An Introduction to Liquid Crystals

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Chapter 1

History

Liquid crystals were first discovered, by accident, in the late nineteenth century at the Karl-Ferdinands-Universität by Austrian botanist and chemist Friedrich Reinitzer (1857–1927) (see figure 1.1(a)). In 1888, Reinitzer was making esters of cholesterol for his studies of plants. While examining the properties of cholesterols extracted from carrots, he noted that cholesteryl benzoate (i.e. $C_{34}H_{50}O_2$) exhibited not one, but two melting points that were associated with *'birefringence'* and vivid iridescent color changes. (The term *'birefringence'* will be introduced in section 4.1. Experimental techniques to determine the birefringence of a liquid crystal will be described in section 5.4.) Strangely, cholesteryl benzoate had the optical properties of crystals, but still flowed like a liquid. Reinitzer was unsure what to do about his discovery so he wrote a letter on March 14, 1888, describing his findings to German physicist Otto Lehmann (1855–1922) at Aachen University (see figure 1.1(b)). In his letter, Reinitzer stated that at 145.5 °C, the substance appeared to be a cloudy, fully liquid melt, while at 178.5 °C, the substance became entirely clear. Reinitzer also noted that these transitions were completely reversible. Reinitzer asked Lehmann, who was one of the first researchers to combine a polarized optical microscope with a hot stage, to confirm the unusual phenomenon of two melting points. Today, the hot stage and polarized optical microscope are considered standard equipment in liquid crystal research. Lehmann, also working on materials with similar behavior, responded by labeling the substances as, *'flüssige krystalle'* or, *'flowing crystals.'* Thus, Lehmann coined the phrase by which these substances are now known: *'liquid crystals.'*

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(a) (b)

Figure 1.1. The *'founders'* of liquid crystal research. (a) Friedrich Richard Reinitzer (1857–1927) and (b) Otto Lehmann (1855–1922).

Etymology:

The word *'liquid'* is derived from the Latin words *'liquere'* or *'liquidis,'* which translate into *'flowing'* or *'capable of flowing.'*

The word *'crystal'* is derived from the Greek word *'krústallos'* that translates into *'clear ice.'*

Reinitzer and Lehmann continued their correspondence and came to realize that they were observing a new, intermediate phase of matter—that is to say, a phase that had properties of both a crystal and a liquid. Reinitzer then published what is considered the first recognized research on liquid crystals: *'Beiträge zur Kenntnis des Cholesterins'* (i.e. *'Contributions to the Knowledge of Cholesterols'*) [1]. While Reinitzer's interest in liquid crystals waned, Lehmann continued researching the mysterious substances. Using his combination hot stage-and-polarized optical microscope, he was able to make high-temperature observations. He learned to control the conditions under which these materials changed phases and could thereby study the properties these substances exhibited while in their various phases. Lehmann's paper, *'Über fliessende Krystalle'* (i.e. *'On Flowing Crystals'*), presented on October 25, 1889, opened a new chapter of materials research and laid the foundation of the science of liquid crystals [2].

At first, liquid crystals were thought to be something akin to *'novelties'* or *'curiosities'* in nature—strange, peculiar substances that were interesting to observe but that provided no practical application. However, liquid crystal research quickly flourished and since that time, thousands of organic compounds have been found to exhibit this same type of behavior [3]. In the early part of the twentieth century,

(a) **(b)** **(c)** **(d)**

Figure 1.2. Pioneers of liquid crystal research. (a) Georges Friedel (1865–1933), (b) Vsevolod Fréedericksz (1885–1944), (c) George Heilmeier (1936–2014) and (d) Pierre-Gilles de Gennes (1932–2007). ((d) credit: Wikimediacommons / CC-BY-SA 2.5 (https://creativecommons.org/licenses/by-sa/2.5/deed.en).)

