2

Crystals that flow: fact or fiction

> There are certainly such things as soft crystals, I am happy to concede flowing crystals, but liquid crystals, never!
>
> G. Tammann's remarks to the 1905 Annual Meeting of the
> German Chemical Society, University of Karlsruhe

The double-melting liquid

The foundation of liquid crystal science is traditionally set in the year 1888, with the work of Friedrich Reinitzer (1857–1927; Figure 2.1). Reinitzer is commonly termed a botanist, although in modern terms he would perhaps be thought of more as a biochemist. He was 30 years old at the time and assistant to Professor Weiss at the Institute of Plant Physiology at the German University of Prague.

Nineteenth century Prague was the capital of the province of Bohemia in the Austro-Hungarian Empire, although in earlier centuries Bohemia had enjoyed periods of independence. What is generally known as the Charles University in Prague was founded in 1347 by the Holy Roman Emperor Charles IV. It is (or rather, as we shall see, was) the oldest German-speaking university in Europe, predating the foundations of the universities of Vienna in 1365 and Heidelberg in 1386.

The late nineteenth century was a time of great political ferment in Bohemia, as political pressure for Czech home rule within the Austrian Empire gathered in strength. In 1882 the Charles University was split into independent German and Czech sections, each following studies in their own language. A majority of students chose the Czech section, in keeping with their political aspirations, but in many ways it was the German section, in which Reinitzer worked, which continued the unbroken traditions which were by now more than 500 years old. Academic staff members included the physicist and philosopher Ernst Mach, who was professor of physics from 1867 to 1895, and, most famously, the young Albert Einstein, who spent 17 fruitful months in Prague in 1911–1912.

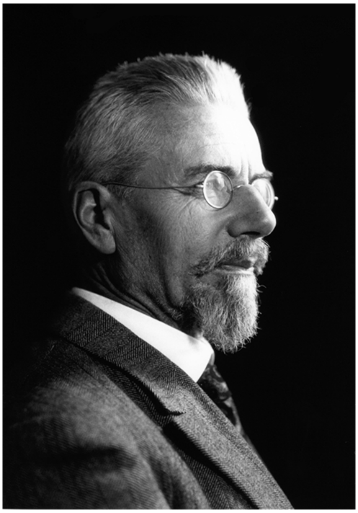

Figure 2.1 Friedrich Richard Kornelius Reinitzer (1857–1927).

If Prague is an unsurprising place to start a technological revolution, the subject matter which starts this revolution is strikingly unexpected. For Reinitzer was obsessed by carrots. More precisely, his experiments involved extracting cholesterol from carrots in order to determine its chemical formula, which at that time was unknown. He thought (wrongly as it turned out) that cholesterol was chemically related to carotene (the red pigment) and thus to chlorophyll. Cholesterol had been detected in plants and in the cells of many animals, and Reinitzer was keen to find out if the cholesterol from carrots was the same as from other sources or whether there were a number of closely related compounds.

Reinitzer examined various compounds formed from cholesterol by the action of other simple chemicals. He first studied the melting behaviour of his compounds, since a number of previous workers had observed some dramatic colour effects on cooling cholesterol compounds from just above the solidification temperature. He himself found the same phenomenon in cholesteryl benzoate, formed from cholesterol and benzoic acid.

The flashes of colours observed near the solidification of cholesteryl benzoate are not its most peculiar feature. Reinitzer found, to his amazement, that this compound does not melt like other compounds. Normal pure substances, in Reinitzer's experience, indeed in most of our experience, form crystals when they are cold and when warmed they melt into a liquid at a precise and repeatable temperature. Cool the liquid down and it freezes, reforming the crystal at the same temperature at which it had previously melted. The transition between the two states is known as either the melting point or the freezing point, depending on whether the normal state is solid (in the former case) or liquid (in the latter).

Cholesteryl benzoate was different. It appeared to have *two* melting points. At 145.5°C the solid melts into a cloudy liquid. Heat up the

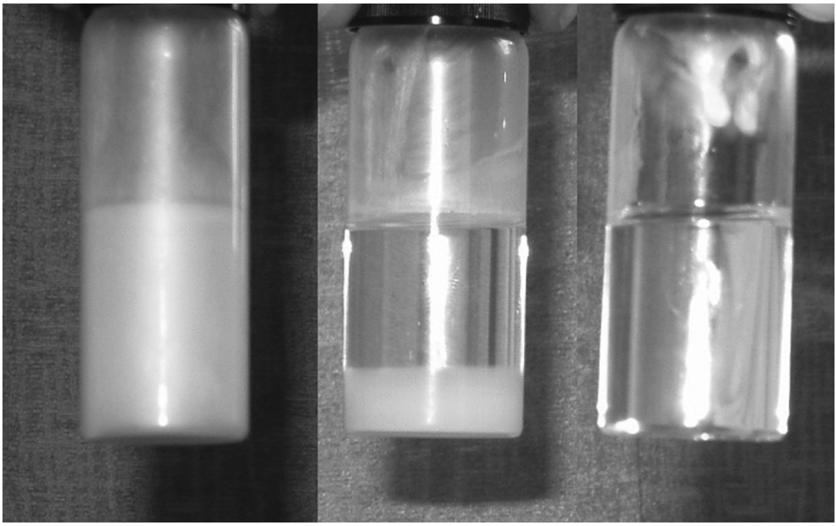

Figure 2.2 Liquid crystal sample in a test-tube, warmed from room temperature. Samples go left to right. The sample starts cloudy then develops a region in which it is clear, with the interface between the two regions advancing until the whole sample is clear. On cooling, the process is reversed. (See colour plate 2.)

cloudy liquid to 178.5°C and the cloudy liquid goes clear (see Figure 2.2). Cool down the clear liquid and the phenomenon appears to be reversible. Near both transition points the system exhibits some dramatic colours. What is going on? Unsure of his ground, and out of his depth in what is now clearly a physics, rather than a chemistry, problem (and remember Reinitzer was not even a chemist; he was merely applying standard chemical methods to what he saw essentially as a biological problem), Reinitzer sought help.

History has not recorded how exactly Reinitzer was able to identify a suitable collaborator. All we know is that somehow, by asking around and reading the scientific literature, he found his man. On 14 March 1888, he wrote to Otto Lehmann,[1] at that time an Extraordinary Professor (roughly equivalent to an Associate Professor in the USA), then the assistant of Professor Wüllner at the Polytechnical School of Aachen, close to the Dutch border in Germany. Lehmann's key skill was as a crystallographer.

