

of liquid crystals 29, 930–44 (1933)	273
nematic state 29, 945–57 (1933)	289
liquid crystals 29, 1060–85 (1933)	303
viscosity of	315
anisotropic liquids	317
on rubbed surfaces: (par les surfaces frottées) <i>Revue de physique</i> 213, 875–76	320
on rubbed surfaces (par les surfaces frottées) <i>Revue de physique</i> 66, 105–30	324

THE INTER-WAR PERIOD: ANISOTROPIC LIQUIDS OR MESOMORPHIC PHASES?

Introduction

As we have seen, the newly emergent field of liquid crystals, crystalline liquids, anisotropic liquids – in the absence of convincing physical pictures, there could not yet be a consensus on terminology – had been started in the German-speaking world and leaked out to France following Lehmann's successful visits to Geneva and Paris in 1909. There was a continuing vibrant interchange of ideas, samples and even visits between Germany and France in the years leading up to the First World War. The Great War, however, temporarily interrupted free scientific interchange, although not by as much as was the case during the Second World War. Thus the important theoretical papers of Born and Grandjean did not seem to penetrate the front line. Although most of the French researchers in the liquid crystal field were allowed to continue their work uninterrupted, their German colleagues were unable to escape war duties. In 1914 Lehmann, at 59, was too old for military service, but Vorländer, already 47, dropped his scientific work in order to become a battery commander on the Eastern and Western Fronts.

With the end of the war, serious research could begin again. The big puzzle remained as to the nature of liquid crystals. Let us summarise the situation as it appeared in 1920. Some substances which were liquid-like from a hydrodynamic point of view (i.e. they flowed), nevertheless seemed crystalline from a crystallographic and optic point of view. Roughly speaking, in the context of *viscosity*, the anomalous materials could be divided into two classes, which had been denoted by Lehmann as flowing (or slimy liquid) crystals on the one hand (with high viscosity), and drop-like liquid crystals on the other (with lower viscosity), with the term 'liquid crystals' serving as an overriding classification. The crystallinity stared out at the observer from the stage of the polarising microscope. Nevertheless, because of their flow properties, some workers had been unwilling to accept these materials as 'crystals', and described them as anisotropic or crystalline liquids. A few stragglers, of whom Tammann remained the most vociferous, continued to reject the observations, still insisting as late as 1922 that the so-called liquid crystals were simply colloidal mixtures of some sort.

Under the polarising microscope, a whole slew of multi-coloured patterns had been observed. The flowing crystals in general seemed to look different from the liquid crystals. The liquid crystals exhibited the Schlieren texture, with bands of bright and dark crossing at special points, named *Kernpunkten* (hard points) in German, with the whole samples labelled by Georges Friedel as *liquides à noyaux* (liquids with cores) in French. Sometimes, when observed from a different aspect, these liquids also displayed long lines threading through them, in which case Friedel names them *liquides à fils* (liquids with threads), and sometimes the threads could be seen running into the cores. Contrast this with the flowing crystals, which exhibited under the microscope peculiar patterns resembling slices of cones, identified by mathematicians as *focal conics*, which Friedel had named *liquides à coniques*. These substances also had been found by Grandjean to exhibit some layering phenomena in drops on surfaces.

Finally there was a class of liquid crystals which rotated the plane of polarisation of light. These materials exhibited some aspects of both the flowing and the ordinary liquid crystals, and the rotatory power could be tuned by mixing materials.

The stage was set for a systematic attempt at classifying liquid crystal properties, and this was the task set for himself by Georges Friedel, at that time newly translated from his Mining School in St Étienne to Strasbourg in the newly reconquered Alsace. Friedel, as an Alsatian by birth, was keen to be a pioneer in this regard, not least because he was able to reoccupy his ancestral family home, from which he had been banished in 1911 following a dispute with what he regarded as the occupying German authorities. In January 1922 he sent a student to Karlsruhe to bring back some samples from Lehmann, and on the 23rd of that month, before even the student had returned, he sent a polite note to Lehmann to thank him for his cooperation.

Otto Lehmann died, unexpectedly, on 17 June 1922. Friedel's review article was published in the *Annales de Physique* in November 1922. We reprint translated extracts as article B1 in our collection. As we shall see below, it was perhaps as well, given the tone of this article, that Lehmann died before Friedel's article appeared. This paper is probably the most influential article on liquid crystals which has appeared, before or since. Even to refer to it as an article fails to do it justice, for in fact it is 201 pages long, and had it not appeared in a review journal, would more merit the appellation monograph than simple review.

Friedel's review marks the coming of age of liquid crystal science; with it, studies of liquid crystals pass from a collection of disparate observations to a unified body of knowledge. So influential has it been that it has acted as a screen between the early years and more modern approaches to the subject. One reason that it has acted as a screen is that it contains remarkably few references; much of the reference to earlier work is implicit rather than explicit, and Friedel is not as generous as perhaps he should have been in recognising the contributions of others. The result is that it has been difficult to follow the subject back directly from this article. Be that as it may, in later years mere citation of this work has

slew of multi-coloured patterns had all seemed to look different from the the Schlieren texture, with bands of named *Kernpunkten* (hard points) in Georges Friedel as *liquides à noyaux*, when observed from a different as threading through them, in which ds with threads), and sometimes the res. Contrast this with the flowing scope peculiar patterns resembling s as *focal conics*, which Friedel had s also had been found by Grandjean on surfaces.

which rotated the plane of polarisa- aspects of both the flowing and y power could be tuned by mixing

pt at classifying liquid crystal pro- If by Georges Friedel, at that time it Étienne to Strasbourg in the newly y birth, was keen to be a pioneer in reoccupy his ancestral family home,

following a dispute with what he s. In January 1922 he sent a student m Lehmann, and on the 23rd of that he sent a polite note to Lehmann to

June 1922. Friedel's review article November 1922. We reprint translated re shall see below, it was perhaps as hmann died before Friedel's article influential article on liquid crystals o refer to it as an article fails to do it d had it not appeared in a review onograph than simple review.

ge of liquid crystal science; with it, ction of disparate observations to a s it been that it has acted as a screen approaches to the subject. One reason remarkably few references; much of r than explicit, and Friedel is not as in recognising the contributions of t to follow the subject back directly years mere citation of this work has

served as a sign that a writer is knowledgeable about the roots of the field. For several years, in fact, following the renascence of interest in liquid crystals in the 1950s and 1960s which we come to in Section C of this collection, the Friedel review was *the* most widely cited paper in the French language scientific literature.

The Friedel paper is unfortunately too long to reprint in its entirety. We nevertheless recommend serious students of liquid crystals and the history of science to follow up the extracts we have chosen to make the effort to read the whole paper, preferably in the original. There are *samizdat* translations (one for example from the US army in the 1960s) which suffice for basic understanding, but which fail to do justice to Friedel's magnificent use of language. As translators we have endeavoured here to maintain the spirit, as well as the meaning, of Friedel's tome.

As an aside, it is worth remarking that Friedel's life was not always easy. He lost his mother when he was still a very small child. He carried the burden of the success of the family Friedel (described in more detail in his biography after the article), and following the Franco-Prussian war he was at least alienated from his family seat in Alsace. As a professional he spent his life in the provinces, in St Étienne rather than in Paris, the result of which was that despite his impressive family pedigree, he was an oppositional figure, not fully part of the scientific establishment. He was never, for example, elected to the Académie des Sciences. Whether as cause or result, he seems to have nursed a kind of private bitterness, in that he did not suffer fools gladly. The article demonstrates this in its vivid language, as we shall see; there is extra evidence from parenthetical written remarks in his archives, and his close colleague Grandjean hints as much in his extremely affectionate 1933 obituary.

We also draw the reader's attention to the reprinted title page of article B1. The article is often wrongly cited. Often the incorrect citation is simply the result of the enthusiasm of the naïve, for of this article more than others it can truly be said (at least nowadays!) that it is often cited but seldom read. In addition, notwithstanding appearances, there was no M.G. Friedel, only a Monsieur Georges Friedel. *Caveat lector!*

We now pass to a brief discussion of the article itself. The very title of the article – *The mesomorphic states of matter* – indicates the change of paradigm that Friedel was advocating. Not for Friedel a gentle opening summarising the present state of play, followed by mild suggestions for improvement. Friedel launches straight into his subject matter, guns blazing, metaphorically speaking. In the very first paragraph he tells us that liquid crystals were wrongly named by Lehmann, and this incorrect terminology had hindered the development of the subject. He, Friedel, will introduce new more appropriate terminology! Furthermore, not only did Lehmann err in denoting these substances as liquid crystals, but all the German scientists were confused... He continues in like vein.

As can be seen in the translated text, he reserves particular scorn for Lehmann's explanation of the mechanism for liquid crystal formation. Lehmann

had posited a molecular directional force (*molekulare Richtkraft*) or structural force (*Gestaltungskraft*). Friedel dismisses this as a *singulière logomachie* – mere mysticism, accusing Lehmann and colleagues of invoking a mysterious German divinity! It is the lack of reference to this exaggerated rhetoric which convinces this writer that the article has been cited by many who have not read it. The natural embarrassment of the scientist when faced with ostentatious display of emotion must be surely balanced, at least in this case, by a sense of exhilaration, as one watches the penmanship of the master cutting up lesser opponents.

