Arrested coalescence of viscoelastic droplets: Ellipsoid shape effects and restructuring

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Abstract

The stable configurations formed by two viscoelastic, ellipsoid-shaped droplets during their arrested coalescence has been investigated using micromanipulation experiments. Ellipsoidal droplets are produced by millifluidic emulsification of petrolatum into a yield stress fluid that preserves their elongated shape. The liquid meniscus between droplets can transmit stress and instigate movement of the droplets, from their initial relative position, in order to minimize doublet surface energy. The action of the liquid meniscus causes the ellipsoidal droplets to undergo rolling and restructuring events because of their unique ellipsoid shape and associated variation in surface curvature. The final configuration of the droplets is shown to be controlled by the balance between interfacial Laplace pressure and internal elasticity, as well as a constraint force that resists complete minimization of surface energy. Geometric and surface energy calculations are used to map the possible and most likely configurations of the droplet pairs. Experimental deviations from the calculations indicate the magnitude and potential origin of the constraint force resisting full equilibration. Droplet aspect ratio and elasticity are both shown to influence the degree of restructuring and stability of the droplets at energy extrema. Higher aspect ratios drive greater restructuring and
better agreement with final doublet configurations predicted by energy minimization. Lower elasticity droplets undergo secondary deformations at high aspect ratios, further broadening the space of possible morphologies.

Introduction

Emulsions are broadly used in food, pharmaceutical, polymeric, petroleum, biomimetic, bijel, and even explosive materials. Coalescence, when emulsion droplets recombine into a larger fluid volume, is a critical dynamic in commercial products that can be harmful, when product instabilities occur or dispersion quality is lost, or beneficial, when a structure of linked droplets imparts rheology modification and desirable texture to a fluid like, for example, whipped cream.

Arrested coalescence occurs when coalescence begins minimizing droplet surface energy but is halted by a physical resistance like interfacial or internal droplet elasticity. Arrested coalescence is commonly observed in dairy products, where a network of solid milk fat crystals forms inside of oil droplets. The poroelasticity of the droplet allows coalescence to begin because of the liquid phase permeating the solid crystal skeleton, but is then halted when the crystal structure can not be deformed enough for full coalescence. Arrested coalescence is important to the study of food products, as it is a key phenomenon used to build structure, texture, and aesthetic perception of most dairy products, but recent work has shown applications of arrested droplets in other materials as well.

Colloidal materials are often developed under conditions when arrested coalescence is significant, as when partially molten metal particles assemble into clusters or when evaporating films of solvent squeeze suspended particles or droplets. The final structure and performance of such systems is highly dependent on the packing and structure of constituent spherical colloids, and it is important to know the effects of dynamic capillary processes in these systems on the evolution of structure as assembly proceeds. For example, it was shown recently that spherical viscoelastic droplets can significantly reorient as a result of
liquid capillary effects during arrested coalescence, spontaneously driving the droplets into more compact packing arrangements even though initially added at less-optimal positions. However, meniscus effects also play a significant role in shape changes by aggregates of non-spherical solid colloids, enhancing self-assembly, sintering of metal structures, additive manufacturing, and aggregation of non-spherical fat solids.

Droplets are typically spherical because interfacial tension acts to minimize surface energy. In some viscoelastic droplets, however, the internal rheology of the droplets can preserve non-spherical shapes, and is used to enhance deposition onto biological surfaces and food emulsion rheology. There is then also a need to understand arrested coalescence and its shape-change dynamics for non-spherical droplets. We are interested in these dynamics for two reasons. One is to understand how non-spherical droplets assemble in systems whose rheology, texture, and quality are determined by droplet microstructure. A second is to map the motion of non-spherical shapes driven by the competing effects of interfacial liquid meniscus motion and droplet mechanical properties. Dynamic shape change using physical mechanisms, like geometry and interfacial driving forces, will be a critical aspect of future directed and active material assembly efforts at the nanoscale, where Brownian motion is significant, and at the microscale, where thermal motion no longer dominates.

