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G. W. Gray
studied chemistry at the University of Glasgow, UK, and received his Ph. D. from the University of London before moving to the University of Hull. His contributions have been recognised by many awards and distinctions, including the Leverhulme Gold Medal of the Royal Society (1987), Commander of the Most Excellent Order of the British Empire (1991), and Gold Medallist and Kyoto Prize Laureate in Advanced Technology (1995). His work on structure/property relationships has had far reaching influences on the understanding of liquid crystals and on their commercial applications in the field of electro-optical displays. In 1990 he became Research Coordinator for Merck (UK) Ltd, the company which, as BDH Ltd, did so much to commercialise and market the electro-optic materials which he invented at Hull University. He is now active as a Consultant, as Editor of the journal "Liquid Crystals" and as author/editor for a number of texts on Liquid Crystals.

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Chapter I
Introduction and Historical Development

George W. Gray

1 Introduction

It is with a sense of responsibility that I begin this summary of the historical development of liquid crystals, because one of the two authors of the original *Handbook of Liquid Crystals* of 1980 [1] was Professor Hans Kelker, a friend and a very well informed authority on the history of the subject and the personalities involved in the earlier stages of its emergence. Those who attended the Twelfth International Liquid Crystal Conference in Freiburg in 1988, which marked the centenary of the discovery of liquid crystals, and heard Professor Kelker's plenary lecture – *Some Pictures of the History of Liquid Crystals* [2] – which was part of a conference session devoted to a historical review of the field, will know this. Here he demonstrated that he was in possession of a very wonderful collection of manuscripts and photographs relating to the scientists who, in the latter part of the nineteenth century and the early part of the twentieth century, laid the foundations of our present-day knowledge of liquid crystals.

I am not in that privileged situation, but I have worked in the field for 50 years, beginning my first experiments on aromatic carboxylic acids in October 1947. I have therefore worked through approaching half of the historical span of the subject, including the most recent years during which the subject has expanded and deepened so markedly. I hope this first-hand experience will counterbalance my lack of detailed historical knowledge of the earlier years, as possessed by Professor Kelker. Were he alive today, I hope he would not disapprove of what I write in this chapter.

The history of the development of liquid crystals may be divided into three phases:

1. The period from their discovery in the latter part of the nineteenth century through to about 1925, the years during which the initial scepticism by some that a state of matter was possible in which the properties of anisotropy and fluidity were combined, through to a general acceptance that this was indeed true, and publication of a first classification of liquid crystals into different types.
2. The period from 1925 to about 1960, during which general interest in liquid crystals was at a fairly low level. It was a niche area of academic research, and only relatively few, but very active, scientists were devoted to extending knowledge of liquid crystals. Two world wars and their aftermaths of course contributed greatly to the retardation of this field during this period. Taking the aftermaths of the wars into account, probably at least 15 years were effectively lost to progress during this second phase.
3. The period from 1960 until today is by contrast marked by a very rapid development in activity in the field, triggered of course by the first indications that technological applications could be found for liquid crystals. These early indications

were justified, and led to today's strong electro-optical display industry. The quest for new applications stimulated research and the flow of financial support into the involved areas of chemistry, physics, electrical and electronic engineering, biology, etc. As a marker of this activity, the numbers of papers and patents published in 1968 was about 2000 and this had risen to 6500 in 1995.

2 The Early Years up to About 1925

The question as to when liquid crystals were discovered must now be addressed. In pinpointing a discovery, it is necessary to distinguish simple observations of an unusual phenomenon or effect from observations that develop into an understanding of the meaning and significance of that phenomenon or effect. If we accept that the latter criteria must be met to justify the word discovery, then the credit for the discovery of liquid crystals must go to Friederich Reinitzer, a botanist of the Institute for Plant Physiology of the German University of Prague, who in a paper submitted on May 3, 1888 [3], described his observations of the colored phenomena occurring in melts of cholesteryl acetate and cholesteryl benzoate. In addition, he noted the "double melting" behavior in the case of cholesteryl benzoate, whereby the crystals transformed at 145.5 °C into a cloudy fluid, which suddenly clarified only on heating to 178.5 °C. Subsequent cooling gave similar color effects (but see later) to those observed on cooling the melt of cholesteryl acetate. Today of course we know that the colored phenomena reported by Reinitzer are characteristic of many cholesteric or chiral nematic (N*) liquid crystal phases.