The crucial thesis of Friedel was that the important feature of the so-called liquid crystals was not their degree of fluidity, but rather their molecular structure. With the help of his daughter Marie, a classicist, he invented the terms *nematic* (from the Greek word νημα = nema = thread), *smectic* (Greek σμηγμα = smegma = soap) and *cholesteric* (for many of the chiral materials, including Reinitzer's original liquid crystals were cholesterol derivatives). The ensemble was neither some peculiar crystal, nor yet a peculiar liquid, nor even a system combining the properties of both, which as we shall see below, became a point of disagreement with other workers. Rather (*and the Germans had missed this!*) one was considering a completely new state of matter, which he denoted *mesomorphic*, from the Greek words μεσος (mesos = intermediate or middle) and μορφη (morphe = shape or form). The state was mesomorphic because it was intermediate between the solid and the liquid phase. In fact Friedel did not use the term *phase*, but employed rather *stase*. The *stase* terminology, as we shall see, excited not a little controversy of its own, and was used as late as 1960 by Luzzati and colleagues in paper E5, but has not entered the canon. Friedel felt it necessary to introduce new terminology of his own here, because of the usage of phase in the context of *solid*, *liquid* or *gas*. Only the classification of phase transitions introduced in the 1930s by the Ehrenfests allowed the identification of states of matter, phases and *stases*.

The nematics could be identified with the drop-forming liquid crystals, his own *liquides à fils*, a term which he now dropped. He discusses at great length what is meant by a crystal, and the relationship between microscopic periodicity and the existence of macroscopic facets. This is a prelude to noting the *lack* of evidence for periodicity in *liquides à fils*. Thus nematics were liquid-like phases in which rod-like molecules were aligned. In fact, this much had been realised by Grandjean in his Forgotten Theory Paper (C1) of 1917. Beyond this Friedel also discusses the structure of what we now recognise as defects, as well as their origin, and makes some remarks as to how defects combine. He seems also to have understood that the nematic turbidity was not an essential property, but rather the consequence of fluctuation, for he notes that a magnetic field can quench the fluctuations and restore the transparency of the material.

Turning to the smectic phases, he was the first to realise, albeit using circumstantial evidence, that these were layered, and he went so far as to suggest that this hypothesis could be tested using X-ray diffraction. What he denoted as the cholesteric phase had hitherto been confusing, possessing some features of *liquides à fils* and some of *liquides à coniques*. Friedel realised that this was

orce (*molekulare Richtkraft*) or structural issues this is as a *singulière logomachie* – and colleagues of invoking a mysterious reference to this exaggerated rhetoric which has been cited by many who have not read it. Artist when faced with ostentatious display least in this case, by a sense of exhilaration, master cutting up lesser opponents.

the important feature of the so-called liquid n , but rather their molecular structure. With ist, he invented the terms *nematic* (from the *smectic* (Greek $\sigma\mu\eta\gamma\mu\alpha$ = smegma = soap) al materials, including Reinitzer's original (atives)). The ensemble was neither some uid, nor even a system combining the pro- below, became a point of disagreement with *ns had missed this!*) one was considering a he denoted *mesomorphic*, from the Greek or middle) and $\mu\omicron\rho\phi\eta$ (morphe = shape or cause it was intermediate between the solid did not use the term *phase*, but employed we shall see, excited not a little controversy) by Luzzati and colleagues in paper E5, but it necessary to introduce new terminology : of phase in the context of *solid*, *liquid* or transitions introduced in the 1930s by the of states of matter, phases and *stases*.

with the drop-forming liquid crystals, his now dropped. He discusses at great length lationship between microscopic periodicity ets. This is a prelude to noting the *lack* of *files*. Thus nematics were liquid-like phases ned. In fact, this much had been realised by per (C1) of 1917. Beyond this Friedel also ow recognise as defects, as well as their o how defects combine. He seems also to ridity was not an essential property, but n, for he notes that a magnetic field can e transparency of the material.

was the first to realise, albeit using circum- ered, and he went so far as to suggest that X-ray diffraction. What he denoted as the confusing, possessing some features of *à coniques*. Friedel realised that this was

a chiral nematic phase, and consequently exhibited some features of layering. There is also a sophisticated discussion of the expected optics of cholesterics, and how this was consistent with the observations, as well as a description of helix inversion in a mixture, passing through the infinite pitch state which was functionally equivalent to a nematic.

Although his article is wide-ranging, Friedel does not claim to have solved all problems, and with the benefit of hindsight, we do find some, though not many, substantive errors. Thus he seems not have realised that nematics could transmit torques, nor that there were several smectic phases. In this latter case he is inclined to dismiss observations of others hinting of what we now call polymesomorphism. He is aware that a set of confocal ellipses and hyperbolae are the focal lines of a family of parallel surfaces. Indeed he uses this, together with his observed focal conics, as a piece of evidence in building up his picture of smectics as layered materials. Nevertheless, he claims in this article to be mystified by the 'peculiar tendency of the smectic liquid to form Dupin cyclides around confocal conics'. It seems to have been the particular existence of the Dupin cyclides which puzzled him, for his general level of understanding seems to have been deep.

To sum up, the impact of this article was profound, and it indeed led to change in world-view and language in the description of liquid crystal science. Mesomorphic phases, nematics, smectics and cholesterics were soon to grace the pages of physics and chemistry journals around the world. Only one battle did Friedel lose comprehensively, and that concerned the term 'liquid crystal' itself. Intellectually his battle was won; liquid crystals were not crystals at all, but peculiar liquids with some hint of solid properties. But the epithet was vivid, and the terminology already widespread. Georges Friedel's righteous hostility to Germans and liquid crystals was insufficient to shift scientific usage of the term. Liquid crystals were here to stay.

As we have seen in Section A, the key experiments confirming the existence of solid crystal lattices were the X-ray diffraction experiments of the Braggs and of von Laue and colleagues. Friedel's article had pointed out that direct confirmation of the existence of smectic layers required an analogous experiment. And indeed, even as his article was appearing, his son Edmond was already collaborating with Maurice de Broglie in an X-ray experiment designed to do just this. The resulting paper was published on 12 March, 1923 in the *Comptes rendus de l'Académie des Sciences*, and we include this as article B2 in our collection. This article, unsurprisingly, uses Georges Friedel's mesomorphic terminology as though it were standard (which it soon would be!).

We may recall that X-ray scattering from a single crystal gives rise to spots in scattering directions related to the lattice parameters of the crystal. A powdered solid redistributes these spots into circles. Likewise, a disordered smectic would be expected to yield a circular diffraction pattern, with a simpler distribution of radii than in a solid. The authors remark that Hückel¹ had carried out the analogous experiment for nematics but had failed to discern any evidence of periodicity. Here, by contrast, the smectic signature rings out loud and clear.

From now on the pace of liquid crystal research quickens. The choice of papers in our collection is now for the first time influenced by language; for the first time there is an accessible relevant literature in English. In a number of cases we (like others) have chosen the easy route, by which we mean the English language version of a paper when equivalents have appeared slightly earlier in German or Russian. It is not quite historically fair, but we have tried nevertheless to give credit where credit is due.

The narrative is further complicated by the fact that there are several contemporaneous subplots. One subplot is the antagonistic development of Bose's swarm theory, in particular by Ornstein and Kast, and of the competing distortion theory by Oseen and later Zocher. Another subplot concerns the discovery by Frederiks* in the Soviet Union of a threshold effect for the alignment of liquid crystals in thin cells subject to a magnetic field. At the same time the long-lasting rivalry of the French and German schools over terminology and intellectual priority continues to simmer. And finally, the realisation of the existence of a scientific field with reams of open questions draws a number of major figures to organise major symposia to explore the important issues.

Paper B3 is the first paper in English by the ultimately tragic figure of Vsevolod Konstantinovich Frederiks, and in it his eponymous effect is described. Let us first remind the reader of the physics of the Frederiks effect. Fields (either electric or magnetic) align liquid crystals. Often they align parallel to the field (*positive* dielectric or diamagnetic anisotropy). So do properly prepared surfaces. Let us suppose competing effects in a thin cell. The field tends to align the liquid crystal (let us say) perpendicular to the walls, and the surfaces are prepared so as to align the molecules along the same (arbitrary) easy axis in the plane of the cell walls. As the field is increased, to begin with nothing happens, but then at some *threshold* field, the molecules in the liquid crystal begin rapidly to realign, and at only slightly higher fields than threshold the system is almost entirely realigned according to the whim of the field.