We study here the binary arrested coalescence of monodisperse ellipsoidal droplets with controlled aspect ratios produced in a microfluidic device. Because of the importance of motion to shape-change, and of final state to self-assembly, we examine both aspects here. We first explore the dynamics of an ellipsoidal droplet being pulled around another by a fluid meniscus as a means of understanding possible shape change and self-assembly mechanisms. Many more configurations are possible for arrested pairs of ellipsoidal droplets than for spherical droplets, and we use the results of an energy minimization model to map the full extent of possible behavior while comparing with our experimental findings.
Figure 1: A) Microscopic images within the millifluidic setup used to produce ellipsoidal droplets. An external yield stress fluid is used as a liquid mold to retain the high droplet aspect ratio during flow and heating. Melting after droplet production ensures a uniformly ellipsoidal shape is produced, even with non-uniform starting shapes like the one on the left. B) Images of three different aspect ratio droplets produced by the millifluidic setup. Scale bar is 200 µm.

**Experimental**

**Methods and Materials**

Oil-in-water emulsions were prepared by combination of an oil and aqueous phase during microchannel flow. The system has been characterized in a number of past works and is a reproducible model of more complex systems like milk fat. The aqueous phase was a dispersion of neutralized 0.15% w/w Carbopol 846. The oil phase was a mixture of petrolatum containing 50% wax solids (Unilever) and varying levels of hexadecane (99% Sigma Aldrich) to form mixtures containing either 30% or 40% w/w wax solids. The two components were heated to 80 °C until the petrolatum melted and fully mixed with the hexadecane. The mixture then crystallized as a dispersion of solid crystals inside a liquid oil phase.
Millifluidics

Droplets were generated in a two-part co-flow millifluidic device made from a round 1.1 mm ID glass capillary (Vitrocom), with a 90 \( \mu \)m ID tip created using a Model P-97 Micropipette Puller (Sutter Instruments), inserted into a 1.1 mm ID square capillary (Vitrocom). Oil phase was pumped through the inner, round capillary while the continuous phase flows through the outer square tube. Droplets with varying size and aspect ratio were produced by adjusting the dispersed phase flow rate between 0.08-1.2 mL/min while keeping the continuous phase at 0.08 mL/min.

As seen in Figure 1A, droplets with irregular shapes were first produced as a result of the yield stress of the droplet phase \((\sigma_y = 1 - 500 \ \text{Pa})\). Relatively uniform ellipsoidal shapes were then produced by immediately passing the dispersion through a section of the channel held at 40 °C by an external heating source. The internal structure of the droplet partially melts during this step, reducing its yield stress and reshaping the droplet to a uniform ellipsoid with a maximum curvature set by the equality of the droplet and continuous phase yield stress values. The yield stress of the 0.15% w/w aqueous Carbol 846 continuous phase \((\sigma_y = 4.25 \ \text{Pa})\) created a “liquid mold” environment that preserved the deformed droplet shape until it could cool and regain its own yield stress. Image analysis of calibrated experimental micrographs was carried out using ImageJ software to quantify droplet size, aspect ratio, and long axis orientation. Doublets are studied only when they are level in the image plane to avoid errors from out-of-plane movements, consistent with our theoretical descriptions.

Figure 1B shows three examples of different aspect ratio ellipsoids produced using this method. Coalescence studies were carried out by carefully transferring droplets to a volume of aqueous 0.3% w/w microfibrous cellulose yield stress fluid. Micromanipulation was performed on droplets, inside a small liquid sample placed on glass slides, using a 3-axis system (Narishige International) mounted on an inverted microscope (Motic AE31). Droplets were grasped, using suction applied by adjusting the height of a small fluid reservoir connected to
a microcapillary in the sample volume, and then the droplets were pushed together by slow manipulation to initiate coalescence\textsuperscript{10}.

Results and Discussion

Arrested coalescence can occur when the elasticity of an internal solid network in two droplets is sufficient to balance the interfacial Laplace pressure driving the coalescence process\textsuperscript{11}. As a result, the balance can be altered by, for example, increasing the internal solids concentration of the droplets in order to increase the droplet elasticity. When the symmetry of the system is broken, for example when a third droplet is added to an existing arrested pair, restructuring can occur when the meniscus pulls the droplets in a direction that minimizes the assembly’s surface energy\textsuperscript{19}. We consider the potential for such effects on ellipsoidal droplets here by studying the simplistic case of an ellipse rolling around a second one.