In his article [3], Reinitzer acknowledges that other workers before him had observed curious color behavior in melts of cholesteryl systems. He mentions that Planar in Russia and Raymann in Paris had noted violet colors reflected from cholesteryl chloride and that Lobisch in Germany had observed a bluish-violet flourescence in the case of cholesteryl amine and cholesteryl chloride. Two things distinguish these earlier observations from those of Reinitzer. These are Reinitzer's recording of the "double melting" property of cholesteryl benzoate, and the fact that Reinitzer carried out preliminary studies on thin films of cholesteryl benzoate and noted the range of spectral colors reflected as the temperature decreased until crystallization occurred and the complementary nature of the colored light when the sample was viewed in transmission. Moreover, Reinitzer knew of the excellent work of the German physicist Professor Otto Lehmann, then at the Polytechnical School at Aachen, in designing and developing polarization microscopes, and recognized that Lehmann could advise on the optical behavior of his cholesteryl esters.

The approach to Lehmann was made in March 1888 and the correspondence is excellently documented in Kelker and Knoll's article [2]. This interaction led to agreement that Reinitzer's materials were homogeneous systems of which Lehmann wrote in August 1889: "It is of high interest for the physicist that crystals can exist with a softness, being so considerable that one could call them nearly liquid." This led quickly to the submission by Lehmann, by then at the University of Karlsruhe, of his paper *Über fliessende Kristalle* to the *Zeitschrift für Physikalische Chemie* [4].

Significantly, this uses for the first time the term liquid crystal. As a consequence of the above events and the development of our understanding of liquid crystals which stemmed from them, we must clearly acknowledge Reinitzer as the true discoverer of liquid crystals and the date of the event as March 14, 1888.

It should be noted that the discovery related exclusively to materials we now class as thermotropic liquid crystals, wherein the liquid crystal phases form either on heating crystals or on cooling isotropic liquids, that is, as a consequence of thermal effects. In addition to thermotropic liquid crystals, a second class of fluid anisotropic materials is known, namely, lyotropic liquid crystals where the disruptive effect on the crystal lattice involves a solvent (often water), coupled where necessary with thermal change. Here, the order of the crystal is broken down by the solvent and the molecules form micelles which then arrange themselves in an ordered way, while allowing fluidity. Excess of solvent completes the decrease in order and an isotropic solution is formed. Observations of anisotropy and optical birefringence in such systems were indeed made well before Reinitzer's discovery, but like the observations of Planar, Raymann, and Lobisch, there was no followthrough to a realization of the full significance of what was being seen. These observations were made by Mettenheimer [5], Valentin [6], and Virchow [7] in the period 1834–1861, and involved studies of biological samples derived from nerve tissue, for example, myelin, a complex lipoprotein which can be separated into fractions and which forms a sheath round nerve cells. In water-containing sodium oleate, these sheaths develop what have been called myelinic forms visible microscopically, especially in polarized light, as fluid, birefringent entities. Progress on these anisotropic systems was however impeded by the complexity and lack of reproducibility of the biological systems involved, and whilst predating the studies of Reinitzer and Lehmann are not generally regarded as marking the discovery of liquid crystals.

Following publication of his paper in 1889 [4], Lehmann continued work with liquid crystals and indeed dominated the scene in the late 1800s and the early part of the twentieth century, continuing to publish on liquid crystals until the year of his death in 1922.