We shall return to Dr Lehmann at greater length later because he plays a central role in our story. For the moment, let us follow the correspondence between Reinitzer and Lehmann. Reinitzer's first letter to Lehmann was 16 pages long and handwritten in Gothic characters. The colour phenomenon in cholesteryl benzoate 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*), Reinitzer 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! 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 others only one. Indeed it is a tribute to the exactness of Reinitzer's experimental method that he observed and recorded rather subtle phenomena whose significance could not have been understood at the time. The explanation itself is complicated and involves concepts that are of extremely recent origin.

Following Reinitzer's initial enquiry there was an exchange of letters with Lehmann, and presumably of samples as well, throughout March and April of 1888.[2] Lehmann examined the intermediate cloudy fluid and reported that he had seen tiny crystals, or crystallites. When the exchange of letters ended on 24 April, although definitive answers to the nature of the cloudy phase had not been elicited, Reinitzer felt that he had enough to publish. His results were presented, with fulsome credits to Lehmann, and also to his Viennese colleague von Zepharovich, at a meeting of the Vienna Chemical Society on 3 May 1888.[3] The important point here is that these first observations of liquid crystals (although not yet recognized as such) were a serendipitous by-product of an apparently unrelated piece of research. Neither for the first nor for the last time, Nature had sprung a surprise on an unprepared investigator.

After accidentally stumbling into ground-breaking territory, Reinitzer more or less disappears from this narrative. He was promoted to professor in Prague and then to a professorship in Graz in 1895, where he later took the position of Rector. His one further contribution to the story came some 20 years later, in a rather unedifying exchange with Lehmann in the pages of *Annalen der Physik* concerning scientific priority.

The scientific puzzle is now taken up by the 33-year-old Lehmann. Reinitzer had stumbled onto an inexplicable observation, but Lehmann realized that he had come across a new phenomenon. Furthermore, Lehmann, unlike Reinitzer, was in a position to launch a systematic research programme to investigate it.

Herr Professor Dr Otto Lehmann

Otto Lehmann (see Figure 2.3) was born in 1855 in Konstanz, close to the Swiss border. His father, Franz Xavier Lehmann, was a mathematics high school teacher. More important for his son's future career was his interest in microscopy, which led him to develop a laboratory at home. In this laboratory he examined carefully the spiral forms on snail shells

Figure 2.3 Otto Lehmann (1855–1922).

and traced around the outside of leaves, seeking always a connection with mathematical formulae.

Otto Lehmann's childhood was peripatetic, for his father's post in the Baden-Würtemberg school system meant that the family was constantly being moved around the state. Successively the family moved from Konstanz to Freiburg, from Freiburg to Offenbach, and finally from Offenbach to Rastatt, near Karlsruhe. Otto was an only child, and the frequent relocations must have interrupted his social interactions with his peers. Instead he created a social life for himself in his father's laboratory. By the age of 17 he was already using his father's microscope to carry out quite sophisticated studies of growing crystals (in particular snowflakes).

These studies prepared him for a life in science in a number of ways. He became adept at self-teaching, requiring only himself and a book to learn new material. He became a careful experimenter, keeping detailed notes and fastidious records. Historians of science must track progress through records that are available. If political history is written by the victors, then scientific history is written by those who keep the most complete notebooks, and Otto Lehmann's notebooks were up with the best. He began to understand the importance of first-hand observation in the development of a scientific picture. Later in life, he faced opponents who treated his observations with scepticism because they did not fit a previously conceived world view. He was hard on such opponents, and would strongly defend his opinions against accepted scientific wisdom. Otto had developed a pride and confidence in his own work, but this later led him easily to take offence when—as naturally occurs as part of the scientific dialectic—his work was challenged. Of all his qualities, perhaps only Lehmann's pride was not always scientifically fruitful.

At 17, in 1872, he was already off to university in *Straßburg*. No longer Strasbourg, the city was then newly reintegrated into the German Reich following the Franco-Prussian war of 1870–1871. Its university was recruiting famous academic names from all over Germany to head up their programmes, and the young Lehmann benefited from contact with the distinguished professors.*

By 1876 we find him receiving a doctorate for a thesis in physical chemistry supervised by crystallographer Paul von Groth (1843–1927). His research involved studies of crystals of different isomeric compounds.† The principal tool in these studies was the so-called 'crystallisation microscope', which, following his youthful experience, he designed and built himself. The important feature of this microscope, which would make it ideal for studying liquid crystals, was that it was equipped with polarizers. Thus the sample could be examined by illumination with polarized light. Crystals had particular optical properties that were only apparent if illuminated by polarized light and examined through a polarizer.

The doctoral qualification that Lehmann achieved also included more general studies of other sciences, philosophy, history, as well as Latin and French. The French, examined orally, would prove of more than just cultural interest. More than 30 years later, as a famous man, he would find himself addressing colleagues in the heart of French academia in their own language.

Following his doctorate, Lehmann then held junior academic posts in Freiburg, *Mülhausen* (Mulhouse, in Alsace, and hence at that time in Germany) and Aachen (where Reinitzer found him). The postdoctoral years were spent building up expertise in crystallography. The principal weapon in his scientific arsenal was experimental microscopy, for which, as we have seen, given his home background, Lehmann was well-prepared. It was Lehmann's jealously guarded and increasingly prestigious microscope, not yet available off the shelf, which had attracted Reinitzer's attention. With Reinitzer's peculiar double-melting liquid, a problem in search of a scientist had met a scientist in search of a problem.

In fact the letters from Reinitzer had not come at the best time. For Lehmann had just been appointed as an extraordinary professor in Dresden beginning in October 1888. However, after a very brief sojourn in Dresden, on 1 April 1889, Lehmann received a call to a full

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* Here Otto was taught by the distinguished petrographer Harry Rosenbusch (1836–1914), by the chemist and (later) Nobel Prize-winner Adolf von Baeyer (1835–1917), and by the crystallographer, Paul von Groth (1843–1927). He himself named the physicist August Kundt (1839–94)—best known to generation of schoolboys for the eponymously named tube, which measured the wavelength of sound waves—as his major influence.

† Isomeric crystals consist of molecules with the same chemical *formula* (i.e. ratios of different elements), but not the same chemical *structure* (i.e. three-dimensional molecular shape). Such molecules are said to be *isomeric* with respect to each other.

professorship of physics at the Technical High School in Karlsruhe. This was a prestigious post, for he was the successor to Heinrich Hertz (1857–1894).[‡] Back in Karlsruhe, where he was to spend the rest of his life, Lehmann now had time for Reinitzer's double-melting materials. He launched a systematic study, first of cholesteryl benzoate and then of related compounds which exhibited the double-melting phenomenon. With his microscope, he was not only able to make observations in polarized light, but also, and this was the original feature of his microscope, was able to make observations while samples were at a controlled temperature. His microscope possessed a sample holder that could be heated or cooled, an accessory that has become known as a *hot stage*.

