THE EARLY PERIOD: LIQUID CRYSTALS OR ANISOTROPIC LIQUIDS?

Introduction

The foundation of liquid crystal science is traditionally set in the year 1888, with the work of Friedrich Reinitzer. Reinitzer is commonly termed a botanist, although in modern terms he would perhaps be thought of more as a biochemist. He was at the time 30 years old and assistant to Professor Weiss at the Institute of Plant Physiology at the German University of Prague. We remind readers that Prague was then the capital of the province of Bohemia in the Austro-Hungarian empire, but that the university in Prague was highly prestigious within the German-speaking world. Reinitzer's experiments involved extracting cholesterol from carrots in order to determine its chemical formula, which at that time was unknown. He thought that cholesterol was chemically related to carotene (the red pigment) and thus to chorophyll. At the same time, cholesterol had been observed to occur in the cells of many animals, and it was of some interest to determine whether this was exactly the same cholesterol, or whether there were a number of closely related compounds. He presented his results to the Vienna Chemistry Society at its monthly meeting on 3 March 1888. This paper is article A1 in our collection.

In the paper Reinitzer examined the physico-chemical properties of various derivatives of the carrot cholesterol. Most of his results are not specifically of interest in a liquid crystal context. Naturally there was much discussion concerning speculations on the exact chemical formula of cholesterol; is it $C_{26}H_{44}O$ as suggested by Gerhardt?[1] He noted that a number of previous workers, such as Raymann,[2] Löbisch[3] and Planar,[4] had observed some dramatic colour effects on cooling cholesteryl acetate or related compounds just above the solidification temperature. He himself found the same phenomenon both in cholesteryl acetate and in cholesteryl benzoate, which has the chemical formula $C_{27}H_{45} \cdot C_7H_5O_2$.

But the coloured light show near the solidification of cholesteryl benzoate was not its most peculiar feature. Reinitzer found, to his amazement, that this compound does not melt like other compounds. Cholesteryl benzoate appeared to have *two* melting points. At 145.5 °C the solid melted into a cloudy liquid. The cloudy liquid lasted up to 178.5 °C, at which point the cloudy liquid suddenly became clear. Furthermore, the phenomenon appeared to be reversible. Near both transition points the system exhibited some dramatic colours.

Both the colours and the double melting were worthy of note. What was going on? There were several different solid modifications, and the colours suggested to Reinitzer that some form of physical isomerism was occurring. Reinitzer sought help from Dr Otto Lehmann, a well-known crystallographer, then the assistant of Professor Wüllner at the Polytechnical School of Aachen. The expectation was that Lehmann's polarising microscope might clarify the situation.

There followed an exchange of letters, and presumably of samples as well, throughout March and April of 1888. Lehmann examined the intermediate cloudy fluid, and reported that he had seen crystallites. When the exchange of letters ended on April 24, although definitive answers to the nature of the cloudy phase had not been elicited, Reinitzer felt that he had enough to publish. The important point here is that these first observations of liquid crystals (although not yet recognised as such) were a serendipitous by-product of an apparently unrelated and unprofound piece of research. Neither for the first nor for the last time, Nature had a sprung a surprise on an unprepared investigator.

Reinitzer's first letter to Lehmann was sent on 14 March 1888. It was 16 pages long, and handwritten in Gothic characters. An extract is shown in Fig. A1. In it Reinitzer relates to Lehmann most of the content of article A1. The colour phenomenon in particular is of interest to the modern observer. When he cooled cholesteryl benzoate below its second melting point at 178.5 °C (later called by Lehmann and others the *clearing point*), he observed that

> ...violet and blue colours appear, which rapidly vanish with the sample exhibiting a milk-like turbidity, but still fluid. On further cooling the violet and blue colours reappear, but very soon the sample solidifies forming a white crystalline mass.

Reinitzer observed the appearance of colours twice! However, in the case of cholesteryl acetate with its *monotropic* cholesteric phase, with a melting point 114.3 °C and a clearing point 94.8 °C, Reinitzer observed the appearance of colours only once on cooling. At that time the mere existence of the double-melting and the colours was sufficient to excite interest. In fact, nowadays we are also able to understand why in one material two sets of colours were seen, and in the other material only one. Furthermore, it turns out that this is not an accident, and indeed a tribute to the exactness of Reinitzer's experimental method that he observed and recorded rather subtle phenomena whose significance could not

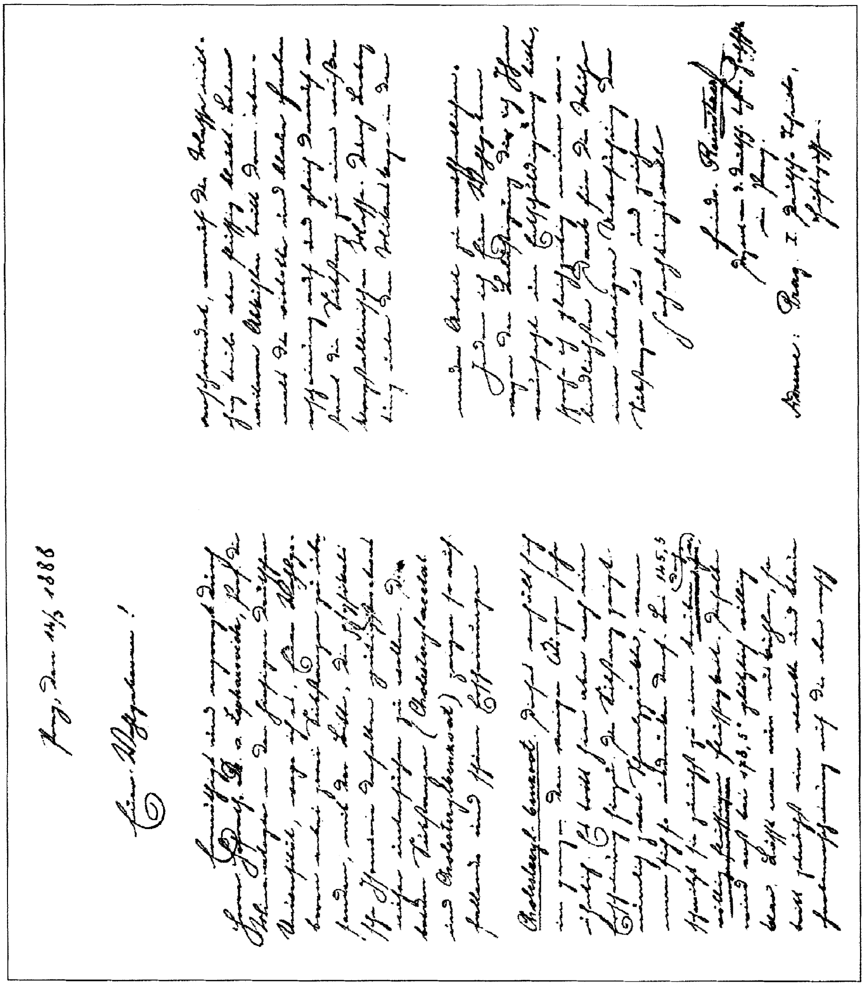

Fig. A1 Reproduction of Friedrich Reinitzer's letter to Otto Lehmann on March 14, 1888, in which he sought help in identifying the properties of cholesteryl benzoate. Note the Gothic script which is very difficult to disentangle.

have been understood at the time. The explanation itself is more sophisticated and involves concepts which are of extremely recent origin.*

Reinitzer wrote a little extra on his work on cholesteryl benzoate,[5] and then more or less disappears from this narrative. His one further contribution to the story comes some 20 years later, in a rather unedifying episode which we shall come to presently.