Rolling ellipsoid model

If the experimental droplets behave as hard solids when moved around one another, a simple rolling model can be used to study some aspects of droplet motion. It also provides a basis for comparison with experimental results using droplets that can undergo some degree of deformation as a result of their internal elastic network\textsuperscript{11}. The two-dimensional path of the center of an ellipse rolling around another, congruent, ellipse is described in Cartesian coordinates by the curve\textsuperscript{17}.

\[
\left( x^2 + y^2 \right)^2 = 4a^2 x^2 + 4b^2 y^2
\]

where \( a \) and \( b \) are the major and minor axes of each ellipse and the aspect ratio is defined as:

\[
AR \equiv \frac{a}{b}
\]
Equation 1 assumes motion of the ellipses begins with the two shapes aligned end-to-end along their long axes and ignores slip between the two shapes during motion. Visualizations of calculated ellipse paths were produced using code developed by Mahieu. Figure 2A shows several plots of the calculated trajectory, in red, of the center of mass of a blue ellipse, rolling around the perimeter of a second, identical, red ellipse. As the aspect ratio of the ellipses increases, the moving ellipse path transitions from perfectly circular, for \( AR = 1 \), to an increasingly complex path. Regions of the path with sharp changes in curvature are evident when the ellipses are aligned edge-to-edge, increasing in magnitude as the ellipse aspect ratio increases. Figure 2B shows a series of images of two ellipsoidal droplets just after coalescence has initiated. Here the images have been rotated to fix the position of the lower droplet and enhance study of subsequent changes. The liquid film bridging the droplets radially moves out from the point of initial contact, reducing overall surface energy, and in the process pulls the two droplets together. Similar behavior was seen for the case of two spherical droplets undergoing arrested coalescence. However, here the non-spherical droplets also experience a change in relative orientation as the interfacial force pulling them together rolls one droplet along the edge of the other, similar to the action of ellipsoidal gears. A red dot has been placed at the center of mass of the upper ellipsoid, allowing us to track changes in orientation as a result of the meniscus movement. The droplets largely move as rigid bodies and never move in a way that increases surface area, consistent with previous observations of spherical droplets moved by meniscus effects. There is also some noticeable deformation of the droplets as the meniscus pulls them together in the last frame of Figure 2B, where overlap with the other ellipse is apparent, also in agreement with the behavior of spherical droplets. We highlight this effect using a drawn ellipse overlay in Figure 2B that indicates the degree of overlap and deformation of the drops as a result of elastic deformation. The last frame in Figure 2B represents the final stable position of this doublet, even though we might naively expect the two droplets to relax further. Some resistance to the reduction of surface energy must be acting to halt further motion, perhaps
because of local friction or deformation of the internal elastic microstructure. Comparison of the center of mass positions in Figure 2B with calculated paths for this doublet will allow us to quantify the magnitude of any effects on trajectory.

In Figure 2C we plot a trajectory calculated following the method used to generate Figure 2A along with the experimentally-determined positions of the center of mass of the upper droplet in Figure 2B to assess any non-idealities. We see good general agreement of the experimental and calculated paths, though the real droplet is systematically closer to the second droplet than predicted. The deviation likely results from the small strain the droplets experience as the internal solid network deforms elastically. The last few points in Figure 2C deviate more significantly from the calculated path, indicating there may be stronger deformation occurring late in the process and that such deviations are time- and position-dependent. Variations in the deformation during arrested coalescence between the two droplets will cause variations in frictional resistance to movement, complicating our description of the process. We do not quantify strain in these systems, as we did for spherical droplets, as the more complex ellipsoidal shape here complicates such a description. The two-dimensional calculations do not fully account for the three-dimensional nature of the ellipsoids produced here, and also ignore the effects of the liquid film between droplets. They do, however, communicate the basic principle at work here: the movement of one ellipsoidal droplet around another’s perimeter is a strong function of the varying curvature of the ellipsoids. Below we improve on the above description, by simulating the three-dimensionality of the ellipsoids as well as the effects of the liquid film that imposes the stress driving motion, providing a more comprehensive understanding of the arrested coalescence behavior of ellipsoidal droplets.