Turning to purely synthetic materials, unlike the cholesteryl esters which were of natural origin, examples of liquid crystal behavior were found in these by Lehmann in 1890. The materials were azoxy ethers prepared by Gattermann and Ritschke [8]. The next ten years or so saw studies of *p*-methoxycinnamic acid and in 1902 the synthesis by Meyer and Dahlem [9] of the first smectogen, ethyl *p*-azoxybenzoate, although not recognized structurally for what it was at that time. Through studying such materials, Lehmann did however recognize that all liquid crystals are not the same, and indeed in 1907 he examined the first liquid crystal material exhibiting two liquid crystal phases. This material had what was later shown to be a smectic A (SmA) and a cholesteric (N*) phase. Significantly in the context of much later work in the field of applications, he also reported on the aligning effects of surfaces on liquid crystals.

Despite the growing number of compounds shown to exhibit liquid crystal phases (and in a short number of years Vorländer contributed about 250), the acceptance of liquid crystals as a novel state of matter was not universal. Tammann in particular [10] persisted in the view that liquid crystals were colloidal suspensions, and was in bitter argument with Lehmann and Schenk who upheld the view that they were homogeneous systems existing in a new state distinct from the crystalline solid and isotropic liquid states. Nernst [11] too did not subscribe to the latter view and believed that liquid crystals were mixtures of tautomers.

There was however a steadily growing body of evidence supporting the view that liquid crystals represent a true state of matter and acceptance of this slowly grew, aided by the excellent reviews of 1905 by Schenk (*Kristalline Flüssigkeiten und flüssige Kristalle*) [12] and Vorländer (*Kristallinisch-flüssige Substanzen*) [13]. There then followed the important review of optical effects by Stumpf [14] and, much later, an important paper was that by Oseen [15] on a kinetic theory of liquid crystals. The real seal of acceptance of liquid crystals for what they are, i.e., a fascinating and distinct state of matter, was however given in 1922 in the famous publication by G. Friedel [16] in the *Annales de Physique*, entitled *Les États Mesomorphes de la Matière*.

Here, in connection with Friedel's article and on a personal note, I well remember my research supervisor, Professor and later Sir Brynmor Jones, sending me to the library to find the appropriate journal, requiring that I produce a complete translation from French of all 273 pages in order to be "fully familiar with all that had been written". This I dutifully did in the fullness of time, and on taking my translation to show my supervisor, he then reached up to a shelf and withdrew a black notebook saying "now you can compare the quality of your translation with mine!" I learned much from that exercise, as will anyone who repeats it today.

In addition to containing a wealth of information on microscopic techniques and materials, Friedel's article represented in 1922 the first classification of liquid crystals into types, i.e., nematic, smectic and cholesteric. Today, of course, cholesterics are known simply as chiral nematics with no need that they be derived from cholesterol, and we recognize the existence of several polymorphic smectic forms, whereas Friedel allowed for only one (today's smectic A; SmA).

Friedel did however understand the layered nature of smectics, firstly through the stepped edges possessed by smectic droplets with a free surface, and secondly through his detailed studies of the optical microscopic textures of thin films of smectic phases. He understood the optical discontinuities, i.e., the defects, of the smectic focal-conic texture and saw the relationship of the black lines delineating ellipses of different eccentricities and their associated hyperbolae in terms of focal-conic "domains" which may be divided into a series of parallel, curved surfaces known as Dupin cyclides. He also understood that the optically extinct homeotropic textures of smectics of the type he studied gave positive uniaxial interference figures consistent with systems of layers lying flat to the surface. His microscopic studies demonstrated the immense value of the optical microscope as a precise scientific instrument in studies of all types of liquid crystal phases.

Friedel's article, coupled with the publications on synthesis and studies of new liquid crystal materials by organic chemists in Germany, notably Vorländer (see, for example, his monograph *Chemische Kristallographie der Flüssigkeiten* of 1924 [17]), firmly cemented in place all the earlier observations, providing a firm basis on which to build the future structure of the subject.