The mantle is taken up by Otto Lehmann, who both realised that he had come across a new phenomenon, and was in a position to launch a research programme to investigate it. In 1888, Lehmann was 33. Up till 1888 Lehmann had enjoyed a rather peripatetic life. His postdoctoral years had been spent building up expertise in crystallography. The principal weapon in his scientific arsenal was experimental microscopy, for which he was well prepared because his schoolmaster father had been an amateur microscopist before him. Lehmann was known to be a coming man, and even at a relatively young age in 1889 he was elected as professor of physics at the Technical University of Karlsruhe, as the successor to Heinrich Hertz (1857–94), who had lately demonstrated experimentally Maxwell's theory of electromagnetism.

It was Lehmann's jealously guarded and increasingly prestigious microscope, not yet available off the shelf, which led Reinitzer to approach him for help. Lehmann was not only able to make observations in polarised light, but also, and this was a key advantage, his microscope possessed a hot stage enabling *in situ* high temperature observations. With Reinitzer's peculiar double-melting liquid, a problem in search of a technique had met a scientist in search of a problem.

Lehmann immediately launched a vigorous programme of intense investigation into the new phenomenon. Already by the end of August 1889 he had his first article ready for submission to the *Zeitschrift für Physikalische Chemie* (Journal of Physical Chemistry). This is article A2 in our collection.

The reader will observe that, even in the imperfect translation presented in this volume, Lehmann's language is particularly flowery. The article is entitled 'On flowing crystals'. What emerges in article A2 is that the cloudiness of the intermediate fluid occurs when what we would now call nucleating droplets merge, and that sometimes the individual droplets exhibited a black cross when viewed between crossed nicols. The cloudiness itself was the macroscopic manifestation of 'large star-like radial aggregates of needles'.

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* In order to appreciate the origin of the colours we have to move forward to the 1970s. They result from selective reflection of circularly polarised light from helically structured chiral liquid crystals. In a careful reinvestigation of selective reflection in cholesteryl benzoate one of the present authors (H. Stegemeyer and K. Bergmann, Springer Ser. Chem. Physics **11** (1980), p. 161ff) was able to show that whereas the low temperature colours are caused by the *cholesteric* phase (a fluid which is nevertheless crystallographically a one-dimensional 'solid'), the high temperature colours are due to selective reflection from a *blue phase* (a fluid which is crystallographically a three-dimensional solid)! Cholesteryl acetate does not exhibit a blue phase, and as a consequence Reinitzer observed colours only once in this compound. It is amazing that the first study of liquid crystals already revealed a structure as complex as a blue phase, whose cubic structure was only disentangled some hundred years later.

Lehmann was certain that the cloudy liquid has all the attributes of a crystal and those of a liquid. He believed truly to have discovered 'crystals that flow'. Much of the rest of the article is concerned with advocating the point of view that the properties of liquidity and crystallinity could indeed coexist, and is not without rhetorical flashes. Given the effort he went to in order to justify his picture, he must clearly have expected to meet with a good deal of opposition.

In a series of papers over the period 1890–1900,[6,7] Lehmann made exhaustive studies of the phenomenon. Because the essence of the phenomenon seemed to occur in droplets, he made a virtue out of necessity and often deliberately prepared fluid mixtures from which the intermediate phase would then precipitate in droplet form. We show in Fig. A2 a series of coloured images of droplets, taken from Lehmann's review article published in 1900.[7] These dramatic pictures, originally taken only in black and white, have been coloured by hand so as to resemble what Lehmann saw under the microscope.

Lehmann found materials some of which exhibited, as in cholesteryl benzoate, two melting points, and some of which even exhibited *three* melting points. He found a phase which he called *Fliessende Kristalle* (flowing crystals) or *Schleimig flüssige Kristalle* (slimy liquid crystals), and another which he named *Kristalline Flüssigkeit* (crystalline fluid) or *Tropfbar flüssige Kristalle* (liquid crystals which form drops). If both phases existed in the same material the latter was always the higher temperature phase. The latter was cloudy, but the former was clear, although very viscous. All this culminated in an enormous and generously illustrated tome, simply entitled 'Liquid Crystals',[8] published in Leipzig in 1904.

Lehmann's first article quickly elicited a response from his scientific colleagues. On 14 March 1890, Ludwig Gattermann of the University of Heidelberg wrote to Lehmann:[9]

> It was with great interest that I read your article on flowing crystals in Zeitschrift für physikalische Chemie. For some time I have had several substances here which also exhibit the same properties. To begin with I thought I was considering mixtures of several materials, but the properties remained unchanged after several crystallisation cycles. Following your article I am now clear as to what is going on.

Later that year Gattermann and his student Ritschke published the first report of the complete synthesis of one of the new substances. This is article A3 in our collection 'On azoxyphenol ethers'. It seems that as with so many organic chemists, the immediate spur to Gattermann's work lay in industrial concerns, for the initial step of the work involved the reduction of *p*-nitrophenetole provided by the Bayer & Co. dyeworks in Elberfeld. The ultimate goal of Bayer was evidently to produce better dyes for textiles and other industrial goods.

In 1890 Gattermann was a 30-year-old Assistant Professor at the University of Heidelberg. Later on he became Full Professor at the University of Freiburg and a

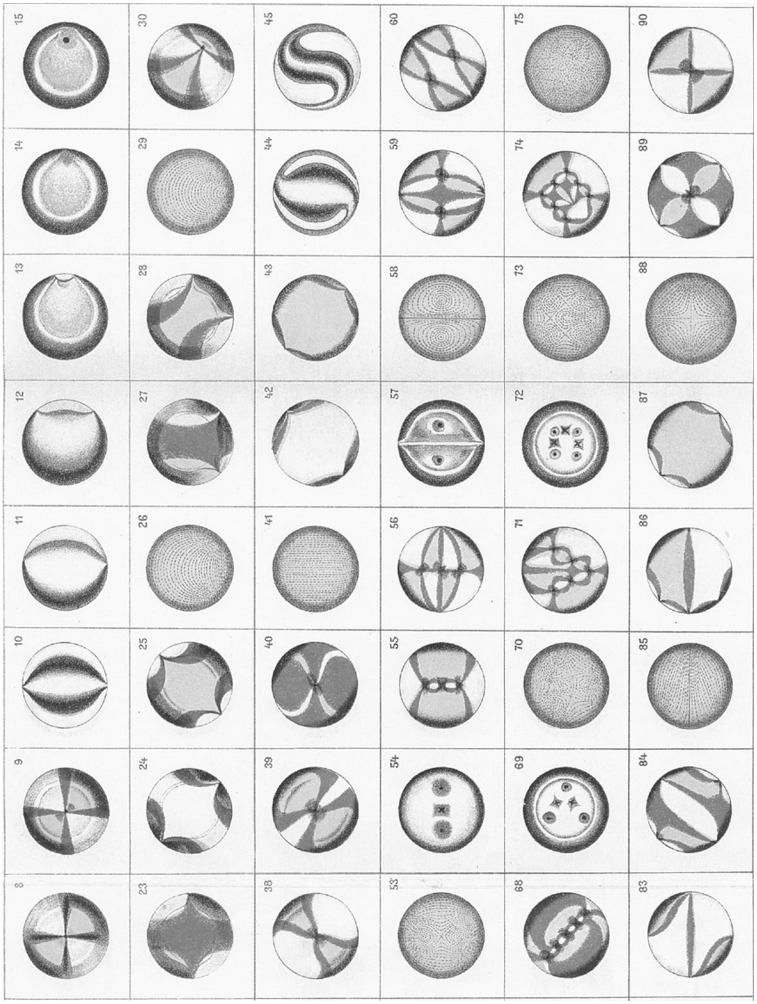

Fig. A2 Extract from O. Lehmann, Annalen der Physik, series 4, vol. **2**, p649ff. The Schlieren texture – the *stains* that so struck the early workers in the field of liquid crystals – can be seen in particular in the images that show what Gattermann and Lehmann called *copulating* drops, in which two drops are amalgamating (e.g. images 55, 56, 59, 74). See Plate I.

famous organic chemist, well-known to generations of chemistry students by his textbook '*Die Praxis des Organischen Chemikers*' (The practice of organic chemistry).

