

THE LIQUID CRYSTALS BOOK SERIES

NEMATIC AND CHOLESTERIC LIQUID CRYSTALS

CONCEPTS AND PHYSICAL PROPERTIES
ILLUSTRATED BY EXPERIMENTS

Patrick Oswald
Pawel Pieranski



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TRANSLATED BY Doru Constantin

With the support of Merck KgaA (LC division), Rolic Research Ltd,
and the Laboratoire de Physique des Solides d'Orsay



Taylor & Francis
Taylor & Francis Group

Boca Raton London New York Singapore

A CRC title, part of the Taylor & Francis imprint, a member of the
Taylor & Francis Group, the academic division of T&F Informa plc.

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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Version Date: 20150121

International Standard Book Number-13: 978-0-203-02301-3 (eBook - PDF)

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Foreword

Having witnessed, thirty or forty years ago in Orsay, the revival of liquid crystal research, Patrick Oswald and Pawel Pieranski's book shows me that this area is still very open. Of course, the impact of new applications probably has shifted from the industrial manufacturing of displays to the understanding of biological processes, and justly so, one may say, since the discoverer of the field, F. Reinitzer, saw in the textures of mesophases the hallmark of life!

This richness of behavior was then thoroughly studied by O. Lehmann, but the main merit of F. Grandjean and my grandfather G. Friedel was no doubt that they obtained, by careful observation of the simplest cases, a clear comprehension of the structure of these bodies at the molecular level. By distinguishing the most ordered state possible and the textures produced by the appearance of defects, they opened the way for a systematic study of the equilibrium phases exhibited by these anisotropic liquids; they also started the study of the defects leading to these deformations, especially the rotation dislocations or disclinations.

If G. Friedel's 1922 paper paved the way, it was P.-G. de Gennes' first book on liquid crystals, in 1974, that rekindled this research activity, still very active to this day. P. Oswald and P. Pieranski participated, among many others, in this revival. This book is a result of thorough personal research and of the graduate courses taught by the two authors, one at the École Normale Supérieure de Lyon and the other at the University of Paris VII (Denis Diderot).

One may wonder about the value of this new work, in an area already covered by a significant number of recent publications, also cited by the authors.

The first immediate answer is found just by reading the table of contents. If the two volumes are split according to the classical separation between what one might call three-dimensional anisotropic liquids (nematics and cholesterics) and those that are liquid only along two directions or even just (smectic and columnar phases, respectively), we notice the important weight given to topics that have only received limited coverage elsewhere in the literature, among them surface phenomena (anchoring, faceting) and the dynamics of growth or deformation. From this point of view, we can only regret the absence of any discussion on mesomorphic polymers.

To me, however, what fully justifies this work is its style, which strives to be as clear and as close to the experimental side as possible. A genuine pedagogical effort was deployed, no doubt a result of the authors' continuous contact with students.

There are only three minor criticisms I would like to offer to the authors:

1. The use of arrows to denote the molecular orientation is only justified in the magnetic case, when the elementary magnets exhibit dipolar order; it is however not adapted to the quadrupolar molecular order observed in liquid crystals. The by now classical use of nail-shaped symbols reminds one of this property and, by the length of the nail, represents the orientation of the molecules with respect to the plane of the image, going from the dash (parallel) to the dot (perpendicular to the plane). Notwithstanding a cautionary note of the authors, I fear that the use of both notations might be confusing to the reader.

2. To simplify their discussion of disclinations, the authors replace the Volterra process of general rotation by de Gennes' process, where the rotation is distributed over the surface of the slit. This is perfectly justified and easier to understand in the case of nematics, where all translations are relaxed by liquid movements. However, the equivalence of the two processes does not hold in the other cases, where liquid relaxation is more complex: in cholesterics, for instance, this presentation poses difficulties in accounting for the distribution of translation dislocations involved in the curvature of disclinations. Similarly, one can also regret the too brief discussion of the topological analysis of defects, which shows its full strength in complex smectics. Finally, concerning the description of Blue Phases, the seminal role of J.-F. Sadoc and M. Kléman in the concepts of projection from a curved space and in the analysis of twist is not sufficiently emphasized.

