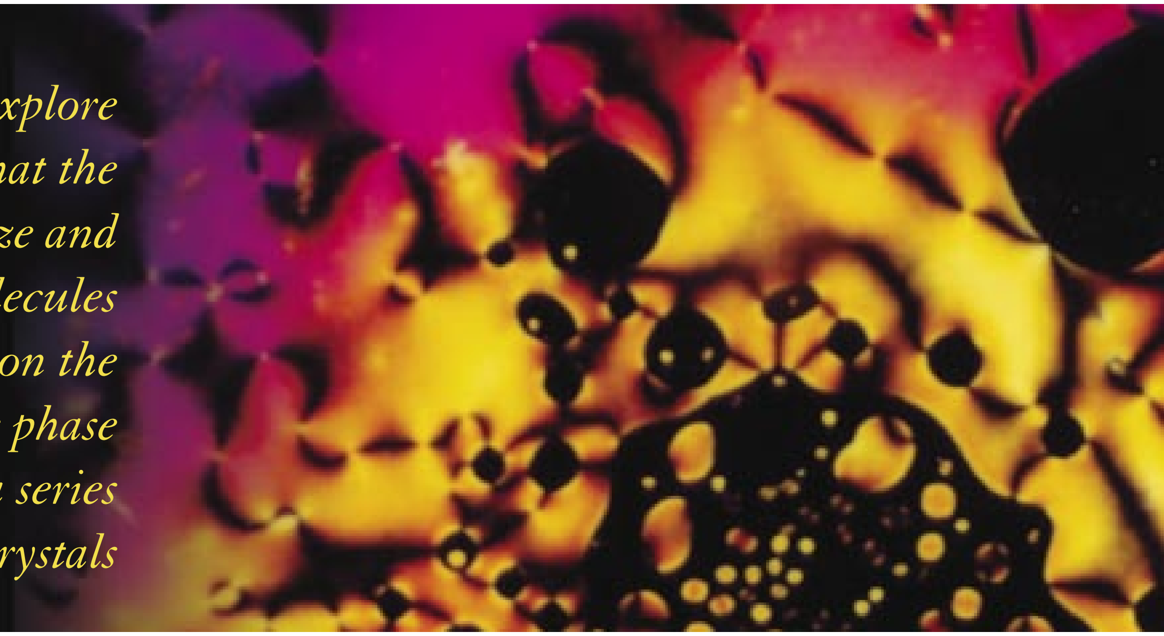
Fats, Oils, & Colors of a Nanoscale Material

Students explore the effect that the nanoscale size and shape of molecules have on the macroscopic phase properties of a series of liquid crystals



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Phase changes and intermolecular forces are important physical science concepts but are not always easy to present in an active learning format. This article presents several interactive activities in which students plot the melting points of some fatty acids and explore the effect that the nanoscale size and shape of molecules have on the material's macroscopic phase properties.

In this article, two sets of suggested active learning questions and activities are posed, followed by answers and concepts that are related to the questions and activities. In the first set of activities, students investigate the connection between molecular shape and the melting point of fats and oils. In the second set of activities, the same shape consideration is then applied to a series of liquid crystals—a key nanoscale material used as sensors (see "Activity: Liquid crystal sensors," p. 34). Liquid crystals with varying composition can illustrate how intermolecular forces affect phase transition temperatures. Although the visible color changes that occur with liquid crystals are not at the phase transition (which is higher), the color change is a measure of changes that are occurring with intermolecular forces as the temperature changes.

Basic phases of matter

Questions for students: *How do solids, liquids, and gases differ at the macroscopic level? Consider shape and volume of the materials. How might you distinguish between a solid, a liquid, and a gas at the nanoscopic level?*

Answer/Concept: Solids, liquids, and gases are the traditional phases of matter taught in physics and chemistry classes. Whether matter is a solid, a liquid, or a gas depends on its temperature. The form of H_2O as ice, water, and steam is a familiar example. Molecules in

FIGURE 1

Saturated and monounsaturated fatty acid melting points.

(IMCJ/JSTA 2006; Gunstone and Herslof 2000)

Saturated fatty acids

Systematic name	Common name	Number of carbon atoms	Fatty acid melting point (°C)	Triglyceride melting point (°C)
Butanoic	Butyric	4	−7.9	
Hexanoic	Caproic	6	−3.4	
Octanoic	Caprylic	8	16.7	9.8–10.1
Decanoic	Capric	10	31.6	32
Dodecanoic	Lauric	12	44.2	46.4
Tetradecanoic	Myristic	14	53.9	58.5
Hexadecanoic	Palmitic	16	63.1	66–66.4
Octadecanoic	Stearic	18	69.6	73.5
Eicosanoic	Arachidic	20	76.5–77.0	78
Docosanoic	Behenic	22	81.5	82.5
Tetracosanoic	Lignoceric	24	87.5–88.0	86
Hexacosanoic	Cerotic	26	87.7–88.5	

Monounsaturated fatty acids [**Note:** The number in the common name indicates the location of the C=C double bond when counting from the carboxyl carbon as number 1.]

