Active motion of nematic oil emulsions in a nematic aqueous environment

Patrick Soltis[a], Karthik Nayani[b], Rahul Mangal[b], Nicholas Abbott[b]

[a]Georgetown University, Candidate for B.S. in Biological Physics
[b]University of Wisconsin-Madison, Department of Chemical and Biological Engineering

Abstract

In this study, we explored the behavior of an uncommon emulsion wherein both the oil and water phase are liquid crystalline. 4-Cyan-4'-pentylbiphenyl (5CB), which is in a nematic phase at room temperature, is used as the oil phase. This oil phase is dispersed in an aqueous solution of disodium cromoglycate (DSCG) at weight fractions that lead to its formation of nematic phase at room temperature. The aqueous phase also contains the surfactant sodium dodecyl sulfate (SDS) at a concentration above its critical micellar concentration (CMC). The limited but finite solubility of the oil in the micelles leads to the dissolution of the oil from the droplets into micelles. This results in a disruption of the surfactant distribution throughout the surface of the emulsion, generating a Marangoni flow, which propels the droplet. Surprisingly, we observed that the motion of the 5CB droplets occurs significantly more on the axis perpendicular to the DSCG director. Additionally, there was an inverse relationship between strength of the DSCG alignment and the magnitude of the active motion of the 5CB droplets. Both these trends could potentially serve as mechanisms for controlling the motion of oil-in-water emulsions for uses in medicine or environmental remediation.

1. Introduction

Active emulsions

Due to the immiscible nature of oil and water, it is commonly known that any hydrophobic substance (oil) will cluster in distinct pockets when introduced into a hydrophilic substance (aqueous solution). When the concentration of oil is significantly less than that of the aqueous solution and when significant mechanical energy is applied to the oil-water mixture, the oil will cluster in small pockets called emulsions. These emulsions are henceforth referred to as droplets. (When the relative concentrations are reversed, of course, the same will happen with the aqueous solution.)

These oil droplets are distinct particles within the aqueous solution, remaining intact because of the immense energy barrier required to force the uncharged hydrocarbon tails of the oil molecules into the partially charged soup of hydrogen bonds within the aqueous solution. In a system with no overall laminar flow, one would expect these droplets to move with only Brownian motion, resulting from constant buffeting of the smaller

water molecules on all sides. In most systems, this is true. However, recent experiments have shown that, under certain conditions, oil-in-water emulsions can exhibit active motion in an otherwise inactive system.[1,2,3] (Water-in-oil emulsions have also been shown to exhibit such qualities.) Such a system of independently active particles has potential to be developed into a controllable micro-scale system, as well as could shed light on fundamental mechanisms of active motion in simple life forms.[3]

These oil droplets become active when a surfactant is introduced into the mixture. A surfactant, defined as a molecule with both a hydrophobic and a hydrophilic end, prefers to rest at the boundaries between the oil and the aqueous solution.[2] This position is more energetically favorable than floating in the oil or in the aqueous solution, as it allows each end of the surfactant to rest in its preferred environment. (That is, the hydrophobic tail rests in the oil emulsion, while the hydrophilic head rests in the aqueous solution.)

This energetic favorability extends to the oil and water molecules themselves. There exists a surface tension across the membrane of the droplet, resulting from the energy lost to the water molecules on the outside through unrealized hydrogen bonds at the surface of the emulsion.[4] A surfactant resting on this surface, consequently, lowers the local surface tension by becoming a hydrophilic component on the surface of the emulsion, with which hydrogen bonds can form.

In some instances, the surfactants come to rest in the droplet's membrane in a way that they are heavily concentrated in one area of the membrane.[2]

(The cause behind this is not yet clear, though it is supposed that, when Brownian motion kicks the droplet in one direction, the surfactants collect on the area of the surface that hits the aqueous solution head-on.) In such an instance, the surface tension in that area is significantly lower than that across the rest of the droplet's surface. Like any physical system, however, the emulsion will tend towards a state of the lowest possible energy.

The surfactants will diffuse around the surface in order to equalize to a decreased surface tension around the entire area of the oil-water interface.[2] As the surfactants travel through the membrane, they catch and drag liquid molecules from both sides of the membrane along with them. On the outside of the membrane, the movement of the water molecules becomes a flow around the droplet. This flow generated by equilibrating surfactants is known as Marangoni flow, the process of which is illustrated in Figure 1.[2] This flow is relative to the position of the emulsion; relative to the surrounding water, the emulsion is, in fact, being propelled. The surfactants act like miniature oars, pushing against the water in one direction in order to move the droplet in the direction opposite the direction of push. As the emulsion travels in one direction, it encounters and absorbs surfactants in its path, maintaining a relatively high surfactant concentration in what can now be imagined as the front side of the moving emulsion. This maintained high concentration on the front side results in continued diffusion of surfactant around the droplet towards the back, maintaining the "forward" motion of the emulsion.[3] (Surfactants have been noted to separate once again from the emulsion surface after joining, although the exact
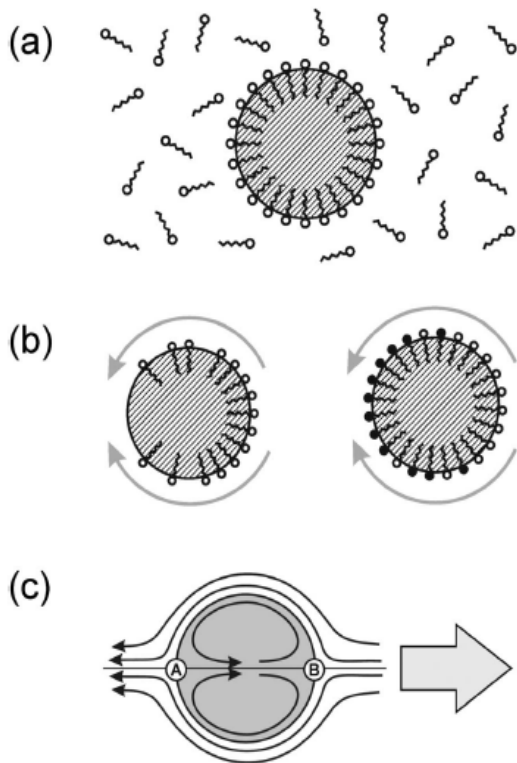
Figure 1.[2] *(a)* Surfactants initially within the aqueous solution also rest at the surface of the oil-in-water emulsion, where it is most energetically favorable for them to rest. *(b)* If surfactants are initially concentrated on one side of the droplet, they will diffuse around the membrane to even out the surface tension. *(c)* Like miniature oars, the surfactants catch and drag water along with them as they move, propelling the emulsion in the direction opposite the direction of diffusion and towards the edge initially oversaturated with surfactants. The flow generated in the aqueous solution (outside the droplet) is known as Marangoni flow.

mechanism and dynamics of separation is not yet understood. The sub-section titled "Geometry of surfactant dynamics" under the "Further Investigation" section discusses some observations which may suggest further investigation on this aspect of the system.)