Surface Minimization Model

To map the energy landscape experienced by the ellipsoidal doublets as a function of their relative orientation, we simulated the fluid-fluid interface with Surface Evolver. The droplets
Figure 2: A) Paths plotted in red for the center of mass of various ellipsoids rolling around a second one. Increasing the aspect ratio alters the path of the center of mass, varying the path curvature when the two shapes are aligned edge-to-edge. B) Experimental micrographs of two ellipsoidal droplets containing 40% solids as they undergo arrested coalescence and restructuring. C) Plotted positions of the center of mass of the upper ellipsoid in B) as compared to the calculated path of a system with the same dimensions using Equation [1].
are modeled as one-sided level set constraints around which the area of the fluid-fluid interface is minimized at fixed enclosed volume as a function of the relative position of the two droplets. In our model, we suppose the interface has uniform surface tension. Hence the area of the interface is proportional to surface energy and minimizing the area is equivalent to minimizing the surface energy. In previous work, this strategy allowed us to correctly predict the critical angle below which the menisci of two spherical droplets overlapped with that of a third droplet being added, causing reconfiguration of the triplet shape\textsuperscript{19}.

Figure 3: The coordinate system used to describe the relative position of two coalescing ellipsoidal droplets.

The computational geometry is depicted in Figure 3: the coordinate system is oriented such that the $y$ axis is along the major axis of one of the ellipsoids. The center of mass of the other is at the zenithal angle $\theta$ from this axis and oriented at an angle $\phi$ to it. Due to the symmetry of the system, the domain of $\theta$ is from $0$ to $90^\circ$ and $\phi$ from $0$ to $180^\circ$. For every $\theta$ and $\phi$, the distance $d$ is calculated using the overlap algorithm proposed by Perram and Wertheim\textsuperscript{51} such that the second ellipsoid is positioned just in contact with the surface of the first ellipsoid. The ellipsoids impose level set constraints on the fluid interface,

$$\mathbf{r} \Sigma^{-1} \mathbf{r} > 1$$

$$\left(\mathbf{r} - \mathbf{r}_c\right)^T R^T \Sigma^{-1} R \left(\mathbf{r} - \mathbf{r}_c\right) > 1$$

where $\mathbf{r} = (x, y, z)$, $\mathbf{r}_c$ is the center of the second ellipsoid at $(0, d \cos \theta, d \sin \theta)$, $R$ is the rotational matrix of $\phi$ around the $x$ axis and $\Sigma$ is the diagonal matrix with entries $(b^2, a^2, b^2)$. The surface is then minimized with a fixed volume $V = 2 \times \frac{4\pi}{3} ab^2 / 0.95$, slightly greater than
the volume of the two ellipsoids in order to allow the formation of a meniscus. The volume of the enclosing fluid is clearly a relevant quantity here, as it will set the available free liquid to act on the droplets during their coalescence and arrest. We use a constant value in the simulations for simplicity.

Figure 4 shows a contour plot of the surface energy, for ellipsoids of aspect ratio $AR = 1.2$, calculated using Surface Evolver simulations for the entire range of values of angles $\theta$ and $\phi$. Three-dimensional renderings of simulated ellipsoidal droplet pairs are also shown for representative regions to aid the interpretation of the results and allow comparison with experiment. Two minimum surface energy regions are visible at high $\theta$ values in combination with either low or high $\phi$ values, consistent with the case when two ellipsoids are joined at their long edges and minimize their total surface area. A maximum in surface energy occurs where the two ellipsoidal droplets are parallel and arranged end on, at low $\theta$ values in combination with either low or high $\phi$ values, maximizing the doublet surface area. A saddle point exists where the droplets are perpendicularly aligned in a ‘T’ configuration. An analogous energy diagram was computed for single nanocylinders at a flat liquid interface, finding similar regions of stability for similar orientations.