The aim of their investigations was a real problem of organic chemistry, namely to test if there existed two or more different isomers (i.e. molecules with the same chemical formula but different structure) of phenol ethers, as was claimed in the literature in the case of azoxytoluenes. In the process of synthesising azoxyphenetole they were indeed able to isolate two different reaction products with quite different crystal structures. However, by skilful chemical analysis they found out that the two substances were not isomers, but rather different compounds which differ in their alkyl groups: *p*-azoxyanisole with a methyl group, and *p*-azoxyphenetole with an ethyl group. Using ingenious chemical procedures, they found evidence that an exchange of alkyl groups had taken place during the synthesis in methanol as solvent (ethyl- *vs*. methyl-group). Consequently, they solved a typical problem of organic chemistry – the replacement of one alkyl group by another.

During the procedure, however, they made an unusual and extremely interesting observation. All the three compounds under investigation (azoxyanisole, azoxyphenetole, anisole azoxyphenetole) exhibited a sharp melting point in the usual way, but were not transformed into the usually observed transparent fluid phase. Rather they gave rise to cloudy liquids, which resembled the cloudy liquid produced by Reinitzer's cholesteryl benzoate.

From our point of view Gattermann and Ritschke's article presents a number of interesting features. For brevity we have omitted some of the technical details not directly relevant to the liquid crystal story. The article reports in particular the synthesis of para-azoxyanisole, which formed a cloudy liquid phase at 116 °C, and what soon became known as a *clearing point* at 134 °C. This compound was to become the material of choice for liquid crystalline studies. The method of synthesis was well defined and relatively easy, and the temperature range over which the anomalous properties were manifest was rather more accessible than in the case of cholesteryl benzoate. In this article too we find the first known reference to the term *Flüssige Kristalle* ('liquid crystals'), although not yet in any precise fashion. The paper emphasises that, although the three compounds under discussion possess different chemical structures and quite different crystalline properties, they exhibit totally the same physical properties above the 'third melting point', i.e. in the liquid crystalline state. Another interesting snippet from Gattermann's report concerns his observations of liquid crystal droplets. These resembled oil droplets, apart from some peculiar 'stains' in the middle of the droplets. The stains, or *Schliere*, have entered the canon as the familiar Schlieren texture.

At the end of his paper Gattermann described a proposal for the structure of the isotropic liquid. He believed that the isotropic, non-birefringent liquid phase of those compounds exhibiting liquid crystalline phases should possess a regular (i.e. cubic) crystal structure. We now know that this speculation went well beyond the facts available and is false. Paper A3 was Gattermann's pioneering publication in the liquid crystal field. Despite the importance of this paper for the development of the subject, only once did he return to liquid crystals. This was in an extensive paper in 1906,[10] in which he briefly mentioned that the condensation products of aromatic aldehydes with benzidine resulted in Schiff bases, which exhibited the properties of Lehmann's 'flowing crystals'. Gattermann's contribution is remarkable not only because it was an assay by a well-known scientist into this field, but also because it provided a solid foundation for much of the work which came later.

Lehmann's slimy liquid crystals were obviously solid-like, if only because of their reluctance to flow. The drop-like variety also showed one physical property which had hitherto been uniquely associated with solidity, that of *birefringence*, which explained the peculiar dark crosses seen through the polarising microscope in droplets in what Lehmann came to call the *erste Hauptlage*, or 'first principal position'. In other circumstances the droplets could be found in the *zweite Hauptlage*, or second principal position. In this case the droplets acted like a lens, with an apparently greater refractive index in the centre of the droplet.

Lehmann continued to insist on his interpretation of his microscope observations as representing materials combining all the properties of fluidity and crystallinity, while freely admitting his ignorance of the precise molecular explanation. By 1900, he was prepared to subsume all the new phenomena under the more general classification of *Flüssige Kristalle*.

It is worth pausing a moment to consider the enormity of the step that Lehmann felt he had to take when he proclaimed the existence of liquid crystals. The distinction between solid, liquid and gas is evident even to the non-scientist. The earliest theories of matter in ancient Greek times emphasise the physical form of matter (under the guise of earth, water and air) over its chemical basis.

Chemistry, by contrast, only slowly developed in the seventeenth and eighteenth centuries out of the medieval art of alchemy. Although atomic ideas had been around since Democritus and Leucippus in the fifth century BC, it was not until John Dalton (1766–1844) published his seminal work, *A New System of Chemical Philosophy*, in 1808, that it was established that chemical compounds came from constituent materials in definite proportions. This gave strong, but not yet decisive, evidence of the existence of atoms.

Similarly by the end of the nineteenth century a basic understanding of continuum mechanics had already developed. Solids possess *displacement* (we would say shear) elasticity, whereas liquids do not. Many solids exhibit crystallinity, which at this time usually meant that under the microscope crystal facets were observed. Crystals were often optically birefringent (i.e. refracted light differently depending on their orientation). Birefringent materials were said to be *anisotropic*, i.e. to possess different properties in one direction as compared to another.

The current picture of crystallinity in terms of periodic atomic lattices is due to the French crystallographer René-Just Haüy (1743–1822). Although this picture had gained wide acceptance by the end of the nineteenth century, it did not yet rest on firm foundations. The debate between Ludwig Boltzmann (1844–1906) and Ernst Mach (1838–1916) – between materialism and idealism – on the atomic nature of matter was still in full swing. Definitive evaluation of the size of the Avogadro number (or equivalently Boltzmann's constant) had to wait for the experiment of Jean Perrin[11] (1870–1942) in 1908, and the definitive experiments in which the crystal lattice was directly observed in X-ray scattering[12] were carried out by Max von Laue (1879–1960) in 1912 and the father–son team of W.H. Bragg (1862–1942) and W.L. Bragg (1890–1971) in 1913.

In any event, notwithstanding the lack of proof of its essential nature, crystallinity certainly seemed incompatible with fluidity. Perhaps not surprisingly given the circumstances and intellectual climate of the day, Lehmann's work elicited not a little scepticism from his scientific peers concerning the very existence of the liquid crystal phenomenon.

Throughout the 1890s, even up till 1905, the physical chemists Georg Quincke (1834–1924)[13] and Gustav Tammann (1861–1938)[14] insisted that the observations were more parsimoniously explained by supposing that the substances which Lehmann labelled as liquid crystals were mixtures of some sort. The multiple melting phenomena must then be explicable in terms of separate transitions for each quasi-separate component of this mixture. Thus, averred Quincke and the theoretical physicist Wulff (later to become famous for explaining why macroscopic solids take their characteristic crystalline shape), liquid crystals must really be colloidal. According to Quincke and Wulff, the existence of a solid component would explain the birefringence. The strong light scattering (i.e. the turbid appearance) in colloids such as white paint results from strong scattering by individual colloidal particles, which are just the right size for maximal light scattering.

An alternative but related picture, supported by Tammann and Walther Nernst (1864–1941), proposed that the so-called liquid crystal phase was rather a colloidal emulsion, akin to milk or vinaigrette, in which droplets of one liquid are suspended in another.

