Research reveals how order first appears in liquid crystals

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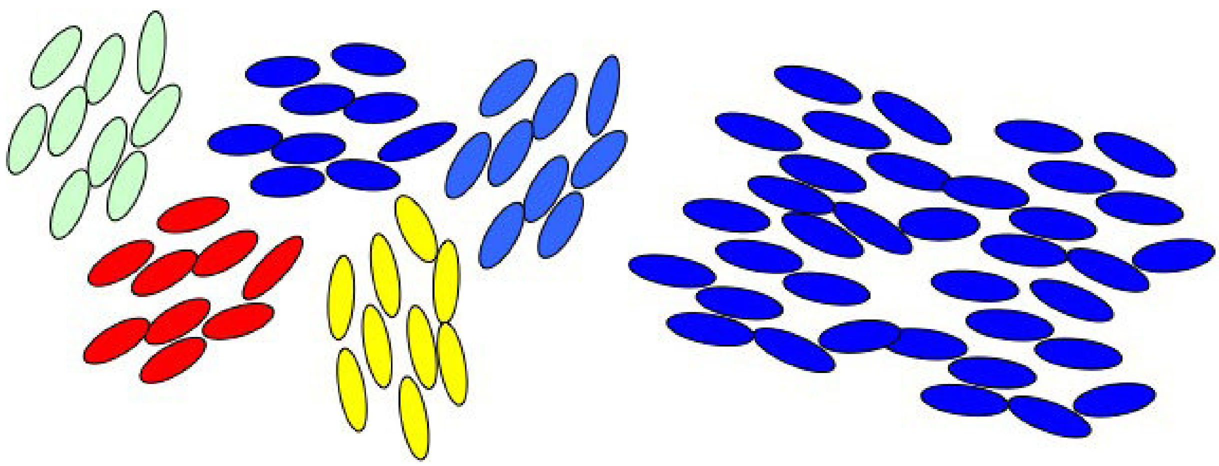

Molecules in liquid crystals go from a disordered jumble to more ordered alignment with changes in temperature. But there's evidence of an intermediate state (left) where order starts to emerge in discrete patches before arriving at the fully ordered state (right). New research by Brown University chemists helps to identify and understand that intermediate state. Credit: Richard Stratt / Brown University

Liquid crystals undergo a peculiar type of phase change. At a certain temperature, their cigar-shaped molecules go from a disordered jumble to a more orderly arrangement in which they all point more or less in the same direction. LCD televisions take advantage of that phase change to project different colors in moving images.

For years, however, experiments have hinted at another liquid crystal state—an intermediate state between the disordered and ordered states in which order begins to emerge in discrete patches as a system approaches its transition temperature. Now, chemists at Brown University have demonstrated a theoretical framework for detecting that intermediate state and for better understanding how it works.

"People understand the ordered and disordered behaviors very well, but the state where this transition is just about to happen isn't well understood," said Richard Stratt, a professor of chemistry at Brown and coauthor of a paper describing the research. "What we've come up with is a sort of yardstick to measure whether a system is in this state. It gives us an idea of what to look for in molecular terms to see if the state is present."

The research, published in the *Journal of Chemical Physics*, could shed new light not only on liquid crystals, but also molecular motion elsewhere in nature—phenomena such as the protein tangles involved in Alzheimer's disease, for example. The work was led by Yan Zhao, a Ph.D. student in Stratt's lab who expects to graduate from Brown this spring.

For the study, the researchers used computer simulations of phase changes in a simplified liquid crystal system that included a few hundred molecules. They used random matrix theory, a statistical framework often used to describe complex or chaotic systems, to study their simulation results. They showed that the theory does a good job of describing the system in both the ordered and disordered states, but fails to describe the transition state. That deviation from the theory can be used as a probe to identify the regions of the material where order is beginning to emerge.

"Once you realize that you have this state where the theory doesn't work, you can dig in and ask what went wrong," Stratt said. "That gives us a better idea of what these molecules are doing."

Random matrix theory predicts that the sums of uncorrelated variables—in this case, the directions in which molecules are pointing—should form a bell curve distribution when plotted on a graph. Stratt and Zhao showed that that's true of the molecules in liquid crystals when they're in disordered and ordered states. In the disordered state, the bell curve distribution is generated by the entirely random orientations of the molecules. In the ordered state, the molecules are aligned along a common axis, but they each deviate from it a bit—some pointing a little to the left of the axis and some a little to right. Those random deviations, like the random molecule positions in the disordered state, could be fit to a bell curve.

But that bell curve distribution fell apart just before the [phase change](#) took place, as the temperature of the system was dropping down to its transition temperature. That suggests that molecules in discrete patches in the system were becoming correlated with each other.

"You now have several sets of molecules starting to cooperate with each other, and that causes the deviations from the bell curve," Stratt said. "It's as if these molecules are anticipating that this fully ordered state is going to take place, but they haven't all decided which direction they're going to face yet. It's a little like politics, where everybody agrees that something needs to change, but they haven't figured out exactly what to do."

Stratt says the work could be helpful in providing insight into what governs the effectiveness of molecular motion. In both ordered and disordered liquid crystals, molecules are free to move relatively freely. But in the intermediate state, that movement is inhibited. This state then represents a situation in which the molecular progress is starting to slow down.

"There are a lot of problems in natural science where movement of molecules is slow," Stratt said. "The molecules in molten glass, for example, progressively slow down as the liquid cools. The protein tangles involved in Alzheimer's disease are another example where the molecular arrangement causes the motion to be slow. But what rules are governing those molecules as they slow down? We don't fully understand it."

Stratt hopes that a better understanding of slow molecular movement in liquid crystals could provide a blueprint for understanding slow movement elsewhere in nature.

More information: Yan Zhao et al, Measuring order in disordered systems and disorder in ordered systems: Random matrix theory for isotropic and nematic liquid crystals and its perspective on pseudo-nematic domains, *The Journal of Chemical Physics* (2018). DOI: 10.1063/1.5024678

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