The existence of a threshold is central to the operation of modern display devices, and it is this fact which forces this effect into the early part of any elementary liquid crystal text. But by itself the effect has little obvious technological significance, although it is of considerable interest as an exemplar of the effects of competing bulk and surface fields. Nowadays the imposed field is

* The literature contains a number of spellings of this gentleman's name. In Russian he was Всеволод Константинович **Фредерикс** and there is no ambiguity. The transliteration to the German literature in 1930s used Fréedericksz (sometimes without the accent) – and seems to have been the original spelling of the Swedish family name. Even so, it seems peculiar given the actual pronunciation. It was also Frederiks's own spelling of his name during the time he spent outside Russia before 1919, and we must presumably give him the benefit of the doubt. Even in the English language literature of the period this transliteration carried the day, but the more-or-less phonetic transliteration which we have used is more usual nowadays. We revert to the early spelling when referring specifically to events which occurred at that time.

research quickens. The choice of papers is influenced by language; for the first time in English. In a number of cases we find, by which we mean the English language, that the papers have appeared slightly earlier in German or French, but we have tried nevertheless to give

credit by the fact that there are several other plots. One is the antagonistic development of Ornstein and Kast, and of the competing theories. Another subplot concerns the discussion of a threshold effect for the alignment of a magnetic field. At the same time the German schools over terminology and, and finally, the realisation of the existence of the questions draws a number of major figures and the important issues.

by the ultimately tragic figure of Vsevolod is the eponymous effect is described. Let us call it the Frederiks effect. Fields (either electric or magnetic) align parallel to the field (*positive* or *negative*). So do properly prepared surfaces. Let us call it the Frederiks effect. The field tends to align the liquid crystal and the surfaces are prepared so as to align with the easy axis in the plane of the cell walls. Nothing happens, but then at some *threshold* the crystal begins rapidly to realign, and at only a small increase the system is almost entirely realigned.

central to the operation of modern display devices is this effect into the early part of any century. It itself the effect has little obvious technical interest as an exemplar of surface fields. Nowadays the imposed field is

ings of this gentleman's name. In Russian he was called Frederiks, and there is no ambiguity. The transliteration to the German is without the accent) – and seems to have been the case, so, it seems peculiar given the actual pronunciation. During the time he spent outside Russia before 1919, there is no doubt. Even in the English language literature of the time, at the more-or-less phonetic transliteration which we find, to the early spelling when referring specifically to

usually an alternating electric field (constant voltages interact with low ionic concentrations to complicate the physics), because the coupling of electric fields with liquid crystal orientations is much stronger than the analogous magnetic effect. And nowadays too, there is much more experience in the surface alignment procedure, a problem we shall return to in papers B11 and B12. But in the 1920s the complications of applying an electric field overwhelmed experimentalists, and bespoke surface preparation was almost non-existent. Thus it was magnetic fields that were the experimental probe of choice.

We may recall that in 1926 Frederiks was working in Leningrad in the then seven-year-old Soviet Union, and was in the process of building up a research group. Frederiks's initial junior co-worker in the liquid crystal field was Alexandra Nikolaevna Repiova,[#] and Frederiks was able to use his German contacts to obtain anisotropic liquid samples from Daniel Vorländer in Halle.

Their original paradigm was Born's theory of the dipolar origin of anisotropic liquids. They reported some initial results at the Congress of the Russian Physical Society, held in Moscow in December 1926. A longer paper was published in the physics section of the Journal of the Russian Society of Physics and Chemistry the following year, entitled 'On the problem of the nature of the anisotropic liquid state of matter'.² Here we find for the first time, amongst other results, what was to become the Frederiks effect. It is interesting to note that Frederiks never refers to liquid crystals, nor even crystalline liquids, despite his Halle contacts. Already in his 1927 Russian paper, he is regularly using the term 'nematic'. As was the custom, a substantively similar paper was published in German in the *Zeitschrift für Physik*.³

The experimental set-up involves liquid crystal trapped between a lens and a flat plate, subject to a magnetic field in the plane of the flat plate which tend to realign the liquid crystal molecules away from the direction normal to the flat plate. The sample is placed between crossed nicols. The basic result is that outside a critical radius, fringes are observed; this corresponds to the region in which the field succeeds in competing with the surfaces. Inside the critical radius, the sample looks black. This is where the surface overwhelms the field.

Thus the critical field, found in a more modern context by scanning through field strengths at constant thickness, was originally observed in inverse fashion as a *critical film thickness* at constant field, and thus clearly visible in a sample of variable thickness. Frederiks and Repiova did change the field as well, and estimated that the critical thickness decreased with field according to a power law of $z \propto H^{-1.75}$. Further work by van Wyk⁴ in Utrecht, a student of Ornstein, published in 1929, found similar behaviour but with a different power law, now with $z \propto H^{-0.93}$.

This work was sufficiently noteworthy to earn Frederiks an invitation to the 55th annual meeting of the American Electrochemical Society, held in Toronto in

[#] c.f. our previous note on the transliteration of Russian names. This is Репиёва in Russian, and we have transliterated phonetically what is Repiewa in the contemporary literature.

May 1929. One imagines that it was the German rather than the Russian version which had attracted the attention of the American electrochemists. By now Repiova's place in this project had been taken by a new graduate student, Valentina Vasilevna Zolina, who carried out further experiments in an attic room just beneath the roof of the Ioffe Institute, increasing the maximum magnetic fields eventually up to 25 kG. The political situation was such that it was impossible for Frederiks to obtain permission to leave the Soviet Union (from his biography we see that things were to get worse), but nevertheless he was able in March to submit his manuscript to be read at the meeting. It is this paper which we include as article B3.

The interpretation of these results was more problematic. Frederiks was initially inclined to regard them as confirmation of the swarm theory; we shall return to this in article B6. Soon after they appeared, an alternative explanation in terms of distortion theory was suggested by Zocher and coworkers (article B7). Eventually around 1934, following a good deal of debate in the liquid crystal community, Frederiks transferred his allegiance from the former to the latter school of thought.

The increase in interest in anisotropic fluids led the eminent crystallographer P.P. Ewald to organise on the subject what we might now call a virtual symposium. The papers were circulated and recirculated, thus including an extensive discussion section, during 1929, and the final result published in the *Zeitschrift für Kristallographie* in 1931. Were it not for the shift in scientific *lingua franca* from German to English in the period between then and now, we should surely have reproduced several papers from this volume. As it is, we nevertheless include extracts from the General Discussion section, as well as reproducing the contents page, in paper B4.

This General Discussion section is extremely long, lasting from page 269 to page 347, and clearly we are in a position to translate only a few highlights. An introductory survey is provided by Rudolf Schenck. It is many years since Schenck worked in the field, but he retains an affection for liquid crystals. We left Schenck in Karlsruhe in June 1905. He had just presented a talk which comprehensively undercut the foundations of Gustav Tammann's emulsion picture of liquid crystals, and subject to the consequent wrath of Tammann himself. We may recall that van't Hoff has intervened from the chair to call for a commission of experts to examine liquid crystal questions and to resolve the raging controversies.

In his introduction, Schenck recalls the drama of the Karlsruhe meeting and further tells us how the commission fared. Sadly, as we might ourselves have predicted, the answer is not so well. Schenck seems to have been the secretary to this committee, for he prepared reports annually over the period 1906–8 for the committee chair, based on work occurring both in Germany and abroad. The final meeting of the committee was set to take place at the 1909 annual meeting of the *Deutsche Bunsen-Gesellschaft*, to be held in Aachen. However, apparently some misunderstanding broke out between van't Hoff and Lehmann, for their correspondence broke down and the final meeting never took place. Van't Hoff promptly

e German rather than the Russian version
merican electrochemists. By now Repiova's
by a new graduate student, Valentina
urther experiments in an attic room just
increasing the maximum magnetic fields
tuation was such that it was impossible for
the Soviet Union (from his biography we
ut nevertheless he was able in March to
the meeting. It is this paper which we

s was more problematic. Frederiks was
nfirmation of the swarm theory; we shall
hey appeared, an alternative explanation in
ted by Zocher and coworkers (article B7).
good deal of debate in the liquid crystal
allegiance from the former to the latter

pic fluids led the eminent crystallographer
what we might now call a virtual sympo-
1 recirculated, thus including an extensive
the final result published in the *Zeitschrift*
not for the shift in scientific *lingua franca*
1 between then and now, we should surely
n this volume. As it is, we nevertheless
cussion section, as well as reproducing the

extremely long, lasting from page 269 to
osition to translate only a few highlights.
y Rudolf Schenck. It is many years since
e retains an affection for liquid crystals.
e 1905. He had just presented a talk which
ions of Gustav Tammann's emulsion picture
sequent wrath of Tammann himself. We may
from the chair to call for a commission of
ions and to resolve the raging controversies.
Is the drama of the Karlsruhe meeting and
fared. Sadly, as we might ourselves have
Schenck seems to have been the secretary to
rts annually over the period 1906–8 for the
rring both in Germany and abroad. The final
take place at the 1909 annual meeting of the
held in Aachen. However, apparently some
an't Hoff and Lehmann, for their correspond-
ing never took place. Van't Hoff promptly

resigned as chair, and the work of the commission came to a premature end. What
was to be done with all the accumulated work? At the suggestion of Johannes
Stark, Schenck collected his reports together and published them (not from our
standpoint using an obvious journal!) in the 1909 edition of the *Jahrbuch der*
Radioaktivität und Elektronik.⁵

In the General Discussion proper, an important issue concerned the nature of
Lehmann's *molekularen Richtkräfte*, the forces which Georges Friedel had so
contemptuously dismissed. Chemists, such as Vorländer, interpreted these in terms
of the chemical forces which lead to compound formation, whereas physicists
sought an electromagnetic origin. There was extensive somewhat heated debate
about swarm theory, including debate between Zocher (*contra*) and Ornstein (*pro*).
Friedel's use of the term *stase* also comes under scrutiny. Finally the debate about
terminology, overlain as it was with emotional significance, continued to drag on.

