

## Lecture 24A • 06/18/12

### Liquid crystals

First, a little story about the discovery of liquid crystals. One of the earliest ones discovered was this compound: cholesteryl myristate; this is the molecule cholesterol that's been attached to a carboxylic acid that is a 14-carbon carboxylic acid. This cholesteryl myristate had very unusual behavior – at least unusual back in the 1800's – because it had the appearance of having two different melting points. Normally, when we do melting, we could observe melting in two different ways: one, we could examine a structure under a microscope and see the fact that, as we go from a solid to liquid, there's a definite change in material. We could also do analysis in terms of temperature versus heat that's added to a substance. If you have a solid, you add energy to it, as it's a solid, there'll essentially be a linear relationship, based on heat capacity, between how much energy is added and the temperature of that solid. At some point we'll go through a phase transition, from solid to liquid. If you're carefully adding heat during that time, the phase transition itself requires energy – a temperature change does not occur while you're at that point, so we'll level out here, until you're fully melted, and then you'll have a liquid, which is going to rise in temperature. This is what should be expected – except that, for cholesteryl myristate, here's what we get: if you look at the energy added versus the temperature, you do start out with a solid. You then go through a transition. This is what confused them, because that material was not fully a liquid. It transitioned into something [that was a fluid but] that was not really a liquid, and underwent yet another transition to a true liquid, which would then be heated up. One of the observations that made researchers back then think something strange was going on was the fact that it appears to have two melting points.

The other thing that was strange was what this did look like under a microscope. Optical rotation [is] this property that chiral materials have. In general, that's just one form of what's known as optical anisotropy, which is a phenomenon in which light travels differently, depending on the pathway it takes through a material. There's different forms of optical anisotropy: for example, calcite [is] the famous doubling stone – you look through it and it appears like you've got a mirror image. Or, you could have what makes it look like an image is transmitted through this stone. Very clear, white-looking material; you put it down on a picture, it looks like the picture's right on top of that crystal that you've just put on it. Optical anisotropy is this idea that you have differences in the way that light travels through a substance, which you can notice when you look at a substance through crossed polarizers.

Crossed polarizers, it's this idea: that you have some kind of light source that, initially, is going to give off light that's travelling in all directions, but also in all orientations, relative to that light beam. Light is really just a wave, or can be represented as a wave, that has both a magnetic and an electric field to [it] that are perpendicular to each other. Even though those fields are perpendicular to each other, they can then be arbitrarily arranged relative to some reference point – in other words, when the light comes out, maybe it's wiggling up and down this way, or at an angle, or flat, or in all of them at the same time, cause it's an unorganized light source. You then put it through a polarizer, which will only allow light travelling in one way to pass through it. If you were then to pass the light through a perpendicularly-arranged polarizer, you won't get any light through, unless, somehow, the light is twisted in between the two polarizers, because if you were block light, let's say, so that it only could oscillate in the vertical orientation, then you pass it through one of these horizontal polarizers, the light simply gets blocked, unless you turn the polarizer to match, and then that would allow the light to pass through, or unless between the two polarizers you had some kind of optical activity. We could change the angle between the two polarizers, and that would be the optical rotation, from which if you know the path length and the concentration, you could calculate this thing called specific rotation. No light passes through orthogonal polarizers, unless a sample twists the light in between. We put the sample in between, and then light change[s] directions.

This kind of behavior was known even back at that time through crystalline samples – you take different rock samples, for example, and make very thin slices of those rocks. You can have some idea of the type of crystals that form, the patterns that form, by looking under polarized light microscopy (PLM). It was thought that, because of the structure of these solids, the crystalline structure, that it caused this optical anisotropy that could be measured under polarized light microscopy. You get all these really interesting, pretty-looking patterns of light through a solid because of the arrangement of atoms that you have. Here's the other piece of evidence to go along with this second melting point that gave people a bit of pause: because this liquid sample, this thing that seemed to have a second melting point, exhibited some of these same types of patterns of light with the liquid-looking sample that you'd normally expect from something that was solid. A true liquid has absolutely no order to it. In a true liquid that's not chiral, so it doesn't have this anisotropy to it, the liquid samples shouldn't cause anything to happen when you put it in between crossed polarizers. Because something happens when you take this apparently-liquid sample and put it between crossed-polarizers, the thought was: there must be something different about the structure of this "liquid". Normally, only chiral liquids or solids such as minerals with a particular structural arrangement display any patterns using PLM. Liquids, since they are normally isotropic, which means structureless, shouldn't show up with any particular patterns under PLM.

