

History of Liquid Crystals Goes from Cloudy to Clear

Liquid crystalline materials display a degree of structural order intermediate between that of crystals and that of isotropic liquids. When samples of liquid crystals were first examined in the mid-1800s, they were not immediately recognized as a novel and exotic phase of matter. For instance, a chemist investigating the properties of natural fats noticed that one material, stearin, appeared to have two distinct melting points. The first transition was from solid to a cloudy liquid, and the second from cloudy to clear liquid. One possible explanation for such behavior could be the presence of an impurity that gives rise to a two-phase coexistence region in the phase diagram, so it was not immediately obvious that the cloudy liquid was anything remarkable.

Another set of early observations in the mid- to late-1800s involved the use of polarized light. Crystals can alter light's polarization, and the effect changes dramatically when a crystal sample is rotated with respect to the light beam. Most liquids have no effect on polarization; liquids containing chiral molecules can alter light's polarization, but the effect shows no variation with rotation of the sample. Thus it was an important discovery that certain biological materials such as the outer covering of a nerve fiber mixed with water could produce changes in light's polarization, and that the effect varied with the angular orientation of the sample. This was perhaps the first clear evidence that such liquids are not isotropic but contain some kind of directional order. A few researchers also noted that some compounds synthesized from cholesterol briefly turned bright blue as they cooled, an effect that was not fully explained until nearly a century later.

A German physicist, Otto Lehmann, was the first scientist to construct a microscope with a heating stage, and later added polarizers. Lehmann's goal was to observe the process of crystallization, and using his microscope he saw that some materials appeared to have an intermediate amorphous phase between crystal and liquid. In 1888 an Austrian botanist, Friedrich Reinitzer, found that an organic material closely related to cholesterol had two distinct melting points, and wondered what the intermediate cloudy liquid phase could be. He sent samples to Lehmann, who examined them in his microscope.

Lehmann concluded that the liquid was a uniform fluid phase—not a two-phase mixture—and observed that it affected polarized light as a crystal would. Thus he coined the name “liquid crystal.”

Daniel Vorlander, a chemist, headed a group that went on to synthesize many liquid crystalline materials, including the first material known to have two distinct liquid crystalline phases. He realized that materials whose molecules were linear and elongated in shape were the most likely to display liquid crystalline phases. Within a few decades the major classes of liquid crystal phases were known. In a 1922 paper, Georges Freidel of France outlined the basic structure of nematic, smectic, and cholesteric phases. In the isotropic liquid,

molecules point in all directions, while in the nematic phase, the molecules tend to align with one another. The local alignment direction is called the director. The name “nematic” is derived from the Greek word for “thread,” and refers to the threadlike defects observed in the director when a sample is viewed in a microscope with crossed polarizers. From careful study of defect structures, Freidel concluded that the smectic phase had not only directional order but also layering. The name smectic is derived from the Greek word for “soap,” as smectic phases have material properties similar to those of soap. The cholesteric phase, also known as the chiral nematic phase, displays local alignment of molecules as in the nematic, but with the local

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director orientation undergoing a periodic twist along one direction. This name was chosen because various materials closely related to cholesterol can take on this phase. Freidel also understood that liquid crystals could be affected by applied electric and magnetic fields, a property that is critical to their use in display devices.

In the years prior to World War II, x-ray scattering experiments verified unambiguously the presence of directional ordering in liquid crystalline materials, and theoretical studies like those made by F.C. Frank in England provided explanations for the forms of the various phases. But by the end of World War II, most researchers lost interest in studies of liquid crystals for lack of any obvious technical application.

The field blossomed again in the 1960s, as an accurate microscopic theory of liquid crystal phases was developed by Wilhelm Maier and Alfred Saupe of Germany, and researchers at RCA invented the first liquid crystal display (LCD) by switching a liquid crystal from cloudy to clear by the applica-

tion of an electric field. LCDs were used in digital watches, calculators, and clocks, and in recent years also for computer displays, telephones, and televisions. The most common display method since the 1970s has been the "twisted nematic," in which a nematic phase material is confined between glass sheets treated to align the director with a 90 degree twist between one sheet and the other. Crossed polarizers are placed above and below, and a reflector beneath. When no electric field is applied, the twisted nematic rotates the polarization of ambient light so that the light is reflected, giving the display a silvery appearance. When an electric field is applied, the alignment of the nematic changes the polarizing effect so that ambient light is absorbed rather than reflected, and the display appears to be black. More advanced technologies make use of other liquid crystalline phases; ferroelectric liquid crystals can provide superior response time and improved contrast and viewing angle.

Modern developments have included

the discovery of discotic liquid crystals, composed of flat, disklike molecules, and the development of polymer liquid crystals, such as Kevlar, which is formed from a liquid crystal phase of polyamide and is used in tires and bullet-proof vests. The bright blue colors first observed in cooling cholesterol-like materials in the 1880s were finally identified in the 1980s as unusual "blue phases" consisting of a liquid crystal with a lattice of defect lines whose periodicity is comparable to the wavelength of light. Liquid crystal science has also produced windows that can be switched electrically from clear to opaque. Liquid crystal phases of biomaterials—such as those first observed in the late 1800s—continue to be discovered, including solutions of DNA, polypeptides, and lipids.

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FOR FURTHER READING: P.J. Collins, *Liquid Crystals: Nature's Delicate Phase of Matter*, Princeton University Press (Princeton, 1990).

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