We can reasonably assume that Otto Lehmann himself would not have been
best pleased with the Friedel classification. Vorländer and Lehmann themselves
were at times bitter rivals, as the following footnote to a 1923²⁶ paper shows:

I cannot agree with O. Lehmann's interpretation of the so-called liquid
crystal characteristics of ammonium oleate hydrate and similar soaps.
These materials, when melted with water, are said to yield liquid crystals.
What Lehmann really observed, photographed and then described, at
least in part, were probably suspensions of swollen soft birefringent phases
in water. In my experience, liquid crystalline phases of fatty acid salts
are only formed at high temperatures, in the molten phase of the (incom-
pletely decomposed) anhydrous salts. Lehmann repeatedly referred to his
discovery, mainly in order to establish his priority with respect to Reinitzer.

Luckily, by this time Lehmann had already been dead for two years and
Vorländer was not called upon to defend his remarks against an irate Lehmann
(and we know that Lehmann was no shrinking violet!). Vorländer was also offended
by Friedel's new 'mesomorphic' classification. Vorländer had his own classification,⁶
dating all the way back to 1907. In this classification, he used the term *pl-phases*
for the higher melting, low viscous liquid crystalline phases, derived from the
first and last letter of the German word of Gattermann's *p*-azoxyanisol.
The lower melting liquid crystalline phase he called the *Bz-phases*, derived from
the letters *B* and *z* of the German word *Benzoessäure* (benzoic acid) because he
observed these phase in the case of benzoate esters. He saw no need for new
nomenclature, as is witnessed in the following sarcastic extract:⁷

If anybody beginning to work in this field wants to introduce new terms –
please, do it with great enjoyment.

Vorländer's contribution to the Ewald symposium was a forceful restatement of
his own position, both academically and as a pioneer in the field. By the time he

had received copies of the papers and it was time to contribute to the Discussion, his blood-pressure was reaching seriously elevated levels, and what his contribution lacked in formal rigour, it gained in richness of language. His words were clearly carefully chosen, and add much to our historical understanding of what it felt like to be a liquid crystal scientist during this period. Unfortunately their emotional content meant that they had less of a persuasive effect on his colleagues. Thus, in spite of Vorländer's high prestige in the field, the terms *pl*- and *bz*- were relatively rapidly replaced – within a decade or so – by Friedel's new terminology. Nevertheless, we do find Vorländer's terminology employed by his own former student Conrad Weygand in 1939,⁸ and even as late as 1955 in a review article by Wilhelm Kast.⁹

His criticisms of the swarm model favoured by Ornstein were matched only by his excoriation of the Friedels, father and son, for their new crystalline liquid nomenclature. Not only did he feel that the data were not well described, but he was also seriously offended (with good reason) by the omission of any reference to his valuable work. We can get a feeling for Vorländer's strong feelings from the following short extracts

There are experiments for recognising correct and incorrect names for scientific phenomena. A name is correct when it is based on fact and experimental observation, but incorrect if it has at its core theories or hypotheses

Mesomorphism, mesophases, or intermediate phases for crystalline-liquid phases, are *incorrect* names because there is not a single fact or phenomenon to prove that the liquid crystals stand between solid crystals and amorphous melts. Give me a *single* property of crystalline liquids that indicates their intermediate position as crucial to the phenomenon. *I know of no such property!* Everywhere, even in X-ray diffraction: sharp, discontinuous change; no intermediate position. In contrast, one could cite more than a *dozen* properties that prove that on the one hand the liquid crystals behave just like solid crystals, and on the other, just like amorphous oils. In other words, hermaphroditism! At best, one could introduce, instead of crystalline liquids, the term crystal-like, crystalloid liquids, or liquid crystalloids, but that does not constitute essential progress.

I reject the words mesomorphic states and mesophases as a designation of crystalline-liquid properties or phases. I consider the expressions mesomorphism and mesophases, as well as the words nematic and smectic, *completely misguided, even if the theory which led to the words at some later time turns out to be correct.*

The italics are ours, but the drift of his remarks is clear! Notwithstanding these problems, always faced by practitioners in a rapidly developing interdisciplinary

ne to contribute to the Discussion, his ed levels, and what his contribution of language. His words were clearly cal understanding of what it felt like riod. Unfortunately their emotional ve effect on his colleagues. Thus, in d, the terms *pl*- and *bz*- were rela- so – by Friedel’s new terminology. ology employed by his own former as late as 1955 in a review article by

d by Ornstein were matched only by on, for their new crystalline liquid ata were not well described, but he n) by the omission of any reference or Vorländer’s strong feelings from

orrect and incorrect names for t when it is based on fact and if it has at its core theories or

mediate phases for crystalline- ise there is not a single fact or crystals stand between solid a *single* property of crystalline te position as crucial to the ty! Everywhere, even in X-ray e; no intermediate position. In en properties that prove that on just like solid crystals, and on other words, hermaphroditism! of crystalline liquids, the term crystalloids, but that does not

id mesophases as a designation es. I consider the expressions ell as the words nematic and ‘the theory which led to the correct.

arks is clear! Notwithstanding these rapidly developing interdisciplinary

field, it is important to reiterate the debt which the liquid crystal community continues to owe to Daniel Vorländer, not only for his work during the pioneer era, but also for his continuing work in the inter-war period. Many of his intuitions did not bear fruit during his lifetime. For example, in paper in 1932,¹⁰ apparently in contradiction to much of his earlier work on molecular shape, he extended his conception to systems with *bent* molecular shape, e.g. derivatives of resorcinol (*m*-disubstitution) and catechol (*o*-disubstitution),^{11,§} writing:

From these facts we may derive some essential results concerning the structure of crystalline liquids. From the crystalline-liquid properties of the *angled* catechol and resorcinol derivatives, one is forced to conclude that, so long as the lateral sides of the angles are sufficiently linearly efficient for liquid crystallinity to occur – as in the present case (caused by) the long *p*-phenobenzoyl groups – the bending by itself in no way completely prevents the crystalline-liquid properties.

By the time of his retirement in 1937, more than 2000 liquid crystalline compounds had been synthesised in his Institute, some of which were used two decades later by Horst Sackmann to work out his system of polymorph smectics, as we shall see in paper C5. A collection of Vorländer’s compounds in sealed glass tubes and kept in attractive cigar boxes can still be inspected in the Institute of Physical Chemistry of the Martin-Luther-University in Halle (see Fig. B1).

Other themes of the Symposium were no less controversial. The dominant theoretical framework was the swarm theory due to Ornstein and collaborators. We last met the swarm theory in an incomplete state as constructed by the unfortunate Emil Bose in 1908. We include extracts from the debate in the Discussion section as to whether Ornstein’s swarm theory is the same as that of Bose. Ornstein drew a distinction between his swarms and Bose’s, averring that, unlike in Bose’s theory, there is no element of emulsion included in his swarm picture. As the memory of the argument between Tammann and Lehmann was still alive, and the emulsion picture of liquid crystals known to be Officially Incorrect, it was important to establish theoretical intellectual credentials by denying any emulsion content.

However, Ornstein’s denials attracted some scepticism from a number of workers, most notably K. Herrmann, who insisted that the two swarm theories *were* the same, that there had therefore to be some degree of isotropy between the swarms, and that anyway the picture was not supported by X-ray data. Behind the swarm theory lay a belief that there had to be what we would call a mean-field

§ Vorländer was not to clarify the reason for the liquid crystal behaviour of his bent molecules. However, very recently workers in the Halle group descended in a direct intellectual line from Vorländer found evidence that actually he had been the first to prepare a *banana phase* (*B_S*) in his resorcine derivatives.¹¹



Fig. B1 One of the cigar boxes in which Daniel Vorländer used to keep his collection of crystalline liquids. See Plate II (courtesy of G Pelzl).

theory which would provide a more solid foundation for the swarms, and that this theory would be the analogue of the Langevin theory of magnetism. We now know, of course, that that theory had already been constructed by Grandjean (article C1), that it had been missed by the liquid crystal community, but that unfortunately it provides no further justification for the swarms.

Zocher was equally unimpressed by the swarm theory, but his objection was more theoretical, for he and Oseen had an alternative theoretical viewpoint, which we shall discuss in more detail when we look at the 1933 Faraday Symposium. There was a vigorous exchange between Ornstein and Zocher on the swarm theory, with Ornstein providing a list of experimental data justifying the swarm picture, and Zocher retorting, roughly speaking, that consistency and justification were different matters. Zocher's problem was that his alternative picture was unable to provide quantitative calculations, a point used to effect in Ornstein's rhetoric. Interestingly Oseen, who might have been in a position to do so, tended to confine his interventions to technical matters, and avoided explicit debate on grand theoretical questions.

