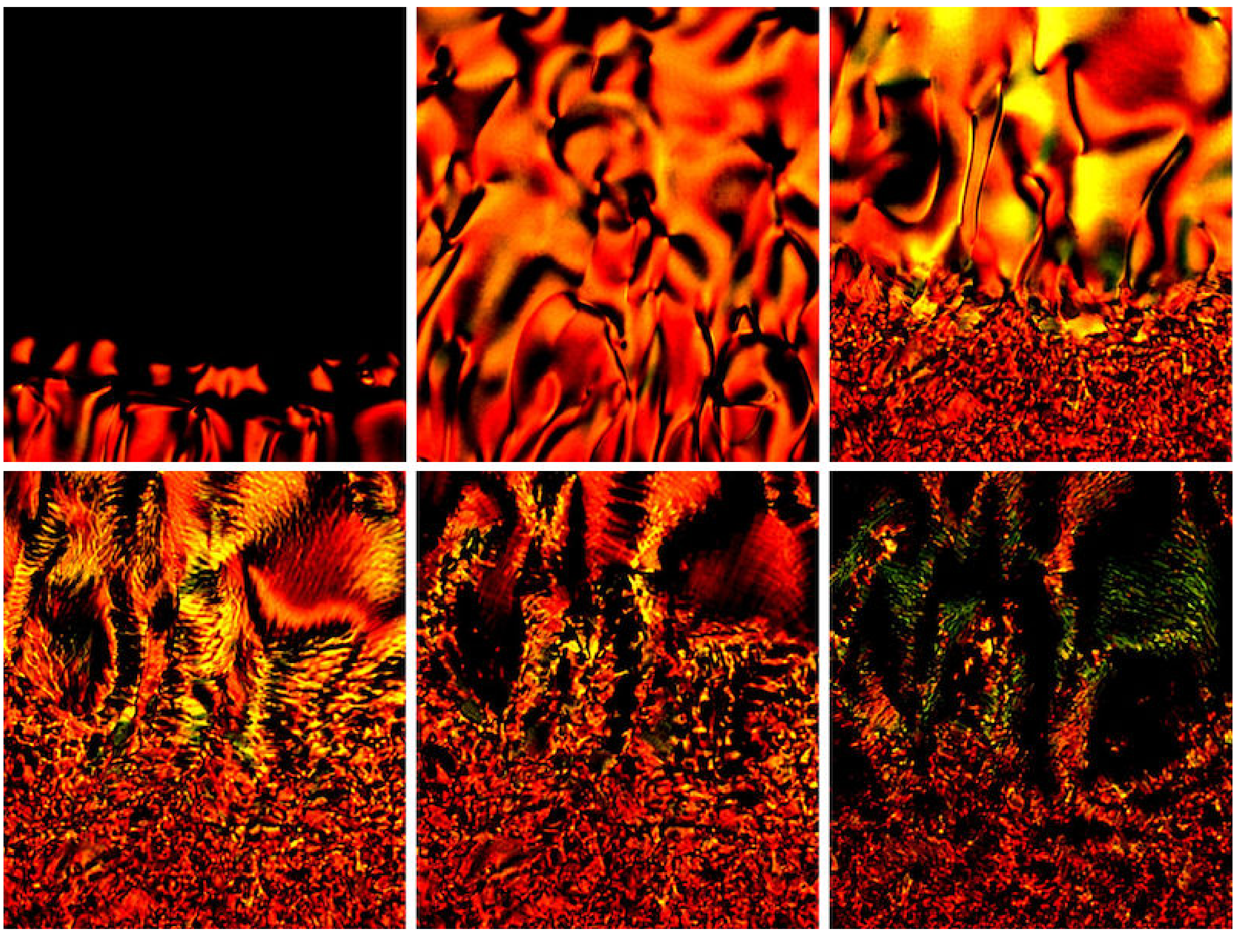
Physicists discover why drying liquid crystal drops leave unusual 'coffee rings'

May 30 2017, by Ali Sundermier



A close-up of the drying progression of Sunset Yellow. Credit: University of Pennsylvania

In previous papers, University of Pennsylvania physicists investigated the "coffee ring effect," the ring-shaped stain of particles left after drops of coffee evaporate. In one paper, they learned how to undo this effect by altering particle shape. Now, in a new paper published in *Nature Communications*, they have uncovered the complex and remarkably different behavior arising in a liquid crystal drop that is drying.