Colloid science was at that stage relatively young, though no longer in its infancy. The founding father is generally reckoned to be the Scottish chemist Thomas Graham (1805–69). It is to Graham that we owe many of the important terms in colloid science, including the appellation itself, *colloid* from the Greek word κολλα, meaning glue.

Tammann's colloidal picture was not supported by detailed theory, but seemed more plausible than the alternative of a liquid which was simultaneously crystalline. Nernst later became extremely famous, winning the Nobel prize in 1920 for discovering the third law of thermodynamics (that the entropy of a material goes to zero at the absolute zero of temperature). But on this occasion he was not right.

The controversy between Tammann and Lehmann was particularly intense, and led to a bitter exchange in the pages of the *Annalen der Physik* in the early years of the twentieth century.[15] Tammann was an Estonian physical chemist who was appointed as Professor of Inorganic Chemistry in Göttingen in 1903. In 1907 he succeeded Nerst as Professor of Physical Chemistry. He is best known now for his contributions to the thermodynamics of metallurgy and glass-formation.

Twice, in 1901 and again in 1902, Tammann wrote articles in *Annalen der Physik* entitled *Über die sogenannten flüssigen Krystalle* (On the so-called liquid crystals). Lehmann was quick to make a response. By the end of 1901 his article *Flüssige Krystalle: Entgegnung auf die Bemerkungen des Herrn Tammann* (Liquid crystals: a rebuttal of Herr Tammann's comment) had already appeared. The second article received similar short shrift.

Tammann's scepticism was at the very least understandable, given the knowledge of thermodynamics at the time. Moreover, the colloidal hypothesis was the obvious parsimonious explanation of the turbidity data. The most difficult question concerned the apparent anisotropic optical properties of the droplets. Tammann was inclined to consider this problem a detail which would be resolved in the course of time, but Lehmann regarded it (correctly, as it turned out) as a central question. The elimination of the colloidal hypothesis, which involved careful experimentation, was an essential step in the understanding of the new phenomenon.

In the end careful experiments by a number of workers, including Lehmann, and, in particular, the physical chemist Rudolf Schenck of Marburg, demonstrated that liquid crystallinity persisted in the limit of chemical purity, the sceptics' contrary prediction notwithstanding. Already in 1904, Both Coehn,[16] and separately Bredig and Schukowsky,[17,18] had attempted to verify the emulsion hypothesis by means of electrophoresis. This effect, sometimes also known as cataphoresis, involves using an electric field to remove colloidal particles from the 'emulsion'. No effect was observed, and the authors concluded that liquid crystals were not emulsions.

The more complete robust demonstration by Schenck of the falsity of the colloidal picture is included in our collection as article A4. This *coup de grace* was administered at a meeting of the *Deutsche Bunsengesellschaft* (the German Physical Chemistry Society), held in Karlsruhe (Lehmann's home territory), in the afternoon of 3 June, 1905. The proceedings of this meeting are reported in the 1905 edition of the *Zeitschrift für Elektrochemie*. Schenck's article (a presumably rather faithful written version of his oral presentation) is designed as a brief overview of the liquid crystal field to prepare the audience for Herr Geheimrat Lehmann's kind demonstrations of liquid crystal behaviour, due to take place later in the afternoon.

Schenck's[19] article emphasised that attempts to obtain the phase separation which must occur if the turbidity were a colloidal phenomenon have failed. Observations in the literature, he claimed, were in fact due to impurities in the system. He himself had personally shown this using the experimental samples of, for instance, Rotarski,[20] who had claimed evidence for phase separation. He had found no evidence of phase separation at the onset of the anisotropic phase, and indeed found discontinuities in density and viscosity. He repeated the experiment for water–phenol mixtures and found an entirely different signature at the transition. He used an elaborate argument due to Eötvos – omitting the source of the argument! – to show that in the clear liquid there could be no isomerism because the specific heat obeys a law of corresponding states.

We also include Tammann's restatement of his position immediately after Schenck's talk. This statement was only barely disguised as a question. The final statement of the official report of the meeting (also included) is replete with irony, as the session chair, the well-known physical chemist van't Hoff, made brave attempts at compromise in order to avoid the real possibility of physical violence. This was socially necessary, but with the benefit of hindsight, scientifically not so. The controversy gradually died down. The most plausible explanations had clearly failed. Nevertheless, there remained neither microscopic explanation nor macroscopic description of the nature of the phenomenon, even if some of the basic elements were now becoming clearer.

The big debate as to the nature of liquid crystallinity may overshadow another fundamental question which still remained in the early years of the twentieth century, and to which the discovery of liquid crystals led to much confusion. This concerned the relationship between thermodynamic phase and chemical constitution. In 1821 the German chemist Eilhard Mitscherlich discovered that many crystal compounds could appear in different solid forms, while retaining identical liquids and vapours. This phenomenon is known as polymorphism. The natural conclusion was that the molecules of the polymorphic modifications are chemically identical, and that polymorphism is only caused by different space lattice structures of the same molecules.

The discovery of *liquid* crystals muddied this picture. For now the lack of a unique liquid modification gave rise to doubts about the original interpretation of polymorphism. Lehmann, who believed firmly in the *physical* existence of his liquid crystals, called for a revision of the dogma. In his 1904 book, he argued:

> The behaviour of flowing and liquid crystals demonstrates that the molecules of polymorphic modifications are unambiguously different from each other. It follows that the optical properties of a substance are not determined by the type of molecular aggregation . . . but must be caused by the special molecular structure.

Shortly afterward he claimed:

> . . . my previous investigations on polymorphism, especially on liquid crystals, have shown that enantiotropic transformations are not caused by the aggregation of the same molecules into another space lattice. Rather changes in the molecules themselves must occur.

The fundamental problem of different molecular structures in different polymorphic phases remained open into the early fifties. Kast,[21] in 1939 claimed:

> . . . the molecules will lose their extended structure [*in liquid crystalline phases*] at the clearing point . . .

and even as late as 1955[22] he maintained the point of view that:

> . . . free rotation of alkoxy side groups does not occur until one arrives at the clearing point.

Eventually, however, the first infrared spectroscopic investigations on liquid crystals, carried out by Maier and Englert[23] in 1957, told a different story:

> The infrared spectrum of a cr.-l. compound is identical with that of the isotropic liquid phase in the band position, in intensity, and in half-width. No significant changes in the structure of a single molecule appear during the phase transition. As a result, the earlier idea — that there is a "thawing" of the intramolecular rotational degrees of freedom at the isotropic-crystalline-liquid phase transition — no longer holds.

The story has a mixed moral. Certainly the vociferousness and vituperation with which Tammann pursued his liquid crystalline quarry turned out to be at the very best misplaced. Indeed Lehmann's liquid crystals did have some liquid and some crystal qualities. For these qualities the term 'liquid crystal' was not wholly inappropriate, at least at the time. We shall see in article B1 that Georges Friedel criticised this terminology with arguments that were formulated in a much better manner than Tammann's. But too literal an attachment to the concept of a *liquid crystal* led to errors which took more than half a century to correct.

Let us now return to 1905. The search for the microscopic origin of liquid crystallinity was now really on, as the number of research groups studying the phenomenon began to increase, though still not transcending the boundaries of the German-speaking world. A prerequisite for any detailed picture involves knowing what kind of materials are able to form liquid crystals. New materials are provided by synthetic chemists, and in this case the synthetic chemists are usually organic chemists, in that liquid crystals without a large number of carbon atoms seemed rare. Gattermann had lost interest in liquid crystals, but a new champion emerged in Daniel Vorländer of the University of Halle.