The intermediate cloudy phase clearly sustained flow, but other features, particularly the appearance under a microscope, convinced Lehmann that his materials were also crystalline. By the end of August 1889 he had his own article on the mysterious flowing crystals ready for submission to the *Zeitschrift für Physikalische Chemie* (Journal of Physical Chemistry).[4] The tone of this article, whose first paragraphs will be of some interest to readers, not only isolated the key problem, but also give some idea of the nature of Lehmann's personality.

> **On flowing Crystals**
> **by O. Lehmann**
> **(With Plate III and 3 wood-engravings.)**[*]
>
> *Flowing crystals! Is that not a contradiction in terms? Our image of a crystal is of a rigid well-ordered system of molecules. The reader of the title of this article might well pose the following question: 'How does such a system reach a state of motion, which, were it in a fluid, we would recognize as flow?' For flow involves external and internal states of motion, and indeed the very explanation of flow is usually in terms of repeated translations and rotations of swarms of molecules which are both thermally disordered and in rapid motion.*
>
> *If a crystal really were a rigid molecular aggregate, a flowing crystal in flow would indeed be as unlikely as flowing brickwork. However, if subject to sufficiently strong forces, even brickwork can*

[‡] Hertz is now a familiar name. He is the Hertz in the '50 Hertz' describing the frequency of the alternating current that powers our houses. In Karlsruhe, Professor Hertz had experimentally verified James Clerk Maxwell's prediction of the existence of electromagnetic waves.

[*] The 'wood-engravings' indicated that special efforts had been made to reproduce pictures in the journal, and there was also a plate, containing two photographs, at the end of the journal issue to which readers' attention was drawn.

> *be set into sliding motion. In a certain sense, the resulting motion corresponds to a stream of fluid mass in which the joints between the individual bricks open. The bricks then run out of control, moving over and rolling around each other in a disorderly manner, rather like single granules in a turbulent mass of sand.*

Lehmann was certain that the cloudy liquid possessed simultaneously liquid and crystal attributes, and believed truly to have discovered ‘crystals that flow’. Much of the rest of the article is concerned with advocating the coexistence of liquidity and crystallinity in the same material, and is not without flashes of rhetoric.

He must clearly have expected to meet with significant opposition, but as to the observations themselves, even if others were sceptical, he was sure:

> *These observations indeed contain many contradictions. For, on the one hand a liquid cannot melt on increasing temperature and also at the same time exhibit polarization colours between crossed nicols [polarizers]. On the other hand, a crystalline substance cannot be completely liquid…Despite all these contradictions, in my own investigations I have really been able to confirm Reinitzer’s results. The impossible here really seems to become possible, but as to an explanation I was at first totally helpless.*

He found that the cloudiness of the intermediate fluid occurred when what we would now call nucleating droplets merge, and that sometimes the individual droplets exhibited a black cross when viewed between crossed polarizers, which he refers to as nicols. The cloudiness itself was the macroscopic manifestation of ‘large star-like radial aggregates of needles’.

Lehmann’s observations were quick to attract the attention of colleagues. As early as 1890, the organic chemist Ludwig Gattermann* (1860–1920) wrote:[5]

> *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 crystallization cycles. Following your article I am now clear as to what is going on.*

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* At that time Gattermann was a mere *Dozent* (Lecturer in UK currency, or Assistant Professor in the USA) at the University of Heidelberg, before moving to a full professorship in Freiburg-im-Breisgau in 1900. He was later to become famous for his ironically labelled eponymous *Gatterman’s Cookbook*, a comprehensive textbook known more formally as the *Practice of Organic Chemistry*.

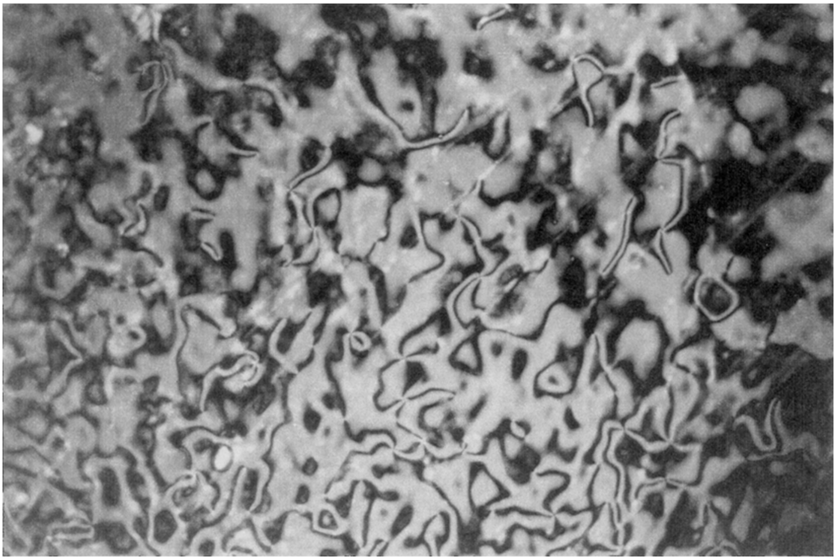

Figure 2.4 The schlieren texture. This is an optical pattern seen in a polarizing microscope, characteristic of Lehmann's liquid crystals. (See colour plate 4.)

Gattermann had made a compound whose properties at first seemed peculiar. After some puzzlement, and correspondence with Lehmann, he realized that his new material—para-azoxyanisole (PAA)—shared the properties of Lehmann's flowing crystals. Gattermann seems to have been the first to use the term *liquid crystals* to describe the strange new materials. For many years, even until after the World War II, PAA was to be the standard material on which to study liquid crystal properties.

The examination of PAA under the polarizing microscope is a testimony to Gattermann's scientific imagination. His bulk samples often exhibited peculiar streaks, *Schliere* (stains), he called them. Later it turned out that many (though not all) of the liquid crystals showed this pattern, which they called a *texture.* An example of what has come to be known as the *schlieren texture* (even in English) is shown in Figure 2.4.