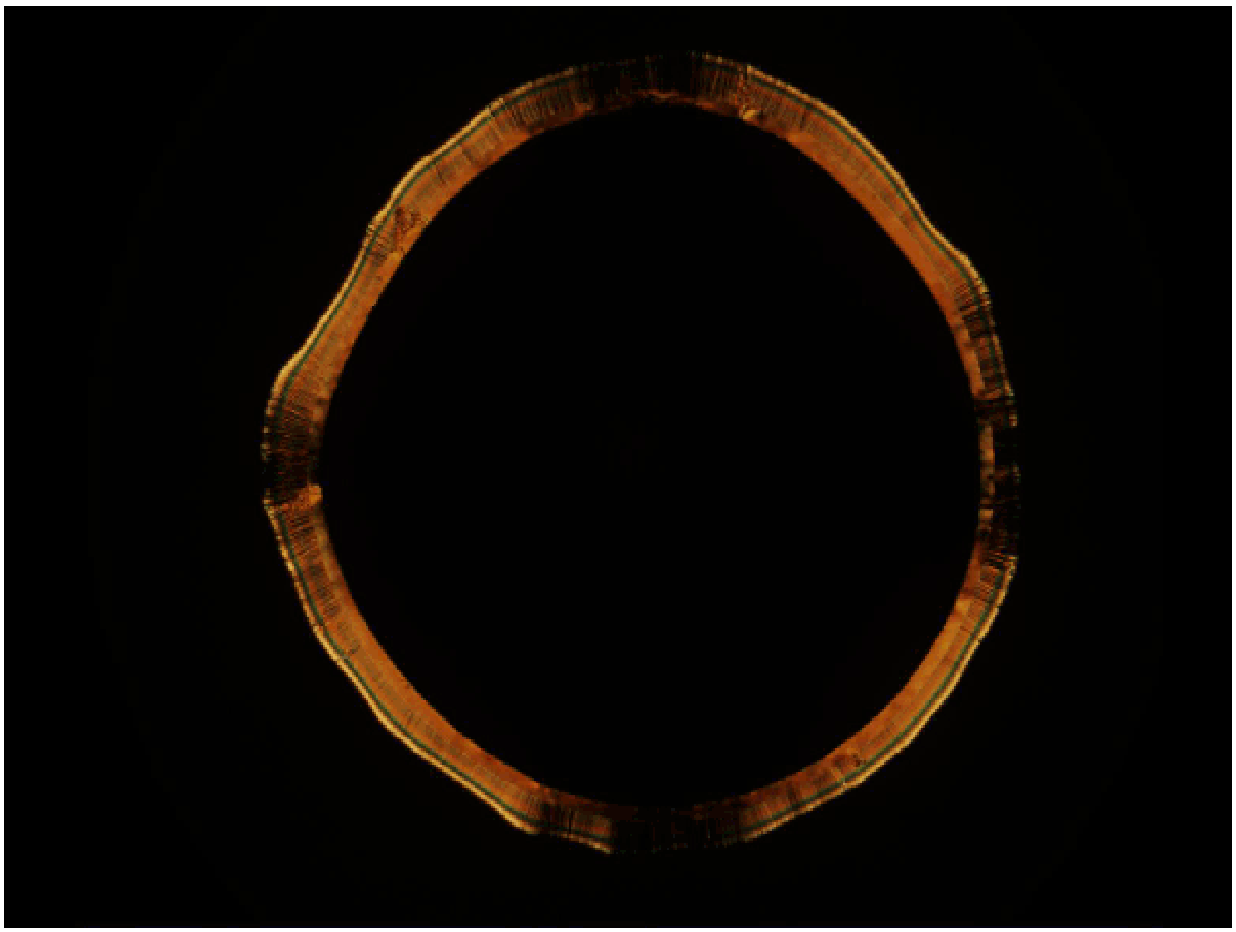
The research, carried out in collaboration with scientists at Lehigh University and Swarthmore College, reveals novel behavior characteristics of liquid crystals, fluids with aligned phases of constituent molecules. The formation of different phases during drying leads to dramatically different fluid movement and solid deposition and also provides insight needed for the control of drying solutions of macromolecules that occur in many dyes and pharmaceutical formulations.