To begin with liquid crystals (or *crystalline liquids*, as Vorländer insisted on calling them right through his long career) cannot have seemed very promising. The first paper which appeared from the Halle group on this subject (which we do not reproduce) was signed only by his graduate students F. Meyer and K. Dahlem.[24] The paper was entitled 'Azo-and Azoxybenzoic acid esters', and was published in the *Annalen der Chemie* in 1903. In a rather detailed commentary on the oxidation of an intermediate chemical, they mention, almost in passing, that they synthesise a material which

> ...exhibits a double melting point,...(which)...reminds one of the strange materials investigated by O. Lehmann and R. Schenck.

Indeed just to check, they asked Schenck to repeat the observation. However, these remarks occupy less than half a page in a fifteen page article, whose main thrust concerns more technical aspects of organic synthesis.

What is noteworthy in this article to the historian of science is that it is not co-authored by Vorländer himself. It was an unwritten but nevertheless extremely rigid convention of the day that the Director of an institute publish the results of his co-workers under his own name. Only in passing would the Director have mentioned that these results had been obtained (in this case) ‘together with F.M and K.D’. It stretches plausibility to suppose that Vorländer omitted his own name out of a spirit of generosity, in order to promote his subordinates’ careers. Much more likely is that Vorländer missed the significance of these observations and, furthermore, aware of the controversial nature of the crystalline liquid hypothesis, was simply keeping his distance from a possibly dangerous scientific controversy.

Whatever his motivation in 1903, the Halle experiments continued, and Vorländer finally realised that he was tapping a rich vein. Three years later he returned to the subject, this time in an article authored by himself alone, in the premier German journal *Berichte der Deutschen chemischen Gesellschaft*. So influential was this journal in its day, that references to articles in it were often abbreviated just by the letter *B*! We include this paper, entitled simply ‘On crystalline-fluid substances’, as article A5 in our collection.

By now it was becoming clear that this was a *class* of substances, and not just a peculiarity. Starting with Reinitzer’s cholesteryl benzoate, and Gattermann’s *p*-azoxyanisole, Schenck recorded the existence of 24 crystalline liquid compounds; by the time Vorländer wrote his article in the following year, the number had increased to 35, and that did not include oleates.

Article A5 is significant for a number of reasons. It is Vorländer’s first major contribution to a subject in which for the next 30 years he was the dominant synthetic chemist. At least partly, Vorländer is simply staking a claim: crystalline fluid research is happening here in Halle. But beyond this, Vorländer is beginning to apply the tools of a trained organic chemist to the problem in hand.

What are the essential molecular properties for a compound to form a crystalline liquid? How can one change a singly-melting fluid into a double-melting fluid? Paper A5 is the first systematic study of how to manipulate organic molecules in order to favour or disfavour liquid crystal properties. He emphasises:

> . . . we have been guided by the idea that the formation of the crystalline-liquid state could be caused or promoted by the same atomic groups which also influence other physical properties, such as light refraction, colour, rotatory power, and so on.

He makes tables of compounds from a homologous series, in order to see which of them possesses a crystalline liquid phase, and which do not; which has the highest first melting point, and which the highest second melting point. Gattermann had found that para-azoxyanisole forms a crystalline liquid. Vorländer finds further that that the para-position of the substituents is important; the analogous ortho- and meta- compounds (with the azoxy group placed differently, and at an angle, with respect to the rest of the molecule) do not give rise to crystalline liquids. However, in this article Vorländer has not yet reached any definitive conclusions from his observations.

It was his next article, published in the following year in *Berichte*, which we include as article A6, which was to have the really long-term influence on the subject. In it he discerned the first important clue to the real nature of liquid crystals. This very short article is entitled ‘On the influence of molecular shape on the crystalline liquid state’ and it reported that most liquid crystalline materials were constructed from molecules with a strongly *rod-like* structure. Over the years Vorländer and his students synthesised hundreds of liquid crystalline compounds. An interesting discovery was that amongst the slimy liquid crystals were many soaps and soap-like compounds. And in 1908, he detected for the first time that a given substance may exhibit more than one liquid crystal phase.[25] Already by 1908 he had enough material to feel able to report his accumulated results, not just in a series of papers, but in a book, which he entitled *Kristallinisch-flüssige Substanzen* (Crystalline-liquid Substances).[26]

One unintended consequence of the book was an unedifying battle, fought out on the pages of the *Annalen der Physik*,[27] concerning priority over who had *really* discovered liquid crystals. We quote the first paragraph of Lehmann’s opening gambit in his battle to defend *his* discovery:

The history of liquid crystals

O. Lehmann

> In a book published recently, the origin of the liquid crystal concept has been described. The book contains many new observations and is a valuable addition to the *chemical* liquid crystal literature. However it presents a picture of the origin of the liquid crystal concept which is seriously misleading. One might suspect from this book that Herr Fried. Reinitzer, who is professor in the Botanical Institute at the University of Graz, had actually discovered the phenomenon in 1888, and I had merely renamed it. I present here, for the first time, the full story.

Reinitzer replied some months later in *Annalen der Physik*. He set the record straight as follows:

> From these arguments it is indisputably clear that the unambiguous concept of flowing crystals was recognised by Lehmann first of all by studying my derivatives. Furthermore, it is obvious that the perception is due to Lehmann, but that I also contributed considerably in this matter.... One should admit that the credit of discovering the phenomenon ought to be attributed to me.

Reinitzer did not continue his investigation of cholesteryl derivatives. This plea for scientific recognition was his last contribution to the liquid crystal story. His career continued as University Rector and Director of the Botanical Institute in Graz.

It was not only against Reinitzer that the barbs of Lehmann's pen were applied. Here he is again, in 1914, in a direct reproach to Vorländer:[28]

> Mr. D. Vorländer believes he should reproach me for some errors, but in reality these errors do not exist. However, his remarks are of value. Misunderstandings between the points of view of Vorländer and myself have often arisen by confusion. Hopefully these misunderstandings can be put behind us. Vorländer has obviously only concerned himself with the investigation of which chemical constitution of a substance is necessary for the appearance of a liquid-crystalline modification. In this endeavour he has achieved great success. However, he has only rarely been involved with physical and crystal optical investigations. As a result it is not surprising that my ideas seem extremely unfamiliar to him.

We shall return in the next section to Vorländer and also to further debates of this type!

A full study of Lehmann's scientific work and impact goes well beyond the scope of this book. One further aspect of his scientific interests of particular interest to the modern reader concerns his correspondence with the zoologist and natural philosopher Ernst Haeckel (1834–1919). Haeckel was an ultra-Darwinist who attempted to combine the natural laws of organic and inorganic matter in the context of the same set of physical laws. This contrasted with traditional ideas of a 'vital force' breathed (by the almighty or otherwise) into living beings.

In many ways he was before his time, in that almost all of the fundamental science which would have enabled him to achieve this task was lacking in the mid-nineteenth century. His programme was premature by at least a hundred years and maybe by a good deal more. Despite Haeckel's commitment to the scientific method, the result was a set of speculations about natural relationships many of which were not in any way empirically based. Some were correct – for example he was the first to suggest that the seat of inheritance was in the nucleus of the cell. Haeckel has developed a reputation as a bit of a crank because of the tenacity with which he held to implausible ideas.

Lehmann was attracted to Haeckel's ideas. Even while at school he had studied Haeckel's books and looked for a link between the areas of minerals, plants and animals. Haeckel was most fascinated by Lehmann's liquid crystal studies and believed liquid crystals to be a missing link between inorganic and living systems. Their correspondence lasted between 1906 and Haeckel's death in 1919, although they never met personally. Lehmann was sufficiently influenced to write a book on the topic.[29] Haeckel's last book *Kristallseelen – Studien über das anorganische Leben* (Crystal souls – Studies on inorganic life), published in 1917, included a chapter entitled *Rheokristalle* (Rheocrystals), devoted to Lehmann's observations of liquid crystals.