The contemporary liquid crystal practitioner should not be too disdainful of this ultimately unsuccessful theory. Ornstein was driven to the swarm theory



Vorländer used to keep his collection of G Pelzl).

adation for the swarms, and that this
vin theory of magnetism. We now
dy been constructed by Grandjean
liquid crystal community, but that
on for the swarms.
warm theory, but his objection was
native theoretical viewpoint, which
k at the 1933 Faraday Symposium.
stein and Zocher on the swarm the-
imental data justifying the swarm
ig, that consistency and justification
as that his alternative picture was
a point used to effect in Ornstein's
e been in a position to do so, tended
ers, and avoided explicit debate on
er should not be too disdainful of
a was driven to the swarm theory

from the success of his theory with Fritz Zernike on the nature of the critical point. He was one of the most successful theoretical physicists of the twentieth century. He had success galore elsewhere to compensate his failure in this problem. What he did not have was the accumulated experience of the behaviour of systems with slowly varying order parameters to warn him off this approach; indeed he did not yet have the concept of order parameter itself.

There was also considerable debate on the various terms associated with what we now call liquid crystal phases. The Friedels were using the terms *stase*, *phase* and *texture*.¹² What was the difference? Without a detailed knowledge of the internal structure of the liquid crystals (or whatever one might call them), it was difficult to answer these questions fully. Could one draw a distinction? Zocher was unconvinced that a stase and a phase were distinct objects, but Ewald was more persuaded. The Gibbs Phase Rule, which gives information as to the number of possible coexisting phases was invoked by Zocher to render less plausible the idea of a stase. Ewald, by contrast, was seeking some intuitions from geometry as well as from thermodynamics. With the benefit of hindsight we can see that symmetry is indeed very important, and this was a fruitful avenue to follow, although the resolution of the problems lay simply in understanding general problems of statistical mechanics better.

Oseen noted that the molecular organisation in the region of apparent singularities would be different from that elsewhere in the system. The Friedels agree, but don't know what it would be like.¹³ In the same way, the Friedels are willing to consider the possibility of the existence of more than just the smectic and nematic phases, but are unconvinced by the experimental evidence. Vorländer has seen more than two phases, and has promised the Friedels to send them a sample, but for some unknown reason, despite the intervention of Ewald as interlocutor, it never arrives.

After the Discussion, Ewald once again sends out all the manuscripts so that some final remarks may be made. At this stage the Friedels realise that they have never seen the intemperate contribution from Vorländer, and have not yet an opportunity to respond. Ewald clearly was a wise man, for by the time the offending article is finally transmitted, their passions have died down, and barely taking the time for a gesture of contempt, they slide it by and on to the next subject. What is striking from the Friedels' final contribution is the articulate plea they make for more experiments, drawing attention to controversy on theoretical questions which they regard as unimportant, and which can in any case as yet only be inadequately resolved on the basis of current data.

Up to 1930, most work in liquid crystals had been carried out in Germany and France, with some contributions from groups in Russia, Sweden and the Netherlands. However, Ewald's virtual meeting was to have an unanticipated influence on broadening interest in the subject. The proceedings of that meeting, as we have seen in paper B4 above, were published, principally in German, but with contributions in French from the Francophone contributors in the *Zeitschrift*

für Kristallographie. Not in English, however, although, as it happened, the English crystallographer Sir William Bragg[†] was an Editorial Board member of the journal.

Perhaps struck by the fact that Anglo-Saxon contributions to liquid crystals had been less than crucial, Sir William resolved not to be left behind. The best way to catch up is to arrange a *meeting*, to which the leaders in the field can be invited. So it was that in May 1933 Sir William Bragg (1862–1942), Director of the Royal Institution, and John Desmond Bernal (1900–71), then a rising young star of the crystallographic world, organised a Discussion Meeting of the Faraday Society[§] in London on *Liquid Crystals and Anisotropic Melts*.

All the major figures in the liquid crystal world were invited (although at least one died before he was able to come, and others, for a variety of reasons, did not show up). The list of invited speakers for the Faraday Discussion was almost a replica of the contributors to the Ewald virtual meeting, though for some reason Ewald himself did not attend. The topics of the papers presented (this time in many cases in person) at the London meeting similarly echo the pages from the *Zeitschrift für Kristallographie* published only two years previously.

Repetition notwithstanding, the record of that Faraday Discussion is the first major document in English on liquid crystals. As we have already emphasised, the peculiar status of English, as the modern *lingua franca* of the scientific world, has conferred on the papers read at the 1933 London meeting a greater historical importance than might otherwise have been the case. The organisers of the meeting went to great trouble to ensure that papers originally written in other languages were translated so as to be accessible to the Anglophone audience. The meeting was fittingly held at the Royal Institution in Albermarle Street in Central London, the academic home of those ancient sages Sir Humphrey Davy (1778–1829) and Michael Faraday (1791–1867).

One hundred and fifty members and visitors attended that meeting, which is a rather impressive number, given the relative novelty of the field. Among eminent foreign visitors at the meeting, the proceedings record, were Professors Leonard Ornstein of Utrecht and Hans Zocher of Prague, and Professor Dr Rudolf Schenck, now of Berlin.* Schenck was a particularly important visitor, not only because of his seminal contribution to the field (in which he was no longer an active participant) but because he was the current President of the *Deutsche Bunsen-Gesellschaft*. Not present, except in spirit – for papers were presented on their behalf – were the distinguished theorist Professor Carl Wilhelm Oseen of the University of Uppsala in Sweden, and the equally

[†]This is the elder Bragg, W.H., to be distinguished from the younger (his son), W.L., later Sir Lawrence (1890–1971).

[§]The Faraday Society much later became the Physical Chemistry and Chemical Physics section of the Royal Society of Chemistry.

*The proceedings record this, but were wrong. Schenck was never a professor in Berlin, and at this point worked at the University of Münster.

ver, although, as it happened, the
was an Editorial Board member of

xon contributions to liquid crystals
lved not to be left behind. The best
which the leaders in the field can be
iam Bragg (1862–1942), Director of
rnal (1900–71), then a rising young
a Discussion Meeting of the Faraday
anisotropic Melts.

al world were invited (although at
and others, for a variety of reasons,
ers for the Faraday Discussion was
Ewald virtual meeting, though for

The topics of the papers presented
don meeting similarly echo the pages
blished only two years previously.

that Faraday Discussion is the first
ls. As we have already emphasised,
lingua franca of the scientific world,
London meeting a greater historical
e case. The organisers of the meeting
originally written in other languages

Anglophone audience. The meeting
Albermarle Street in Central London,
ir Humphrey Davy (1778–1829) and

sitors attended that meeting, which
elative novelty of the field. Among
proceedings record, were Professors
Zocher of Prague, and Professor
k was a particularly important visitor,
on to the field (in which he was no
he was the current President of the
t, except in spirit – for papers were
stinguished theorist Professor Carl
psala in Sweden, and the equally

hed from the younger (his son), W.L., later

cal Chemistry and Chemical Physics section of

henck was never a professor in Berlin, and at

distinguished experimental physicist Professor V.K. Fredericksz of the Physico-Technical Institute of Leningrad, who had once again been refused an exit visa by the Soviet authorities.

Dominating the meeting (and, reading between the lines, also the Organising Committee) was the ebullient figure of Bernal. An Irish-born polymath, Bernal was to become a dominant figure in twentieth century crystallography, known as well for his left-wing views, his womanising and his contributions to the history of science. So learned was Bernal, that he was known, at least to his co-workers and acolytes, as ‘Sage’. Bernal’s own interests were so wide that he was never able to win the Nobel prize in his own right, but several of his students did win the Nobel prize for ground-breaking work in the resolution of the structure of molecules important in molecular biology. In the discussion it is always Bernal who is first on his feet with some point or other.

The first paper in the Discussion proceedings is by Oseen, and we include this in our collection as article B5. In fact in these discussions the papers are circulated beforehand and taken as read at the meeting, with perhaps five minutes of introduction from the author. As a result Oseen’s physical absence at the meeting would not have been a major inconvenience. In 1933 Oseen had been working on anisotropic fluids for 12 years, and had already published 20 papers and he had also written a monograph¹⁴ on the subject published in 1929. All in all he was to publish 26 papers on the topic.

His first three papers were entitled *Versuch einer kinetischen Theorie der anisotropen Flüssigkeiten* – Essay on a kinetic theory of crystalline fluids – and apart from this one, all the others were entitled, in one language or another, ‘Contributions to theory of anisotropic fluids’. In 1934 he switched from German to French as a protest against the rise of Nazism in Germany. Paper B5 is his only paper in English, and judging from the published proceedings (in which translators were acknowledged on the title page), he nevertheless wrote it himself with presumably only minor editorial help. So by May 1933 his ideas were somewhat mature. It is worth retreading our steps back to 1923 to follow some of the early steps in Oseen’s thinking.