There's this example molecule that we're working on, the unusual behavior it has is two-fold: one, when melting it carefully, it appears to go through two separate melting transitions. During this middle transition, it's that middle form that appears to have some kind of activity under polarized-light microscopy. Polarized-light microscopy is exactly this type of thing involving crossed polarizers, except we're not simply looking for when the light has a maximum or minimum as you're twisting these polarizers – that's how optical rotation is measured: you find out where, if you have the crossed polarizers, you have complete darkness, find out how that compares to the original polarizer, you how much light has twisted. This time, we're not just looking at the potential for optical rotation, we're looking for the specific patterns generated, the visual patterns, which can be used to say something about the structure of the material. Under PLM, you saw this kind of activity, which means there's some kind of optical anisotropy, which means there's some kind of structure there. Pure liquids shouldn't be visible, not with these kind of patterns, under PLM. Isotropic means completely the same structure throughout, pass through that material in any direction and you encounter pretty much the same thing. [is a racemic mixture isotropic?][calcite] What was thought was going on is that this must be some kind of mesophase – something that's in between a solid and a liquid, something that has the ability to flow liquid does, because after this first melt, you have a fluid, something that was not a solid – like a goo, you could say. And yet, it had the structure of a crystal. So it moved like a liquid, but it had the structure of a crystal – that's where the term liquid crystal comes from. That's a little bit about the history of the early discoveries involving liquid crystals.

The problem, if you want to express it that way, is it appears to melt twice, and the first melt forms an optically-active material under PLM. This solution is this idea of a liquid crystal mix: liquid, which means that it's fluid, meaning it's mobile; and crystal, which means it has internal structure. Mesophase – a phase in between a solid and liquid that has the properties of both.

#### Classes of liquid crystals

There are two main categories: those in which the type of phase formed by a liquid crystal is mainly temperature-dependent; and then are those that the form of the liquid crystal it exhibits depends on the concentration. We have what are known as thermotropic liquid crystals and lyotropic liquid crystals. There are other [classifications]. Thermotropic liquid crystals can be further divided into two sub-categories: nematic and smectic. [nematic – nemata? thread: thread-like structures that are seen under PLM][smectic – related to soap]

#### Thermotropic liquid crystals

They change phase primarily based on temperature. They usually form a liquid crystal [LC] without a solvent. What's the general structure of one of these liquid crystals? Cholesteryl myristate had a long carboxylic acid tail that was very flexible in nature; it was long, but then it had the ability to wiggle around. And, it had this multi-ring core. That's the general shape of a thermotropic liquid crystal. Imagine that you've got this juxtaposition between the much more randomly-oriented, flexible tails that much more easily can slip past each other and start having liquid behavior, versus these more rigid cores that are more likely to more efficiently stack with each other and stay crystalline in nature. This is one way to generate this liquid crystal phase: to have the cores that are so attracted to each other that, even as the rest of the compound melts, these try to maintain some kind of spatial relationship with each other. But, the more random, wiggly chains do allow the compound to melt more easily. It's caught in between the influences of these two parts of the molecule. These cores try to maintain order due to intermolecular forces (IMF). [phospholipids are lyotropic; lecithin] Because that has charge, there's a dichotomy of its phase compatibility, whether it wants to go into oil versus water things. This doesn't involve phases, just attractions between individual molecules. The mechanism of forming a mesophase is a different type of thing in these type of lyotropic systems that you would have in the phospholipid bilayers, which are lyotropic, they're sensitive to concentration. [thermotropics in LCDs] The chains melt more easily, since there's not as efficient packing; they're more flexible. Thermotropic mesophases are generated in liquid crystals due to the contrast of the flexibility of the chains and the order caused by the cores.

As far as the different types of phases, the two main classes, nematic versus smectic, it's degrees of order. In terms of order versus disorder, you go from a solid first to smectic phases (smectic C and smectic A); they then go to nematic phases, and then to liquid. There can be multiple stopping-off points, depending on the type of crystal; there can be multiple transitions. Here's smectic C, smectic A, and nematic. Nematic liquid crystals have random arrangement in terms of layers; if you go through [the] material, there's no macroscopic [layering] order. However, they all tend to have a certain slant to them, and they all seem to be pointed in one direction. That average orientation is known as the director. You can have different domains. A domain is a region in space in which the molecules are all similarly aligned. In a larger sample, you can have regions where the director is pointing in one direction; you move to just a little different place in the sample, the director's pointing somewhere else. The nematic phases are characterized by having a director. The difference between a nematic phase and a smectic phase is that in the smectic phases, there'll be these rows that form. They're not rigid: molecules can move between the different rows; this is a liquid-like phase, there is fluidity. But, they also self-organize into these strata. If you put even more order to it, you can have a smectic C phase in which the molecules all have an average slant to them within each row. There's even a version of this that's often important in making materials [NLO] called a chiral smectic C phase, where the rows, as you go from row to row to row, the director twists around like a helix from one row to the next. If you have some kind of asymmetric in structure, if you have something that's a little bit different about it, then either through an electric field or a magnetic field, it gives you a grip on the molecule.