Here he discusses the entire life of these rheocrystals, which he thought of as an intermediate stage between simple materials and life itself:

> By critical comparison between spherical rheocrystals (myelin spherules) and primitive cytodes (*chroococcus*) the traditional as well as artificial border between inorganic and organic nature is finally removed.

As we have seen, Lehmann's ideas about the nature of his liquid crystals did not meet with uncritical acceptance by his peers. His links with Haeckel were a further hindrance to his credibility. Indeed, following one of his lectures on liquid crystals a colleague ironically asked him, 'What's this about your liquid crystals? Can they now eat?'

What was lacking now was any input from theoretical physics. In the years 1907–9 the first serious attempt at a mathematical theory of liquid crystals was made by Emil Bose from the Physical Chemistry department of the University of Danzig (now Gdansk in Poland, but then a free German-speaking city). He published three papers[30] in the *Physikalische Zeitschrift*. The first of these was entitled 'For and against an emulsion structure for crystalline fluids'. The basic conclusion (perhaps for the first time, but certainly not for the last time, in the history of the subject!) is that rather than talk of liquid crystals or crystalline fluids, it would be better to refer to *anisotropic* fluids, for there is no real crystal structure. At any rate, following Schenck, Bose finds against the emulsion picture despite having been initially attracted by it.

We include Bose's second paper in our collection as article A7. This is the most influential of the three articles; the third is an attempt to compare theory with experiment. At this time there were really only two sets of statistical mechanical models on which to base a theory. One of these strands was van der Waals's 1873 model of the fluid equation of state.[31] This leads naturally to the idea of a liquid–gas phase transition. The other strand included Pierre Weiss's (very new) model of ferromagnetism,[32] now known as the Curie-Weiss theory, as well as the ideas of Paul Langevin.[33]

Bose tried, not entirely successfully, to draw eclectically from both of these. He was led to introduce the idea of molecular *swarms (Molekülschwärmen)*. We include this paper, despite the eventual failure of Bose's ideas, because this idea remained influential in liquid crystal science for a long time. For many years the literature contained earnest but awkward discussions about the difference between a *chemical* molecule (the real one!) and the *physical* molecule. The latter was supposed to be the swarm of molecules pointing more or less in the same direction. In any event the swarm theory, as it became known, passed, albeit temporarily, into the canon. As late as 1957, it was quoted approvingly in the major review article of the day in *Chemical Reviews*.[34]

What is wrong with Bose's paper is that although his physical motivation was correct (he is searching for a theory of anisotropic fluids), his mathematical starting point was not, in that he started out from the van der Waals theory of fluids. He was compelled to introduce molecular anisotropy in a forced, unnatural and essentially phenomenological manner. The result was that he missed the point, despite realising that the important physics lay in the Weiss and Langevin theories of magnetism. Shortly afterwards Bose died tragically young at only 37. Had he lived, it seems likely that he would have been able to reformulate his ideas and obtain a good molecular field theory of liquid crystals before the First World War.

In the spring of 1909 Lehmann, by now 54 and an established figure, visited Geneva and Paris, and at each venue gave a long seminar accompanied by experimental demonstrations.[35] The visits seem to have been a success, for they inspired the formation of a French school of liquid crystal science which has remained influential to this day.

His host in Paris was the eminent crystallographer and member of the Academy of Sciences Fréderic Wallerant, who held a chair at the École Normale Supérieure. Amongst those influenced by Lehmann's visit were Charles Mauguin, Georges Friedel and François Grandjean. Mauguin was at the time Wallerant's assistant in Paris, Friedel was director of the School of Mines at St Étienne, with Grandjean his assistant. Lehmann's lecture turned Mauguin toward a study of liquid crystals. He must have established a warm relationship with Lehmann, for two years later he paid him a return visit in Germany. Both groups started working in liquid crystals.

We include two of Mauguin's early papers, published in 1911 as articles A8 and A9 in our collection. It is noteworthy that in fact a digest of this work was also published in the *Physikalische Zeitschrift*, presumably at the behest of Lehmann, who felt that they should be available in the German literature as well. Mauguin's studies were carried out using Gattermann's by-now-standard liquid crystals azoxyanisole and azoxyphenetole. The more substantial of these, article A9, simply entitled 'On Lehmann's liquid crystals', was published in the *Bulletin de la société française de mineralogie*.

Mauguin concentrated on the behaviour of a liquid crystal confined between plates in thin layers, of thickness between 10 and 150 microns, i.e. roughly of the dimensions on which present-day studies are carried out. This is to a certain extent in contrast to Lehmann's work, in that much of Lehmann's studies concerned droplets. His studies involved both parallel light and converging light, and of course he used a polarising microscope. The use of converging light – conoscopy – was necessary in order to detect birefringence in the direction of view, for otherwise the sample appeared isotropic.

A number of important ideas appear in Mauguin's article. The extinction reappears when the sample is heated and subsequently cooled. In modern language, it is the director whose orientation is retained by the surface. The *memory effect*, as it has come to be known, was thought by Lehmann to depend on films of oriented molecules adhering to the glass slides. Mauguin further noticed that the optical phenomena persisted in a moving liquid, a fact apparently inconsistent with Lehmann's conception of a liquid crystal as a crystal which flows. He was able to calculate the degree of optical birefringence from his experiments.

Most profoundly for the subsequent history of the subject, he examined 'birefringent liquid films with a helicoidal structure'. These were films with non-coincident surface films which no longer extinguished light between crossed polarisers. Mauguin found that under certain circumstances the polarisation of incident light is twisted in such a sample, and in general that an incident linearly polarised beam exits the sample elliptically polarised. Furthermore he was able to show theoretically that this is the consequence of what we would now call a twisted nematic cell. He demonstrated that if the ratio of the twist pitch to the wavelength of light is long, the polarisation does indeed follow the twisting birefringence. Following these observations, to this day, light undergoing weak polarisation rotation under this circumstance is said to be in the *Mauguin régime*.

Article A9, which appeared in the premier French scientific journal, the *Comptes rendus de l'Académie des Sciences*, is but a brief note, but once again of great importance. The problem he had had in his previous work had always been to obtain sufficiently large so-called crystalline (and in reality oriented liquid crystalline) domains. In this paper he reported observations that large domains could be obtained using magnetic fields. In other words, fields orient liquid crystals. He then went on to discuss the competing effects of glass plates orienting in the plane of the sample and a magnetic field orienting in the plane perpendicular to it, and vice versa. Extinction between crossed nicols could be induced or destroyed by the application of the field.

His final observation is particularly significant with hindsight. The initial sample is set up with what we would call random planar boundary conditions, so that (as we now know) the static fluctuations are sufficient to cause the sample to appear cloudy. A magnetic field is applied perpendicular to the sample. The molecules reorient giving the '... equivalent of a film perpendicular to the axis, except for a thin layer next to the glass plates ....'

The experimental programme of Friedel and Grandjean was contemporaneous with that of Mauguin. There was a healthy rivalry between the two research groups. In part this was born from the competition between Parisian patricians and provincial practical men. Reading between the lines it is clear that experimental progress ran in parallel, and that there was an understandable unwillingness by either group to grant priority to the other (this spirit is also observable in early German work!). Perhaps this purely French rivalry explains the ease with which Mauguin and Lehmann had established a warm rapport.

