Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Controlled generation of spiky microparticles by ionic cross-linking within an aqueous two-phase system

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Time-series Images of a DEX-alginate droplet surrounded by continuous phase PEG free alginate, inside a polymerization bath of PEG-$CaCl_2$

Figure S1 demonstrates time-series images of a 30 w/v% DEX - 1 w/v% alginate droplet, surrounded by an intermediate 10 w/v% PEG phase free of alginate molecules, in a bath of 10 w/v% PEG - 2 w/v% $CaCl_2$. We do not observe any spike formation across the surface of the DEX-alginate droplet, over a course of 24 hours, which is indicative of the importance of the presence of alginate molecules, in the intermediate PEG phase, for spike formation across the DEX-alginate droplets.

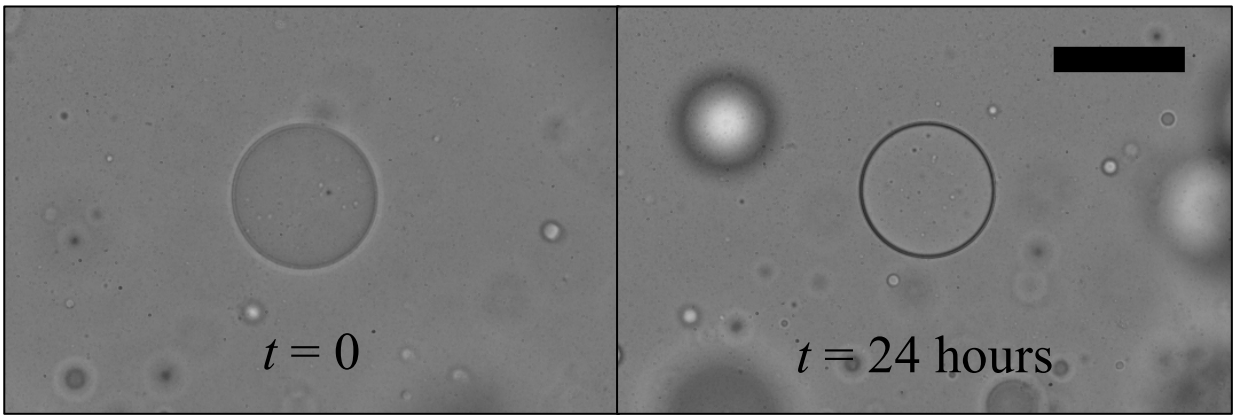

Figure S1. Time-series images of a DEX-alginate droplet, inside the polymerization bath of PEG-$CaCl_2$, surrounded by continuous PEG phase free of alginate molecules. Scale bar indicates 50 μm.

The effect of droplet size on the spike length

Based on our experimental observations, the radius of the curvature of the droplets does not appear to affect the diffusion rate. As seen in Figure S3 below, spikes of similar length are formed on two droplets of different sizes, suggesting that the diffusion rate is similar.

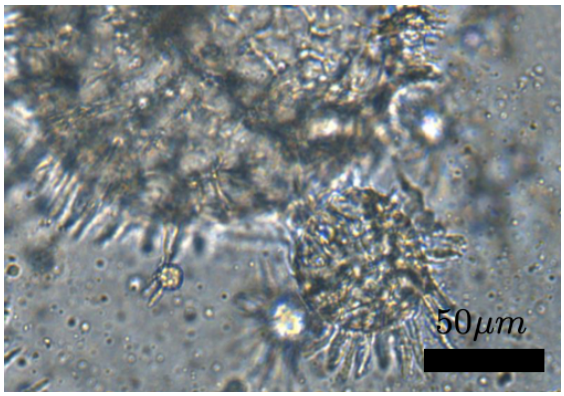

Figure S2. Image of droplets inside a 30 w/v% PEG – 2 w/v% $CaCl_2$. Spikes of the same length grow on the droplets, indicating that the radius of the curvature of the droplets does not affect the diffusion rate and the spike length.