Generally, when the droplets initially make contact at arbitrary angles we expect their orientation to evolve down the energy gradient towards the minimum because the motion occurs in a viscous quasistatic regime, a prediction that will be robustly tested in the subsequent section. The droplets in the doublet are, however, also subject to forces from the internal structure and the opposing meniscus driving forces on the ellipsoid surface. Divergence from the behavior predicted by surface energy alone therefore allows us to assess the relative importance of these other terms to the final shape of the doublet.

Figures 4B-H show several examples of experimental ellipsoidal doublets forming and restructuring, to various degrees, before reaching their final arrested state. The droplets all have an aspect ratio of $AR \sim 1.2$ and contain 40% solids by weight. As a result, the droplet deformation is expected to be relatively low during arrested coalescence and any
observed restructuring by the fluid meniscus will be reproducible and easily compared with
the predictions of Figure 4A. Figure 4A suggests we might only find stable configurations of
ellipsoidal doublets at the two energy minima. However, Figures 4B-H show a much wider
range of final doublet states can be formed, without necessarily exhibiting the restructuring
we might expect. Figures 4B and H show the largest amount of restructuring, with $\phi$ varying
by 40° and 20°, respectively. In Figure 4B, the restructuring halts with the two ellipsoids
oriented at angles of $\theta = 67^\circ$ and $\phi = 139^\circ$, close to the energy minimum in Figure 4A but
several contour lines outside of it. Clearly some type of constraint force, possibly the elastic
resistance of internal structure, affects the restructuring process and can arrest the system
at a point that is not stationary with respect to the surface tension term. In Figure 4H, an
energetic minimum is attained by the pair of ellipsoids at values of $\theta = 89^\circ$ and $\phi = 170^\circ$.
Other initial states lead to much less restructuring, expanding the range of forms that can
be obtained by ellipsoidal droplet arrested coalescence. Because the ellipsoidal droplet shape
is anisotropic, this implies that the initial orientation of the droplets’ major axes will have a
strong effect on the subsequent restructuring brought about by the meniscus.

Figures 4C-G restructure very little from their initial position, moving at most 5° in
Figure 4E. In Figure 4C, two ellipsoids initiate contact at angles of $\theta = 1^\circ$ and $\phi = 3^\circ$ and
do not experience any restructuring over time, despite this representing the highest energy
configuration calculated in Figure 4A. This is because the meniscus forces that normally
drive restructuring vanish at an energetic maximum, creating an unstable stationary state.
However, additional influences present, such as elastic resistance of the internal structure,
may stabilize the stationary state against collapse. Figure 4D shows the case when two
ellipsoids are initially brought together into the minimum energy configuration at the top
right of Figure 4A. Here the system restructures only very slightly. Figures 4E-G also do not
restructure significantly, and they all come into contact in various realizations of the saddle
point conditions in Figure 4A, an area of intermediate stability where two ellipsoids are
arrested at, or near, right angles to one another. The system may be stabilized at the saddle
point, as in Figure 4F. If the doublet is initially configured slightly away from the saddle point, as in Figures 4E and G, the system evolves towards the energy minimum slightly but nonetheless is arrested close to the saddle point. Again, this may be explained by the additional constraint forces from the internal structure.

Figure 4: A) A density plot of surface energy as a function of $\theta$ and $\phi$ for ellipsoid aspect ratio $AR = 1.2$. High-energy regions are colored cyan while low-energy regions are brown, with neutral colors indicating intermediate saddle regions. Six three-dimensional renderings of exemplary configurations are shown for representative energy extrema. (B-H) Stable experimental examples of some of the simulated shapes are shown for droplets with a solids content of 40% and aspect ratio $AR = 1.6$.