Much, though not all, of Oseen’s work was in theoretical hydrodynamics, and it is within this perspective that he approached the theory of anisotropic fluids. His first efforts were directed towards a hydrostatic theory, and we quote from the introduction to his third article in 1923:¹⁵

The first question which strikes a theoretician in this field is the origin of the two forms in which anisotropic liquid drops appear: the sphere-forming “liquid crystals”, and the “flowing” crystals which also appear crystalline. Lehmann gave the answer to this question, which was that in liquid crystals the structural force is insufficient to overcome the surface tension. That this explanation is valid is hardly open to doubt. The task of the theoretician is to define this concept of structural force, and connect it to the usual molecular forces

There follow almost 40 pages of almost impenetrable algebra, before Oseen emerges again with something we can recognise . . .

The number of independent constants is therefore four.

Difficult as the working is, we are already seeing the four elastic constants of what has come to be called the continuum theory of liquid crystals, which are now traditionally labelled K_{11} , K_{22} , K_{33} and K_{24} . But let us compare Oseen's Swedish tone to that exuded almost simultaneously by Friedel in Strasbourg. Whereas the fierce Friedel castigated the structural force in forceful terms as essentially meaningless, the milder Oseen merely noted that some further progress was necessary in order to connect this idea with more normal physics!

By 1933 his formulation of the elastic energy had settled down, although it is not yet quite in its modern form. The detailed form of the terms is probably equivalent but differently stated, and the conventions are of course different from today. We may note also that the paper is focussed in a rather modern way: in successive sections Oseen deals with statics, defect structure, optics, dynamics and finally smectics. The modern eye is drawn to the use of the term 'aeolotropic' (from the Greek αιολος = 'changeable'), which is now no longer used in a liquid crystal context. There are speculations about the molecular origin of the 'cholesterine-nematic' (cholesteric) phase.

In the dynamics section he presents new work by his Ph.D student Adolf Anzelius (1894–1979). That work was not entirely successful, at least partly because it does not use the time derivative of the director as a dynamical variable in the theory. This is to some extent the result of a lack of careful experiments in the literature at the time to direct the theorists. The deficiency is made up later by Mięsowicz (articles B9 and B10) and by Tsvetkov¹⁶ from the Leningrad school, whom we shall come across again in article C2. Anzelius's theory would nevertheless be the starting point for the successful 1968 Ericksen-Leslie theory, which we shall come across later as article C6.

What is interesting is that, despite his technical brilliance, Oseen seems to have had some difficulty with the basic physics of anisotropic liquids (we can perhaps sympathise!). He seems, for example, to have believed that anisotropic fluids no longer obeyed Newton's laws of motion. From the perspective of 2002, what is missing is a well-defined scale separation between continuum theories on the one hand and molecular theories on the other.

Article B6, entitled 'New arguments for the swarm theory of liquid crystals' is by Ornstein and Kast. This article is included because it represents the eventually unsuccessful swarm theory at the height of its influence. The swarm theory, we underline, was a brave attempt to formalise physical intuition into a viable calculational scheme. Ornstein had developed the swarm theory beyond the rather limited picture of Bose, and his swarms were much more concrete than those of Bose. He really believed that inside liquid crystals there existed macroscopic entities which could be aligned by magnetic fields, and which could be regarded

most impenetrable algebra, before Oseen emerges
arise . . .

stants is therefore four.

re already seeing the four elastic constants of
num theory of liquid crystals, which are now
and K_{24} . But let us compare Oseen's Swedish
neously by Friedel in Strasbourg. Whereas
uctural force in forceful terms as essentially
erely noted that some further progress was
ea with more normal physics!

lastic energy had settled down, although it is
The detailed form of the terms is probably
d the conventions are of course different from
aper is focussed in a rather modern way: in
ith statics, defect structure, optics, dynamics
e is drawn to the use of the term 'aeolotropic'
ul'), which is now no longer used in a liquid
lations about the molecular origin of the
phase.

sents new work by his Ph.D student Adolf
was not entirely successful, at least partly
ivative of the director as a dynamical variable
the result of a lack of careful experiments in
e theorists. The deficiency is made up later by
d by Tsvetkov¹⁶ from the Leningrad school,
n article C2. Anzelius's theory would never-
uccessful 1968 Ericksen-Leslie theory, which
C6.

his technical brilliance, Oseen seems to have
ysics of anisotropic liquids (we can perhaps
le, to have believed that anisotropic fluids no
otion. From the perspective of 2002, what is
ration between continuum theories on the one
other.

nts for the swarm theory of liquid crystals' is
included because it represents the eventually
height of its influence. The swarm theory,
to formalise physical intuition into a viable
developed the swarm theory beyond the rather
arms were much more concrete than those of
le liquid crystals there existed macroscopic
magnetic fields, and which could be regarded

as 'physical' – as opposed to the usual chemical – molecules. In B6 he and Kast
marshal a whole slew of experimental evidence in support of the swarm theory.

Article B7, by Hans Zocher, entitled *The effect of a magnetic field on the
nematic state*, is concerned with the explanation of the Frederiks threshold experi-
ments. To some extent this article recapitulates a paper which appeared in 1929
in the *Zeitschrift für physikalische Chemie*.¹⁷ Note the use of the term *nematic*,
despite Zocher's German background. In ten years, Friedel's terminology had
achieved clear victory. Apart from Oseen, Zocher was the other main protagonist
in this period for the continuum theory (called the 'distortion theory' by Zocher).
Whereas Oseen somewhat regally simply ignored the swarm theorists, Zocher
was more inclined to confront it head-on, as we find in the very first paragraph of
his paper:

. . . . It is extremely important to decide which is the correct (theory), not
only for the particular problem dealt with in this paper, but for the whole
general question of the structure of these phases

There is also experimental work by his colleague Eisenschimmel (also present
at the conference with his wife), who is acknowledged underneath the title, but
nevertheless not elevated to full co-authorship.

Zocher discusses various different possible Frederiks geometries, and refers
back to the van Wyk experiment. Van Wyk had used the distortion theory to
examine the spatially dependent behaviour of the optic axes. Zocher shows by
way of example that this same theory will indeed give rise to threshold behaviour. He
addresses experimental work, including that which Kast¹⁸ previously adduced in
favour of the swarm theory. Although the distortion theory apparently does
not reproduce Kast's result in the low field régime, Zocher has a host of excuses –
probably, with the benefit of hindsight, more-or-less correct – concerned with
implicit assumptions about the experimental set-up, which provide himself with a
satisfactory excuse. There are hints of a discussion of what we would now call
anchoring (and which he calls variable surface tension), and a remark that with
plausible anchoring energies there would be negligible differences in (in modern
language) pretilt.

Eisenschimmel's experimental section makes a number of innovative contri-
butions. He first notes that by choosing suitable material it is possible to align
the optic axes perpendicular to the magnetic lines of force, whereas in previous
experiments it had always been found to be parallel. He then carries out a somewhat
qualitative experiment demonstrating the Frederiks effect with parallel aligned
in-plane easy axes, positive diamagnetic anisotropy, and an in-plane magnetic field.
There is a final experiment essentially showing that when the surfaces are antag-
onistic (in this case, one easy axis is in-plane and one normal to the surface) and
there is a perpendicular in-plane field, the critical field is substantially increased.
Although the geometry is not the same as for the twisted nematic phase, the physics
is, and this paper provides a link between the work of Mauguin in articles A8 and

A9 (which are cited by Zocher) and the twisted nematic device itself, in particular Leslie's article D5.

The importance of Zocher's article lies in the progress that had been made since the Ewald symposium. In 1930–1, Zocher had been fending off demands by Ornstein not merely to criticise the swarm theory but actually to provide some viable alternative. The rhetoric is unconvincing, even if Zocher himself was sure of his ground. But the Frederiks experiment provided a specific procedure to calculate the elastic constants. Now the distortion theory was up and running, and the writing was on the wall for the swarm theory. As we have seen, soon the Frederiks group also was to begin to conceptualise not in terms of Ornstein's swarms but in terms of the Oseen–Zocher elastic constants.

Before passing onto extracts from the General Discussion section (article B8), it is of some interest to survey briefly other highlights of the Symposium. As an echo of the 1905 meeting in Karlsruhe in which Lehmann had given demonstrations (article A4), the introduction records that:

After Professor Oseen's Introductory Paper had been taken as read and discussed, very beautiful demonstrations were given by Professor Vorländer, Professor Van Iterson and Dr. A.S.C. Lawrence. Further experimental demonstrations were given on Tuesday by Professor van Iterson and Mr. Bernal.

