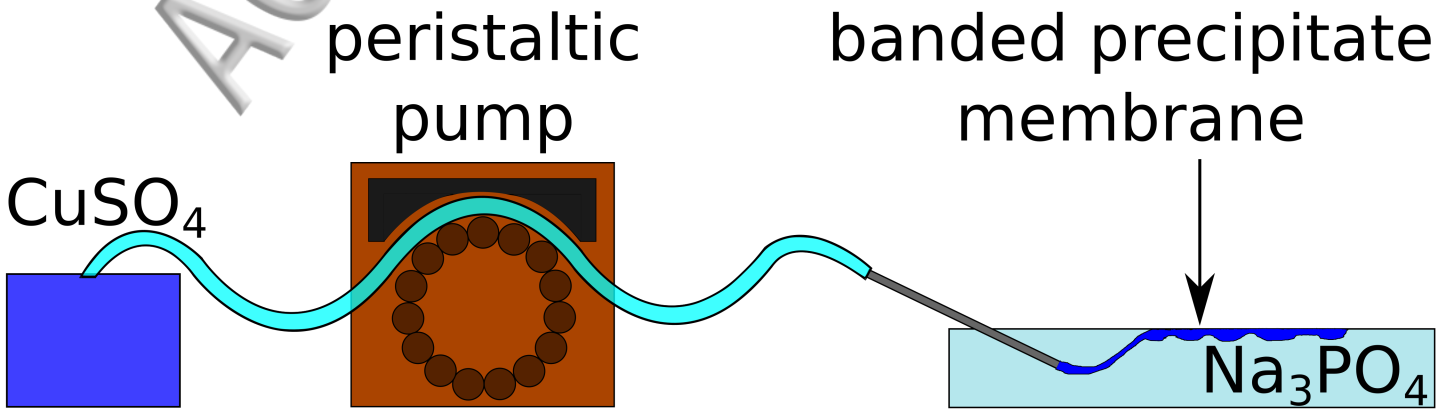
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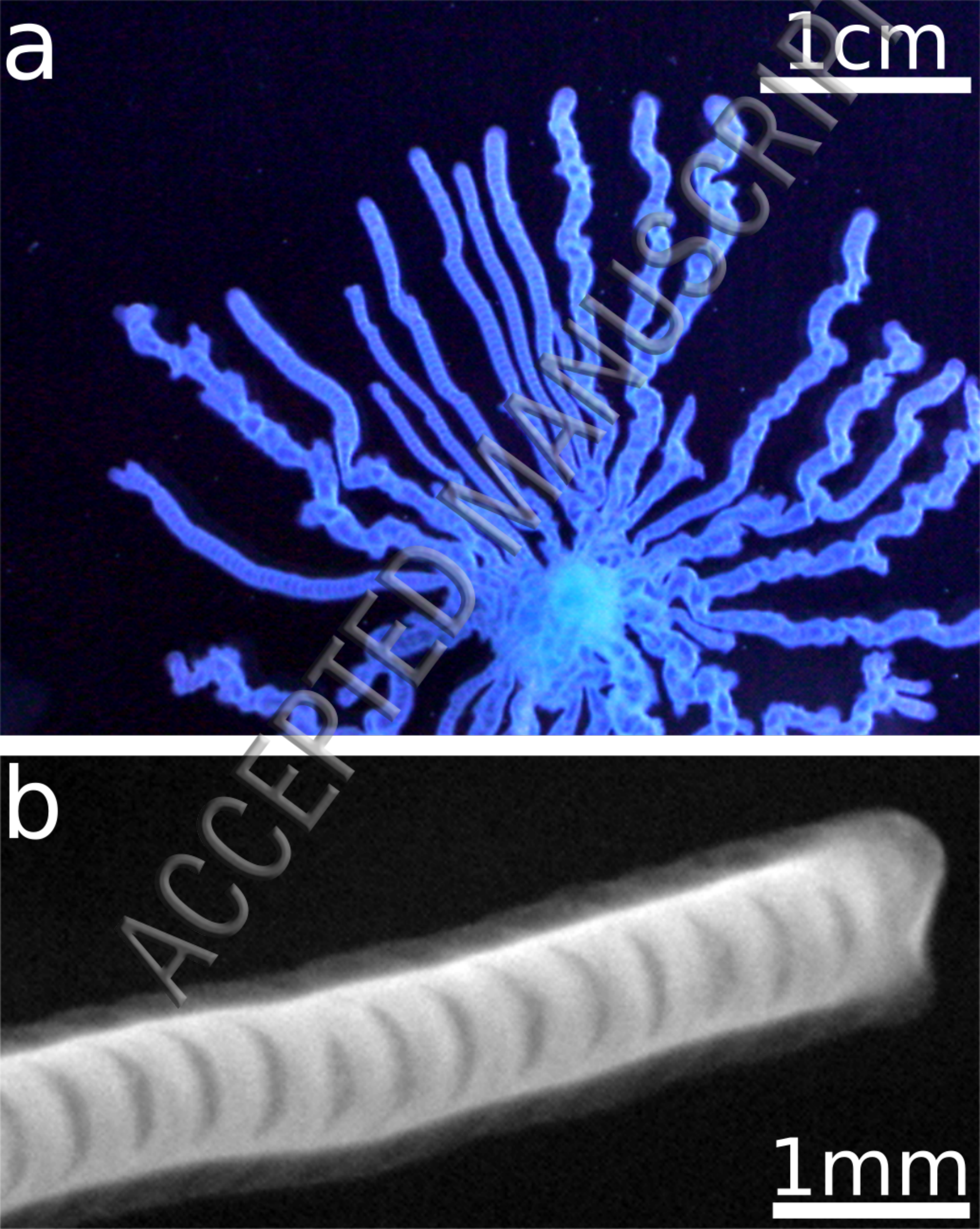