Liquid crystal droplets also exhibit dramatic and striking optical patterns, and can sometimes amalgamate. When they do so, the patterns change rapidly. Gattermann defined this phenomenon as *copulation*. It was not to be the last time that comparison would be made between the physical properties of the liquid crystals and biological process and function. As time passed, as we shall see presently, the comparison would be made with a deeper purpose than that of mere rhetorical flourish.

In the years following, Lehmann made exhaustive studies of the optical properties of what were being called flowing crystals.[6] Because

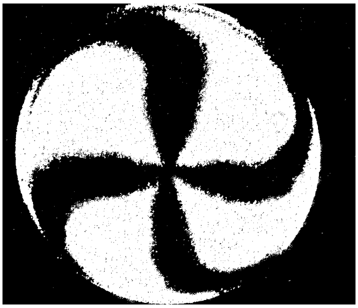

Figure 2.5 Liquid crystal droplet showing the characteristic dark cross when viewed through crossed polarizers.

the essence of their unusual optical behaviour seemed to occur in the droplets, he made a virtue out of necessity. Often he deliberately prepared fluid mixtures from which the flowing crystal phase would settle out in droplet form.

Lehmann found other materials which exhibited, as in cholesteryl benzoate, two melting points. Some materials even exhibited *three* melting points. He found a phase which he sometimes called *Fliessende Kristalle* (flowing crystals) or sometimes called *Schleimig flüssige Kristalle* (slimy liquid crystals). There was another phase with different properties which he named *Kristalline Flüssigkeit* (crystalline fluids) or *Tropfbar flüssige Kristalle* (liquid crystals which form drops). If these two 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.

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 that had hitherto been uniquely associated with crystallinity, that of *birefringence*, which explained the peculiar dark crosses seen through the polarizing microscope in droplets (Figure 2.5).

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* (liquid crystals). The amount of material that he had collected was multiplying to an encyclopaedic degree. By 1904 Lehmann had published 10 papers on his new substances. It was time to pause for breath, take stock, sort the wheat from the chaff, and summarize his findings for posterity. This he did in a generously-sized 260 page tome, including no less than 483 illustrations drawn from his microscopic observations, which was published by Wilhelm Engelmann in Leipzig. Never one at a loss for words, Lehmann

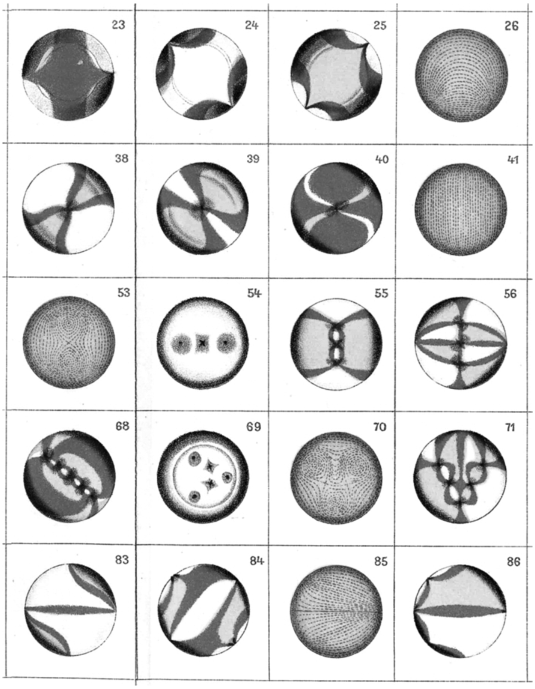

Figure 2.6 Coloured pictures of liquid crystal droplets. Reproduced from Lehmann's 1904 book. These are a few from an enormous collection of similar images. (See colour plate 3.)

entitled it *Flüssige Kristalle sowie Plastizität von Kristalen im Allgemeinen, molekulare Umlagerungen und Aggregatzutandänderungen* (liquid crystals as well as crystal plasticity in general, structural changes and changes in the state of aggregation), or just plain *Flüssige Kristalle* for short.[7]

Lehmann had long experience of preparing sketches and photographs from microscopic observation. However, the pictures of liquid crystal droplets which emerged when he developed the (black and white) images from his camera did not do justice to what he saw as he gazed through the eyepiece of the latest in his series of beloved microscopes. The blacks and whites, and even greys, failed to communicate the brilliance of the visions nature was presenting him. He was not the last to find liquid crystal textures addictive.

Nowadays we can faithfully reproduce nature's colours electronically. Lehmann was forced to resort to a more labour-intensive solution. His research assistant was set to work laboriously colouring in the camera's black-and-white reproduction, so as to simulate the real thing. It must have taken months, but the result is dramatic. Some of the images are reproduced in Figure 2.6.

Supporters and opponents

Notwithstanding the lack of proof of its essential nature, crystallinity certainly seemed incompatible with fluidity. Lehmann's assertion that he had observed liquid crystals was not, as we have seen, made trivially. The liquidity of his materials was plain for all to see. The crystallinity was less obvious, but here too the grounds were strong. He had two principal reasons for believing that he had crystals. One was simply the evidence of his own eyes. You could *see* the crystals in the microscope.

The other reason was more subtle. The liquid crystals looked dramatic, but only under the polarizing microscope, that is, between crossed polarizers. This meant that somehow birefringence was playing an important role. The cloudy double-melting phase appeared (at least to Lehmann) to break up into many regions when looked at as a layer under the microscope. Each region itself seemed to be transparent but anisotropic and birefringent. The cloudiness visible to the naked eye was the result of the light constantly changing direction as it was refracted at the boundaries between different regions, each of which had a different special direction. The cloudiness was therefore a secondary, rather than a primary, characteristic, that is, it depended on how you looked at the sample. Finally, Lehmann knew that birefringence only occurred in crystals because this was the only circumstance in which it had been observed, and this was the only circumstance in which mathematical theory seemed to allow it. Lehmann had followed Sherlock Holmes's adage of eliminating the impossible and had arrived at what he regarded as merely the improbable. Liquid crystals it had to be.

All pioneers in strange territories acquire acolytes willing to seek their fortunes in the new country. Gattermann can partly be regarded as such, even though most of his time was spent exploring elsewhere. A more enthusiastic acolyte was the young Rudolf Schenck (1870–1965) of the University of Halle. The ancient city of Halle, birthplace of the composer George Frideric Handel (1685–1759), 250 km to the south west of Berlin in Saxony–Anhalt, has played, and indeed continues to play, an important role in the history of the liquid crystal phases.

