Supplementary Information: Self-propulsion of a calcium alginate surfer

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1 Density, surface tension, viscosity, and droplet weight measurements

Density of the reactants was measured with a density meter (Anton Paar DMA-500) at 25 °C. Density difference ($\Delta\rho$, see Table S1) was calculated as $\Delta\rho = \rho_{Ca^{2+}} - \rho_{ALG}$. At 0.5 M $CaCl_2$, the droplet fully immersed (1.5% w/V ALG) or stationary floated (0.3-1% w/V ALG) and did not self-propel. Thus no experiments were recorded at this concentration.

Table S1: Calculated density differences ($\Delta\rho$) between the used concentrations.

$\Delta\rho$	1.5% w/V ALG	1.0% w/V ALG	0.5% w/V ALG	0.3% w/V ALG
6 M $CaCl_2$	0.4553 g/cm^3	0.4576 g/cm^3	0.4598 g/cm^3	0.4606 g/cm^3
4 M $CaCl_2$	0.3051 g/cm^3	0.3074 g/cm^3	0.3096 g/cm^3	0.3104 g/cm^3
2 M $CaCl_2$	0.1564 g/cm^3	0.1587 g/cm^3	0.1609 g/cm^3	0.1617 g/cm^3
0.5 M $CaCl_2$	0.0359 g/cm^3	0.0382 g/cm^3	0.0404 g/cm^3	0.0412 g/cm^3

Surface tension, viscosity and drop weight results are collected in Table S2. Surface tension was measured with a stalagmometer by measuring the mass of 10 droplets. Viscosity of the alginate solutions was measured with a rotational viscometer (Anton Paar ViscoQC-300). In Table S2, surface tension difference between the outer $CaCl_2$ solution and the exerted water is calculated as $\Delta\gamma = \gamma_{Ca^{2+}} - \gamma_{water}$.

Table S2: Surface tension, surface tension difference compared to water, dynamic viscosity and droplet weight measurements.

	γ [mN/m]	$\Delta\gamma$ [mN/m]	η [mPa·s]	m_d [mg]
water	72	0	–	–
2 M $CaCl_2$	79	7	2.2	–
4 M $CaCl_2$	86	14	4.6	–
6 M $CaCl_2$	91	19	14.9	–
0.3% w/V ALG	78	–	17,6	11.9 ± 0.2
0.5% w/V ALG	92	–	58.2	12.0 ± 0.1
1.0% w/V ALG	93	–	296.2	12.0 ± 0.1
1.5% w/V ALG	–	–	1312	12.0 ± 0.1

2 Nuclear Magnetic Resonance (NMR) measurements

To characterize the sodium alginate reagent, we first identified the proper peak groups from the measured NMR spectrum (Fig. S8) and then calculated the guluronate amount ($G\%$).[1] The $G\%$ determines the gelation properties of the sodium alginate because only guluronate blocks are able to react with calcium ions. We used a Bruker Avance 500 MHz NMR spectrometer with a standard water suppression (`zgesgp`) pulse program, and 250 number of scans was recorded.

The sample contained 3.5% w/V alginate (MW = 110 ± 6 kDa), where the powder was dissolved in D_2O with stirring and by sonication. For the evaluation, we used `TopSpin 4.0.5`. From the integrated areas of the proper, baseline-corrected peak groups (Table S4), G% was calculated as

$$G\% = \frac{\text{integrated area of A}}{\text{integrated area of B} + \text{integrated area of C}} = \mathbf{27.9\%}. \quad (1)$$

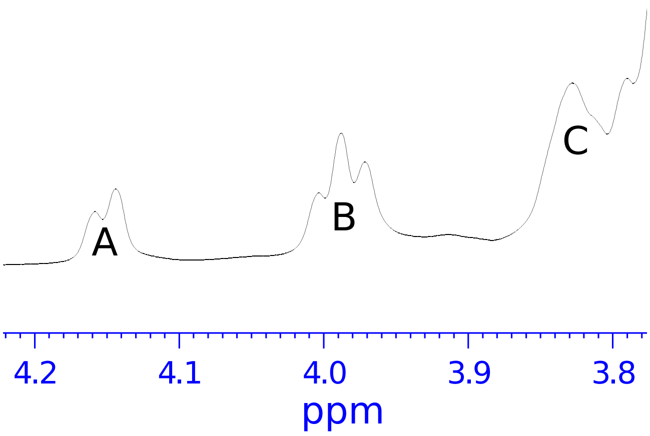

Figure S1: NMR spectrum of 3.5% w/V sodium alginate.