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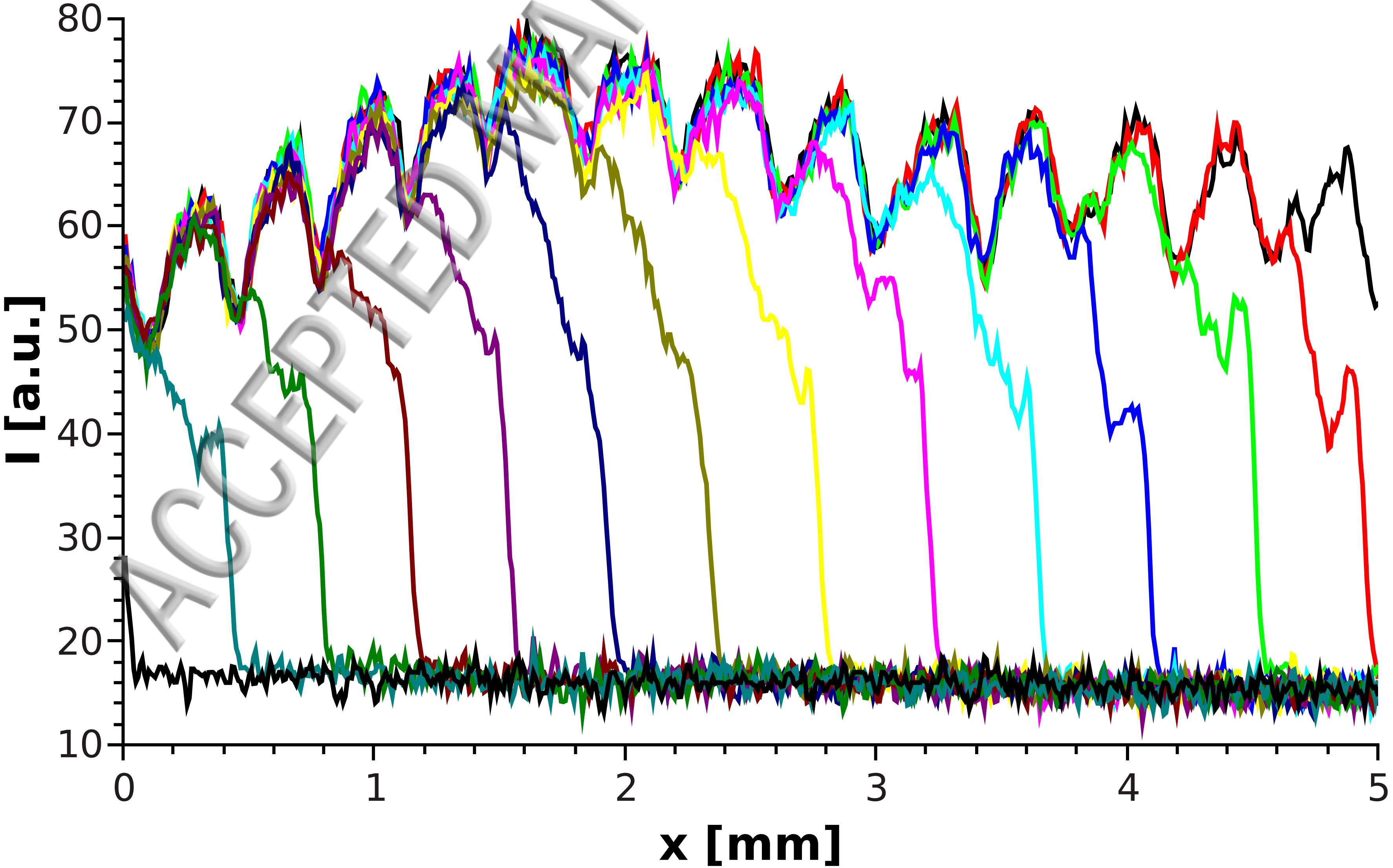