Using LC oil to visualize internal configuration

The general alignments of liquid crystal (LC) domains are visible under polarizers in a microscope, and the alignment defects are often distinguishable even without polarizers. In particular, defect points, formed where the alignment within the LC droplet cannot be defined or ascertained, are visible not only under polarizers but also often under a non-polarized bright field. The position of the defect point relative to the edges of the droplet provides information on the alignment within the droplet (Figure 2).[2] In general, the director of LC within the droplet can be approximated as an arrow starting in the center of the droplet and pointing towards the defect point (Figure 3).
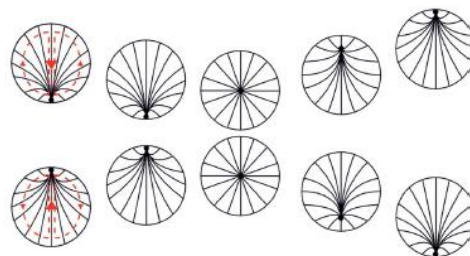

Figure 2.[2] The alignment of liquid crystal within the oil droplets (lines) can be determined by the location of the defect point (black spot) within the droplet. Because alignment directors from all directions meet at the defect point in a homeotropically anchored (radially aligned) droplet, it is easy to imagine the alignment at various points in the droplet by drawing a line perpendicularly through any edge and to the defect point in the fastest possible route.
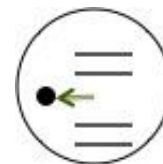

Figure 3. When the defect point is close to a particular edge, the dominating LC director is parallel to an imaginary arrow (green in this image) that would start at the center of the droplet and end at the defect point.

Tangentially, liquid crystal alignments and defects in the emulsions serve as excellent proxies for visualizing the flow within the emulsion. Past experiments have utilized LC oil for this reason; this experiment uses LC oil for the same reason.[2] Given that the mechanism for active oil emulsions in aqueous environment remains to be fully defined, rigorous investigation of the emulsion defects are required to understand the active motion of liquid crystal oil emulsions.

The role of the aqueous fluid outside the emulsions is just as important as the fluid within, however. Suspending the emulsions in an LC aqueous environment allows us to visualize the flow of the outside motion in a similar manner. The observable interactions between the alignments of the aqueous environment and of the oil within the emulsions provide an optimal system to observe specific flow patterns that can, hopefully, be matched to detailed quantitative models of active motion.

Motion control using liquid crystal field

The primary importance of using an aqueous LC solution, while allowing us to visualize flow, is actually to study the LC's effect on direction of motion. Because liquid crystals are anisotropic, certain qualities of a liquid crystal field change depending on the direction from which the property is being observed or experienced. Therefore, it is reasonable to suspect that active motion of a particle suspended in an aqueous LC field (such as a droplet of oil) would vary depending on the direction it travels relative to the director of the LC field. (Recall that the director is the average direction of an LC field's alignment.)

A primary goal of this investigation is to determine whether anisotropy of an LC aqueous solution can be used to control the motion of an oil droplet suspended within. Prior to the investigation, we suspected that a droplet would move further along the axis parallel to the director compared to the axis perpendicular to the director, because the aligned LC molecules would form a "track" for the emulsions to follow.

Any correlation between the LC alignment and preferred axis of motion, however, could have implications for nanotechnology. Given that the droplets are small objects mere microns in diameter, they exist at a size scale appropriate for targeted chemical delivery in biological and environmental systems. The ability to confine motion to a specific axis could prove useful in designing and implementing methods of targeted chemical delivery, directing the motion of the micro-sized particles to the intended targets.[5]

Characterizing physically induced component of active motion

Studying active emulsions is the primary step in understanding the fundamental properties of active nanoparticles, which promise to have wide-ranging applications from medicine to environmental remediation. Aside from the prospect of direct applications, there is another more abstract motivation stemming from this fact. While bacteria and plankton are plentiful, natural examples of active nanoparticles, their active motion results from a mixture of both extremely complex biological and simpler (but still complex) physical processes. This makes active motion due to physical processes difficult to distinguish, making it difficult to build basic theories of active motion based on studies of these living organisms. These theories, after all, must be applicable to the design and deployment of synthetic nanoparticles not

endowed with the complexities of a biological system. Active emulsions are among the simplest of systems that exhibit active motion, making them primary candidates from which the most basic principles of active motion can be derived.[3]

2. Evolution of Hypotheses

Initial

Originally, the goal of this investigation was to determine the preferred alignment of the LC within the oil droplet with respect to that in the LC aqueous environment. Given that the defect point in the oil droplet tended overwhelmingly to touch the front edge of the droplet as it moved, we could potentially associate the direction of the droplet's motion with the direction of the alignment within the droplet, which could then be compared to the alignment of the aqueous LC environment. Collecting statistics on the directions of kicks relative to the director, we hoped, could provide valuable insight into the alignment of the LC in the droplets at the critical moments of motion.

Complications

Despite the jerky motion of the droplets, it was difficult to count distinct kicks in each direction. Statistics on kick directions could easily be collected by tuning an image analysis tool to distinguish and count kicks according to an algorithm. However, we found it simpler (and potentially providing the same breadth of information) to quantify the overall displacement of the droplets relative to each axis with respect to the director. (A future attempt to quantify this is advised, however.)

Given time constraints, we instead focused on quantifying the overall displacement of the droplets relative to each axis. Finding such a preferred axis of motion would, if it existed, would also be able to shed light on the relationship between the alignment of the oil droplets and the alignment of the aqueous environment, all while being more easily measured with the image processing tools available.

Throughout the early trials with our oil-in-water, LC-in-LC system, we noticed that it was difficult to construct a sample with both strong alignment in the aqueous LC environment and significant motion of the LC oil droplet. Particularly, the strongest and clearest LC alignments in the environment appeared to host little to no motion, while the most significant motion appeared to occur in aqueous environments which maintained little to no significant alignment. Additionally, side experiments showed (1) that the alignment of the aqueous LC environment strengthened over time and (2) that this alignment occurred more slowly where the oil droplets were moving through the system than where there were no oil droplets. Consequently, we decided to investigate whether there truly was a relationship between alignment in the LC environment and magnitude of the oil droplet motion.