Table S3: Identified peaks and their integrated areas.

peak group	peak position(s)	integrated area
A	4.18; 4.16	1.3341
B	4.02; 4.01; 3.99	3.3496
C	3.85	1.4378

3 Particle image velocimetry (PIV)

To reveal the flow profile in the $CaCl_2$ solution during the reaction, we used particle image velocimetry (Fig. S2). A plexi container held 9 mL 4 M $CaCl_2$ solution. This also contained 72 μg/mL latex beads ($\varnothing$ = 6.4 μm). One droplet of 10 μL 1% w/V sodium alginate was dropped with a pipette into the middle of the plexi container, to which a metal thread was attached and the end of it was bent to the center of the container. The drop was pinned to the thread's end by dropping on it, so the droplet would not float to the wall. The container was illuminated with a laser beam plane (λ = 660 nm, 70 mW, width ~1 mm, Roithner Lasertechnik), while a convex lens (F = 15 cm) in front of the laser beam was placed 1 cm apart. The experiment was recorded from above (Fig. S3) or from side view (Fig. S4) and the laser beam was accordingly set horizontally in the top 1 mm or vertically crossing the droplet. A black-and-white camera (Adimec) equipped with 20 mm focal length lens was used for recording continuously with ~7.5 fps. Initially, images were cut to exclude the unimportant sections thread's area in `ImageJ`, which were evaluated in `Matlab(PIVlab)` and plotted in `Tecplot`, where flow vectors determined from the displacement of the latex beads.

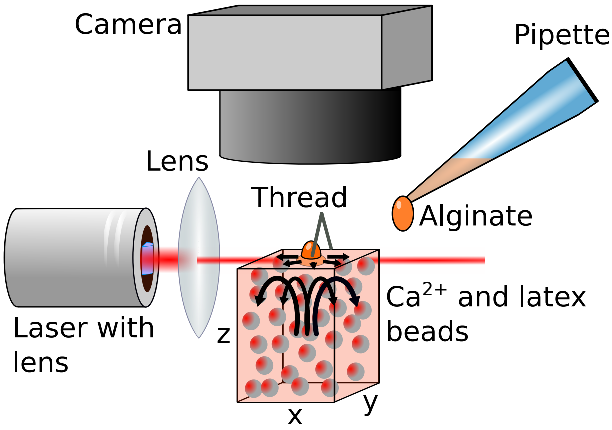

Figure S2: PIV experimental setup. The red laser beam marks the horizontally propagating light plane.

From above the container, we observed receding flow from the surfer (Fig. S3), which is induced by water expulsion. Accordingly to this, the same receding flow appears in the uppermost layers of the liquid from the side view (Fig. S4). However, we see flow heading towards the droplet underneath. These two flow together generates complex fluid motion in both sides in the calcium chloride solution.