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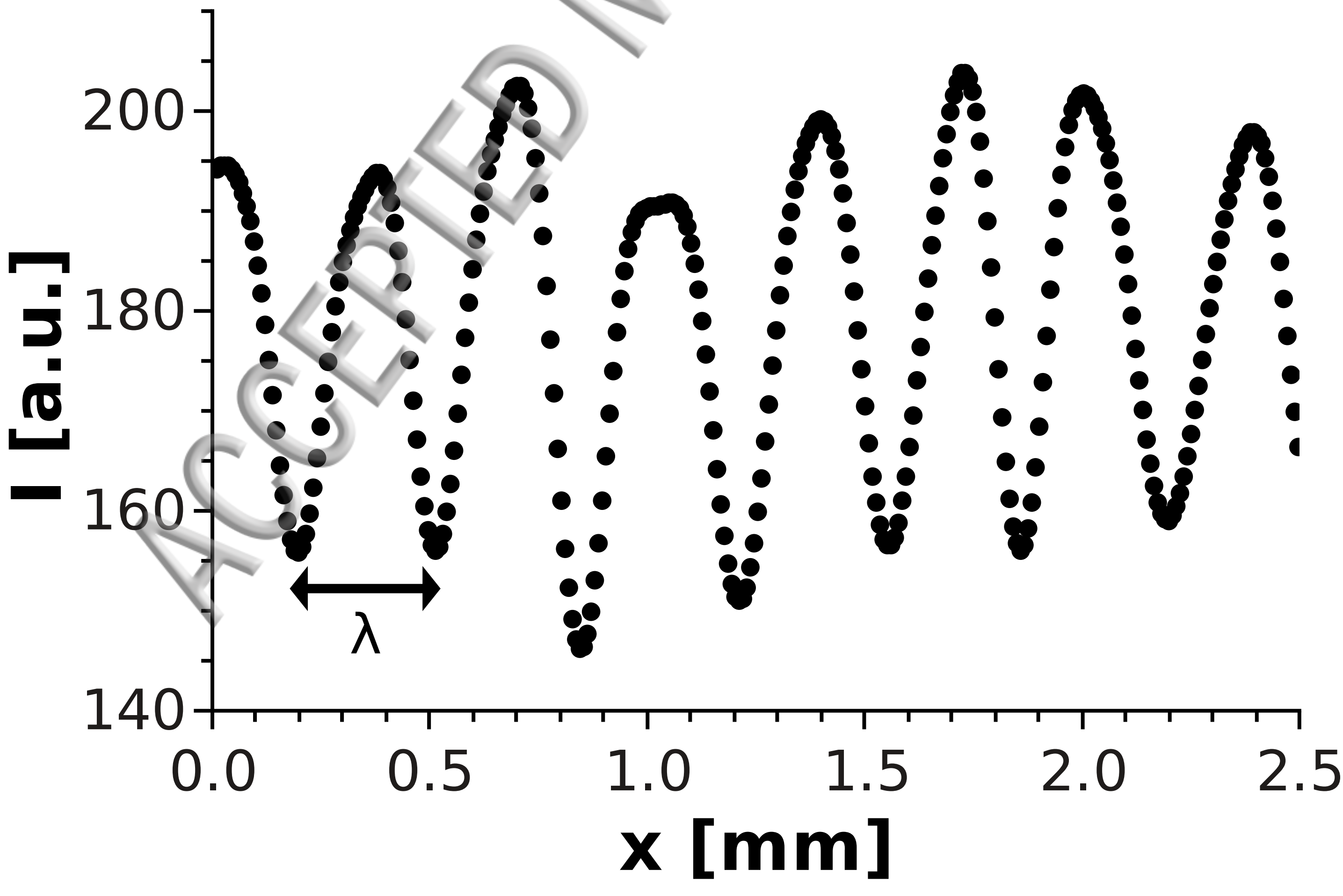
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