The proceedings include fully four separate articles by the by-now-veteran Vorländer, including his demonstrations. There are two articles on liquid crystal viscosity, one by Wolfgang Ostwald (son of the Nobel prize winner), and one by Herzog and Kudar. At this stage the role played by symmetry and geometry in defining exactly what was meant by viscosity in a liquid crystal was as yet unclear. We also note a contribution, entitled *Lyotropic Mesomorphism*, by A.S.C. Lawrence (at that time in Cambridge, but later to be a professor in Sheffield). We return to lyotropic substances in more detail in Part E, but the following extract from the first paragraph summarises the analogies between thermotropics and lyotropics as well as any textbook:

It is interesting to recall that Lehmann's liquid crystals of ammonium oleate, which formed the foundation of the subject under discussion, were deposited from solution; and also that the amount of water present profoundly modified their form. Since that time, however, most of the substances studied have been in the form of anisotropic melts of single compounds. The action of heat and of a solvent are not dissimilar insofar as they both loosen the directive forces holding the molecules in their normal crystal lattice. For a mesoform to appear, it is necessary for these forces to persist in either one or two dimensions after loosening of the third. But even when this occurs and a mesoform exists it is unlikely that heat and all solvents will bring this about equally well.

a twisted nematic device itself, in particular
 lies in the progress that had been made
 1, Zocher had been fending off demands by
 warm theory but actually to provide some
 convincing, even if Zocher himself was sure
 experiment provided a specific procedure to
 the distortion theory was up and running, and
 swarm theory. As we have seen, soon the
 conceptualise not in terms of Ornstein's
 other elastic constants.

the General Discussion section (article B8),
 other highlights of the Symposium. As an
 in which Lehmann had given demonstrations
 hat:

tory Paper had been taken as read and
 onstrations were given by Professor
 n and Dr. A.S.C. Lawrence. Further
 e given on Tuesday by Professor van

ir separate articles by the by-now-veteran
 ons. There are two articles on liquid crystal
 (son of the Nobel prize winner), and one by
 role played by symmetry and geometry in
 y viscosity in a liquid crystal was as yet
 entitled *Lyotropic Mesomorphism*, by A.S.C.
 e, but later to be a professor in Sheffield).
 i more detail in Part E, but the following
 arises the analogies between thermotropics
 :

hmann's liquid crystals of ammonium
 ation of the subject under discussion,
 d also that the amount of water present
 Since that time, however, most of the
 the form of anisotropic melts of single
 id of a solvent are not dissimilar insofar
 e forces holding the molecules in their
 form to appear, it is necessary for these
 two dimensions after loosening of the
 and a mesoform exists it is unlikely that
 is about equally well.

The key word here is 'loosening'. The word *lyotropic* comes from the Greek
 verb λυειν, to loosen,¹⁹ known to generations of classical scholars because it is
 the *only* regular verb in Ancient Greek!

Finally we note an article by Bernal and Crowfoot, who conclude:

....the mesophases, far from being an anomalous manifestation, take
 their place in a regular procession from the disorder of the ideal liquid to
 the regularity of the ideal crystal....

The young Dorothy Crowfoot, later Hodgkin (1910–94), would later be
 celebrated for determining the atomic structure of Vitamin B₁₂, an achievement
 for which she was awarded the 1964 Nobel Prize in Chemistry.

The General Discussion ranged widely. The transcript of the Discussion is not
 a true and accurate representation, of course. There are inserted contributions,
 and Discussants are able to edit their words so as to make it appear that what they
 said is more intelligent than it appears on the day. But, by contrast with the Ewald
 Symposium, underlying this transcript there is here the record of a human
 occasion. Is this why the debate seems to have taken a more sedate path than its
 Ewald counterpart? Or is it simply that Anglo-Saxons are more measured in their
 expression of emotion? Or perhaps the absence (presumably due to illness, for he
 was to die in December of the same year) of a Georges Friedel who might have
 provoked Vorländer?

Ornstein reiterates again and again his belief in the swarm theory, emphasising
 the manner in which surfaces affect the local orientation in their neighbourhood.
 He stresses that swarms are necessary to understand the turbidity of liquid
 crystals – this seems to underlie his real belief in the theory – but Zocher says no,
 statistical fluctuations and static deformations are quite sufficient. Zocher has
 evidently had more time to think about his debate with the swarm theorists.
 He now is able to point to internal contradictions: different calculations of the swarm
 size from experimental data give very different answers. He finds an articulate
 ally in Bernal, who yet again points out that although the swarm theory does
 explain the experiments of Kast and Ornstein, it does not necessarily *compel* this
 explanation.

Hermann suggests the existence of a tilted smectic (in general agreement with
 Vorländer's point that there are many unexplored liquid crystalline phases), but
 Bernal is extremely sceptical. Mention is made of the existence of the Dupin
 Cyclides in the smectics – a problem left open in Friedel's review – and Sir William
 Bragg presents an impromptu explanation, which, it was felt, was sufficiently
 important to codify *ex post facto*; a short paper about this thus appears in the
 proceedings.²⁰

In papers B9 and B10 we return to the viscosity of anisotropic fluids, which
 have been addressed, albeit imperfectly, in the Faraday Symposium. It had long
 been known that the dielectric response of a liquid crystal depended on liquid
 crystal orientation; this is the essence of what is understood by an *anisotropic* fluid

when observed in an optical experiment. As far back as 1913, Neufeld had attempted to find a magnetic field dependence of the viscosity, but he reported a negative result.²¹ The problem was revived again by Marian Mięslowicz in 1934, a student of Professor Mieczysław Jeżewski in the Mining Academy in Cracow, Poland.

Much of the early French progress, we may recall, had been made by Friedel and Grandjean, working in a School of Mines. Despite the implication of its rather practical name, *L'École de Mines* was a centre for the fundamental study of geology, geophysics and more generally earth science. As such the classification of minerals and crystal types fell within its legitimate sphere. Liquid crystals were thus a natural extension. No doubt the long-term aim of governments in funding such institutions involved a practical pay-off, eventually. The Poles followed a similar train of thought, though whether the Polish Government could visualise liquid crystal displays as the long-term technological result is doubtful. Be that as it may, Jeżewski had been making dielectric studies of liquid crystals. Mięslowicz returned to the viscosity problem with apparatus considerably improved compared to that available to Neufeld in 1913.

In contrast to Neufeld, Mięslowicz obtained positive results. Paper B9, published in *Nature* in 1935, reported proof of principle. A fuller set of results was presented in a paper in German in the Bulletin of the Polish Academy of Sciences in 1936. However, this journal is not widely read and so a paper for *Nature* was in preparation when the war intervened. Paper B10, published after the war, reports these detailed results. It is said that at the outbreak of war, Mięslowicz's apparatus was summarily wrecked by the invading German forces. In fact, Mięslowicz never returned to serious study in the liquid crystal field (after the war he became a nuclear physicist). Luckily the results were not completely lost.

The important point about Mięslowicz's results is that by applying a magnetic field, he was able to anchor the nematic director in a specific orientation with respect to a flow field. He is then able to determine the viscosity when the director is parallel to the flow, or alternatively parallel to the velocity gradient, or out-of-plane. This makes three viscosities altogether. Nowadays they are known as the *Mięslowicz* viscosities. The highest viscosity (the second of the three) is between four and seven times the lowest (the first of the three). Averaging viscosities is a very dangerous thing to do!

This section is concluded with two papers with the same title – *On the orientation of liquid crystals by rubbed surfaces* – by Pierre Chatelain, which appeared during the war. For many years gentle rubbing was the method of choice in order to create a surface with suitable liquid crystal alignment properties. In the technological era this has been a very important imperative. In this problem the skill of the engineers has by far outpaced the understanding of the scientist. It is probably fair to say that even today a detailed and reliable model for rubbing-induced surface anchoring is lacking. Only recently have other surface orientation methods begun to compete with the noble art of rubbing.

Chatelain did not invent rubbing. Already in 1927, Zocher and Coper²² had found that rubbing a glass surface oriented a nematic phase, and Eisenschimmel

back as 1913, Neufeld had attempted viscosity, but he reported a negative result. Mięsowicz in 1934, a student of the Polish Academy in Cracow, Poland. My recall, had been made by Friedel and Chatelain. Despite the implication of its centre for the fundamental study of liquid crystal science. As such the classification of liquid crystals is a legitimate sphere. Liquid crystals have been a long-term aim of governments in Poland, but eventually. The Poles, whether the Polish Government could achieve a technological result is doubtful. dielectric studies of liquid crystals. With apparatus considerably improved. Positive results. Paper B9, published in the Polish Academy of Sciences in 1936. I so a paper for *Nature* was in pre-1940, published after the war, reports a break of war, Mięsowicz's apparatus was destroyed by German forces. In fact, Mięsowicz's liquid crystal field (after the war he became a physicist) was not completely lost. Results is that by applying a magnetic field in a specific orientation with the flow to determine the viscosity when the flow is parallel to the velocity gradient, or perpendicular to it. Nowadays they are known as the first and second viscosity methods (the first of the three). Averaging with the same title – *On the orientation of liquid crystals* by Chatelain, which appeared during the war, is the method of choice in order to align liquid crystals. In the technological problem of the skill of the scientist. It is probably the model for rubbing-induced surface orientation methods begun in 1927, Zocher and Coper²² had a nematic phase, and Eisenschimmel

had employed just this approach in his Frederiks-like experiment presented in article B7. However, in the articles we have translated, Chatelain is the first to investigate systematically rubbing effects. B11 is a short note in *Comptes rendus*, submitted by Charles Mauguin, who by this time was an eminent crystallographer and holder of a chair at the *Laboratoire de Minéralogie* at the Sorbonne in Paris. The follow-up B12 is a longer account in the *Bulletin de la Société Française de Minéralogie* (Mauguin's journal of choice), and from this article we have chosen some extracts.