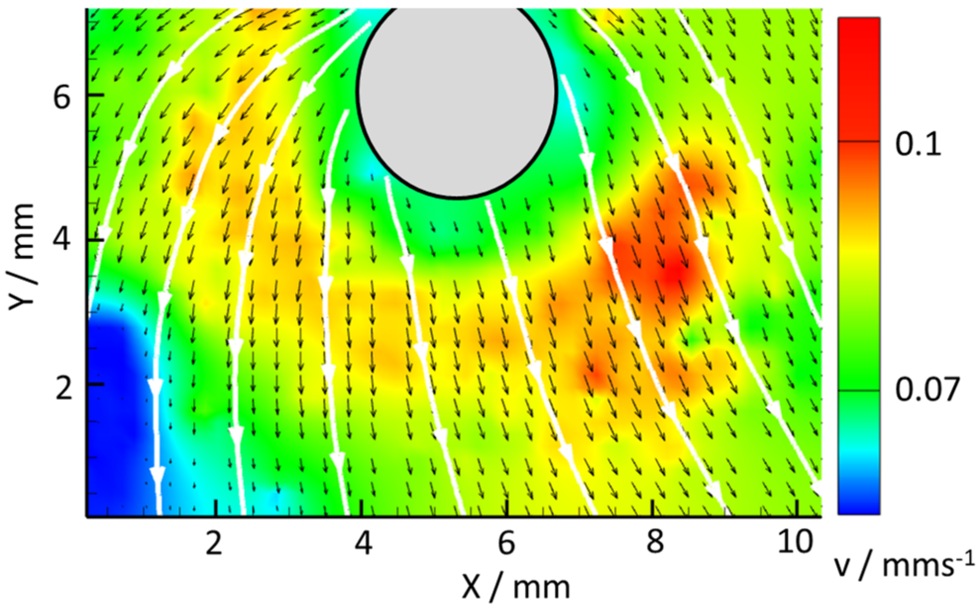

Figure S3: PIV image made from above the surfer in the *xy*-plane, capturing the flow in the uppermost layer of the calcium chloride solution. The gray circle covers the area of the surfer. The white arrows illustrate the direction of the flow in the calcium chloride solution. Small black arrows show the displacement of the latex beads. Colors illustrate the velocity of the latex beads.

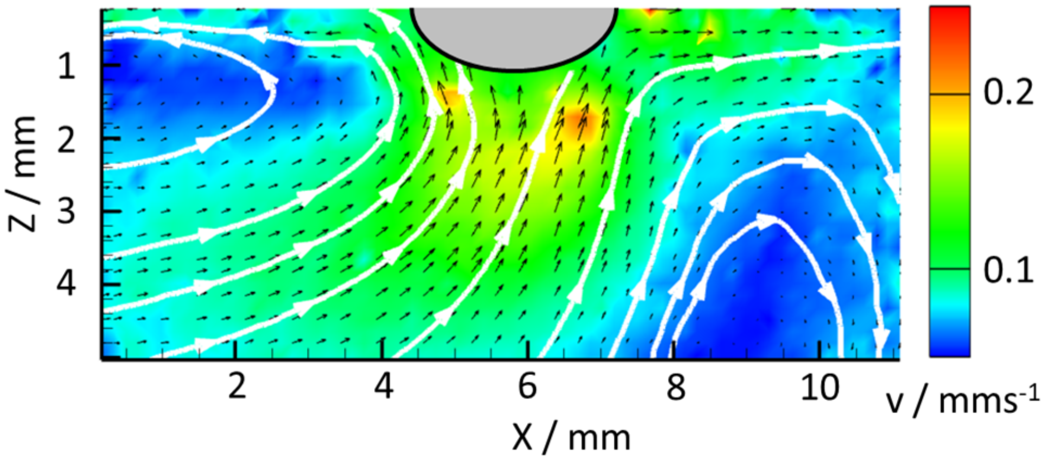

Figure S4: PIV image captured form the side in the *xz*-plane. The gray circle covers the area of the surfer. The white arrows illustrate the direction of the flow in the calcium chloride solution. Small black arrows show the displacement of the latex beads. Colors illustrate the velocity of the latex surfers.