Penn alumnus Zoey Davidson, now a postdoc at the Max Planck Institute for Intelligent Systems in Germany, had been experimenting with Sunset Yellow, a dye that gives Doritos and orange soft drinks their bright colors, when he accidentally spilled some of the material.

"I noticed that the spill pattern left behind by the drop was sort of similar to coffee-patterns we had studied before, but there were also differences," Davidson said. "The drying drops had a macroscopically visible interior structure, too."

Davidson, along with Arjun Yodh, director of the Laboratory for Research on the Structure of Matter and the James M. Skinner Professor of Science in the Department of Physics & Astronomy in the School of Arts & Sciences at Penn, and Peter Collings of Swarthmore, an adjunct professor at Penn, then decided to investigate this in a more controlled fashion. Penn Professor Randall Kamien, undergraduate alumnus Adam Gross and postdocs Angel Martinez and Tim Still also contributed to the study. The group collaborated with Chao Zhou of Lehigh and his Ph.D. student Yongyang Huang.

Unlike the particles in a coffee drop, the [liquid crystal] drop they studied was a solution of Sunset Yellow molecules that spontaneously combine to form rod-like macromolecular assemblies, similar to how rod-like molecules order to form the liquid crystals used in LCDs.



Credit: University of Pennsylvania

"Liquid crystals are a phase of matter," Collings said, "just like the more well-known solid, liquid and gas phases. They are fluids, which means they take the shape of their container, but unlike liquids there is some order among the constituents that make up the substance. So, although the constituents diffuse around much like what happens in liquids, they maintain some orientational and sometimes positional order."

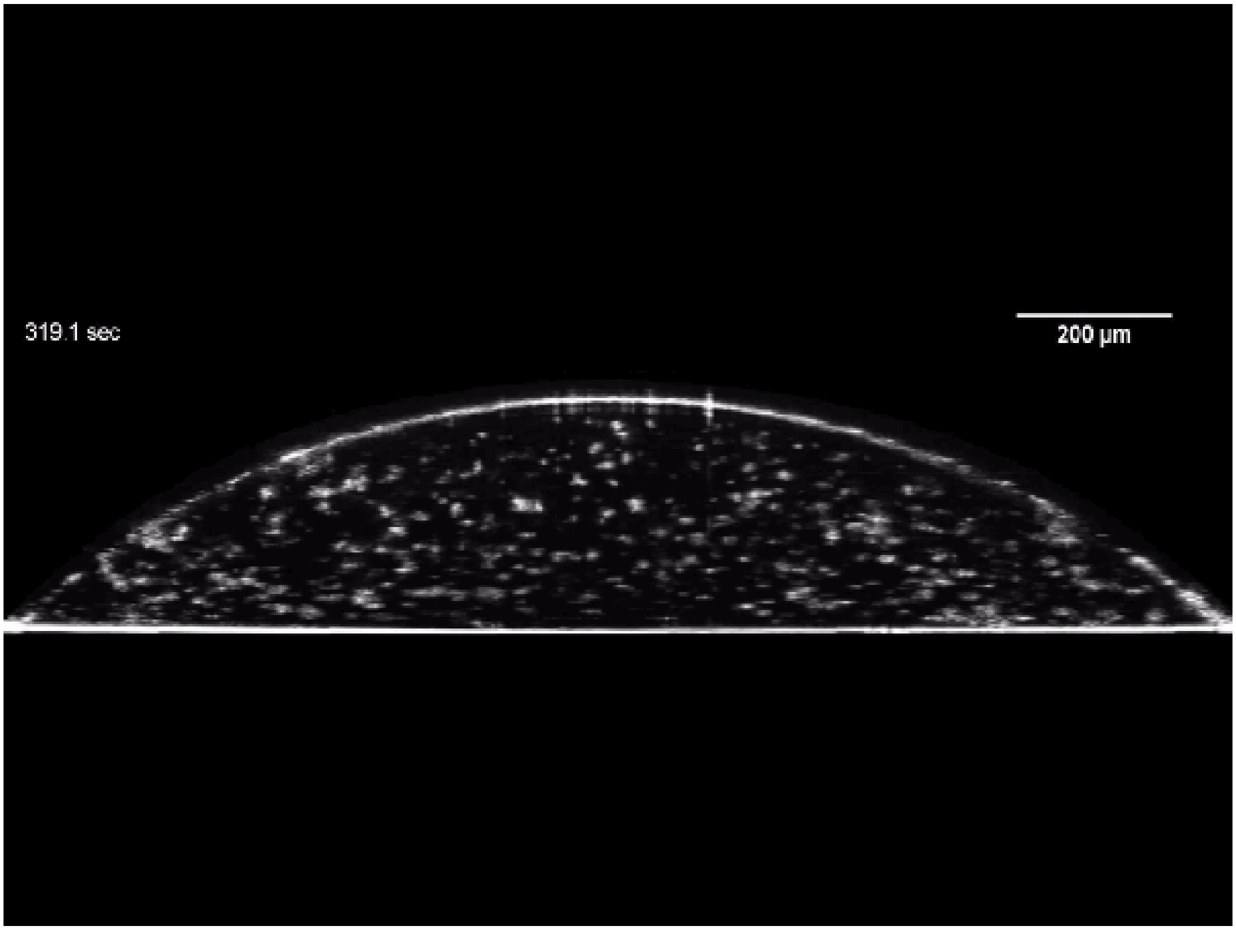
While the liquid crystals used in LCDs, called thermotropic liquid crystals, are made of molecules with nothing else added, the liquid crystals used in this experiment were chromonic liquid crystals. Chromonic liquid crystals consist of assemblies of molecules dispersed in liquid water.