Before moving on to phase two of the history, we might just return to Reinitzer, the discoverer of liquid crystals, and recognize the quality of his powers of observation, for not only did he focus on the color effects and double melting, but also he noted the blue color appearing in the isotropic melt just before the sample turned into the cloudy cholesteric phase. About this, he said the following: "there appeared (in the clear melt) at a certain point a deep blue colour which spread rapidly through the whole mass and almost as quickly disappeared, again leaving in its place a uniform turbidity. On further cooling, a similar colour effect appeared for the second time to be followed by crystallisation of the mass and a simultaneous disappearance of the colour effect." The turbid state and the second color effect were of course due to the cholesteric phase, but the first transient blue color we now know was associated with the optically isotropic 'blue phases' we are familiar with today. Although Lehmann believed that this transient effect represented a different state, the full significance of Reinitzer's observations had to wait until the 1980s when these isotropic cubic phases became a focus of attention in condensed matter physics.

A further point concerning the first phase of our history of liquid crystals is about nomenclature, a matter about which scientists of today still love to argue. In the early years, however, the debate was sparked by Friedel who strongly objected to Lehmann's term liquid crystal, on the basis that liquid crystals were neither true liquids nor true crystals. The term does of course remain in widespread use today, simply because the juxtaposition of two contradictory terms carries an element of mystery and attraction. Friedel preferred the term mesomorphic to describe the liquid crystal state, and the associated term mesophase, reflecting the intermediate nature of these phases between the crystalline and isotropic liquid states. These terms are again widely used today and coexist happily with the Lehmann terminology. A useful term springing from Friedel's nomenclature is the word mesogen (and also nematogen and smectogen), used to describe a material that is able to produce mesophases. The associated term mesogenic is used by some to indicate that a material does form liquid crystal phases and by others to indicate that a compound is structurally suited to give mesophases, but may not, if, for example, the melting point of the crystalline state is too high. Then the isotropic liquid is produced directly from the crystal, and, on cooling, crystallization may occur too quickly for even a monotropic liquid crystal phase to form. Yet this compound may show strong tendencies to be mesomorphic if binary phase diagrams of state are examined using a standard material as the second component. My view is that the term mesogenic should be used to describe a structural compatibility with mesophase formation, without the requirement that a phase is actually formed. After all, if the compound does really form a mesophase, the description of it as mesomorphic is perfectly adequate.

Finally, on the subject of nomenclature, Friedel of course gave us today's terms smectic and nematic with their well-known Greek derivations.

3 The Second Phase from 1925 to 1959

In the first part of this period, Vorländer and his group in Halle contributed strongly to the growing number of compounds known to form liquid crystal phases, some showing up to three different mesophases. Based upon his work came the recognition that elongated molecular structures (lath- or rod-like molecules) were particularly suited to mesophase formation. His work also showed that if the major axis of a molecule were long enough, protrusions could be tolerated without sacrifice of the liquid crystal properties. Thus 1,4-disubstituted naphthalenes with a strong extension of the major axis through the 1,4-substituents were liquid crystalline, despite the protruding second ring of the naphthalene core. It is interesting that Vorländer records that the materials behaved as liquid crystallline resins or lacquers (an early thought perhaps about the potential of liquid crystals for applications).

In his book *Nature's Delicate Phase of Matter*, Collings [18] remarks that over 80 doctoral theses stemmed from Vorländer's group in the period 1901–1934. Further evidence of Vorländer's productivity is found in the fact that five of the 24 papers presented at the very important and first ever symposium on liquid crystals held in 1933 under the auspices of the Faraday Society in London, Liquid Crystals and Anisotropic Fluids – A General Discussion [19], were his. Perhaps the most important consequence of Vorländer's studies was that in laying down the foundations of the relationship between molecular structure and liquid crystal properties, attention was focused upon the molecules as the fundamental structural units of the partially ordered phases. Up to then, even Lehmann had been uncertain about the units involved in the ordering and what occurred at the actual transitions.