Final

Taking into account both our original goals and the complications encountered early on in the experiments, we identified two ultimate objectives for the investigation:

1. Determine preferred axis of motion of droplets relative to the director of the aqueous phase. *We expected that the preferred axis would be along the director.*

2. Demonstrate correlation between motion and aqueous alignment strength. *We expected that there would be an inverse relationship.*
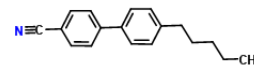
3. Experimental

Materials

The oil used was 4-Cyano-4'pentylbiphenyl, more commonly known as 5CB (Figure 4). 5CB typically exhibits a nematic phase at room temperature.
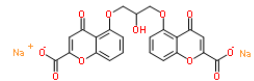
The aqueous liquid crystal solution used was disodium cromoglycate, or DSCG, dissolved in purified, deionized water (Figure 5). The relative amount of DSCG was maintained at 17 weight percent through all the trials.
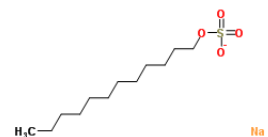
The surfactant used was sodium dodecyl sulfate, commonly known as SDS (Figure 6).

In order to induce the aqueous solution to align, the mixture was placed in a cell lined with a polyimide coating, N-Methyl-2-pyrrolidone, brushed to line up in one direction.

Plain slides made of Swiss Glass by Fisher Scientific were used to create all cells.

Setup

After fine-tuning the relative amounts, the mixture used in all samples observed contained a volume ration of 1:40 5CB to aqueous solution. The aqueous solution contained 17 weight percent DSCG and 80 mM SDS.

Figure 4.₆ Schematic of 5CB

Figure 5.₇ Schematic of DSCG

Figure 6.₈ Schematic of SDS

The 5CB was added to an aqueous solution in which the DSCG was already dissolved. The mixture was then held on a mechanical vortex stirrer for a period of time between 1 minute and 1 minute and 30 seconds in order to break up the 5CB into small enough droplets. The SDS was then added to the mixture. Next, the mixture was sonicated for 1 minute in order to help distribute the SDS more evenly. (The water containing SDS frequently formed tactoids of isotropic aqueous solution, completely separate from the LC aqueous solution containing the SDS, making this further mixing necessary.) Significant time was spent altering this sample preparation process in order to achieve a mixture that rendered more consistent results.

The mixture was then pipetted into a glass cell 100 microns thick and viewed with transmitted light under a microscope. Cells both with and without the polymer coating mentioned in the previous section were used. (This is because cells with strong alignment and cells with no alignment were both needed for observation.) Objective lenses of magnifications 10x, 20x, and 50x were all used, though the results discussed in this report were achieved using the 20x objective.

The coated cells were created by spin-coating the polyimide on plain glass slides, which were then baked at 250° C for over 1 hour. The polyimide was diluted using an appropriate thinner at a ratio of 1:9 polymer to thinner. After baking and cooling, the slides were rubbed with a velvet cloth 8 to 12 times in a single direction with a velvet cloth. (The number of rubs varied between batches of coated glass, but not across any single batch.)

For coated cells, both the top and bottom were coated.

Observations

Under the microscope, two types of observations were taken. The first was videos, made of moving droplets in order to analyze their motion. The videos were taken at 4 frames per second and under a bright field.

The second was pictures, taken with the sample between crossed polarizers after each video. Each set of pictures included pictures taken after rotating the polarizers (remaining crossed) by intervals of 30°, from 0° to 180°. (Both 0° and 180° settings were oriented such that one polarizer was roughly parallel with the approximate alignment, while the other was, obviously, perpendicular.)
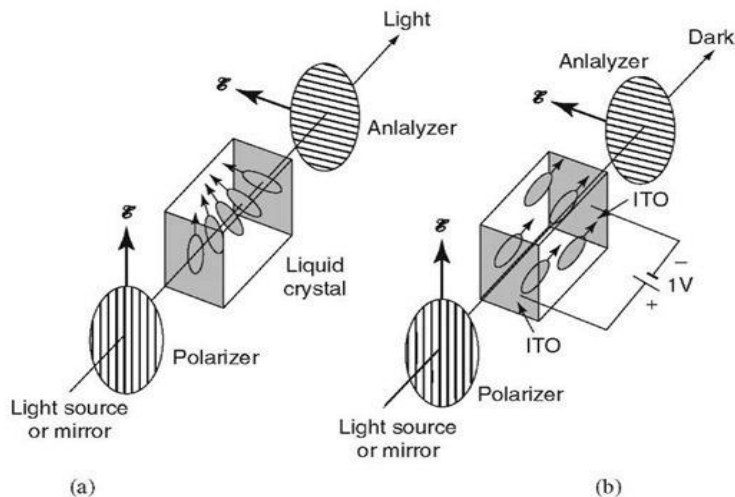

Figure 7.9 Light polarizers are set both above and below the sample. The polarizations are perpendicular to each other. *(a)* The front polarizer blocks light that is polarized perpendicular to its polarization, C. This leaves only light polarized parallel to the front polarizer's C, which is perpendicular to the back polarizer's C. The liquid crystal in the sample box repolarizes the light coming through the front polarizer so that there is once again light polarized perpendicular to the front polarizer C, which is able to pass through the back polarizer. *(b)* Normally, as in the case of an isotropic sample, the light is not repolarized between the polarizers, and so there is no light able to pass through the back polarizer because the front polarizer eliminated all that is capable of passing through.

The pictures under crossed polarizers were taken to roughly quantify the strength of the alignment in the aqueous solution. The sample is between the two polarizers, fixed at a right angle relative to each other, as illustrated in Figure 7. One would normally note expect any image to shine through in a microscope with polarizers crossed, as a basic understanding of electromagnetic waves would suppose that any passing through the first polarizer would be absorbed by the second polarizer, as light emerging from the first polarizer would be perpendicular to the orientation of the second polarizer.

Understandably, any individual liquid crystal molecule will appear dark when aligned parallel to either of the polarizers. If the molecule is not parallel to a polarizer, however, some light will shine through and the area occupied by the molecule will be lighted in the field. (This occurs because, although the light emerging from the first polarizer is perpendicular to the second polarizer, the liquid crystal between the polarizers is able to repolarize the light to once again have a component that is parallel to the second polarizer and thus able to pass through to be viewed in the microscope.[10]) Thus, the darker that the liquid crystal field appears between any particular orientation of the crossed polarizers, the more LC molecules that are parallel to either of the polarizers. The more LC molecules with the specific orientation parallel to either of the polarizers, of course, the stronger the alignment at that angle.

Image Analysis

The trajectories were generated by processing the videos using the plugin Mosaic on ImageJ, which utilizes an algorithm that tracks patterns of changing pixel brightness within a video.[11] The list of trajectory coordinates were then processed by a MatLab script so that the displacement could be quantified.