4 Trajectories and their characterization

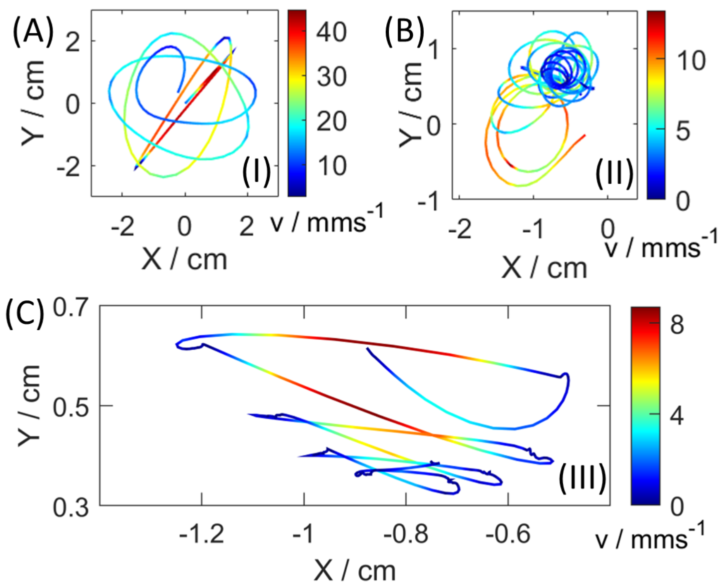

Figure S5: Trajectory in the *xy*-plane of (A) translational, (B) rotational and (C) stop-and-run motion at 6 M $CaCl_2$ and 0.5% v/V sodium alginate, corresponding to Fig. 4. Colors show the instantaneous speed of the surfer.