The Faraday Meeting of 1933 was of great importance in bringing together the small number of active, but often isolated, scientists involved at that time in liquid crystal research. This propagated knowledge and understanding, but, as we shall see, it also generated some dispute.

As early as 1923, de Broglie and E. Friedel (the son of G. Friedel) had shown [20] that X-ray reflections could be obtained from a system of sodium oleate containing water, and that the results were consistent with a lamellar or layered structure. This X-ray work was extended [21] in 1925 to Vorländer's thermotropic ethyl *p*-azoxybenzoate, confirming G. Friedel's conclusions of a layered structure stemming from his microscopic studies of smectic defect structures. Further, in the period 1932–1935, Herrmann [22], who also contributed to the 1933 Faraday Discussion, was decisive in confirming the lamellar nature of smectics by X-ray studies which included Vorländer's material exhibiting more than one smectic phase. The latter work substantiated a change from a statistical order in the layers of one smectic to a hexagonal ordering in the lower temperature phase. A tilted lamellar structure was also found by Herrmann for some thallium soaps [23].

Amongst other names of historical interest featured on the Faraday Discussion program were, for example, Fréedericksz and Zolina (forces causing orientation of an anisotropic liquid), Zocher (magnetic field effects on nematics), Ostwald, Lawrence (lyotropic liquid crystals), Bernal, Sir W. H. Bragg (developing the concept of Dupin cyclides in relation to Friedel's earlier studies of focal-conics), and also Ornstein and Kast who presented new arguments in favor of the swarm theory, which was first put forward in 1907–1909 by Bose [24]. This theory had proposed that the nematic phase consisted of elongated swarms of some 10^6 molecules, and in the 1930s much effort was given to proving the existence of these swarms, which were used to explain some, but not all, of the physical properties of nematics. However, at the 1933 Faraday Meeting, the presentation of Oseen [25] and the strong reservations expressed by Zocher during the discussions were already casting shadows of doubt on the swarm theory. Today of course we accept that definitive proof of the existence of swarms was never obtained, and by 1938 Zocher was expressing further strong reservations about the theory [26], proposing alternatively that the nematic phase is a continuum, such that the molecular orientation changes in a continuous manner throughout the bulk of the mesophase. This was called the distortion hypothesis and together with Oseen's work marked the beginning of the modern continuum theory of liquid crystals. However, developments here had to wait until after the second world war when Frank [27], at a further Faraday discussion in 1958, and consequent upon his re-examination of Oseen's treatment, presented it as a theory of curvature elasticity, to be advanced in the next historical phase by names such as Ericksen, Leslie, de Gennes, and the Orsay Group in France.

The period following the war up until the 1950s is also significant for the work of Chatelain [28], in collaboration with Falgueirettes. Using surface alignment techniques, they measured the refractive indices of different nematics, and Chatelain produced his theoretical treatment of the values of the ordinary and extraordinary indices of refraction of an oriented nematic melt.

Following Vorländer, other chemists were now becoming interested in new liquid crystal materials, and in the early 1940s we find publications on structure/property relations by Weygand and Gabler [29]. Later, in the 1950s, Wiegand [30] in Germany and the author in the UK were also making systematic changes in the structures of mesogens to establish the effects on liquid crystal behavior. The author's work included not only systematic modifications to aromatic core structures, but also studies of many homologous series, establishing clearly that within series systematic changes in transition temperature always occur, within the framework of a limited number of patterns of behavior. In the period 1951–1959, the author published some 20 papers on structure/property relations in liquid crystals. These are rather numerous to reference here, but in the account of the third historical phase from 1960 until today, reference to relevant reviews and books is given.

Lyotropic liquid crystals also progressed during this second phase. Lawrence's paper at the 1933 Faraday meeting discussed the phase diagrams for different compositions of fatty acid salts, recognizing the different phase types involved and the transitions undergone with change of temperature and/or water content. Examples of aromatic materials, including dyes, giving lyotropic phases were also found, and solvents other than water as the lyophase were explored.