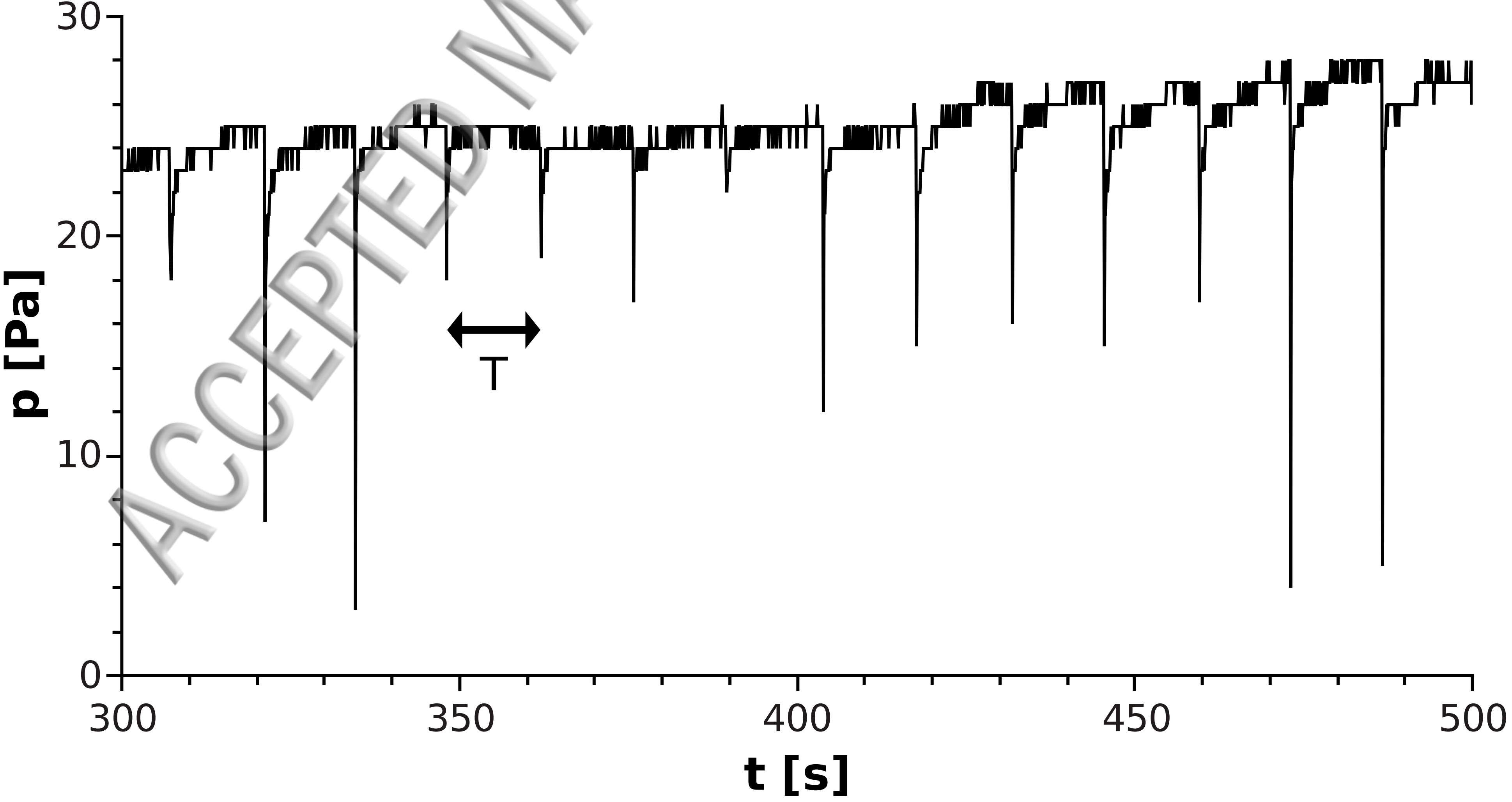
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