3. The growth instabilities as such merit a short appendix, rather than an entire chapter. The role of B. Chalmers as a forerunner might have been mentioned, without necessarily proceeding all the way to the distinction made by G. Friedel, in his crystallography lessons (1926), between equilibrium facets, characterized by the law of P. Curie and the Wulff construction, and the development of slow growth facets in dendritic growth. I am nevertheless certain that it was by studying the shapes of mesomorphic "rods" that G. Friedel was able to make this distinction, in the early 1920s.

Overall, this book leaves both a solid and stimulating impression. Everything relating to molecular configuration, to optics (however complex, as shown by Ch. Maugin), to dielectric properties and to (anti) ferroelectrics, to elasticity, the laminar flows and the buckling towards the first instabilities, is described in an authoritative and detailed manner, as are the properties of textures and plastic deformations, involving the appearance of the defects typical for these

phases. But, if the authors were directly involved in the study of these aspects, it might have been noted that the topic itself is more complex and this study is far from complete.

Of course, I appreciate the emphasis given, at the beginning of the book, to the contribution of G. Friedel to the field. The 1922 paper in *Annales de Physique*, which established his reputation, was written upon his arrival at Strasbourg University in 1919 to head the Institute of Mineralogy. Coming from the École des Mines in Saint-Étienne, where he worked and which he directed, he could not become a university professor, according to the rules of the time, for lack of both B.Sc. and Ph.D degrees. He most certainly wrote this paper, mainly describing his own activities, in order to prove that a thesis posed him no problems. This paper struck a note among the specialists and, notably, defined the main terms of the domain, inspired by his penchant for the humanities and a daughter who was good at Greek. This success undoubtedly overshadowed in the minds of readers the original contributions of Friedel's friend F. Grandjean, as Y. Bouligand likes to point out. On the other hand, of course, this paper cannot mention the subsequent work of G. Friedel. It is for instance certain that he saw the Grandjean walls in cholesterics as singular lines, bordering the additional half-pitch on one side of the wall, initially sketched by Grandjean as in Figure B.VII.18 of the present work. His joint paper with my father E. Friedel states this clearly at the liquid crystal conference in 1930, published in *Zeitschrift für Kristallographie* (1931, pp. 1 and 297). After having situated this line on one of the surfaces of the mica wedge (used by Grandjean long before Cano), it appears, according to my father, that G. Friedel realized it was more obvious to place it in the middle of the sample, as proposed much later by researchers in Orsay (cf. figure B.VII.26). At any rate, it is certain that he likened the Grandjean wall to what later would be called a translation dislocation line of the edge type, that he observed its thermal displacement, its pinning on impurities as well as the possibility, in the wedge geometry, of producing a weakly disoriented sub-grain boundary between two slightly mismatched ordered phases. It was only in 1939 that J.M. Burgers predicted such sub-grain boundaries in crystals, and only as late as 1947 did P. Lacombe find them in aluminum. This 1931 conference also discusses the direct X-ray measurements of the layered structure of smectics, performed by E. Friedel in M. de Broglie's laboratory (*C. R. Acad. Sci.* **176**, 738, 1922 and **180**, 209, 1925, cf. *Zeitschrift für Kristallographie*, 1931, pp. 134 and 325).

More generally, it is noteworthy that such a rich and varied area of research went unnoticed by the mainstream scientists until the end of the 1960s. And when recognition finally came, the surge of interest was prompted by the applications. At first glance, this is very surprising, especially since the experiments, though not always easy to perform, are not complex, and since in the 1940s and 1950s the physicists were absolutely ready for the mesoscopic scale arguments, constantly employed ever since. A paper by F.C. Frank in the

1940s had even emphasized the existence of rotation dislocations, but no one, least of all myself, understood the essential role of liquid relaxation in the creation and movement of these lines in liquid crystals. P.-G. de Gennes would certainly point out that the applications relaunched the scientific investigation. The lack of interest in liquid crystals may also have resulted from their apparent lack of applications, at a time of intense research on crystal dislocations and their role in plasticity and growth. At any rate, this example should inspire a certain modesty and warn us against too early abandoning a research field considered to be exhausted.