Because the ellipsoid dimensions determine the amount and distribution of surface area in the droplets, we also explore the effects of droplet aspect ratio on our above results. Calculated energy contour plots are shown in Figure 5 for several ellipsoidal droplet aspect ratios, as well as two different internal droplet solids levels. Our simulation can account for changes in solids level by varying the volume of fluid enclosed by the simulated interface, but we use a fixed value here because it doesn’t change the shape of the energy contour plot. The contours in each plot are labeled with surface energy relative to the surface energy minimum. Increasing aspect ratio alters the shape of the regions of energy minima and maxima as a result of the geometric changes in the droplets. For example, the width of the minimum energy region for the three aspect ratios with 30% solids in Figure 5 increases as
AR increases, spanning a wider range of θ values. The effect is geometric, and is caused by
the higher ellipsoid edge length at larger AR values.

The instantaneous values of θ and φ for a number of experimental doublets, during
coalescence and restructuring, are plotted as colored trajectory lines on top of the contour
plots in Figure 5 to show the extent of restructuring that occurs for different starting positions
and compositions. The contour plot provides a useful map to summarize many different
experiments and compare the effects of multiple system variables. For droplets containing
30% solids, at all aspect ratios, the trajectories plotted in Figure 5 all move in the direction
of decreasing energy. Interestingly, for AR = 1.3, most do not reach a minimum, consistent
with the example in Figure 4B, likely because of inherent solid and fluid resistance to flow
and movement. As the aspect ratio of the droplets containing 30% solids is increased in
Figure 5, the lengths of the trajectories increase significantly, indicating a greater degree of
movement and restructuring during arrested coalescence. Although fewer data were taken
for the larger aspect ratios, droplets with AR = 2.5 and AR = 3.25 reproducibly move
from an intermediate stability level, at a calculated saddle point, entirely into the minimum
energy region. Despite the simplicity of the model, agreement between experiment and
predicted final configurations is surprisingly good when meniscus-induced restructuring is
this significant. It is reasonable to expect that longer ellipsoids will have stronger driving
forces to reduce surface energy, restructuring much more significantly than droplets with
smaller aspect ratios. The concept of a driving force, here reduction of surface energy, and
a resistance, here an elastic or frictional force, suggests that increasing droplet solids level
and elasticity will also affect the restructuring process.

Figure 5 plots trajectories for a number of doublet systems containing 40% solids as they
restructure. For an AR = 1.3, the trajectory sizes are of similar or smaller size compared to
the trajectories of the droplets containing 30% solids in Figure 5. At the higher solids level in
Figure 5, most of the restructuring observed at both aspect ratios moves the doublets down
the energy gradient, but does not move them into the calculated energy minimum state,
likely because of a larger elastic resistance to deformation. Interestingly, we observe two instances at 40% solids where the droplets move up the energy gradient, possibly because of heterogeneities in the solid structure of the droplet. Even more extreme effects of the larger aspect ratios are observed at the lower solids concentration studied.

Figure 5: Experimental pathways of ellipsoidal doublets relaxing to their final configuration are plotted on several calculated surface energy contour maps for different ellipsoidal aspect ratios. Arrows indicate direction of movement on each trajectory. Increasing the aspect ratio changes the shape of the extrema regions, as a result of the changes in ellipsoid geometry, and also enables relaxation to lower energy states for 30% solids.

The top row of Figure 6 shows a time sequence of images of two ellipsoids containing 30% solids, with $AR = 3.7$, as they are brought together, begin coalescence, and then arrest. The images in Figure 6 are captured between crossed polarizers to highlight the solid phase regions of the structures as they move. In the first few frames of Figure 6, the droplets move together steadily because of migration of the fluid meniscus, reducing doublet surface area and moving it from a relatively high energy configuration, near the saddle-point in the middle of Figure 4A, toward the low-energy region of the upper-right quadrant of Figure 4A. The time interval is the same for each frame, but the distance moved from the frame at $t = 3 \text{ s}$ to the frame at $4 \text{ s}$ is about $300 \mu m$, a significant acceleration. Much like elliptical gears, we find that ellipsoidal droplets can convert a relatively constant driving force, expansion of the fluid meniscus, into a variable speed movement. Such forces also have a strong effect on the
individual droplets.