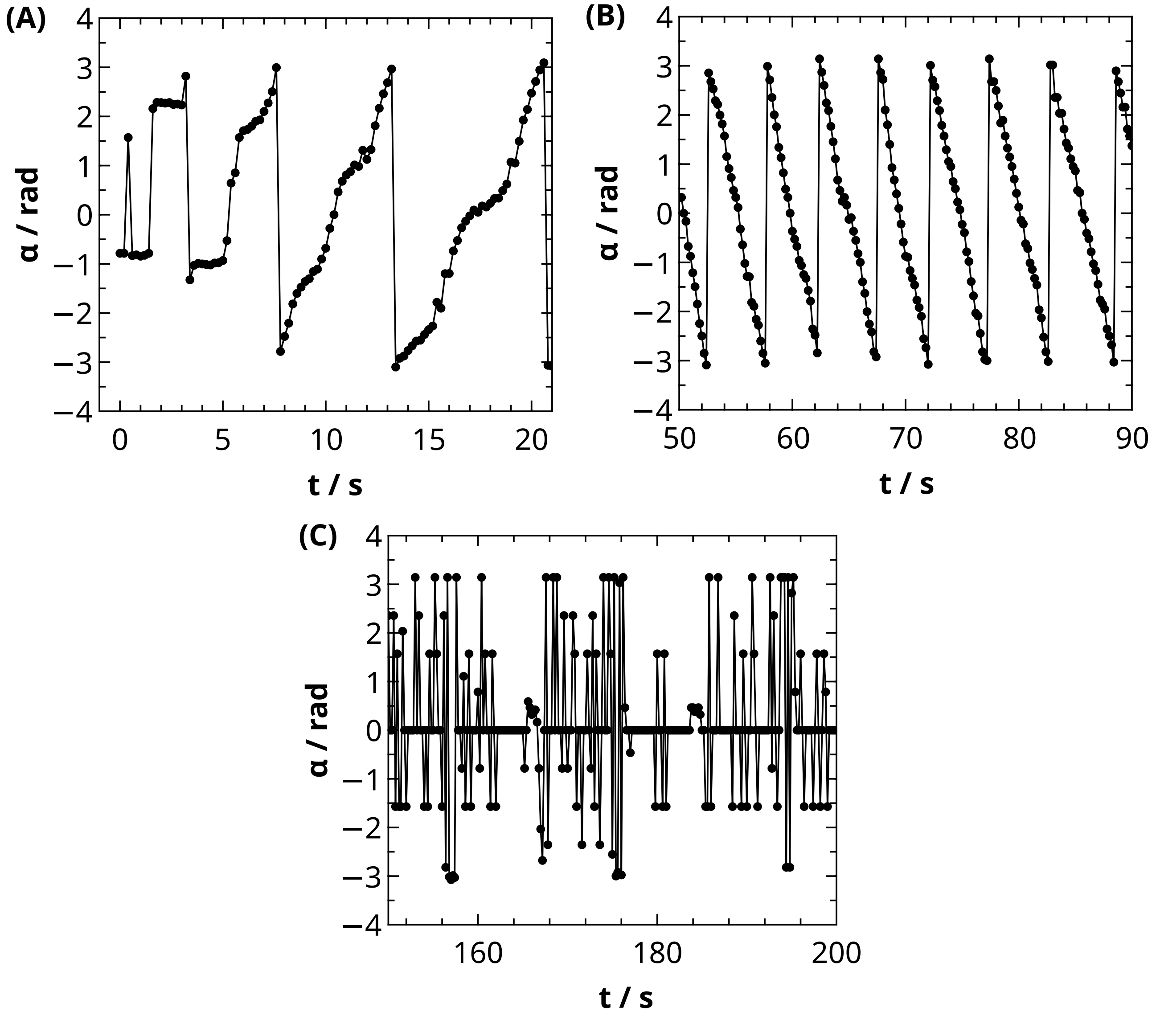

Figure S6: Characterization of the motion: (A) translational, (B) rotational and (C) stop-and-run motion at 6 M $CaCl_2$ and 0.5% v/V sodium alginate, corresponding to Fig. 4.