The early work of Robinson et al. [31] was also done in this period. This involved solutions of poly-γ-benzyl-L-glutamate in organic solvents. These solutions exhibited the selective light reflecting properties of thermotropic cholesteric liquid crystals.

This period of history also saw the publication of work by Eaborn and Hartshorne [32] on di-isobutylsilandiol, which generated a mesophase. This was a puzzling result at the time, as the molecular shape was inconsistent with views of the time that liquid crystal formation required rod-shaped molecules. Light would be shed on this only after the discovery of liquid crystal phases formed by disc-shaped molecules in the early 1970s.

Finally, it should be noted that in this period, in 1957, a very important review on liquid crystals was published by Brown and Shaw [33]. This did much to focus the attention of other scientists on the subject and certainly contributed to the increase in liquid crystal research, which was to herald the strong developments in the early 1970s.

The period 1925–1959 may be usefully summarized now. Although the level of activity in the field was limited, important developments did occur in relation to:

- the influence of external fields (electric and magnetic) on liquid crystals;
- the orienting influences of surfaces;
- measurements of the anisotropic physical properties of aligned liquid crystals;
- the range of new liquid crystal materials and structure/property relationships;

- the development of theories of the liquid crystal state ranging from the swarm theory to the emerging continuum theory;
- increased awareness of the value of polarizing optical microscopy for the identification of mesophases, the determination of transition temperatures, and reaching a fuller understanding of defect textures.

4 The Third Phase from 1960 to the Present Time

The first ten years of this period saw several important developments which escalated interest and research in liquid crystals. Among these, there was the publication by Maier and Saupe [34] of their papers on a mean field theory of the nematic state, focusing attention on London dispersion forces as the attractive interaction amongst molecules and upon the order parameter. This theory must be regarded as the essential starting point for the advances in theoretical treatments of the liquid crystal state which followed over the years.

There was also much activity in the field of new liquid crystal materials, notably by Demus et al. [35] in Germany and by the author who, in 1962, produced his monograph *Molecular Structure and the Properties of Liquid Crystals* [36], published by Academic Press.

Also, further X-ray studies began to advance knowledge of the structure of liquid crystal phases, particularly smectics. The work of de Vries and Diele should be mentioned, and later on, notably that by Levelut and co-workers in France and Leadbetter in England (see, for example, [37, 38]), work which culminated in the 1980s in a clear structural elucidation and classification of smetic liquid crystals. This distinguished the true lamellar smectics with little or no correlation between layers from lamellar systems, previously regarded as smectics, which possess three-dimensional order and are really soft crystals. Today, the true smectics are labeled SmA, for example, and the crystal phases are referred to simply by a letter such as K, or by CrK. The phase once known as SmD and first observed by the author and co-workers in laterally nitro substituted biphenyl carboxylic acids [39] is now recognized [40] as a cubic liquid crystal phase. Several other examples of cubic thermotropic liquid crystal phases are now known [41, 42].

Such studies focused attention on the microscopic textures of liquid crystal phases. The defects characterizing these textures are now well understood through rather beautiful studies by workers such as Kléman [43], and from textures it is now possible to go a long way towards characterizing the phase behavior of new materials. A great deal of work on phase characterization has been done, and two reference sources are important [44, 45]. Through such detailed studies of phase behavior, new phenomena were often recognized and explained, for example, the re-entrance phenomenon through the work of Cladis [46], and the existence of the blue phases (BPI, BPII, and BPIII) through the work of several groups [47]. We should remember of course that Reinitzer did observe blue phases many years earlier and knew, without understanding the situation, that something occurred between the isotropic liquid and the N^* phase on cooling many chiral materials. Reflectance microscopy played a big part in the eventual elucidation of these phases as cubic phases involving double twist cylinders.

The widened interest in liquid crystals exemplified above had its origins in a number of events, such as the publication of the Brown and Shaw review [33] and the