German chemist Daniel Vorländer (1867–1941) began synthesizing various liquid crystalline samples and, by his retirement in 1935, determined methods for creating most of the known liquid crystals at that time. In 1922, French mineralogist and crystallographer Georges Friedel (1865–1933) published a 200 page work *'Les États Mésomorphes de la Matiere'* (i.e. *'Mesomorphic States of Matter'*) in which he proposed the classification scheme of liquid crystalline phases that are still used today (see figure 1.2(a)) [4]. Friedel's classification scheme will be discussed in more depth in chapter 4. In 1927, Russian physicist Vsevolod Fréedericksz (1885–1944) applied external fields to produce phase transitions in liquid crystals (see figure 1.2(b)). When a sufficiently strong electric or magnetic field is applied to a liquid crystal in an undistorted state, a phase transition will result as components of the crystal align to the field. This transition, labeled the *'Fréedericksz transition,'* is discussed in chapter 5. Starting in the 1940s, Scottish organic chemist George Grey (1926–2013) characterized the phases of various samples under different conditions and essentially systematized the field of liquid crystals. His book, *'Molecular Structure and the Properties of Liquid Crystals,'* published in 1962, became instrumental in laying the foundation of the liquid crystal display industry [5]. Despite Grey's work, the high-temperature needed to cause samples to undergo various phase transitions made initial attempts at displays very impractical. Over time, chemists learned to mix various compounds to produce samples capable of operating over a wide temperature range.

Once chemists synthesized samples that could undergo these phase changes at room temperatures, practical display devices soon became possible. As a result, research into flat panel liquid crystal displays took off in the 1960s, thanks in large part to researchers at the RCA Corporation in Princeton, New Jersey. There, in 1962, physical chemist Richard Williams (1927–) was working on the concept of a TV that was light enough to mount directly to a wall. He applied a voltage to a thin layer of liquid crystals and generated *'zones'* or *'domains'* of striped patterns as the sample changed its alignment in response to the applied field. These *'Williams Domains'* were the precursors of the pixels found in today's liquid crystal displays.

In the late 1960s, George Heilmeier (1936–2014), also at RCA and working on the *'TV-on-a-wall'* concept, continued Williams' research and discovered several new electro-optical effects in liquid crystals. He demonstrated the first liquid crystal display, using what he called the *'dynamic scattering mode,'* soon afterwards. Heilmeier and his team are usually credited with the invention of the liquid crystal display (see figure 1.2(c)). In the 1970s, Indian physicist Sivaramakrishna Chandrasekhar (1930–2004) synthesized disc-shaped molecules for use in liquid crystal research, followed shortly thereafter by Chinese physicist Lui Lam (1944–), who did the same for bowl-shaped molecules (called *'bowlics'*) in the 1980s. The shapes of the components of liquid crystalline systems will be addressed in chapter 3.

By the 1990s, research into liquid crystals had clearly grown and evolved into a field rich in its potential for advancing fundamental science as well as its innovative applications beyond the realm of display technologies. As a testimony of how far the field has come in the brief time since Reinitzer's discovery, French physicist Pierre-Gilles de Gennes (1932–2007) was awarded the Nobel Prize in Physics in 1991 for his work on liquid crystals (see figure 1.2(d)) [6]. The citation on his prize reads: *'for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymers'* [7]. However, to date, de Gennes is the only scientist to receive the prize in the area of liquid crystals.

References

[1] Reinitzer F 1888 Beiträge zur kenntniss des Cholesterins *Monatsh. Chem.* **9** 421–41

[2] Lehmann O 1889 Über fliessende Krystalle *Z. Phys. Chem.* **4** 462

[3] Chandrasekhar S 1988 Recent developments in the physics of liquid crystals *Contemp. Phys.* **29** 527

[4] Friedel G 1922 Les États Mésomorphes de la Matiere *Ann. Phys.* **9** 273–474

[5] Gray G W 1962 *Molecular Structure and the Properties of Liquid Crystals* (Cambridge: Academic)

[6] de Gennes P G 1974 *The Physics of Liquid Crystals* (London: Oxford University Press)

[7] Nobel Media *The Nobel Prize in Physics 1991* Nobel Prize.org (15 April 2019). Retrieved from https://nobelprize.org/prizes/physics/1991/summary/ on 4 April 2019