In fact Schenck's interest in liquid crystals was somewhat serendipitous. He was a student in Halle, his home town, and his interests were turning from organic chemistry to physical chemistry. He was trying to carry out a difficult experiment involving heating up gases. The work was relatively unsuccessful, but then came to an abrupt and dramatic end when a cleaning lady in the department accidentally smashed his apparatus. Following this incident he retired grumpily to the library. There, whiling his time away reading the latest periodicals, he came across Gattermann's recent publication on PAA. This stimulated him to study liquid crystals.[8] He continued this work at the University of Marburg, where he obtained his Habilitation* degree in 1897 and was then appointed to a lectureship. He made contact with Lehmann and although they did not publish together, they influenced each other's work and Schenck joined the small but growing group of liquid crystal scientists.

Others were less keen. Perhaps this is not surprising, given the circumstances and intellectual climate of the day. Lehmann's point of view elicited more than a little scepticism from some of his scientific peers concerning the very existence of the liquid crystal phenomenon. They were worried by the apparent explicit contradiction between the existence of a crystal lattice and liquid crystals.

For them, Lehmann's unlikely explanation was impossible. They sought more conventional explanations. This usually involved some sort of colloidal mixture that combined solid and liquid components. In such a case properties intermediate between those of a solid and those of a liquid would be less surprising.

The first such suggestion seems to have been made in 1894 by Georg Quincke (1834–1924), professor of physics in Berlin and later in Heidelberg.[9] It was clear therefore, averred Quincke and the Russian theoretical physicist Georg Wulff (1863–1925),† that liquid crystals must really be colloidal, suspensions of small crystallites inside a liquid. An example of such a colloid is white paint (at least while it is still in the tin!), which consists of crystallites of titanium dioxide suspended in a polymer resin. According to Quincke and Wulff, the existence of a solid component would explain the birefringence. The opaqueness or strong light scattering, called turbidity, in colloids results from the interaction of light waves with individual colloidal particles, which are just the right size to reflect the light in all directions. Interestingly, the theory which showed this explicitly was produced by Gustav Mie (1869–1957), a former assistant of Lehmann's, in 1908, but the general phenomenon had been known for a long time and had been investigated by, amongst others, Michael Faraday.

The most prominent and most vigorous and persistent sceptic was the physical chemist Gustav Tammann, later distinguished as a pioneer of modern metallurgy (Figure 2.7). Tammann was a Baltic German, born in Jamburg (since 1922 Kingisepp), near St Petersburg, in 1861. All his early career in chemistry was at the by no means undistinguished

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* The Habilitation degree is the requirement in Germany to be appointed to a Professorship.

† Later to become famous for explaining why macroscopic solids take on their characteristic crystalline shapes.

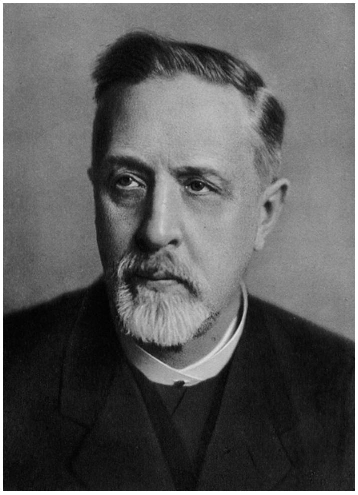

Figure 2.7 Gustav Heinrich Johann Apollon Tammann (1861–1938). The physical chemist Tammann vociferously and aggressively opposed Lehmann's idea of liquid crystals.

University of Dorpat (now Tartu, in Estonia), which despite then being part of Russia, used German as its principal language. After 1893 the medium of instruction switched to Russian and the increasingly alienated faculty (many from Germany itself) looked for other positions. Tammann himself was invited to apply for the professorship of physical chemistry at Göttingen in 1903, where he remained for the rest of his life, dying in 1938.

Those not familiar with German culture should be aware of the premier position held by Göttingen in the German-speaking world—comparable to Oxford and Cambridge in England—so the move from Dorpat to Göttingen should be seen as real recognition of Tammann's perceived promise and talent. Indeed, in the late 1890s and early 1900s he was gaining an impressive reputation as *the* up and coming man in thermodynamics. In particular his specialities were the study of the effects of heat and pressure on materials, and the phase behaviour and mixing properties of complex mixtures. With its peculiar phases, the behaviour of liquid crystals was a natural theoretical problem for him to tackle. Peculiar phases required peculiar talents, and Tammann was certainly not a man who lacked self-confidence.

Tammann vociferously propounded the view that the underlying cause for the anomalous 'liquid crystal' behaviour would be found when the purity of these substances was carefully examined. His first contribution to the debate in 1897 only elliptically referred to liquid crystals,[10] but in an article submitted to *Annalen der Physik* on 27 December 1900, sarcastically entitled 'On the so-called liquid crystals',[11] he suggested an alternative viewpoint. He made an analogy with the behaviour of water–phenol mixtures. The simple organic compound phenol, commonly known as carbolic acid, in former times was the cleaning agent that gave rise to the characteristic smell in hospitals and other institutions. Phenol is only partially miscible with water, depending on the relative amounts of phenol and water. Below a certain *lower critical temperature*, mixing does not occur and the resultant mixture of water and phenol appears cloudy.

Perhaps, suggested Tammann, the so-called liquid crystals were really a mixture of some sort. These mixtures were also exhibiting a lower critical temperature, he proposed, but of a type not previously observed. Tammann compounded his legitimate scientific disagreement by suggesting that a volume change observed by Schenck in Marburg at this critical temperature, the clearing point, was probably the result of poor measurement, and that the sensitivity of the clearing point to impurity concentration was good evidence that the whole phenomenon was impurity driven. In a mixture, no abrupt change in volume is observed when it separates. Incidentally, he remarked, since the liquid crystal patterns observed in the microscope were not easily disrupted by poking the sample, almost certainly everything was occurring at the surface anyway. The tactless suggestion of error and careless experimentation transformed a disinterested scientific discussion into an unpleasant personal confrontation that lasted many years, and which still echoes through the ages.

Tammann's underlying objections were really twofold. On the one hand it was known that colloids with particles whose sizes were of the order of magnitude of the wavelength of light strongly scatter light. In fact Tammann preferred the idea that liquid crystals were *emulsions*, in which droplets of one liquid are suspended in another. Emulsions are often thought of as a particular form of colloids. Familiar emulsions include milk (oil droplets in water) and vinaigrette (oil droplets in vinegar). Both systems are cloudy, and in this way superficially resemble the turbid liquid crystal state. It was the strong physical resemblance of liquid crystals to such systems which convinced Tammann, on the basis of what we now know to be inadequate evidence, that this was also the case here. His other objection was due to his strong attachment to the as-yet-unproven lattice theory of solids. Liquid crystals, he believed, really were a contradiction in terms.