Systematic name	Common name	Number of carbon atoms	Cis melting point (°C)	Trans melting point (°C)
Tetradecenoic	9-Myristoleic	14	−4	
	9-Myristelaidic	14		18–18.5
Hexadecenoic	9-Palmitoleic	16	−0.5 to +0.5	
	9-Palmitelaidic	16		31
Octadecenoic	9-Oleic	18	12	
	9-Elaidic	18		44.5–46.5
	11-Vaccenic	18	14.5–15.5	
	11-Vaccenic	18		44
Eicosenoic	9-Gadoleic	20	23–23.5	
	9-Gadelaidic	20		54
	11-Gondoic	20	23–24	
	11-Gondoic	20		52-53
Docosenoic	11-Cetoleic	22	33–33.7	
	13-Erucic	22	34.7	
	13-Brassidic	22		61.9
Tetracosenoic	15-Nervonic	24	42.5–43	
	15-Nervonic	24		65.5

a solid have a fixed orientation and position, so the bulk solid has a volume and a shape. When the temperature of a solid is sufficiently increased, the solid melts to become a liquid. Molecules in a liquid are more weakly attracted to each other, so liquids have a volume but flow to take the shape of their container. When the temperature of a liquid is sufficiently increased, the liquid boils to become a gas. Molecules in an ideal gas act independently, so gases expand to fill the entire volume of their container.

Fats and oils

Most students are familiar with fats and oils. Fatty acids are components of the fats and oils we eat and cook with. Fats and oils, also called *triglycerides*, are made of three fatty acids plus a sugar alcohol called *glycerol*.

The triglyceride's melting point is usually very similar to that of the fatty acid of which it is composed (Figure 1). Triglycerides that are liquids at room temperature are called oils. Examples are corn, safflower,

Nanotechnology.

Liquid crystals self-assemble, which means they are an example of "bottom-up" synthesis to form a more ordered structure. [Editor's note: For an activity to model molecular self-assembly, see "Self-Assembly: How Nature Builds," p. 54 in this issue.] That structure can be controlled by surface patterning, using nanoscale features on a surface to orient a film of liquid crystals. Liquid crystals have been used as templates for further synthesis. The movement of liquid crystals in an electric field has promise in the development of molecular motors.

FIGURE 2

Examples of the chemical structures of *trans*-monounsaturated and *cis*-monounsaturated fatty acids.

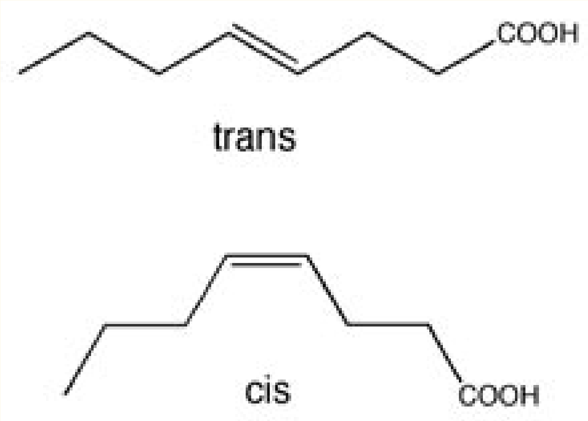
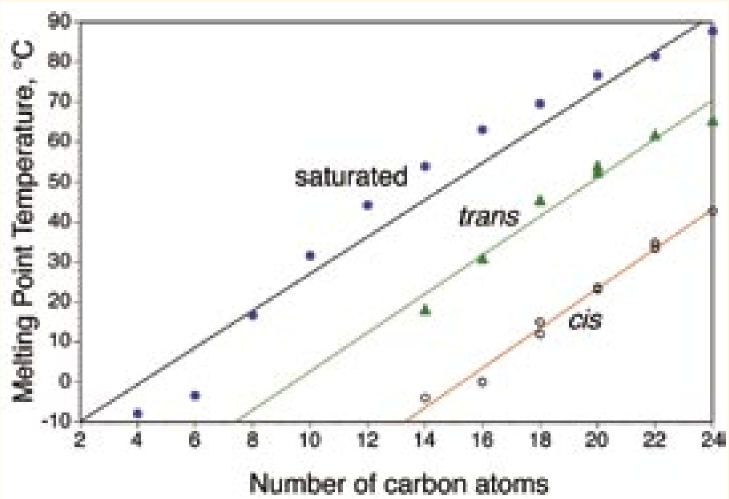


FIGURE 3

Melting point trends in fatty acids.