The motion was quantified separately along each axis in terms of mean squared displacement. Mean squared displacement was used to account for the total motion within the period of observation, as average displacement alone can sum to zero even when the motion along the given axis is significant. Mean squared displacement (MSD) can be defined as:

$$MSD \equiv \langle [r_i(\Delta t)]^2 \rangle = \frac{\sum_{i=1}^{t/\Delta t}[r_i(\Delta t)]^2}{t/\Delta t}$$

where r_i is the total displacement of an object over an interval of time with length Δt, and t is the total length of time in which the displacement of an object is being considered.

Motion of an object can be determined as active or Brownian by plotting MSD as a function of Δt (Figure 8). With Brownian motion, such a plot exhibits a linear trend line because the amount of motion scales at a one-to-one ratio with increasing time interval sizes. With active motion, such a plot exhibits a quadratic trend line at low values before decaying to a linear trend line at high values.
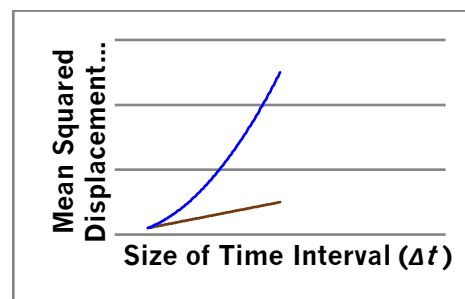

Figure 8. When plotted as a function of increasing time interval size, mean squared displacement makes (blue) a quadratic curve if the motion being considered is active and (brown) linear if it is Brownian.

The polarized photographs were compared using the average brightness of the pixels across all pixels and pixel colors in any given photograph. The average brightness was then charted at each 30° interval from 0° to 180° as a decimal fraction of the maximum pixel brightness, 255, and compared to the average brightnesses from 0° to 180° of other photographed regions in the same sample. As each set of photographs imaged the region through which an oil droplet was moving in an analyzed video, the trends in brightness of the given region could provide information on the strength of the alignment in the region through which the was moving.

For this investigation, both MSD and alignment strength were measured in atypical units: the MSD in pixels squared and the alignment strength in pixel brightness. Although these units processed on the computer must be converted to other units in order to be useful to physical applications of this system, they are sufficient to achieve the goals of this investigation. This is because each set of data (both the MSD along a particular axis and the brightness of one set of pictures) must only be compared relative to another set of data of the same units in order to generate meaningful results.

## 4. Results and Discussion

1. Preferred axis of motion

Based on the limited number of quality observations made during this investigation, there appears to be a preference for oil droplets to move along the axis that is *perpendicular* to the director. The motion on the parallel axis is significant, but the values of MSD along the parallel axis tends to exist as fractions of those values. The preference for the perpendicular axis was by no means universal, though the perpendicular axis did appear to, statistically, be the more popular axis. Figure 9 depicts the MSD graphs of three droplets from the same sample over the same period of time. As is apparent in Figure 9b, the parallel axis was, in fact, the preference of some droplets, though it was in general the less popular preference, as represented by the majority preference for the perpendicular axis as shown in Figures 9a and 9c.

This less than decisive victory for the perpendicular axis leads to significant uncertainty about the result. As can be seen in Figure 9b, all droplets do not follow this pattern. The relatively small number of successful, quality-controlled observations considered in the results provides a reasonable basis for uncertainty; a larger sample size would certainly be preferred in order to absolutely confirm or deny this trend.
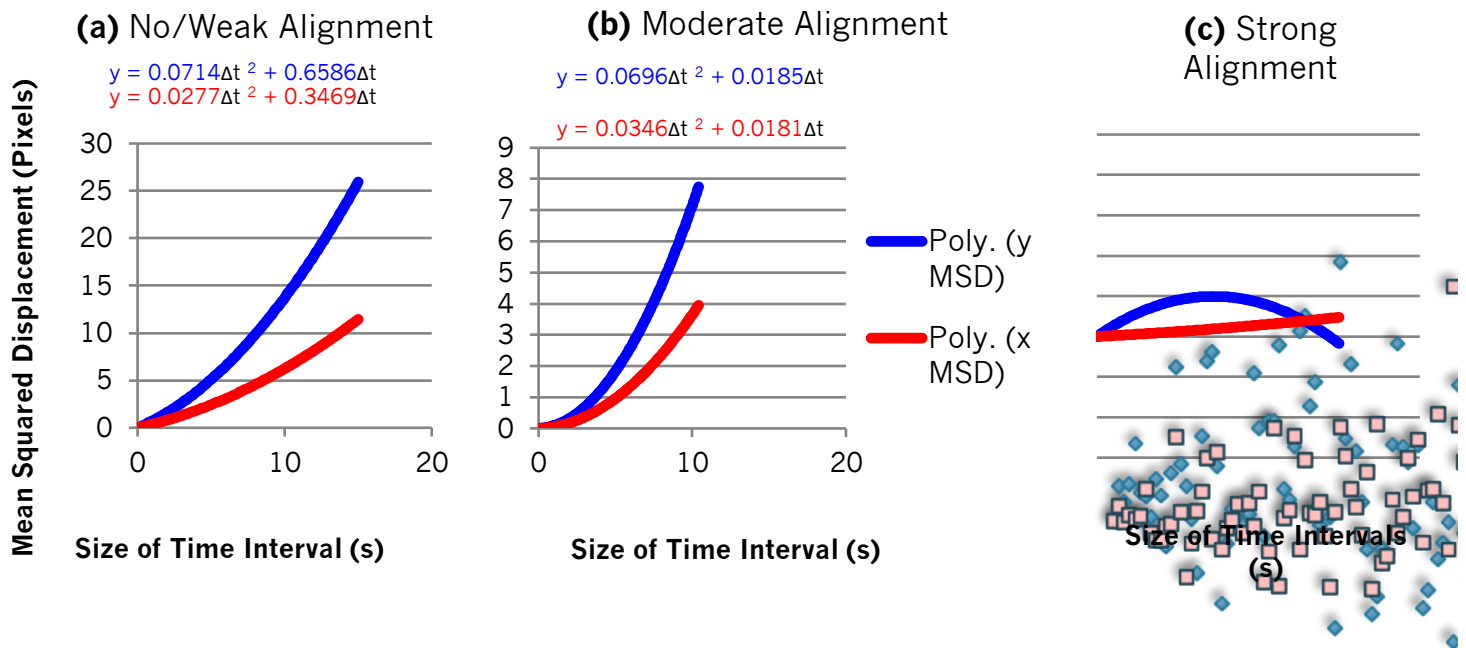
Size of an oil droplet may be a significant factor in its trends of motion. The droplets shown in Figure 9 are each of significantly different sizes, and this difference may affect the directions that they are most easily able to move. Qualitatively, it appeared during some of the observations that many of the small droplets appeared to prefer the parallel axis to the perpendicular axis. (The rough percentage of small droplets that had this preference cannot be estimated, however, since many small droplets also appeared to prefer the perpendicular axis. No rigorous counting of very small droplets was undertaken.) It is possible that, if a droplet is below a certain size in relation to the molecular spacing of the liquid crystals in the aqueous environment, it will move more easily in the parallel direction because the space between the aligned molecules is large enough to form a path that the droplet can force its way through.