Tammann's published article enraged Lehmann. On 25 February 1901, he fired off a lengthy reply.[12] In principle Tammann could be right, he admitted (and he had himself seen some examples of such phenomena in other materials), if only there had been no other observations. But there *were* other observations! Indeed (Lehmann too was no slouch with heavy irony) in a lengthy recent article he had explained how he had been led to the idea of a liquid crystal, but this article seemed to have escaped Tammann's notice, for it was not mentioned in Tammann's paper.

Lehmann's points of rebuttal were somewhat technical. He noted the existence of a surface tension between the cloudy and clear phases, which is inconsistent with the picture of an impurity-induced phase. He pointed to the fact that one could observe clear extinction directions (regions of destructive optical interference) in his polarizing microscope (and which, as we have seen, should only occur in real honest-to-goodness crystals). As to Tammann's comment that the effects must really be confined to the sample surface, if that were really the case, then the colours exhibited by the liquid crystal samples under the polarizing microscope would always be the same, but actually they depend on sample thickness. Then, if Tammann could be rude about Lehmann's experimental technique, he could return the compliment. Tammann's attempts to purify the sample, he asserted, had actually had exactly the opposite effect! Tammann's (but not his own or Schenck's!) experiments had been carried out on impure samples. No wonder Tammann had observed impurity effects! But if pure materials are used, in this case, not much is changed. As a final warning shot, he also escaped from Tammann's criticisms of experiments on cholesteryl benzoate by pointing out that anyway this compound is not strictly a 'liquid' crystal, but a 'flowing' crystal.

Tammann was unconvinced, but remained silent for a year. On 3 March 1902, however, he was back, submitting yet another paper to *Annalen der Physik*, with the same title as before.[13] Given Lehmann's rather robust response to his previous missive, Tammann shifted his ground somewhat. Look, he said (implicitly, one has to read between the lines), last time I only skated the surface with my objections. Let me put them with full force. Lehmann's liquid crystals do not 'shake' like real solids (technically, they possess no shear elasticity, so they cannot possess an underlying lattice). The (re)definition of cholesteryl benzoate as a flowing crystal was *ad hoc* (i.e. invented just for the purpose of explaining these experiments) *and* otherwise implausible. Liquid crystals, pointed out Tammann, were *all* milky and equally milky, but solid crystals, on the other hand, were perfectly clear, so where was the commonality? And then, if liquid crystals really were mixtures or emulsions, then distillation (i.e. boiling them off in a special apparatus in such a way as to eliminate the impurities) would lead to a shift in the clearing point, and his former student Rotarski had shown experimentally that this was indeed the case. Tammann concluded by re-emphasizing that all so-called liquid crystal phenomena were typical of emulsion behaviour.

Lehmann was by now incandescent. His reply,[14] submitted on 31 May 1902, was 15 pages long, with again a numbered list of points. By now, however, battle lines were drawn, and many of Lehmann's explanations only made sense within the liquid crystal paradigm. An example of this is his assertion that liquid and solid crystals differ because of their lack of shear elasticity. The substantive point made by Lehmann was, as we have already seen, that the cloudy phase is not really cloudy at all, contrary to Tammann's assertion. Under a microscope, magnified 700 times, it becomes clear, just like a solid crystal. Each droplet is *anisotropic*, and the cloudiness is because the whole system is an aggregate of differently ordered droplets. Lehmann's irony degenerated into sarcasm as he remarked that Tammann was persuaded by the new and untested lattice theory of solids, but unconvinced by the old well-tried and well-tested crystal optics. As for the remaining disagreements, they reduced to doubting the opposing experimentalist's competence. Little wonder that Lehmann was offended.

In fact Tammann's doubts were widely shared in the chemical community. Probably only Tammann—an expert in thermodynamics—was motivated and articulate enough to express them in public. However, the distinguished but elderly Russo–German organic chemist Friedrich Konrad Beilstein (1838–1906) from St Petersburg exhibited this scepticism in a 1905 letter to his Halle colleague Jacob Volhard (1834–1910).* Beilstein noted that (Georg) Quincke had shown him some work on ice and glacier formation that proved conclusively that liquid crystals were an optical illusion. Not only that, but 'Lehmann was a man who knew neither physics nor chemistry...!' Volhard was a friend of Beilstein's, but he had also supervised the Ph.D. work of Rudolf Schenck, who was contemporaneously playing a major role in the opposing camp; Schenck's reaction to this clash of loyalties is not known.

Karlsruhe 1905

It was in this climate that in late May 1905 the German physical chemistry community gathered together in Karlsruhe for the annual meeting of their society, the *Deutsche Bunsen Gesellschaft* (The German Bunsen Society).† The proceedings, published in the *Zeitschrift für Elektrochemie*, give us a grandstand view of the whole event. The meeting started on the evening of Thursday June 1—Ascension Day according to the proceedings—with a greeting party in the *Stadtgarten*, and finished with an excursion to the Old Castle in Baden–Baden on Sunday 4 June. In the event of bad weather, the walk round the castle was to be replaced by a visit to Baden–Baden itself. We are not told, however, whether (or how many of) the 166 participants actually made it to the *alter Schloss*.

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* We are grateful to Professor Horst Stegemeyer for providing us a with a copy of Beilstein's letter to Volhard.

† A good deal of detail about this meeting is provided by Knoll and Kelker (1988). We have augmented this from the outline of the meeting programme in pp 299–300 of *Zeitschrift für Elektrochemie* **11** (1905).

The meeting was a general physical chemistry meeting, with an eclectic choice of talks. Friday saw no fewer than 17 papers, including a presentation on a geological thermometer by the society's president, the Dutch physical chemist Prof. Dr Jacobus Henricus van't Hoff (1852–1911) from Berlin, another on the teaching of physical chemistry in schools, and yet another on the physical chemistry of wine.

The Saturday morning session was set to start, as the programme rigorously instructed, at *precisely* 8.30 a.m. The session was honoured to have as chairman the society's president. Van't Hoff had been professor of chemistry in Amsterdam, but bureaucratic pressures (and too high a teaching load!) had led him to accept a research-only post in Berlin in 1896. Many were envious then, but the level of his research was unquestioned. He had been the winner of the very first Nobel Prize in chemistry in 1901. His eminence meant that his authority was accepted by all. It is not impossible that the organizers had anticipated that the exercise of that authority would be required.