In conclusion, I would like to cite again G. Friedel at the 1930 Conference (p. 320), saying that none of the three approaches – the naturalist, the physicist, and the mathematician – should be neglected and that a healthy balance must be preserved amongst them! It is no doubt in this spirit that the present work was written.

Jacques FRIEDEL

To our wives, Jocelyne and Hélène

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Preface to the English edition

Liquid crystals were discovered at the end of the 19th century. With properties intermediate between those of solids and liquids, they are known primarily for their widespread use in displays. However, even more important is the fact that they allow us to perform (sometimes very simple) experiments which provide insight into fundamental problems of modern physics, such as phase transitions, frustration, hydrodynamics, defects, nonlinear optics, or surface instabilities. It is in this spirit that we conceived this book, without attempting to exhaustively describe the physical properties of liquid crystals. From this point of view, the book is far from complete; it only reflects a very small part of the enormous work done on this subject over the last thirty years. On the other hand, it provides a thorough treatment of topics reflecting the research interests of the authors, such as growth phenomena, flow and thermal instabilities, or anchoring transitions, which are not described in detail in the fundamental (and already well-known) treatises by P.-G. de Gennes and J. Prost [1], S. Chandrasekhar [2], or P. J. Collings and M. Hird [3]. We also recommend M. Kléman's book on the physics of defects [4] as well as P.M. Chaikin and T.C. Lubensky's book [5], which discusses the general principles of condensed matter physics, often using liquid crystals as an illustration.

We would also like to warn the reader that we use the tensor conventions usually employed in mechanics, and not those of Ericksen, which are employed in references [1] and [2]. Thus, if $\underline{\sigma}$ is a second-rank tensor and $\mathbf{n}$ a vector, $\underline{\sigma} \mathbf{n}$ is a vector with components $\sigma_{ij} n_j$ (and not $\sigma_{ij} n_i$). This difference is essential for all materials exhibiting orientational order, such as nematics, where the stress tensor $\underline{\sigma}$ is not symmetric. Similarly, $\text{div } \underline{\sigma}$ is a vector of components $\sigma_{ij,j}$ (and not $\sigma_{ij,i}$) and the torque associated with the antisymmetric part of the tensor is given by $-e_{ijk}\sigma_{jk}$ (instead of $e_{ijk}\sigma_{jk}$). Let us also point out that we sometimes use arrows $\uparrow$ to represent the director field $\mathbf{n}$ in uniaxial nematics, while the classical representation, which takes into account the $\mathbf{n} \Leftrightarrow -\mathbf{n}$ symmetry is by "nails" ($\perp$). In our case, these two representations are strictly equivalent, the head of an arrow corresponding to the head of a nail. Finally, we added at the end of this volume a chapter on growth instabilities. Although it goes beyond the domain of liquid crystals, this chapter is very useful for understanding the growth experiments described in chapter B.VI, as well as two other chapters in the second volume, entitled *Smectic and Columnar Liquid Crystals: Concepts and Physical Properties Illustrated by Experiments*, dedicated to the growth of columnar and smectic phases.

In conclusion, we would like to thank all those who contributed to the French and English versions of this book. We thank first of all Professor

J. Friedel for his thorough reading of the French manuscript and his observations and informed comments on the history of liquid crystals. We are also grateful to Mr. J. Bechhoefer who suggested many very useful corrections and to Mrs. J. Vidal who corrected the numerous errors which had found their way into the chemical formulas and the associated nomenclature; we also owe her thanks for the calculation and the graphical representation of several molecular configurations.