Figure 9. Mean Squared Displacement by Axis
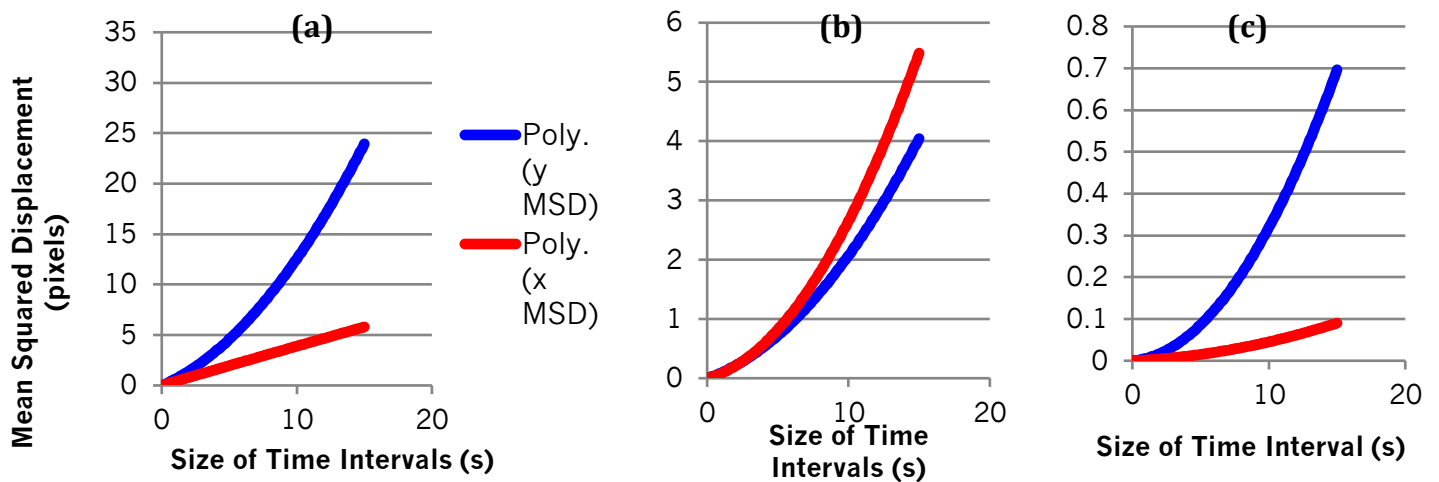
These graphs each depict the mean squared displacement, split by axis, of an individual 5CB droplet. The three droplets here are all from the same sample and all the graphs describe trajectories that were recorded through the same interval of time. The nematic director of the aqueous solution was along the x-axis. (The MSD graph of motion along the x-axis is colored in blue.) Among these three droplets, motion along the y-axis was preferred (graph colored in blue), although this was not universally true, as demonstrated by *b.* This trend held in general across all samples. Notice that the distance scale varies greatly between each graph.

Figure 10. Correlation between Amount of Motion and Alignment Strength

These graphs ch depict the calculated mean squared displacement (MSD), split by axis, of an individual 5CB droplet. The three droplets whose MSD graphs are represented come from the same sample, although at different times and in regions with different intensities of alignments. Note the difference between magnitude of the scales on the y-axis of charts *a* and *b*. *(a)* In the region showing the weakest alignment, the MSD is largest. *(b)* In the region showing moderately strong alignment, the MSD graphs increase much more slowly but the increase is still definite. *(c)* In the region showing the strongest alignment, there was so little motion that the algorithm broke down while trying to calculate the MSD. This is apparent in the blue curve, which exhibits negative values, while all MSD values are positive by definition. The data points have been included (color matched to the corresponding trend lines) to show that there is realistically no correlation between MSD and Δt. The y-axis values have been deleted since they are too small to be relevant. *(a-b)* The equation for the curves are listed above the appropriate chart area, each in a color (blue or red) matching the curve that it describes. (In *a* and *b*, additionally, the motion perpendicular to the nematic director, charted in blue, comfortably exceeds the motion parallel to the nematic director, charted in red. This supports the data in Figure 9.)

In light of this, it is possible that a human experimenter might be slightly biased towards choosing to analyze droplets that exhibit perpendicular motion. A human eye is more naturally inclined to focus on droplets that are more easily visible (i.e. larger) in any image and that move more noticeably throughout a video recording. If larger droplets do tend significantly more towards perpendicular motion than the overall sample of droplets, then a human eye may be more inclined to notice perpendicular motion. It is possible, additionally or instead, that some other bias exists. Ideally, the motion of every droplet in every sample would be analyzed. However, many of the droplets, especially smaller ones, appear to blurry in the recording for the image processing algorithm to pick out a trajectory. In general, since every sample is in fact a three-dimensional system, there is no way to keep every droplet is in focus during every recording. (In addition, the large amounts of time necessary to perform such a thorough investigation suggests that this approach may be impractical.) Instead, future investigations would need to take steps to ensure that a wide range of droplet sizes is represented. In order to account for this, future observations might need to take observations across a greater variety of magnifications, in order that droplets of different sizes may be viewed with the same clarity.

This preference for perpendicular motion is consistent with previous investigations of active emulsions and aqueous liquid crystal environments. In this investigation, the defect point of a moving droplet typically rested near or touched the front edge of the droplet, or the edge that collided with the oncoming molecules of aqueous solution head-on. This matches observations in a previous investigation.[3] First, such a defect position demonstrates that the general alignment of the LC within the droplet tends to be approximately parallel with the direction of motion. Second, an investigation of the LC anchoring across the oil-water interface of LC-in-LC emulsions shows that a 5CB droplet finds it energetically favorable to align its domains perpendicular to that of the external DSCG field.[12] It is suggested that this arrangement is a result of anisotropic van der Waals forces between the 5CB molecules and the aqueous DSCG molecules. Given that (a) motion appears to occur parallel to the internal alignment and that (b) the internal alignment appears to energetically prefer being perpendicular to the external alignment, motion perpendicular to the external alignment agrees with these previous observations of this system's characteristics.

Mechanically, the preference for perpendicular motion could be explained in terms of torque on each LC domain in the aqueous solution. An object (such as a droplet) hitting an LC domain perpendicular to its director would cause molecules on the incident edge of the domain to spin, colliding with LC molecules further in the domain, causing those too to spin and disrupt the integrity of the alignment within the former domain (Figure 11a). Of course, as the droplet continues to move into the area occupied by the former domain of alignment, the droplet itself also contributes to the disruption of the domain.