The session concluded, eight seminars later, with a presentation by *Privatdozent* R. Schenck from Marburg, entitled 'The nature of crystalline fluids and liquid crystals'. Lunch was then due to be taken in the *Stadtgarten* at 1.30 p.m. The proceedings also fail to inform us how many delegates lasted until Schenck's presentation, read presumably at around 1 p.m. Could some less committed delegates perhaps only have persisted until the seminar by Prof. Dr Cohen of Utrecht, on the explosive properties of antimony (with demonstration!), before tiring of the morning session?

Those few delegates—and this included Tammann—who were patient enough to wait until Schenck's paper witnessed an event in scientific history. Schenck's point of view is best presented in his book, *Kristallinische Flüssigkeiten und flüssige Kristalle* (Crystalline fluids and liquid crystals),[15] which appeared almost contemporaneously with the meeting. Originally intended as a thermodynamic appendix to Lehmann's 1904 book, it finally appeared on its own a year later, but with a blessing from Lehmann (and published by the same publisher). Perhaps the delay turned out well, for the Schenck book is shorter, less pretentious, more focused on possible objections, and altogether easier to read than Lehmann's effort. But the Karlsruhe paper provided a theatrical dimension to what turned out to be surgical unpicking of the Tammann point of view.

If previous exchanges between Tammann and Lehmann had been noted for their heat rather than their light, Schenck's presentation dragged the experimental status of the field into new pastures.[16] By 1905, the book reports, citing each of them in a list in the first chapter of the book, there had been 41 publications on or referring to liquid crystalline phenomena. By 1905 all of 21 liquid crystal compounds had been identified (there are now, in 2010, approaching 100,000!).

Schenck's paper made a number of points, all of which pointed strongly against the idea of liquid crystalline properties depending on the lack of material purity. One was to do with the dependence of the turbidity on the birefringent drops. Then there were the jumps observed in both density and viscosity at the onset of the cloudy phase. If the liquid crystal were an emulsion, there would still be a clearing point, but no discontinuities, and (as Tammann had chosen to cite this example, although of course Schenck politely did not point this out) here were some explicit results on water–phenol mixtures to stress the point. Furthermore, Schenck had actually carried out experiments on the *exact same* experimental samples used by Tammann, generously provided by Herr Professor Dr Tammann himself. Apparently Tammann had been careless in preparing his materials. Indeed they were not pure, but if the materials *are* purified, it makes no difference.

The light absorption in crystalline liquids is temperature-independent, which would not be the case in an emulsion because the droplet number would change with temperature. Emulsions can be made to separate if a high voltage is applied, but experiments by the German physical chemist Georg Bredig (1868–1944) and his student Schukowsky had failed to cause phase separation of the presumed emulsion.[17] They failed at the usual 12 volts and they failed at a higher value of 70 volts. They even failed at the *enormous* value of 48,000 volts! There was no demixing, and if there was no demixing, it must be because there was no mixture.

Not only had Bredig been unable to separate out the 'mixture' into its components, but similar experiments by Coehn, working with Tammann in Göttingen, had likewise led to a negative result.[18] In an attempt to rescue the Tammann hypothesis, Coehn had suggested that perhaps some mixtures could not be separated in this way, a suggestion treated by Bredig with laughable contempt. For Bredig, for Schenck, and for Lehmann the circumstantial evidence against the mixture idea was overwhelming.

Finally, noted Schenck, the Hungarian physicist Baron Loran von Eötvös (1848–1919) had predicted in 1886 that in pure liquids the surface tensions varied in a regular way with temperature. This would not work in a mixture, as was suggested by Tammann for liquid crystals. In fact the surface tension of liquid crystals varied with temperature in the manner expected for pure liquids, so there was no *a priori* reason to suppose that the liquid crystals were impure.

As soon as the lecture was over, up popped Tammann with a long, involved, and impressively tactless restatement of his by now well-known position, thinly disguised as a question:

> *I am familiar with liquid crystals from personal experience. I want to discuss the central question: Are these materials anisotropic or isotropic? Equivalently, has birefringence in these cloudy liquids been conclusively established?*
>
> *First: the materials in question have been observed in parallel films between crossed Nicols. Professor Lehmann has described a situation in which the image is divided into segments. When the sample is rotated, their brightness changes. This seems to demonstrate birefringence, and I would not object to calling these liquids crystals. But then one observes that the segmentation and the change in brightness are not properties of the liquid itself. Rather there seems to be an anisotropic dust adsorbed onto the glass plates surrounding the sample. If the liquid is shaken violently the picture does not change. The phenomenon is thus not a property of the liquid. It can be disrupted by interfering with the adsorbed dust. Then no segmentation can be observed. I have made such observations on many occasions, and Professor Lehmann has essentially described the same thing. I conclude from this that the liquid is not itself birefringent.*

On and on and on he thundered (or perhaps droned, for the high emotion of the meeting sadly has to be inferred from the words on the page). We omit some of the rhetoric:

> *The anisotropy relates only to optical properties. In all other contexts there is complete isotropy, and this even applies to growth phenomena. All liquid crystals are optically turbid media. They are thus emulsions, and contain at least two components. However, a complete analysis of this phenomenon has not yet been successfully carried out. In my own view, distillation of the liquid crystals offers the best prospect for the resolution of the problem, but this is an extremely difficult task.*

Unsurprisingly (and correctly) he was focusing on the importance of identification of 'liquid crystals' for the lattice theory of solids.

> *We must also take into account that Dr Schenck has found discontinuous changes in certain properties as a function of temperature. However, a discontinuous change in any given property is difficult to establish beyond doubt. Finally I would like to come to the so-called flowing crystals. There are certainly such things as soft crystals. I am happy to concede flowing crystals, but not liquid crystals. The existence of liquid crystals is a key question when considering the lattice theory of solids. I would thus assign enormous theoretical importance to the question of the existence of liquid crystals!*

So the experiments were wrong and the interpretation was wrong. The lattice theory of solids trumped everything. According to Tammann, the key observation was the turbidity. Although the birefringence at this stage was not yet understood, in the fullness of time, it would sort itself out. Lehmann, of course, took a different view.

A reply was clearly necessary, but at this point session chair van't Hoff curiously and abruptly closed the discussion. Whether eight successive papers had caused delegates' stomachs to rumble so loudly as to impede further fruitful interaction, or whether simply the chair merely wished to prevent bloodshed, is not recorded. We read that the 'discussion ran out of time…and that consequently a reply to Professor Tammann's points was impossible.' In lieu of a reply on the spot to what was clearly a contentious issue which raised important scientific issues, van't Hoff proposed the setting up of a Commission of Experts. This could examine liquid crystal problems further at its leisure. It would, of course, include, among others, Tammann and Lehmann. Meanwhile they should all reconvene in the afternoon for a demonstration in Lehmann's own laboratory.