Although even after these papers, rubbing remained as much an art as a science, the art was now considerably more educated and experienced. We may note how Chatelain systematically changed the amount of rubbing, the rubbing material, the nature of the slides, the mesogenic material; everything indeed that could in principle be altered. From a contemporary perspective, the degree of concentration seems all the more wonderful when we reflect on the difficult political situation in France caused by the Second World War. We may speculate that perhaps only by restricting his interest to mundane and repetitive scientific tasks was Chatelain able to divert his attention from these difficulties.²³

With Chatelain's articles we conclude Section B. Liquid crystal science then began a somewhat somnolent phase which lasted almost 20 years. The war and its attendant instability surely played a major role in generating this sleepy period. Frederiks was *de facto* a victim of Stalin, and Ornstein similarly a victim of Hitler. As we have seen, the foundations of liquid crystal science were laid in Germany and France, and in both cases, recovery from the war was not easy. By the end of the war Vorländer had died of old age, and his younger colleague Weygand²⁴ had fallen in battle, a victim of German desperation in the last days of the war. Oseen also was dead, and Zocher,²⁵ regarded as politically unreliable by all sides, eventually emigrated to Brazil where he made a successful new career. Finally the technological promise of liquid crystals was not yet obvious, so that many workers in the field of anisotropic fluids (on all sides) had been diverted to more pressing war work.

It was not till the late 1950s before progress was resumed. We shall return to discuss this in Section C.

References

1. E. Hückel, *Zerstreuung von Röntgenstrahlen durch anisotrope Flüssigkeiten* (*Scattering of X-rays through anisotropic fluids*) *Phys. Z.* **22**, 561–3 (1922). Hückel's main contribution to physical chemistry is through his molecular orbital theory. He is also known for the Debye–Hückel theory of electrolyte screening in colloids. This paper is his only contribution to liquid crystal science, and is often, perhaps unjustly, neglected because of its negative result. Hückel's interest in colloids may well have been inspired by his contacts in Göttingen with Richard Zsigmondy (see article E1), whose daughter Annemarie later became his wife.

2. A. Repiova and V. Frederiks, к вопросу о природе анизотропно-жидкого состояния вещества (*On the problem of the nature of the anisotropic state of matter*), Zh.R.F.Kh.O **59**, 183–200 (1927).
3. V. Freedericksz and A. Repiewa, *Theoretisches und Experimentelles zur Frage nach der Natur der anisotropen Flüssigkeiten* (*Theory and experiment concerning the question of the nature of anisotropic fluids*), Phys. Zeit. **42**, 532–46 (1927).
4. A. van Wyk, *Die orientierenden Einflüsse von Magnetfeld, Wand und gegenseitiger Wechselwirkung auf die Schwärme des flüssig-kristallinen p-Azoxyanisols* (*The orientational influence of a magnetic field, a wall and mutual interactions on swarms in the liquid crystal p-azoxyanisole*), Ann. Phys. **3**, 879–933 (1929).
5. R. Schenck, *Bericht über die neueren Untersuchungen der kristallinen Flüssigkeiten* (*Report on recent studies of crystalline liquids*), Jahrbuch der Radioaktivität und Elektronik **6**, 572–639 (1909).
6. D. Vorländer, *Neue Erscheinungen beim Schmelzen und Kristallisieren* (*New observations of melting and crystallisation*), Z. phys. Chem. **57**, 357–64 (1907).
7. D. Vorländer, E. Däumer, W. Selke and W. Zeh, *Die einsachige Aufrichtung von festen weichen Kristallmassen und von kristallinen Flüssigkeiten*, Z. phys. Chem. **129**, 435–74 (1927). The remark cited is on p. 468.
8. C. Weygand (Discussion remark on an article by W. Kast on *Anisotropic fluids*), Z. Elektrochemie **45**, 200–2 (1939).
9. 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).
10. D. Vorländer and A. Apel, *Die Richtung der Kohlenstoffvalenzen in Benzolabkömmlingen II*, Ber. Dtsch. Chem. Ges. **65**, 1101–09 (1932).
11. G. Pelzl, I. Wirth and W. Weissflog, *The first 'banana phase' found on an original Vorländer substance*, Liq. Cryst. **28**, 969–72 (2001).
12. Note, however, that in the ground-breaking 1922 article B1, Georges Friedel tended to use *structure* to describe a specified set of defects, when later workers would have used *texture*. Later, however, when X-ray crystallographic investigation of these effects took off, the term *structure* was reserved for X-ray crystallographic patterns.
13. This is of particular interest to one of the present authors, who studied just this problem (without realising its historical provenance!), calculating the local order close to a defect line: N. Schopohl and T.J. Sluckin, *Defect core structure in nematic liquid crystals*, Phys. Rev. Lett. **59**, 2582–5 (1987). However, this was not a problem which exercised Georges Friedel greatly, and we may speculate that this is because he realised the relevant length scales were not amenable to analysis under the microscope. He understood perfectly well that at a defect the optical axis directions converged.
14. C.W. Oseen *Die anisotropen Flüssigkeiten. Tatsachen und Theorien* (*Anisotropic liquids: experiments and theories*) (Fortschritte der Chemie, Physik und physikalischer Chemie, Vol. 20, no. 2, Berlin 1929).
15. C.W. Oseen, *Versuch einer kinetischen Theorie der kristallinen Flüssigkeiten, III. Abhandlung* (*Essay on a kinetic theory of crystalline fluids, part 3*), Kungl. Svenska Vetenskapakademiens Handligar. **63**, no. 12 (1923).
16. See e.g. G.M. Mikhailov and V.N. Tsvetkov, *Влияние электрического поля на скорость течения анизотропно-жидкого p-азоксианизола в капилляре*; (*Influence of an electric field on the speed of flow of the anisotropic liquid p-anoxyanisole in a capillary*), Zh.E.T.F. **9**, 208–14 (1939).

17. H. Zocher and V. Birstein, *Beiträge zur Kenntnis der Mesophasen* (Zwischenaggregatzustände) V: Über die Beeinflussung durch das elektrische und magnetische Feld. *Z. phys. Chem.* **142**, 186–94 (1929). Note that already by 1929 Zocher has switched to using the term ‘mesophase’, although he does still feel the obligation to explain himself; *Zwischenaggregatzustände* literally means ‘intermediate aggregation state’.
18. W. Kast, *Dielektrische Untersuchungen an der anisotropen Schmelze des para-Azoxyanisol* (Dielectric studies of the anisotropic melt of para-azoxyanisole), *Annalen der Physik* **83**, 391–417 (1927).
19. The principal meaning of λυειν is ‘to loosen’, and it is clearly to this meaning that Lawrence is making allusion in the extract just cited. However, a derived meaning of the word is ‘to dissolve = lösen’, or ‘to break into constituent parts’. It is with this meaning that the root ‘lyo’ first enters the physical chemistry literature, for example in ‘lyophobic’ = ‘fearful of being dissolved’ = ‘water repellent’. See H.G. Liddell and R. Scott, *A Greek-English Lexicon* (The Clarendon Press, eighth edition, Oxford, 1897). We have not been able to identify the first time the term ‘lyotropic’ was used in the liquid crystal literature, but it seems likely that this term too was an invention of Marie Friedel’s.
20. The mathematics of the Bragg paper, although somewhat heavy going for a contemporary theoretical physicist, contained relatively standard nineteenth century undergraduate-level geometry. This paper is not universally felt to have added greatly to the understanding of the Dupin cyclide problem already achieved by Friedel. Note also that as Bragg co-organised the meeting, the decision to include this exposition in the proceedings might not be thought of as entirely dispassionate.
21. M.W. Neufeld, *Über den Einfluß eines Magnetfeldes auf die Ausflußgeschwindigkeit anisotroper Flüssigkeiten aus Kapillaren* (On the influence of a magnetic field on the flow velocity of an anisotropic fluid through capillaries), *Phys. Z.* **14**, 646–50 (1913) cited in M. Mięslowicz, *Mol. Cryst. Liq. Cryst.* **97**, 1–11 (1983). *Liquid Crystals in my memories and now – the role of anisotropic viscosity in liquid crystals research.*
22. H. Zocher and K. Coper, *Über die Erzeugung der Anisotropie von Oberflächen* (On the production of surface anisotropy) *Z. phys. Chem.* **132**, 295–302 (1928).
23. The present writers do not know anything about Chatelain’s politics. Chatelain worked at the University of Montpellier, which was in the so-called ‘unoccupied’ (Vichy) part of France in the period 1940–42. The role of the middle classes in Vichy France, and the extent to which they collaborated with Hitler, is a subject of much contemporary historical debate.
24. Hans Kelker, in his fascinating article *History of liquid crystals*, *Mol. Cryst. Liq. Cryst.* **21**, 1–48 (1973), reports that Weygand ‘died as a storm-trooper in the last days of the war’. Another conjecture is that Weygand died by his own hand. Indeed he was an active member of the Nazi party and published a dubious book entitled “*Deutsche Chemie*”.
25. For reasons more fully explained in his biography. As an ethnic German he was super-numerary in post-war Czechoslovakia, despite family and other reasons for opposition to Nazism.
26. D. Vorländer, *Die Erforschung der Molekularen Gestalt mit Hilfe der Kristallmischen Flüssigkeiten*, *Z. Phys. Chem.* **105**, 211 (1923).