On the other hand, an object hitting an LC domain parallel to its director would press the molecules on the incident edge of the domain without significantly disrupting their alignment (Figure 11b). The force of collision, being along the director, pushes the molecules on the edge inwards along the director. However, as the molecules are

already packed into an LC structure, there is little space to give to the edge molecules that are
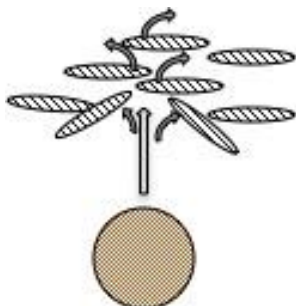

Figure 11a. An oil droplet (tan sphere) collides with a domain of aligned aqueous LC molecules (shaded ellipses), hitting the domain perpendicularly to its alignment. The incident motion (light grey arrow) of the droplet pushes the LC molecules so that they turn out of the way (dark grey arrows), allowing the droplet a low-resistance passage through the LC domain.
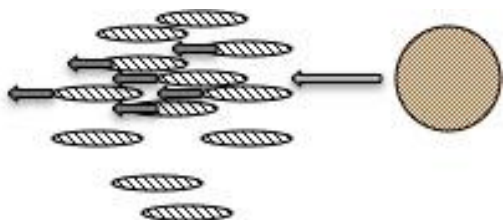

Figure 11b. An oil droplet collides with a domain of aligned aqueous LC molecules, hitting the domain parallel to its alignment. The incident motion pushes the LC molecules so that they slide forwards, but the resistance put up by the molecules behind those hit by the droplet make going through the domain more difficult for the droplet. The molecules cannot spin out of the way as easily since the force applied to them is parallel to their longer axis, resulting in little applied toque on each

suddenly pushed inwards. The push is then transferred largely to the molecules in contact with the edge molecules, then transferred backwards along the entire domain. Unlike the perpendicularly incident droplet, the parallel incident droplet must either push the entire domain backwards or split the domain along its entire length. It is possible that the droplet has enough

force to do so, but the energy required is much greater.

The droplet moving through the LC domain can be compared to the hand of a karate master attempting to chop through a board: the hand (the droplet) can much more easily bust the board (the LC domain) when chopping against its long side, perpendicular to the grain of the wood, than chopping along the full length of the board from the end. This analogy is also well-suited to the investigated system since the LC domains appeared to be longer along the director than across it, the relative proportions matching those of the LC molecules themselves.

As was found in the second part of the investigation, the oil droplets could move much more easily through regions of disrupted alignment. Therefore, a droplet is able to move more easily in the direction in which it can more easily disrupt alignment. This torque-based model, however, has abstracted an incredibly nuanced system into a rather simple one, and so requires rigorous investigation, perhaps by simulation, in order to verify or reject its veracity.

**2. Correlation between amount of motion and alignment strength**

There appears to also be an inverse correlation between the ability of a 5CB droplet to move and the strength of the local DSCG alignment near the considered 5CB droplet. Although the quantitative data supporting this conclusion does not yet include an appropriate sample size, the vast amount of qualitative observations of this correlation leave us relatively certain that this correlation does, in fact, exist. Figure 10 shows the MSD graphs of three 5CB droplets in the same sample over the same period of times, but in

Figure 12. These are pictures of different regions of the same sample under crossed polarizers. The same intensity of light was kept for all pictures shown. The column headings indicate the angle at which the polarizer under the sample was set. The polarizer above the sample was consistently kept perpendicular to the polarizer below. In the first row, the alignment of the DSCG is weak if not nonexistent. The brightness is practically consistent through all orientations of the polarizers, meaning that there is about an equal amount of molecules oriented parallel to either of the polarizers across every orientation between which pictures were taken. In the second row, the image is significantly darker at 0°, 90°, and 180°. This indicates that a much greater number of DSCG molecules are oriented parallel to one of the polarizers at these settings than at the other settings (i.e. 30°, 60°, 120°, and 150°). Additionally, one can see distinct blurs of color in all images in the second row, indicating long domains of DSCG that have the same alignment.

	0°	30°	60°	90°	120°	150°	180°
Weak/No Alignment							
Strong Alignment							

Figure 13. This chart shows the average pixel brightness of every picture across the polarizer settings from 0° to 180°, at 30° intervals. Each line shows the brightness trend across the varied settings for a different region. The pictures analyzed in this chart are pictures of the same regions through which the droplets in Figure 10 moved. Even though the data points are connected, the spaces between the polarizer angle settings at 30° intervals do *not* represent average brightnesses at angle settings between those at 30° intervals. No pictures were taken at these settings.

Brightness of Analyzed Regions under Polarizers
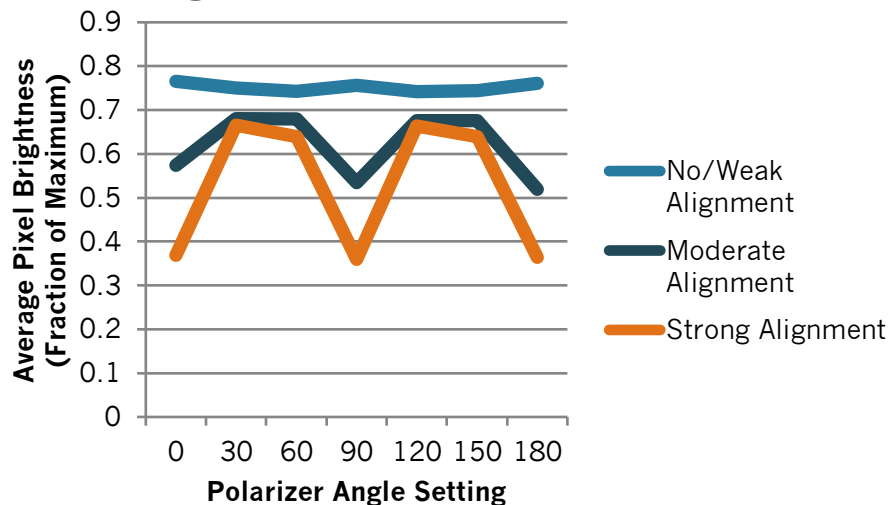
different levels of surrounding DSCG alignment strength. As described in the experimental methods section, the relative alignment strengths of each region were determined by comparing the levels of brightness in each region through 180° of crossed polarizer orientations around the sample (Figure 12). Figure 13 shows a graph of the brightness at

30° intervals for each of the droplets featured in Figures 10 and 12.