The aftermath of the meeting was no less unhappy than the meeting itself.[19] It was not just a scientific mistake for Tammann to take on Lehmann on his home turf. Lehmann felt humiliated and insulted by what he saw as an unanswered public attack on his scientific competence and integrity. There was a bitter exchange of letters. Turning down an offer of a private meeting to sort things out, Lehmann wrote to Tammann on 12 June:

> *The treatment in the meeting must have convinced all the students that my work is completely unreliable…I must assume that you are aware that a private discussion just between us cannot repair the offence to my honour in the meeting. The people in front of whom this injustice has been perpetrated will necessarily discover that things are not like this at all…*

Tammann claimed, in a seemingly disingenuous manner, that he was merely involved in a disinterested search for truth, claiming in a letter of 14 June that he 'valued (Lehmann's) work very highly'. Retreating somewhat (in a letter of 18 June), he claimed social rather than professional offence:

> *Concerning the course of the meeting, I obviously made an error, since I could not see well in the auditorium. So I concluded that when van't Hoff kept to time, it meant that no-one disagreed with me…*

There followed a list of scientific questions. Did, for example, the turbidity disappear when you looked at it between crossed polarizers?

Lehmann answered this and other questions curtly in a letter written on 21 June. Yes it did. But he concludes the letter by remarking that although he is grateful for the opportunity of achieving understanding in a spirit of friendly cooperation, he cannot but suspect that maybe Tammann has not had actually had the opportunity to make the observations himself.

The emotional effort of all these exchanges was clearly telling on Lehmann, as he was confiding to Schenck in a parallel set of letters. Schenck, in what we might think of as pusillanimous mode, remarks on 17 June:

> *I was very interested by the letter from you which I received today. The shady tricks by Dr T which you recount are even worse than I had expected…You mustn't make any concessions. This so-called honourable man, who denies all facts…must be offered no forgiveness. As far as negotiations with T are concerned, in order to prevent later shady tricks, one must establish a protocol, which he must sign. The presence of an expert in theoretical optics and a chemist is an absolute precondition…*

War, indeed! Meanwhile, insult or no insult, Tammann's mind was also not for changing. Lehmann was turning his attention to the relationship between liquid crystals and the life sciences, a story which we shall relate in Chapter 6. We note here only that the discouraging interaction, and the emotional frustration and effort which accompanied it, led to two further books, one of which is phrased as a Socratic dialogue.

Lehmann had been exhausted by their public disagreements, but retained an emotional commitment to the subject matter. Tammann, however, although unpersuaded, was on the point of retiring hurt. He made but one further assay into the liquid crystal literature, the following year (1906), again in *Annalen der Physik*. This time it had been Lehmann who had fired the first shot.[20]

Tammann contrived a weak, if complex, reply.[21] No longer did he refer to 'so-called' liquid crystals. Unsure of his ground, he simply entitled his paper 'On the nature of liquid crystals III'. The III was understandable; it was indeed the third in the series, but normally one would expect it to have the same title as I and II! The article contains a number of excessively complicated binary liquid phase diagrams, but continued to lack a convincing explanation of the huge birefringence.

As it turned out, even the commission of experts also turned out badly, with Lehmann and van't Hoff finishing daggers drawn, but Schenck was able to retrieve something in the form of an extensive review article in 1909 in the *Jahrbuch der Radioaktivität und Elektronik*.[22] None of these personal problems impeded the progress of liquid crystal science, as we shall see in the next chapter.

TECHNICAL BOX 2.1 Optical anisotropy, the optic axis, and the director

The problem that confounded Lehmann and others in understanding liquid crystals was the optical anisotropy they observed in the polarizing microscope. Anisotropy could be easily understood for crystals in terms of lattice theory, since if the lattice dimension along one direction was greater, or less, than that in another direction, then it was obvious that the properties of the crystal, that is, the refractive index, would differ along these two directions.

However, there can be another source of anisotropy other than lattice anisotropy. If we want to locate ourselves, or indeed anything else, in the map of the Universe, then we certainly need position, as on a lattice, but we also need to know which way up the map is, that is, the direction. On a microscopic scale, a lattice provides position, but what about direction?

On Earth, we know which way is up and which is down thanks to the force of gravity (a force in technical terms is called a field). Direction on the surface of the Earth is given us by the Earth's magnetic field, which runs from the North Pole to the South Pole in lines of force, which more or less follow the lines of longitude. But we can also gain directions from looking at things—the sun, the stars, and even a boundary marker in the distance, and we can do this because light has direction.

Thanks to Newton and Huygens a great deal was understood about the directional properties of light, and all scientists working at the beginning of the twentieth century knew everything about macroscopic optical anisotropy: refraction, the polarization of light, double refraction, and birefringence.[23] If the optical anisotropy of liquid crystals didn't come from a lattice, however, where did it come from? The crystal optical anisotropy that Lehmann and others could understand was a consequence of the positional anisotropy associated with a non-cubic lattice, but nobody was thinking about other indicators for direction on a microscopic scale.

The director

The answer is clear, but it took a long time to demonstrate it. Under suitable conditions of density and temperature, molecules having an extended shape will pack together such that they minimize their collisions with each other. Such an arrangement is often likened to a shoal of fish swimming in a river. There is a difference between fish and liquid crystal molecules, which is that the latter mostly don't care whether they are facing forwards or backwards, but otherwise they will flow like a shoal of fish. The local direction is determined, and we now give it a name, the *director*, but it need not be fixed in space. The director may wander around in a fluid, or be constrained by boundaries, or, as we shall see, it can be changed by flow or external forces. Having defined a director, the optical anisotropy is easy to understand.

The optic axis

At last the origin of the optical anisotropy in liquid crystals is explained. The speed of light is different along the director from the speed of light perpendicular to the director: in fact it is faster. The direction of maximum speed of light was something that optics specialists could easily determine for crystals and liquid crystals, and it was called the optic axis. It was a special direction, since not only did light travel fastest along it, the polarization of the light was unchanged. If you looked at a crystal or a liquid crystal film between crossed polarizers down the optic axis, then you saw nothing: it was as though you were looking at an isotropic liquid . . . or nothing. But slightly tilt the crystal, or liquid crystal away from its optic axis and light was transmitted by the crossed polarizers: a clear signature of a birefringent material. *The optic axis is the director.*