When all other things are equal, melting point increases with molecular weight as indicated here by the number of carbon atoms. Data from Figure 1, p. 31, is shown here for saturated fatty acids, *trans*-monounsaturated fatty acids, and *cis*-monounsaturated fatty acids.



and olive oil. Triglycerides that are solids at room temperature are called fats. Examples are butter and lard. In general, animal sources are high in saturated fat and plant sources are high in *cis*-monounsaturated oils. An unsaturated molecule contains carbon-carbon double bonds, and therefore contains less hydrogen than a saturated molecule. Thus, a saturated fat is "saturated" with hydrogen atoms. Hydrogenation of the double bond can convert an oil to a fat; food labels often indicate "partially hydrogenated vegetable oils," or *trans*-unsaturated fats, that have been chemically modified to increase their melting point (Figure 2). *Trans*-unsaturated fats rarely occur in plants and animals and mainly result from an isomerization during the hydrogenation reaction. Food labeling regulations now require inclusion of the *trans*-fat content in foods because both *trans*-fat and saturated fat have been linked to an elevated risk of coronary heart disease.

Questions and activities for students: *Consider the relationship between the sizes and shapes of molecules and their melting point. Plot the data in Figure 1, p. 31, to show the melting point as a function of the number of carbon atoms for* cis-*monounsaturated fatty acids and* trans-*monounsaturated fatty acids. How does the melting point change as the molecular size increases? Compare the two plots. How are the plots similar? How are they different?*

Answer/Concept: The strength of the forces between molecules determines the melting and boiling points of the material. One force that holds molecules together is called the London dispersion force. This force generally increases with the size of the molecule. An example is shown in Figure 3 for long chain fatty acids, $CH_3(CH_2)_nCOOH$, where the number of carbon atoms (n + 2) in the molecule is taken as an indication of the size of the molecule.

Figure 3 also shows similar data for *cis* and *trans* monounsaturated fatty acids. As the molecular size increases—again as indicated by the number of carbon atoms in the molecule—the melting point increases. Different series are shifted relative to one another, such that for a given molecular size, the saturated fatty acid has a higher melting point than the *trans* fatty acid, which has a higher melting point than the *cis* fatty acid.

Questions for students: *What is the smallest fatty acid that is solid at room temperature? What is smallest* trans*-monounsaturated fatty acid that is solid at room temperature? What is the smallest* cis*-monounsaturated fatty acid that is solid at room temperature? Consider the shape of the molecules and how they pack together at the nanoscopic level to explain the data.*

Answer/Concept: The bent shape of *cis*-unsaturated fatty acids makes them less able to pack together; the melting point decreases by more than 50°C when comparing a saturated fatty acid with a *cis*-monounsaturated fatty acid for the same number of carbon atoms. Since the *trans* acids are straighter than their bent *cis* isomers, they can pack

FIGURE 4

Each popsicle stick represents the direction of the molecules in a layer of liquid crystal.

In a cholesteric liquid crystal, stacks of layers are rotated with respect to one another, similar to a spiral staircases or screw threads. The model on the left depicts a liquid crystal at a higher temperature, and the model on the right depicts a liquid crystal at a lower temperature. The rotation angle from one layer to the next increases with temperature, so the pitch or distance between layers with the same orientation decreases with temperature.

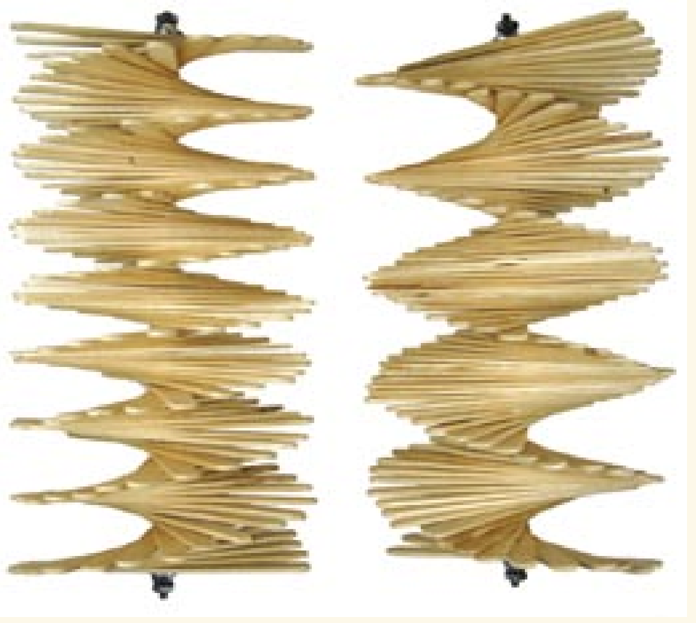


FIGURE 5

Some liquid crystal compositions.