This relationship could be explained qualitatively in terms of the LC molecule density. Where the DSCG is strongly aligned, we can hypothesize that the molecules are more densely packed than in a region where it is weakly or not aligned. LC molecules allow little space between them when perfectly aligned. In contrast, LC molecules would tend to be more spaced out when not aligned. It is improbable to think that LC molecules could be strongly aligned without being close to each other, as the physical influence of other LC molecules has a major role in forcing any given LC molecule to align with the rest of the field. If the molecules were aligned but equivalently spaced to the unaligned molecules, there would be no energetic restriction keeping the aligned molecules from spinning to become unaligned. Any object moving through a field of smaller particles would require less energy to travel in regions where the particles are more widely spaced, as the moving object must expend less energy to push the smaller objects out of its path. Given that a weakly aligned region would be less dense by this theoretical model, a particle moving through a less dense LC region would obviously be able to move more, and vice versa.

We have described a system in which alignment strength within an LC region influences the extent to which an active particle is able to move through this region. The direction of influence could, in fact, exist both ways. As mentioned previously, DSCG alignment appeared to be delayed by the presence of active oil droplets. Qualitative observations indicated that, as droplets move through aligned areas, they disrupt the alignment of the area and leave a trail of unaligned LC in their wake (Figure 14). This effect could be explained as a result of swim pressure. Swim

Figure 14. A 5CB droplet has moved across the region pictured, leaving a wide path of DSCG that is much less strongly aligned than the rest of the visible field. The path goes between the 5CB droplet near the bottom left corner of the picture and the largest 5CB droplet visible along the top edge. It is unclear which of the two 5CB droplets made the path, though such a feature is known to be created by a 5CB droplet moving through an aligned region.

pressure is a component of pressure in a fluid or gaseous field resulting from the aggregate force of active particles colliding with the material that contains them, distinct from the traditionally understood pressure that results from collisions due to thermal energy.[13,14] Some systems containing active particles have the tendency to clump into pockets of dense and dilute phases. Swim pressure of active particles can be a thermodynamic tool for understanding this tendency.[13] In this system, the 5CB droplets generate a swim pressure that shakes and sometimes disrupts the crystalline DSCG structure that attempts to contain them.

5. Further Investigation

Uncertainties

As described in the results section above, a number of uncertainties exist surrounding the meaning of what was observed during this investigation. Sample preparation and observation should be done more carefully to investigate whether a droplet's preferred axis of motion depends on its size. A method for controlling droplet size could be helpful in this respect, as could simply taking the time to measure and confirm the radius of the droplets whose motions are analyzed. Additionally, the sample size in general must be increased in order to verify whether or not these trends are universal. Both of the previous uncertainties could be addressed by improving the experimental setup in order that the maximum percentage of 5CB droplets in every sample could be visible to the image processing software for analysis. This could be done by altering the depth of the glass cells or controlling for droplet size in each sample. A method to quantify the position of the defect in each droplet would be useful, as this investigation only qualitatively took its placement into account. Steps to increase homogeneity of the aqueous solution and decrease backflow would also be useful to further generalize the results.

Quantifying energy

As discussed, the 5CB droplets have different behaviors along different axes relative to the director. They appear to move in short bursts, or kicks, and appear to disrupt the DSCG alignment in any region through which they move. In between bursts of motion, the defect structure within the droplets continue to fluctuate, unless the droplets are no longer in motion.

The fluctuation of the defect structure between bursts suggest that a droplet may have potential for active motion at these points. After all, there is activity in the droplet, suggesting energy is being used, just not for translational motion. When the droplet moves with a burst of energy and disrupts the LC alignment through whichever regions it moves, we can imagine that the droplet has suddenly generated enough energy to overcome the barrier presented by the crystalline structure in its path.

Understanding the approximate value of these energy barriers is important for further characterizing the anisotropic motion of the droplets in this LC environment. Given that there is a preference for motion along the axis perpendicular to the nematic director, we would learn much by quantifying the relative height of the energy barrier in the perpendicular direction with respect to that in the parallel direction. An attempt to quantify the energy contained in the Marangoni flow might be interesting. All of this could give insight into the strength of the aqueous liquid crystal's structure, as well as into important thresholds for controlling motion for potential applications. For example, one could fine-tune the energy capacity of the droplets, either by temperature or surfactant concentration, to be above the threshold to move perpendicularly but below the threshold to move parallel to the director, creating droplets that would only move along the perpendicular axis.

System path memory

As discussed, we suspect that the relationship between alignment strength and droplet motion is biconditional. We noticed that, as droplets moved through aligned areas, they disrupted the alignment of that area and left a trail of unaligned LC in their wake (Figure 14). We also verified that the 5CB droplets moved more depending on how weak the

alignment DSCG alignment was. The trails of unaligned DSCG that the 5CB droplets leave, then, are paths through which future 5CB droplets would easily move if the droplets were to encounter them. Using this concept, a system with path memory could potentially be created, creating a network of preferred motion paths, which are reinforced as preferred motion paths whenever a particle travels through one of them.

Directing motion

Both of the main results from this investigation could be used to develop systems that manipulate and direct the motion of oil droplets to a desired end. The alignment of small regions within an aqueous LC environment could be fine tuned in order to direct a droplet's motion when the droplet is in that region. The direction of the alignment could be adjusted to determine the droplet's axis of motion, and the strength of alignment could be adjusted to determine the droplet's overall capacity to move.

Geometry of surfactant dynamics

The mechanism for active motion is still not adequately understood. We do not understand by what pathway the SDS leaves the droplet after it has diffused around to the back of the droplet while generating a Marangoni flow. The SDS must leave the droplet because, if it did not, the droplet's surface would quickly become saturated, meaning that no more SDS would attach to the droplet's surface and thus no more SDS would diffuse around the side of the droplet to generate the Marangoni flow which is necessary to propel the droplet. There are competing pathways, dubbed molecular and micellular, by which the SDS departure could be explained.[3]

In one of the videos, smaller droplets could be seen fizzling out the sides of a main 5CB droplet into the aqueous solution (Figure 15). This could be seen of other 5CB droplets in a few other videos, as well. Characterizing the direction, fizzle rate, and identity of the smaller droplets could shine some light into the surfactant dynamics.

In the best example, the smaller droplets were seen fizzling out the back of the droplet in two separate streams at an obtuse angle from each other but beginning at roughly the same place near the back of the 5CB droplet. Generalizing such a pattern of fizzle jet directions could help determine the exact mechanism of the droplet motion more effectively.