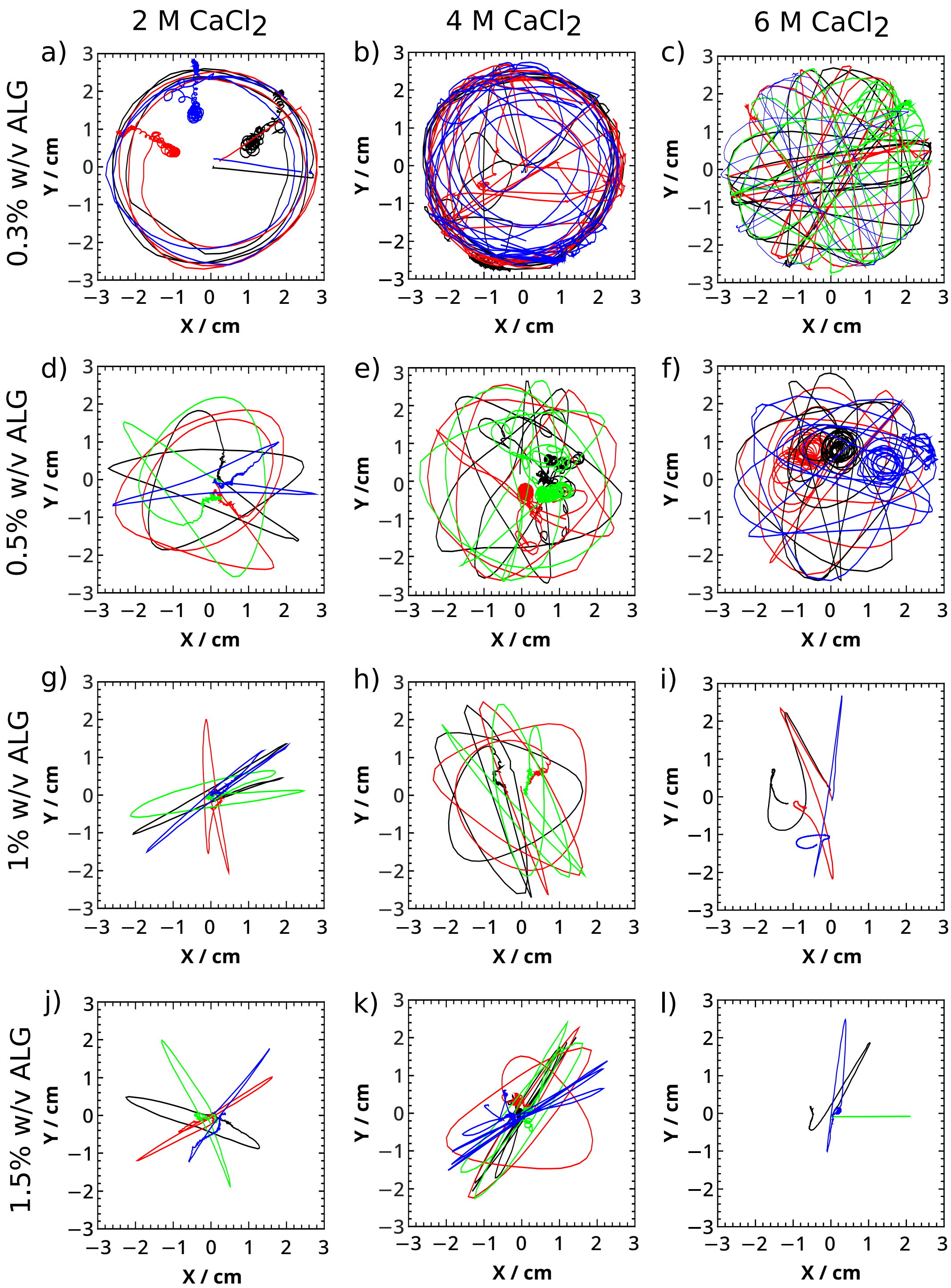

Figure S7: Trajectories in the *xy*-plane at various conditions. Different experiments are illustrated with different colors.

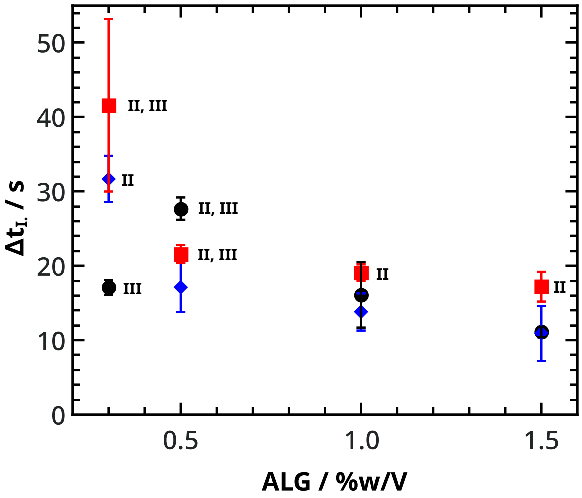

Figure S8: Duration of period I at different calcium chloride (♦: 2 M $CaCl_2$, ■: 4 M $CaCl_2$, •: 6 M $CaCl_2$) and sodium alginate concentrations.

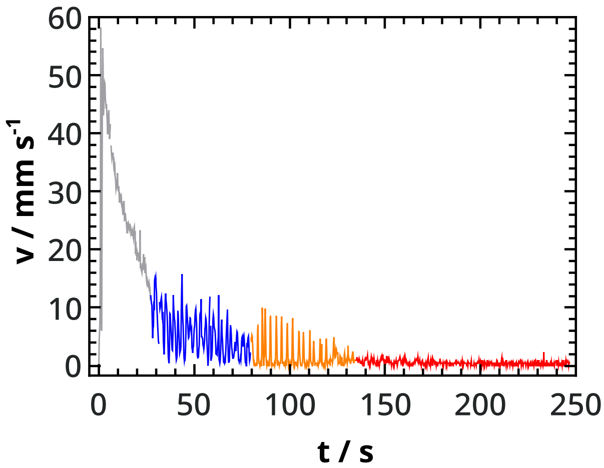

Figure S9: Speed profile at 4 M $CaCl_2$ and 0.3% w/V ALG. The figure shows another example when all four periods are present in the surfer's motion.

5 Supporting video information

Movie S1: Motion of the calcium alginate surfer with 6 M $CaCl_2$ and 0.5% w/V sodium alginate shown at 10X the actual speed.

Movie S2: PIV made from above the surfer in the *xy*-plane corresponding to Fig. S3 with conditions of 4 M $CaCl_2$ and 1.0% w/V sodium alginate shown at 1.6X the actual speed.

Movie S3: PIV made from the side of the surfer in the *xz*-plane corresponding to Fig. S4 with conditions of 4 M $CaCl_2$ and 1.0% w/V sodium alginate shown at 1.6X the actual speed.

6 Bibliography

[1]T. Salomonsen,"Chemometric prediction of alginate monomer composition: A comparative spectroscopic study using IR, Raman, NIR and NMR," Carbohydr. Polym. **72**, 730–739 (2008).