The bottom row of Figure 6 highlights the behavior of the two droplets after reaching a near-final conformation: edge-to-edge alignment in a low energy state. An overlaid line, connecting the lower ellipsoid’s endpoints with its midpoint, is used to visualize the subsequent deformation of the ellipsoid as the meniscus continues to expand completely across the length of the doublet. Here the deflection of the lower ellipsoid is $\sim 120 \mu m$ in the last frame, about 10% of the ellipsoid length. The significant deformation of the ellipsoids by the meniscus force only occurs once the droplets have been brought together at the energetic minimum with respect to their relative orientation. At this point, no further reduction in the meniscus area can occur by rotations; however deformation of the ellipsoids can bring their ends into closer contact, reducing the overall contact area at the expense of elastic reorganization of the internal structure. The lower solids level of the ellipsoids means that this deformation is feasible. Past measurements of the petrolatum system\textsuperscript{26} indicate droplets containing 30% solids have a yield stress, $\sigma_y \sim 1 Pa$ and an interfacial tension $\gamma \sim 10 mN/m$. The stress needed to deform the droplet must then be of the same order as the droplet yield stress\textsuperscript{26}. Assuming the Laplace pressure sets the magnitude of applied stress, we can calculate the necessary maximum radius of the fluid meniscus, $R$, to cause such a change from:

$$R = \frac{2\gamma}{\sigma_y} \quad (5)$$

Using Equation 5, we solve to obtain $R = 20 mm$ and, since the measured meniscus radius is more on the order of $R = 150 \mu m$, conclude that the meniscus force is more than sufficient to cause the changes observed in Figure 6. Such deformation is only observed when droplets have low solids levels and high aspect ratios, but Equation 5 indicates it could be avoided by increasing the elastic resistance to droplet deformation\textsuperscript{26,28}. 

16
Figure 6: Arrested coalescence of high aspect ratio ellipsoidal droplets, $AR = 3.7$, containing 30% solids. The doublet exhibits deformation of the ellipsoid being moved, curving it around the second droplet.

Conclusions

The processes of self-assembly and restructuring of pairs of ellipsoidal droplets undergoing arrested coalescence have been studied here using stable droplets, produced in a millifluidic process, with varying aspect ratios. The ellipsoidal shape of the droplets enables restructuring and deformation behavior that is significantly different from that exhibited by spherical droplets\cite{19}. Ellipsoidal droplets exhibit more complex trajectories, and a wider range of motion, than spheres\cite{19} during meniscus-driven restructuring. The experimentally observed dynamics approach, but don’t always attain, theoretical predictions of the most stable configurations with respect to geometry and surface energy. Small amounts of deformation occur for all droplets, reducing the radius of their path when compared to that predicted by the locus of an ellipse rotating around a second ellipse. The final configuration of the droplets also deviates from more developed three-dimensional simulations of arrested coalescence of ellipsoids, likely because of elastic and frictional resistance to the stresses transmitted by the fluid meniscus. The resistance can be tuned by adjusting the dimensions and solids fraction of the droplets, potentially allowing control of larger structure assembly and restructuring.

We are particularly interested in how irregularly-shaped, non-Brownian, particles and droplets can be assembled and organized by the action of a fluid meniscus to achieve changes in shape and to form larger-scale structures. This work demonstrates limits on the ability
to control shape change and other dynamics using droplets containing solid particles or viscoelastic microstructures. Varying the aspect ratio of the droplets controls the extent of restructuring that is possible before a stable configuration is reached. All ellipsoidal droplets experience some restructuring, mostly moving toward lower surface energy states. Low aspect ratio ellipsoids form mostly metastable configurations during restructuring, while higher aspect ratios mostly converge to energy minima, though increased elasticity can offset such effects. Tuning the rheology of the droplets impacts the final configurations, likely by affecting the significance of local and variable deformation of individual droplets. The importance of this work is its droplet-level study of arrested coalescence and restructuring mechanisms for non-spherical shapes. It is hoped the insights can be used to create accurate predictions of larger-scale aggregates formed via assembly and meniscus-driven restructuring, enabling design of emulsion microstructures and their mechanical properties. Applications are possible in areas as diverse as food product development, advanced material creation, and additive manufacturing.

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