We have chosen as article A10 in our collection an important contribution by Grandjean in 1916. He was trying to distinguish intrinsic and extrinsic liquid crystalline effects. His article 'Orientation of anisotropic liquids on crystals' is a careful examination of the effect of crystal cleavage planes on the liquid crystals sitting on the crystal substrates. Although most of this article is devoted to detailed observations of liquid crystalline anomalies induced by defects in the crystal surface, probably the most significant observation is almost buried in one paragraph at the top of the fourth page in an article which continues for forty-nine.

Grandjean was observing drops of what he identified as focal-conic liquid crystals. These are Lehmann's flowing crystals, identified not by their degree of fluidity, but rather by their optical signature. The focal conics are the characteristic curves seen in the microscope when the flowing crystals are viewed. The focal conic liquid crystals were to be contrasted with the liquid crystals '*à noyaux*' ('with nuclei'), which is how the French school described the Schlieren texture.

The drops were attached to crystal surfaces. He found an effect which he called *phénomène des gradins*. His drops were divided into regions of apparently more or less constant height separated by narrow steps. These have passed into current liquid crystal terminology as *Grandjean terraces*. These terraces turned out to be the essential clue to the nature of the liquid crystals, for they were in fact the borders between regions in which n and $n+1$ smectic layers were to be found on a surface. We shall see how this story plays out in Section B.

Before ending this section, it is interesting briefly to discuss two further theoretical attempts at a mathematical theory of liquid crystals during this initial period. In 1916 the liquid crystal problem came to the notice of Max Born (1882–1970), professor of theoretical physics in the premier-division university of Göttingen. Born, it will be recalled, was an instrumental figure in the development of quantum mechanics during the 1920s.

We have included Bose's article on the swarm theory because of its influence, notwithstanding the fact that theory does not explain the data and is theoretically incomplete. Born's paper of 1916[36] adapted the Curie-Weiss molecular field theory of magnetism to the liquid crystal context. His basic assumption was that liquid crystalline molecules carried an electric dipole and that this quantity drives the liquid crystallinity. This theory is theoretically consistent – it *is* the Curie-Weiss theory for all intents and purposes – but unfortunately the basic assumption is wrong, because it soon turned out[37] that there were non-dipolar molecules which exhibited liquid crystalline phases. As a result, this paper has been relegated to the status of a historical footnote.

In 1917 it was the turn of Grandjean to construct a molecular field theory for liquid crystals. Because of the war he was unaware of Born's work. Perhaps for the same reason his article too remained unread and thus *ipso facto* also a historical footnote. We have included this paper elsewhere in this collection as C1, where we shall discuss it further.

The heroic period of the liquid crystalline state comes to an end around 1920. By this time a large amount of data on liquid crystals had been collected, and the number of compounds exhibiting liquid crystallinity was growing by the day. The time was ripe for the emergence of a correct picture of the molecular basis of the phenomenon, and the beginnings of a sensible description both on the molecular and macroscopic scales. This will be the topic of Section B of our collection.

References

1. Quoted by Reinitzer from an article by Gmelin in the Handbuch der Organischen Chemie **4**, 2093ff.
2. B. Raymann, Bull. Soc. Chim. (Paris) **47**, 898 (1887).
3. W. Löbisch, Ber. **5**, 513 (1872).
4. P. Planer, Ann. **118**, 25 (1861).

5. F. Reinitzer, Wiener Sitzber. **94**, 719 (1888), *ibid.* **97**, 167 (1888). These are papers presented to the Vienna Scientific Society covering more or less the same material as paper A1. The latter paper deals with the double melting properties of cholesteryl acetate and hydrocarotene benzoate.
6. An incomplete list of Lehmann's early papers includes:
   Einige Fälle von Allotropie (*Some cases of allotropy*), Zeitschrift für Kristallographie und Mineralogie **18**, 464–7 (1890);
   Ueber tropfbarflüssige Krystalle (*On drop-forming liquid crystals*), Wiedemann's Annalen für Physik und Chemie **40**, 401–23 (1890);
   Ueber krystallinischer Flüssigkeiten (*On crystalline liquids*), Wiedemann's Annalen für Physik und Chemie **41**, 525–37 (1890);
   Die Struktur krystallinischer Flüssigkeiten (*The structure of crystalline fluids*), Zeitschrift für physikalische Chemie **5**, 427–35 (1890);
   Ueber künstliche Färbung von Krystallen und amorphen Körpern (*On artistic colours in crystals and amorphous bodies*), Wiedemann's Annalen für Physik und Chemie **51**, 47–76 (1894);
   Ueber Contactbewegung und Myelinformer (*On contact motion and myelin formation*), Wiedemann's Annalen für Physik und Chemie **56**, 771–88 (1895).
7. *Struktur, System und magnetisches Verhalten flüssiger Krystalle und deren Mischbarkeit mit festen* (*Structure, system and magnetic behaviour of liquid crystals and their miscibility in solid crystals*), Annalen der Physik (series 4) **2**, 649–705 (1900).
8. O. Lehmann, *Flüssige Kristalle* (Wilhelm Engelmann, Leipzig, 1904).
9. Lehmann op. cit. p. 52.
10. L. Gattermann, *Synthese aromatischer Aldehyde* (*Synthesis of aromatic aldehydes*), Liebigs Ann. Chem. **347**, 347–86 (1906).
11. J. Perrin, *Brownian movement and molecular reality* (Taylor and Francis, London, 1910).
12. See e.g. W. Friedrich, P. Knipping and M. Laue, Sitzber. Bayer. Akad. Wiss. **303**, 363 (1912); also: W. Friedrich, *Die Geschichte der Auffindung der Röntgenstrahlinterferenzen*, Die Naturwissenschaften **10**, 363–6 (1922), Paul Knipping, *Zehn Jahre Röntgenspektroskopie*, Die Naturwissenschaften **10**, 366–9 (1922);
    W.H. Bragg and W.L. Bragg, *The reflection of X-rays by crystals*, Proc. Roy. Soc. **A88**, 428–38 (1913);
    W.L. Bragg, *The structure of some crystals as indicated by their reflection of X-rays*, Proc. Roy. Soc. A**89**, 248–77 (1913).
13. Quincke was professor of physics first in Berlin and later in Heidelberg.
14. See e.g. G. Quincke, *Ueber freiwillige Bildung von hohlen Blasen, Schaum und Myelinformen durch ölsaure Alkalien und verwandte Etrscheinungen besonders des Protoplasmas*, Wied. Ann. **53**, 593–631 (1894); G. Tammann, *Ueber die Grenzen des festen Zustandes*, Wied. Ann. **62**, 280–99 (1897).
15. See: G. Tammann, *Ueber die sogenannten flüssigen Krystalle*, Ann. Physik **4**, 524–30 (1901); O. Lehmann, *Flüssige Krystalle, Entgegnung auf die Bemerkungen des Hrn G. Tammann*, Ann. Physik **5**, 236–9 (1901);
    G. Tammann, *Ueber die sogenannten flüssigen Krystalle II*, Ann. Physik **8**, 103–8 (1902);
    O. Lehmann, *Ueber künstlichen Dichroismus bei flüssigen Krystallen und Hrn. Tammann's Ansicht*, Ann. Physik **8**, 908–23 (1902);
    O. Lehmann, *Näherungsweise Bestimmung der Doppelbrechung fester und flüssiger Kristalle*, Ann. Physik **18**, 796–807 (1905);
    G. Tammann, *über die Natur der "flüssigen Kristalle"* III, Ann. Physik **19**, 421–5 (1906).