The translation of the first volume into English is the masterpiece of Mr. Doru Constantin to whom we address especially warm thanks for a very enthusiastic, careful, and punctual accomplishment of this task. Our thanks also go to the financial sponsors of this translation: Mr. B. Bigot from École Normale Supérieure de Lyon, Mr. J. Charvolin from Laboratoire de Physique des Solides in Orsay, Dr. M. Schadt from Rolc Ltd, and Drs. J.-P. Caquet, W. Becker, and J. Gehlhaus from Merck. We also thank Mr. V. Bergeron who was the first critical reader of the English version. The final proof was made by Prof. G.W. Gray, the editor of the Taylor & Francis series on Liquid Crystals. We are grateful to him for numerous corrections and informed comments on the historical and chemical aspects of liquid crystals.

We also thank warmly Ms. C. Andreasen who helped us prepare the PDF printer-ready final files of this book.

Last, but not least, we thank all those with whom we collaborated on the topics presented in this book. In particular, one of the authors (P.P.) wishes to acknowledge his friendly and fruitful collaboration with R. Hornreich on Blue Phases.

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Part A

OVERVIEW

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Chapter A.I

Some history

In this introductory chapter we briefly recall the pioneers in liquid crystals. The first experimental observations date from the 19th century, but liquid crystal physics really began in the early 1920s with G. Friedel. This period was followed by almost half a century of inactivity. It was only in the early 1970s, particularly under the influence of P.-G. de Gennes, that liquid crystal physics entered a stage of expansion that continues to the present day.

Useful complementary information on liquid crystal history can be found in the two papers by H. Kelker published in 1973 and 1988 in *Molecular Crystals and Liquid Crystals* (vol. 21, pp. 1–48 and vol. 165, pp. 1–43) and in a special issue of *Liquid Crystals* (vol. 5, 1989).

I.1 Georges Friedel and liquid crystals

Georges Friedel (Fig. A.I.1), the famous French crystallographer of the early 20th century, was the first to suggest that liquid crystals are states of matter in their own right, intermediates between isotropic liquids and crystals. Before Friedel, several scientists of the 19th and 20th centuries had observed liquid crystals without understanding that they were dealing with new states of matter, separated from the liquid state and the crystalline solid state by sharp boundaries (phase transitions). Friedel took this decisive step and described his discovery in the now famous treatise entitled “Mesomorphic States of Matter,” published in *Annales de Physique* in 1922 [1]. It is well worth citing some of the crucial passages from this fascinating work. From the very beginning, Friedel declares without false modesty that he intends to bring some order into the state of confusion created by his famous but ill-inspired forerunner, Otto Lehmann:

“By this name (“**mesomorphic states of matter**”) I will designate the uncommon states exhibited by the bodies that Lehmann reported on since 1889 under the name of **liquid crystals** or **crystalline fluids**. Upon these denominations, ill-chosen but incessantly repeated for thirty years, many people imagine that the peculiar bodies to which Lehmann had the great merit of drawing attention, but that he was wrong to misname, are nothing more than

crystallized substances, differing from the previously known ones simply by their higher or lower degree of fluidity. In fact, all this is about something else completely and infinitely more interesting than merely more or less fluid crystals."



Fig. A.I.1 Georges Friedel, author of "Mesomorphic States of Matter" [1].

Friedel further details his way of understanding the nature of the bodies Lehmann called **fliessende Kristalle** or **flüssige Kristalle**:

*"The specificity of Lehmann's substances lies not in their more or less fluid state, but rather in their extremely particular structures, always the same and whose number is very small. I hope that the rest of this work will demonstrate that the bodies reported by Lehmann represent two **entirely new forms of matter**, invariably separated from the crystalline form and the amorphous form (isotropic liquid) by discontinuities, as the crystalline form and the amorphous form are always separated by a discontinuity."*

Finally, Friedel names the new states of matter (nematic, cholesteric, and smectic) drawing his inspiration from the Greek language:

*“I shall call **smectics** (σμεγμα, soap) the forms, bodies, phases, etc. of the first kind (part of the fließende Kr., Schleimig flüssige Kr. of Lehmann; liquids with conics), because soaps, in usual temperature conditions, belong to this group and because potassium oleates, in particular, are the first bodies of this group to have been signaled. I shall call **nematics** (νημα, thread) the forms, phases, etc. of the second type (flüssige Kr., Tropfbar flüssige Kr. of Lehmann; liquids with filaments) because of the linear discontinuities, winding like threads, that are their salient feature.”*