During drying, the Sunset Yellow concentration varied within the drop, and microscope images revealed the formation of different fluid phases such as the isotropic liquid (random), liquid crystal nematic (aligned) and liquid crystal columnar (cylindrically packed) phases that segregate to different regions of the drop.

"When you look at the drop over time," Yodh said, "it's not uniform; it has a lot of structure."

The central region of the drop was isotropic, and it was surrounded by the aligned nematic phase. The boundary between the two phases moved toward the center as the droplet dried, and then other regions with different structures appeared, such as the columnar and crystal phases.

"It's a qualitative jump to go from a drop that is one phase that just gets more concentrated," Yodh said, "to a drop that can change into several different phases depending on concentration. The different phases segregate and affect the viscosity and convection in different regions of the drop."



Credit: University of Pennsylvania

They noticed unusual dynamics in the drying process but found it difficult to discern these processes with simple microscopies. Thus they joined forces with Zhou and Huang to employ optical coherence microscopy to track the flow inside of the droplets. The new microscope revealed circular flow patterns, or Marangoni currents, circulating in a direction opposite to that seen in other solutions. This circulation anomaly was due to the unusual surface tension properties of Sunset Yellow.

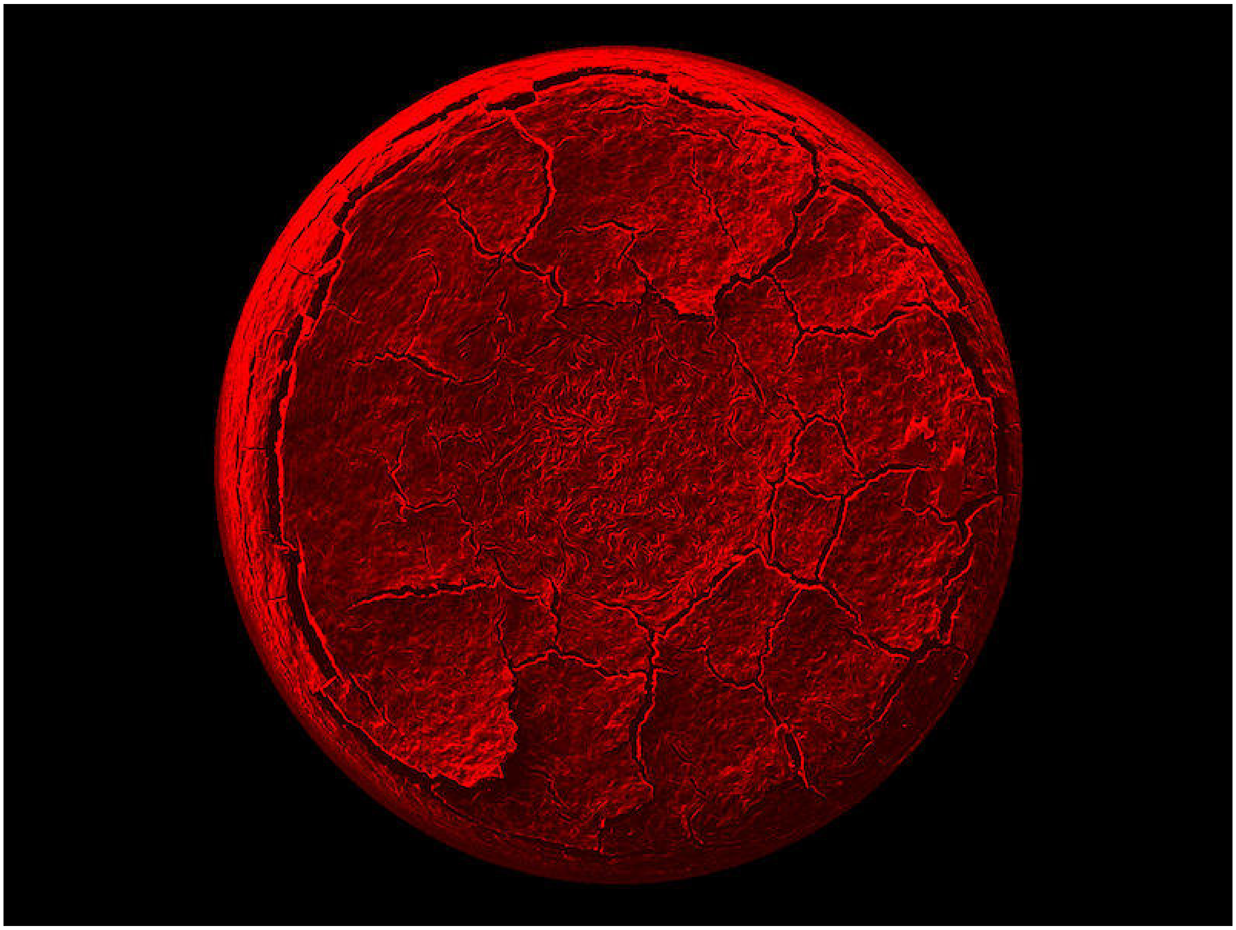
Because evaporation happens fastest at an outer edge in a drying drop of coffee, solid material inside the drop is transported from the center of the droplet to the outer edge, bringing more and more coffee grains with it.

"These coffee grains accumulate at the edge," Collings said, "and after the drop has completely dried a nice, dark ring of coffee particles results."

In the end, deposition from the drying liquid crystal drop was not ring-like or uniform.

"In many cases," Collings said, "the existence of liquid crystal phases raises the viscosity and lowers the speed material moves at, so the final shape looks like a volcano or sunken souffle."

Although there have been other investigations in which multiple phases arise in drying and evaporating drops, especially near the drop edge, this is the first time researchers have investigated multiple liquid crystal phases and understood how viscoelastic effects and other properties of liquid crystals affect the final drying deposition pattern.



Credit: University of Pennsylvania

"We're pushing a frontier," said Yodh, "We know that lots of systems actually can have these properties, and this research is important if you want to understand what they're going to do."