These cholesteric esters can be obtained from Aldrich Chemical (catalogue numbers 151157, C78801, and C75802, respectively) (Sigma-Aldrich 2006) as well as other suppliers. Use these materials with normal chemical precautions. [**Safety note**: Do not inhale solids; avoid contact with skin, eyes, or clothing. Wash thoroughly after handling.] The values are approximate since they can depend on sample thickness, but the same order of transition temperature is observed for any constant thickness.

CAUTION

*Color changes observed for liquid crystal sandwiches as shown in Figure 6, p. 34.

Cholesteryl oleyl carbonate	Cholesteryl pelargonate	Cholesteryl benzoate	Transition temperature (°C) *
0.70	0.20	0.10	22
0.65	0.25	0.10	23
0.60	0.30	0.10	24
0.55	0.35	0.10	25
0.50	0.40	0.10	26
0.45	0.45	0.10	27
0.40	0.50	0.10	28
0.35	0.55	0.10	29
0.30	0.60	0.10	30

FIGURE 6

Liquid crystal in a contact paper sandwich.

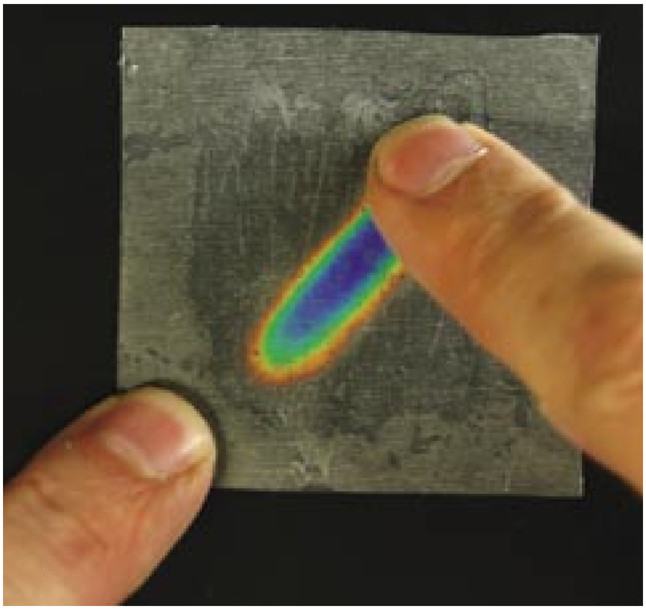
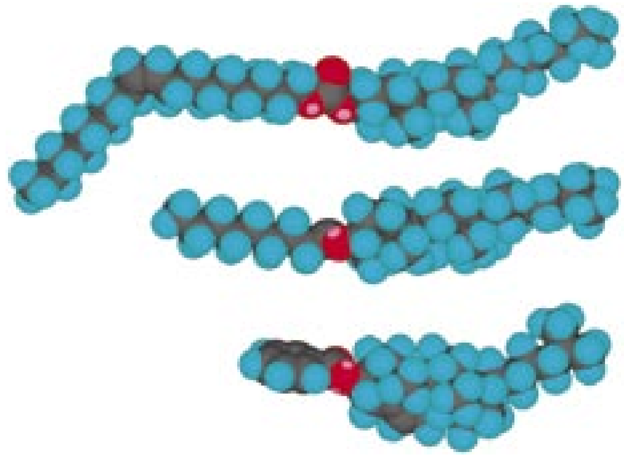


FIGURE 7

Molecular shape for cholesteryl oleyl carbonate (top) with a *cis* double bond, cholesteryl pelargonate (center), and cholesteryl benzoate (bottom).



Activity: Liquid crystal sensors.

1. Place your hand on the tabletop to warm the table. Keep your hand still.
2. Remove your hand and look closely at the table. Can you see a handprint on the table with your eyes? Place a commercial liquid crystal sheet on top of your handprint. Can you see your handprint now?
3. Take turns holding different objects (e.g., coins, keys, pencils) without showing each other. Use the liquid crystal sensors to detect which object had been held. Do some objects work better than others? Why? Do some of the liquid crystal sheets work better than others?