It is also important to specify that Friedel put forward the distinction between two types of nematic mesophases:

*“One should distinguish in nematic bodies two different types, between which one can observe **continuous transitions**, as we shall see. I will call the first type: **nematics proper** (liquids with filaments or noyaux, positive nematic liquids); and the second: **the cholesteric type** (liquids with Grandjean planes, negative nematic liquids).”*

These four excerpts from Friedel’s treatise merit a few historical remarks, especially concerning the forerunners of Friedel.

I.2 The discovery of birefringence in fluid biological substances by Buffon, Virchow, and Mettenheimer: lyotropic liquid crystals

The seeds of the idea that condensed matter can exist in states different from the isotropic liquid and the crystalline solid appeared about the mid-19th century.

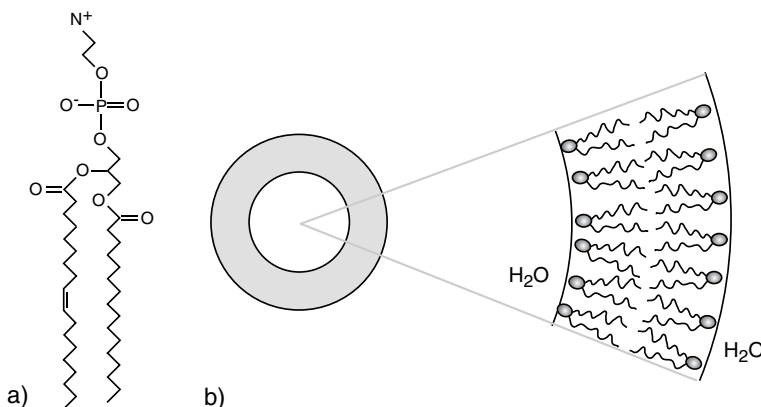


Fig. A.I.2 Phospholipids are the main ingredients of the cell membrane. a) Chemical formula of phosphatidylcholine (lecithin); b) in aqueous solution, phospholipids gather in bilayers.