This exchange unearthed previously neglected papers on the double-melting phenomenon, going back all the way to W. Heintz in 1849. He was quoted as having written an article in the 1849 Yearly Report on Progress in Chemistry, p. 342 in which he made just such an observation. (A more accessible reference to Heintz's work is in W. Heintz, J. prakt. Chem. **66**, 1 (1855).) Lehmann is sceptical as to whether Heintz's double-melting is the same phenomenon as occurs in liquid crystals, stating that 'allegedly all fatty acids have double melting points.' For the fatty acid case in fact, surprisingly, Lehmann is a supporter of the Tammann school of thought, noting (while citing Gibbs) that 'a liquid does not have necessarily to be a single phase. Milk, ink, colloidal gold solution and egg-white are examples of two-phase fluids'.

16. G. Coehn, *Über Flüssige Kristalle*, Z. Elektrochemie **10**, 856–7 (1904).
17. G. Bredig and N. Schukowsky, *Prüfung der nature der flüssigen Kristalle mittels Kataphorese* (*Test of the nature of liquid crystals using cataphoresis*), Ber. Dt. Chem. Ges. **37**, 3419–25 (1904).
18. Georg Bredig was a leading German physical chemist in the early part of the 20th century. Born in 1868 in Glogau, he obtained his Ph.D in Leipzig in 1894 as a student of Wilhelm Ostwald. After postdoctoral periods with van't Hoff and Arrhenius, he obtained his habilitation in 1901, subsequently working in Heidelberg and Zürich. In 1911 he became full professor of physical chemistry in Karlsruhe, and became Rector there in 1921. His main scientific activities concerned catalysis and optically active compounds, decomposition processes of metal sols, and kinetics of reactions catalysed by protons. In 1933, following the Nazi rise to power in Germany, he was removed at the age of 65 from his post because of his Jewish background. He emigrated to the Netherlands in 1939, escaping to America in 1940, where even at the age of 72 he was offered a post at Princeton. This he was unable to take up as a result of ill-health. He died in New York in 1944. Schukowsky was probably his graduate student.
19. See also: R. Schenck: *Kristalline Flüssigkeiten und flüssige Kristalle* (Wilhelm Engelmann, Leipzig, 1904).
20. T. Rotarski, Ann. Phys. **4**, 528 (1901).
21. W. Kast, *Anisotrope Flüssigkeiten*, Z. Elektrochemie **45**, 184–200 (1939).
22. W. Kast, *Die Molekul-Struktur der Verbindungen mit kristallin-flüssigen (mesomorphen) Schmelzen (Molecular structure of compounds with crystalline-liquid (mesomorphic) melts*), Angew. Chem. **67**, 592–601 (1955). Recent studies, however, suggest that in "banana"-shaped mesogens, with a complex molecular structure, different conformations in different liquid crystalline phases can in fact occur. See I. Wirth *et al.*, J. Mater. Chem. **11**, 1642–1650 (2001).
23. W. Maier and G. Englert, *Infrarotspektroskopische Untersuchungen an Substanzen mit kristallin-flüssigen Phasen* (*IR spectroscopic studies of compinds with crystalline liquid phases*), Z. Physik. Chem. **12**, 123–7 (1957).
24. F. Meyer and K. Dahlem, *Azo- und Azoxybenzoäureester*, Ann. Chemie **331**, 331–46 (1903).
25. D. Vorländer, *Neue Erscheinungen beim Schmelzen und Krystallisieren*, Z. Physik. Chem. **57**, 357 (1907).
26. D. Vorländer, *Kristallinisch-flüssige Substanzen* (Stuttgart, 1908).
27. O. Lehmann, *Zur Geschichte der flüssigen Kristalle*, Annalen der Physik **25**, 852–60 (1908);

    F. Reinitzer, *Zur Geschichte der flüssigen Kristalle*, Annalen der Physik **27**, 213–24 (1908);

O. Lehmann, *Bemerkungen zu Hr. Reinitzers Mitteilung über Geschichte der flüssigen Kristalle*, Annalen der Physik **27**, 1099–1102 (1908).

28. O. Lehmann, *Die optische Anisotropieder flüssigen Kristalle*, Physikal. Zeit. **15**, 617 (1914).
29. First he wrote an article: O. Lehmann, *Scheinbar lebende Kristalle* (Apparently living crystals), Biolog. Zentralblatt **28**, 513–26 (1906); and then two years later followed it up in a longer monograph: O. Lehmann, *Die scheinbar lebenden Kristalle* (Apparently living crystals) (Verlag Schreiber, Esslingen and München, 1908). By this time Lehmann was aware of the liquid crystalline potential of certain organic molecules, in particular myelin. This had been studied by Virchow as early as 1854, and its birefringent properties had been observed by Mettenheimer in 1858. We discuss this subject in more detail in Section E.
30. The two papers in this series not reprinted here are:
    E. Bose, *Für und wider die Emulsionsnatur der kristallinischen Flüssigkeiten*, Phys. Zeit. **8**, 513–7 (1907); *Zur Theorie der anisotropen Flüssigkeiten*, Phys. Zeit. **10**, 230–44 (1909). These are not the only papers by Bose on liquid crystals. He took an active interest in the Tammann–Lehmann controversy, only rejecting the colloidal hypothesis after much thought. See also E. Bose and F. Conrat, *Über die Viskositätsanomalien beim Klärpunkt sogenannter kristalliner Flüssigkeiten*, Phys. Zeit. **9**, 169–73 (1908) and E. Bose, *Über Viskositätsanomalien anisotroper Flüssigkeiten im hydraulischen Strömungszustande* (*Ein Experimentalbeitrag zur Schwarmtheorie der kristallinen Flüssigkeiten*), Phys. Zeit. **10**, 32–86 (1909).
31. J.D. van der Waals, *Over de continuiteit van den gas- en vloeistoftoestand* (*On the Continuity of the Liquid and Gaseous State*) [in Dutch; Ph.D thesis, University of Leiden (Netherlands), 1873]. This thesis explained, at least qualitatively, experimental results by Thomas Andrews, the successor of Michael Faraday at the Royal Institution in London. Andrews was studying the pressure–volume–temperature relations in CO_2, and presented his results to the Royal Institution in the Bakerian lecture in 1869. It was in this lecture that he introduced the term ‘critical point’ to describe the thermodynamic point at which liquid and vapour become identical.
32. P. Weiss, *L’hypothèse du champ moléculaire et la propriété ferromagnétique*, J. Phys. Rad **6**, 661–90 (1907); see also the German version in: *Molekulares Feld und Ferromagnetismus*, Phys. Zeit. **9**, 358–67 (1908). Note that Bose cites the German version.
33. P. Langevin, Ann. Chim. Phys. (Paris) **5**, 70 (1905).
34. G.H. Brown and W.G. Shaw, *The mesomorphic state: liquid crystals*, Chem. Rev. **57**, 1049–1157 (1957). This encyclopaedic review article played a (perhaps *the*) major role in the post-war revival of interest in liquid crystals; see Section C.
35. O. Lehmann, *Les cristaux liquids*, J. Phys. (Paris) **7**, 713–35 (1909);
    O. Lehmann, *Cristaux liquids et modèles moléculaires*, Archives des sciences physiques et naturelles (Geneva) **28**, 205–26 (1909).
36. M. Born, *Über anisotrope Flüssigkeiten. Versuch einer Theorie der flüssigen Kristalle und des elektrischen KERR-Effekts in Flüssigkeiten*, Sitzungsber. Preuss. Akad Wiss. **30**, 614–5 (1916). (This is the report of the maths and physics session of the Prussian Academy of Sciences dated 25 May 1916).
37. G. Szivessy, *Zur Bornschen Dipoltheorie der anisotropen Flüssigkeiten*, Z. Physik. **34**, 474–84 (1925).