Imagine that the cores of these liquid crystals, even in the nematic phase, had something that was sensitive to an electric or magnetic field. You apply a field, that means you can change the direction, you can move the director for that phase. What if in one direction the liquid crystal phase is transparent, but because these are non-anisotropic materials, if you flipped it the other direction, maybe it becomes opaque – liquid doesn't pass well through. What if it changes color if you flipped them? There's your basis for LC technology for display screens. You have layers of liquid crystals that you apply an electric current so they're being flipped around one direction of another. Of course, that brings up tons of design considerations: what is the viscosity of this material that you're trying to flip the molecules around in? How much current does it take? Will that current itself cause a decomposition of the molecule? How long will these molecules persist in whatever binding layers you use to trap them between the plates that end up being the screen?

The difference between the [smectic] C and the [smectic] A? [Smectic] C has molecules tilted within the layers. That's like another degree of order, which makes it more like a solid. The reason I listed these phases in the order that I did is because if you had a liquid crystal that can exhibit all of these different phases – that's a huge issue in liquid crystal design: aside from making a core that might be sensitive to magnetic or electric fields, so that you can manipulate them, how does putting one more carbon affect the range of temperatures that liquid crystals can be seen at? By varying structure, maybe the smectic C [phase] won't appear for a typical molecule; maybe a [smectic]A phase will appear. But if there are multiple phases, the [smectic] C [phase] will be the one closer to solid, so it forms first cause there's more order; the smectic A, since you lose that directionality, now the molecules across all layers are oriented the same way; that's less order; they're more similar, so that'll form next. You lose the layers and it just becomes a sea of molecules that are oriented one way – that's the smectic; and then, once those molecules no longer have an average order, they're just randomly oriented, that's a liquid. That's the difference between these phases.

#### Lyotropic LCs

Lyotropics are liquid crystals that mainly change phase based on concentration. Let's take a phospholipid as an example. This is ammonium palmitate [16-carbon]. If we take two of those and attach them to glycerol. [lecithin] Here's how we're going to represent it: this would correspond to the ionic headgroup. Notice we do have something that's got charge on it. [chalkboard screech] Here's that ionic portion of the molecule. Look at all this long organic tail group we have here. If we reduce this to having this hydrophobic group and this hydrophilic group – hydrophobic means water-fearing which means something like this that's non-polar that doesn't want to go into the water layer, versus hydrophilic which is something like this charged species that does want to go into the water layer. The molecule wants to do both, in fact. We call this type of molecule an amphiphile – compatible with both polar and non-polar phases. There's another term often conflated with this, which is surfactant [surface-active] You have the junction point between an organic and an aqueous phase, that interface between those two phases, that's what these surfactants act at.

Micelle. What is a micelle? There's what known as the critical micelle concentration, which is the minimum amount of this surfactant, this amphiphile, that you have to have around before it spontaneously starts forming these structures. Depending on how big these hydrophobic tails are, depending on how intense the charge is on this headgroup, depending on how small or large that headgroup is, if you change the physical parameters of this molecule – what if you ended up with a tailgroup that was broad versus a tailgroup that was really narrow – how might that affect the packing of this molecule? Certain structural changes can change how much you need around in order to make a micelle [or some other phase]. Once you get above a certain minimum concentration, they hydrophobic portions of the molecule, in water ... the only reason these micelles form is to minimize energy, to make it so that the organic bits dissolve in other organic bits, because the ends up being thermodynamically favorable, and the polar bits end up dissolving in the water. The reason that oil and water don't mix is entropy; it turns out to be entropically unfavorable because you end up organizing water. To keep the two separate, that's more thermodynamically favored. Like dissolves like is a thermodynamic process. The organic bits try to find each other here, because the majority of this is a water environment; that's why the organics get pushed to the inside. The way that soaps like ammonium palmitate – that's a really rudimentary form of soap: you have the non-polar tail, but you have the ionic headgroup. You add soap to a mixture, it forms, in low concentration, these micelles. Grease, fat, whatever, dissolve on the inside, then it gets carried away by water, because the outside of that structure's surface is hydrophilic.

Put more liquid crystal in, though, and you can form a variety of other phases [phospholipid bilayers]. Lamellar phase, which means you get sheets of these liquid crystals where all the head groups will be oriented one way, and all the tail groups will be oriented another. You might get stacks of these sheets that form. Sometimes the layers will fold on top of themselves, so that maybe you'll get headgroups on either side of these layers, so they're called bilayers. These are the types of structures that phospholipids form that are found in membranes. Besides the lamellar phases, you could have columnar phases, which look like this. Instead of a micelle, you have what looks like a micellar structure, except that it is extended into these indefinite-length tubes. Imagine that the entire surface of this tube is hydrophilic and the inside is organic, hydrophobic. These tubes can then pack into cubic, which means square, or hexagonal phases, which means it's like big, long hexagons. Using x-ray [diffraction], you can prove that these columns form. You can also have inverse hexagonal, if your soap concentration gets high enough where there's only a little bit of water.

Now, the organic tails become the outside of these columns, so they'll still pack in a hexagonal fashion, but the main medium between all of these will be an organic phase. All of these lyotropic liquid crystals are just liquid crystals, which means that they're mobile. [polymerize]

---

Structures not available for this lecture.