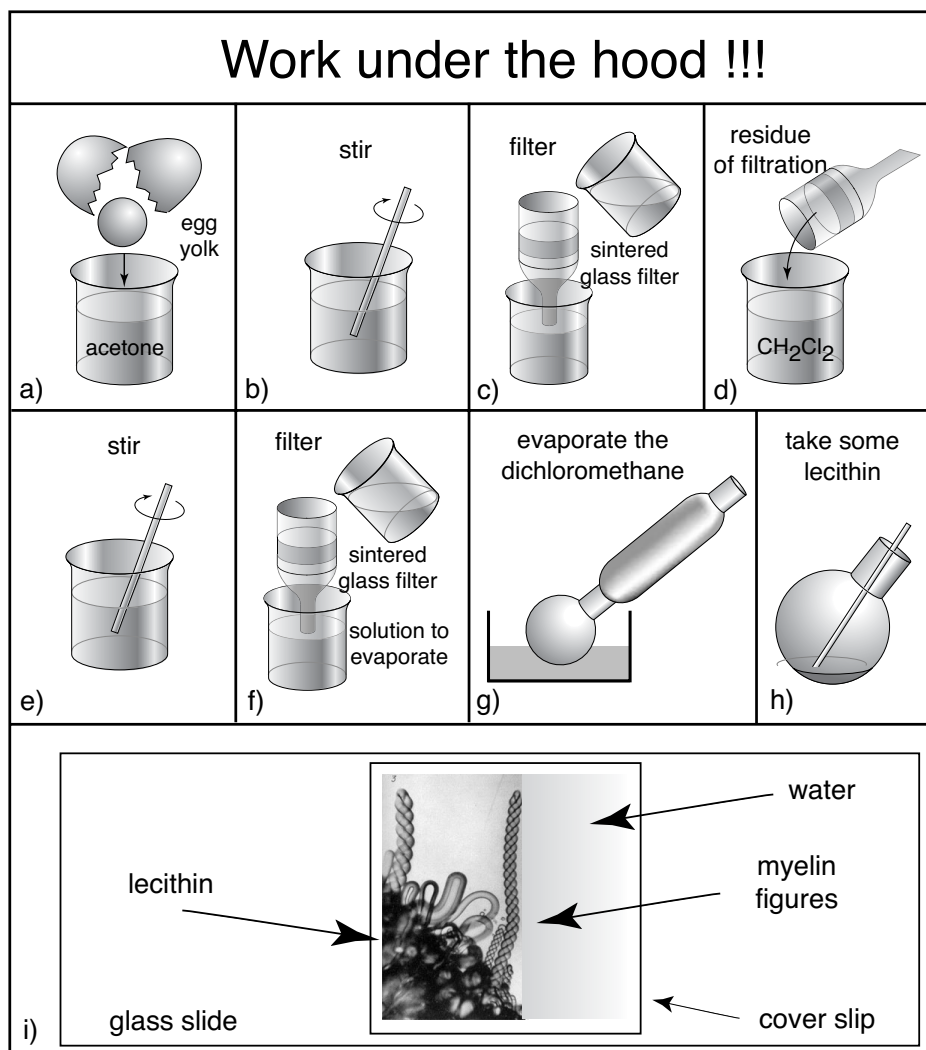


Fig. A.I.3 Recipe for extracting lecithin from egg yolk and producing myelin figures: a-b) mix an egg yolk with 40 ml of acetone; c) filter; d-e) mix the residue of filtration with 40 ml of dichloromethane (CH_2Cl_2); f) filter; g) evaporate the dichloromethane using an appropriate device (rotating evaporator); h) take some lecithin, place it on a microscope slide, and squeeze it under a cover slip; i) add water to the preparation and observe the myelin figures under the polarizing microscope.

At that time, biologists started using the polarizing microscope for studying vegetable and animal tissues, as well as the substances extracted from them (the publication in 1861 of a manual entitled “Die Untersuchung der Pflanzen und Tiergewebe im polarisierten Licht” by G. Valentin shows that the polarizing microscope was among the biologists’ instruments at that time).

Observed in 1857 under the polarizing microscope by the ophthalmologist Mettenheimer, myelin, a soft substance extracted from the nerves, and identified by Virchow in 1850, turned out to be particularly interesting. Indeed, by placing myelin in contact with water, Mettenheimer observed the growth of tubular objects at the myelin-water interface. However, Mettenheimer was not the first (as it is often maintained) to have observed these tubes, now called myelin figures [2]. Similar observations can be traced back to Buffon's complete works, published in 1840, where he speaks of "writhing eels" obtained by dilacerating wheat or rye ergot in water. Obviously, it was not fish, but myelin figures formed by the ergosterol and lecithins contained in these substances.

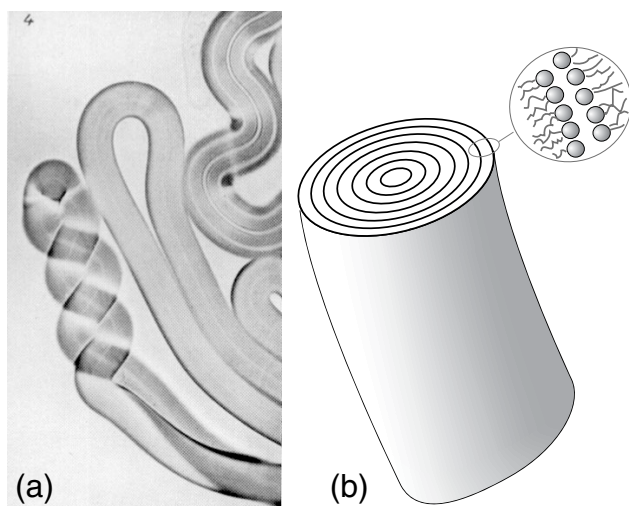


Fig. A.I.4 Myelin figures: a) observed under a microscope (by J. Nageotte); b) concentric cylinder structure made of phospholipid bilayers.