Because the color of a liquid crystal depends on the alignment of its molecules, anything that disrupts that alignment can be detected by a color change. Liquid crystals are used in displays where an electric field changes the alignment of the molecules to affect the polarization of light passing through them. Liquid crystals are even being studied to detect chemicals that interfere with the alignment of the molecules, including liquid crystals spread over antibodies attached to a surface.

Temperature sensitive liquid crystal sheets can be obtained from various commercial suppliers.

together more easily and therefore have an intermediate melting point. The saturated hydrocarbons are the most flexible and pack together most easily; therefore they have the highest melting points.

Liquid crystals

A liquid crystal is a state of matter with properties intermediate between solids and liquids. Not all molecules have a liquid crystalline state. The molecules in a liquid crystal can move independently as in a liquid, but remain somewhat organized as in a crystalline solid. A good analogy is a school of fish; in any region all fish swim in the same direction, but the fish can change position with respect to each other and the orientation of the school can respond to external stimuli. Liquid crystals are ordered at the nanoscale but lack long-range order (see "Nanotechnology," p. 32). Intermolecular forces that govern the interactions at the nanoscale are responsible for both the macroscopic behaviors we observe in fats and oils and the color changes we observe in liquid crystals.

Cholesteric-phase liquid crystals are those that contain molecules aligned in layers rotated with respect to one another. The name comes from cholesteryl benzoate, which was the first known example of this type of material. The rotation angle from one layer to the next increases with temperature, so the distance between layers with the same orientation, called the *pitch*, decreases with temperature (Figure 4, p. 33). When the pitch is about the same size as the wavelength of light (a few hundred nanometers) the liquid crystal diffracts light. The wavelength of the reflected color is proportional to the pitch and will change with temperature and viewing angle. As the temperature of a liquid crystal is increased, all the colors of the rainbow will be observed from red to orange to yellow to green to blue.

A series of liquid crystals can be prepared by weighing out the compositions shown in Figure 5 (p. 33) and melting the solids together with a hair dryer or hotplate. It is easier to have these samples prepared ahead of time. Cholesteric liquid crystals can degrade when exposed to moisture or air, but as long as they are stored in a sealed container, the mixture can be prepared months in advance. [**Note:** For more information and instructions, complete with video demonstrations, on how to prepare cholesteric liquid crystals visit *http://mrsec.wisc.edu/Edetc/nanolab/LC_prep/index.html* (UW MRSEC 2005).]

Questions and activities for students: *Use a spatula or popsicle stick to transfer a small amount of one liquid crystal to the sticky side of one piece of contact paper. Smear it uniformly around in the center, leaving at least some sticky area around the edge. Cover with a second piece of contact paper, sticky sides together. Rub your finger on the sandwich. Does the color change? What colors do you see?* [**Note:** *Demonstration videos for this activity are available for teachers at* http://mrsec.wisc.edu/Edetc/nanolab/LC_prep/index.html.]

Answer/Concept: If the transition temperature is lower than their body temperature, students should see a color change as they rub their finger over the contact paper sandwich (Figure 6). The liquid crystal reflects different colors depending on its temperature. As the molecules of the liquid crystal warm up, their rotation relative to each other changes, which in turn changes the observed color. A color will be reflected when the pitch is approximately equal to that color's wavelength of light. This change in pitch causes the color changes seen when we heat, cool, or apply pressure to the cholesteric liquid crystals.

Questions and activities for students: *Place the liquid crystal sandwich on the side of a beaker of warm water with a thermometer. As the water cools, record the temperature when the first color appears. Record the temperature when the last color disappears. Use the average of these two temperatures as the color transition point. Compare your value with someone else who used the same sample. Compare your value with someone else who used a different sample. Explain at the nanoscopic level why the color transition temperature is different for different compositions. (Hint: the molecular shapes of the components are shown in Figure 7.)*

Answer/Concept: The shape of the *cis*-unsaturated chain in cholesteryl oleyl carbonate (Figure 7, top) makes the molecules less able to pack together; the color transition point of the liquid crystal mixture decreases as the percent composition of cholesteryl oleyl carbonate increases.

The same intermolecular forces and molecular shapes that control whether a fat or oil is solid or liquid and whether a particular brand of margarine should be stored in a refrigerator to keep it from melting also affect the phase transitions of cholesteric liquid crystals. Just as molecular shape affects the melting points of fats and oils, shape affects the color transition of liquid crystals. Mixtures of different shape liquid crystals can be adjusted so that they reflect colors at different temperatures in order to create a thermometer. Using molecular interactions to disrupt the nanoscale structure of liquid crystals has potential for providing a whole range of biological, medical, and environmental sensors. ■

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