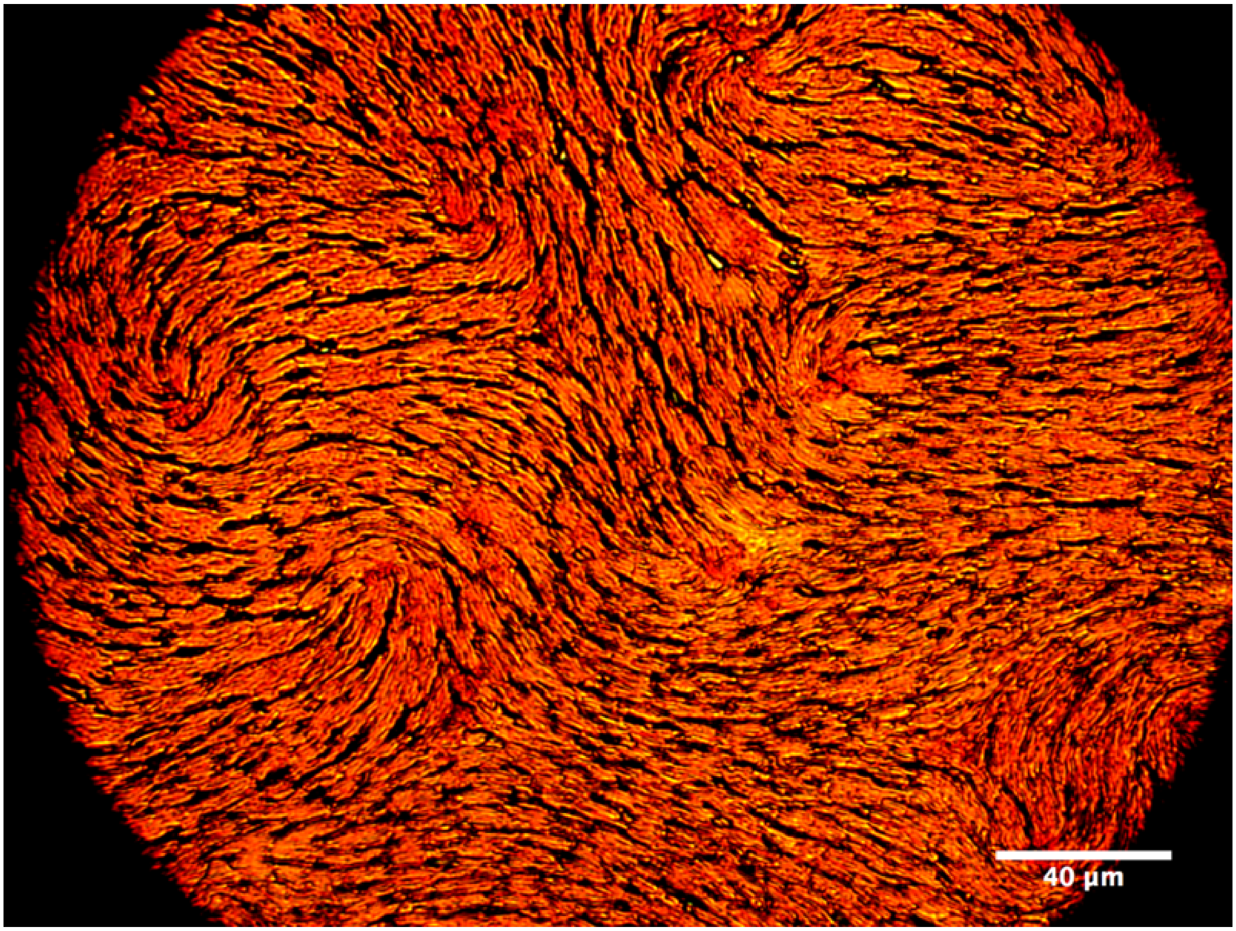
Many technologies depend on depositing material in a precise way through the evaporation of a solvent. Since liquid crystal-like phases are common among dyes and pharmaceuticals, this research could have potential applications down the line.

"One need only think about ink-jet printing," Collings said, "to realize an extremely common and useful example. If such processes involve substances that form liquid crystal phases, as many dyes and drugs do, then the understanding gained through our experiments is going to be important in achieving whatever results are desired."

But much of the importance of this work lies in the realm of basic science.

"Our newfound understanding of how droplets of another class of materials dry," Collings said, "substantiates some concepts developed before but also extends our knowledge into realms where the behavior is different."

The researchers hope to follow up on some of the interesting observations they made about the structures that form as the material dries.



Fast dried drop center. Credit: University of Pennsylvania

"The patterns of material that form," Yodh said, "are influenced both by traditional equilibrium thermodynamics and by fluid convection and new structures with novel locked topologies form as a result."

To be able to control this phenomenon would be an exciting next step.

"That's the funny thing about watching paint dry," Davidson said. "There's actually all this cool stuff happening inside the drop."

More information: Zoey S. Davidson et al, Deposition and drying dynamics of liquid crystal droplets, *Nature Communications* (2017). DOI: 10.1038/ncomms15642

Provided by University of Pennsylvania