Influence of backflow

The droplet pictured in Figure 15 also appeared to move almost directly against the direction of an

Figure 15. This 5CB droplet is in the process of resisting a laminar flow attempting to drag it along. The flow comes from the bottom left corner, tugging the droplet towards the top right corner. The droplet swims against the current, swimming fast enough for a few moment to hold itself in the same position instead of being washed back with the flow. Above and to the right of the droplet, the faint outline of a string of smaller droplets is visible. These smaller droplets are fizzing out of the droplet both upwards and to the right. It is supposed that these droplets are SDS micelles.

unintended bulk laminar flow in the sample. Many other droplets, when a flow was present, could also have seemed to prefer motion against a backflow. If this tendency to "swim upstream" actually exists, induced laminar flows could serve as a mechanism to control the exact direction of a droplet. This relationship is theoretically feasible, as well. The oncoming flow could deliver surfactant to the front of the droplet, creating a high concentration there, necessitating diffusion towards the back of the droplet, generating a propulsive Marangoni flow which can overcome the resistance of the laminar flow. Additionally, the flow could help whip away surfactants collecting at the sides or back of the droplet, further necessitating the backward diffusion. The steady stream of smaller droplets fizzling out the back also brings to mind an image of jet propulsion, raising the question whether the departure of surfactants from the droplet is a negligible effect on the droplet's overall motion.

Liquid crystal knapsacks

One of the most fascinating things to watch in this experimental system was the product of a sub-environment that originally was not supposed to exist. The SDS absorbed in water often did not mix well into the DSCG absorbed in water. Typically, the SDS water formed isotropic pockets of various sizes within the main LC aqueous environment containing DSCG. These tactoids of SDS were seen as nuisances for most of the investiagion, as they had a habit of luring 5CB droplets into them and not letting them leave. (5CB droplets usually swam in circles around the edge of such an SDS tactoid once they were inside.) Since the interior of the SDS tactoids were isotropic, the motion of the droplets within them was not valid for our LC-in-LC investigation.

However, in many of the larger SDS tactoids, an interesting structure formed. Droplets of 5CB appeared to pick up small pockets of DSCG water and drag it behind them through the SDS tactoid (Figure 16). These pockets could not be verified as DSCG water, but had the same rainbow-like pattern as the external DSCG water. The supposed pockets of DSCG water appeared completely distinct from the SDS water, forming emulsions in their own right. These pockets of DSCG water were always towed directly behind the 5CB droplet as it moved, hence why they are dubbed as "knapsacks". Even when the 5CB droplet turned while moving, the DSCG knapsack rotated to the end directly opposite the end facing the direction of motion. The 5CB droplets in the SDS tactoids preferred to be skirt around the edge of the tactoid, always in contact with the wall of DSCG water outside the tactoid, but also spent a significant amount of time swimming through the center of the isotropic pocket.

This droplet-and-knapsack structure could be a particularly useful mechanism for transporting

Figure 16. 5CB droplets tug along droplets of what appear to be an aqueous solution containing DSCG. The 5CB droplets are the two large brownish spheres and the DSCG droplets are the rainbow-tinted spheres overlapping with them. The light brown medium in which the 5CB droplets swim is an isotropic aqueous solution, believed to contain SDS. The DSCG droplets, dubbed as "knapsacks" hang behind in the direct opposite direction that the 5CB droplets move, readjusting when the 5CB droplets turn.
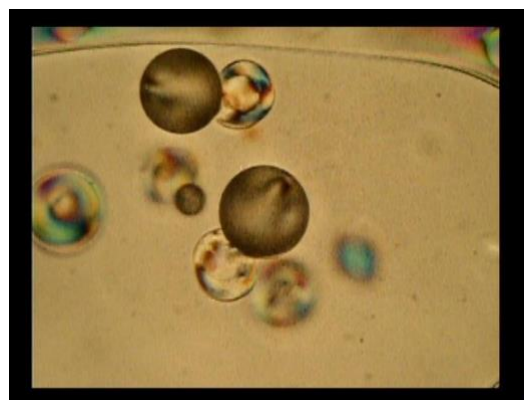
chemicals to a target destination. While the direction of the 5CB head could potentially be controlled, the aqueous solution in the knapsack could contain the water-soluble compound that needs to be transported. Studying this structure in more detail could also render information on the anchoring of the 5CB to aqueous DSCG, as well as information on the dynamics of the sufactants.

Magnetic controls

The investigation by Mushenheim and Abbott indicates that the 5CB droplets energetically prefer alignment perpendicular to the DSCG director. The study also indicates that applying a magnetic field could reorient the 5CB alignment to rest in parallel to the director as long as the field remained present.[12] Since direction of motion for the 5CB droplet seems to depend at least in part on the orientation of its director relative to the DSCG's director, magnetic fields could become an external control for actively controlling the axis of motion.

Assess utility of system for practical applications

While there is much yet to be learned from this particular type of system, any researcher considering further investigation must consider whether the necessary time and money required to undertake the investigation are worth the results. To better inform the value of LC-in-LC emulsion research, the compatibility of this system with potential applications for it must be deemed significant before intense pursuit. Knowledge itself is, of course, a worthy pursuit, but given that resources for such research is often a sacrifice made by society, such research should aim to benefit society in return.

References

1. Peddireddy, Kumar, Thutupalli, Herminghaus, Bahr. "Solubilization of Thermotropic Liquid Crystal Compounds in Aqueous Surfactant Solutions." *Langmuir,* 2012, 28, 12426-31
2. Herminghaus, Maass, Krüger, Thutupalli, Goehring, Bahr. "Interfacial mechanisms in active emulsions." *Soft Matter,* 2014, 10, 7008-22
3. Maass, Krüger, Herminghaus, Bahr. "Swimming Droplets." *Annu. Rev. Condens. Matter Phys.,* 2016, 7, 171-93
4. Nicholas Abbott. Discussion. <date>
5. Lavrentovich. "Active colloids in liquid crystals." *Curr. Opinion in Colloid and Interface Science,* 2016, 21, 97-109.
6. Royal Soc. of Chem. "4-Cyano-4'-pentylbiphenyl." *ChemSpider.* Web. 2015
7. Royal Soc. of Chem. "Cromolyn Sodium." *ChemSpider.* Web. 2015.
8. Royal Soc. of Chem. "Sodium Lauryl Sulfate." *ChemSpider.* Web. 2015.
9. "Applications (Optical Properties of Materials) Part 7." *What-When-How.* Web. Accessed July 2017.
10. Peter J. Collings. *Liquid Crystals: Nature's Delicate Phase of Matter.* Princeton U. Press: Princeton. 2002.
11. Sbalzarini, Koumoutsakos. "Feature point tracking and trajectory analysis for video imaging in cell biology." *Structural Bio.,* 2005, 151, 182-95
12. Mushenheim, Abbott. "Hierarchical organization in liquid crystal-in-liquid crystal emulsions." *Soft Matter,* 2014, 10, 8627-34

13. Takatori, Yan, Brady. "Swim Pressure: Stress Generation in Active Matter." *Phys. Rev. Lett.,* 2014, 113, 028103

14. Marchetti, Fily, Henkes, Patch, Yllanes. "Minimal model of active colloids highlights the role of mechanical interactions in controlling the emergent behavior of active matter." *Current Opinion in Colloid and Interface Sciences,* 2016, 21, 34-43