The effect of shear on the spikes as a result of washing the particles

When the spike growth has stopped, and the polymerization has been completed, it is possible to manipulate the particles inside the PEG bath, without the particles losing their stability. We have tried transferring the particles from the PEG bath to a water bath. However, the soft nature of spikes formed on the droplets cannot withstand the shear stress applied as the result of the transfer (shear due to pipetting the solution). Therefore, during the washing process, the spiky microparticles tangle together, and the spike features become distorted, as seen in the example in Figure S2.

For future work, we are planning on tuning the concentration of both the alginate and $CaCl_2$, and explore different types of alginates (such as higher G block alginates) to create spiky microparticles which are more versatile and withstand their shape and integrity during post-processing transfer and washing steps.

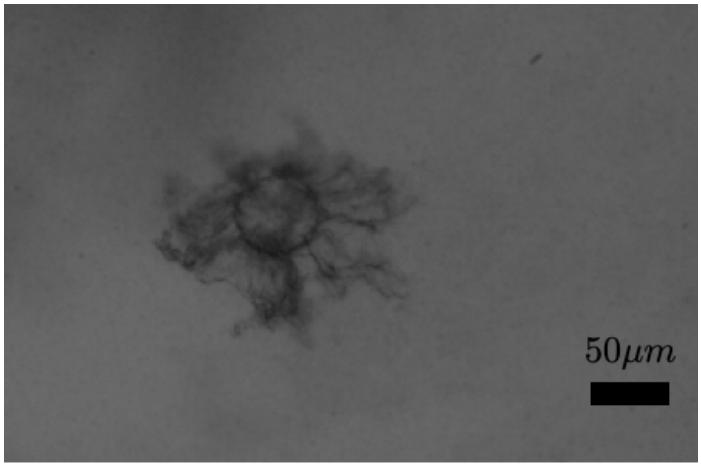

Figure S3. Image of a spiky microparticle after wash and transfer to an aqueous solution. The shear applied as a result of the pipetting results in tangling and distortion of spikes features of the microparticles.

Qualitative discussion on order-of-magnitude estimation of diffusion and electrostatic energy

To better understand the effects of diffusion, and electrostatic transport, we compare the diffusion energy (thermal energy) with the electrostatic energy between positive and negative ions of $CaCl_2$ and alginate, respectively (based on Coulomb's law) at the beginning stages of the experiment (when the droplets have just reached the polymerization bath. We emphasize that the following estimation does not encompass the complexity of the chemical reactions occurring during the spike formation process. However, this estimation allows us to just compare the difference in order of magnitude of energies associated with diffusion, and the electrostatic energy, at the onset of the spike formation.

An order of magnitude approximation reveals that the thermal energy, $kT = O(10^{-21})J$, where k is the Boltzmann's constant, and T is the temperature. The electrostatic energy, $k_e q_+ q_- / l_d =$

$O(10^{-25})J$, where k_e is the Coulomb's constant, q_+ is the charge of the positive ion (in this case Ca ions), q_- is the charge of the negative ions (charged groups of sodium alginate), and l_d is the width of the intermediate PEG phase, which separates the droplets from direct contact with PEG - $CaCl_2$ solution. From this simple order of magnitude estimation, it is evident that the process is diffusion driven. However, it is important to note that the magnitude of the electrostatic energy increases with time as the intermediate PEG phase and the PEG – $CaCl_2$ solution mix, which allows for polymerization of the spiky microparticles.

Supplementary Material Movie Captions

Supplementary Information Movie 1:

Video is a compilation of images taken every 5 minutes, illustrating spike formation across the surface of a 30 w/v% DEX - 1 w/v% alginate droplet, surrounded by an intermediate 10 w/v% PEG phase, inside a polymerization bath of 20 w/v% PEG - 2 w/v% $CaCl_2$. Spike growth terminates at t = 100 minutes.