We know today that myelin consists mostly of phospholipids, molecules that are the main ingredient of cell membranes [3]. The extent of these membranes in nerves is enormous, because of their ramified shape, explaining their high phospholipid content. Egg yolk is another source for phospholipids, and has an important lecithin concentration (Fig. A.I.2). The recipe for extracting lecithin from egg yolk is very simple (Fig. A.I.3), and allows one to reproduce the Virchow-Mettenheimer experiment very easily.

At high concentrations, phospholipids in water are arranged in bilayers. We shall see later (in chapter C.III of Vol. 2 on defects in smectics) that bilayers can take various forms and organize in different manners. For instance, they can fit into each other under the form of concentric cylinders. These cylinders are birefringent and constitute the main elements of the myelin textures visible in figure A.I.4.

The arrangement of phospholipids in bilayers is a consequence of their hybrid (**amphiphilic**) molecular anatomy. Indeed, one end of the molecule is hydrophilic, while the other is hydrophobic. The same amphiphilic character is found in soaps which, chemically speaking, are nothing other than fatty acid salts, and therefore derivatives of biological substances. In his treatise (last phrase in section I.1), Friedel alludes to potassium oleate (Fig. A.I.5) whose aqueous solutions, studied at that time by Perrin, also presented, in certain concentrations, a structure of stacked-up bilayers.

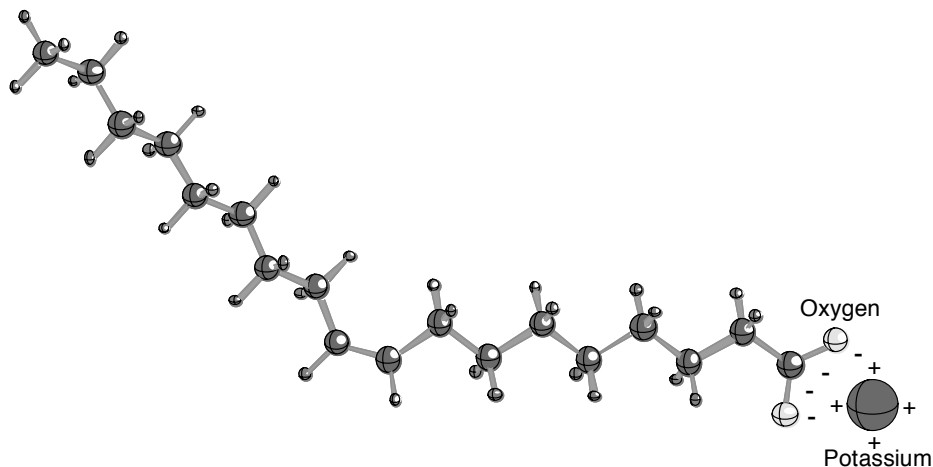


Fig. A.I.5 Molecular structure of potassium oleate. The chain is unsaturated, with a double bond at C₉.

In conclusion, the first mesophases were **discovered in aqueous solutions of amphiphilic molecules**. Today, they are termed **lyotropic liquid crystals**, in contrast to **thermotropic** phases that do not contain water.

I.3 Observation of the surprising behavior of cholesteryl esters by Planer and Reinitzer: thermotropic liquid crystals

Friedel knew that liquid birefringent phases existed not only in solutions, but also in pure bodies. Once more, it is the biologists who set the physicists on the right track. The story begins with cholesterol [3], a substance extracted from plants. In the 19th century, its chemical structure was still unknown;

however, it was classified among alcohols, since one could prepare cholesteryl esters (Fig. A.I.6) by reaction with fatty acids. The biologists Planer in 1861 [4] and Reinitzer in 1888 [5] noticed its opaqueness and the iridescent colors exhibited by these esters upon melting from the crystalline phase or upon cooling from the isotropic liquid. Reinitzer also knew that the optical properties of materials interested some physicists of his time.

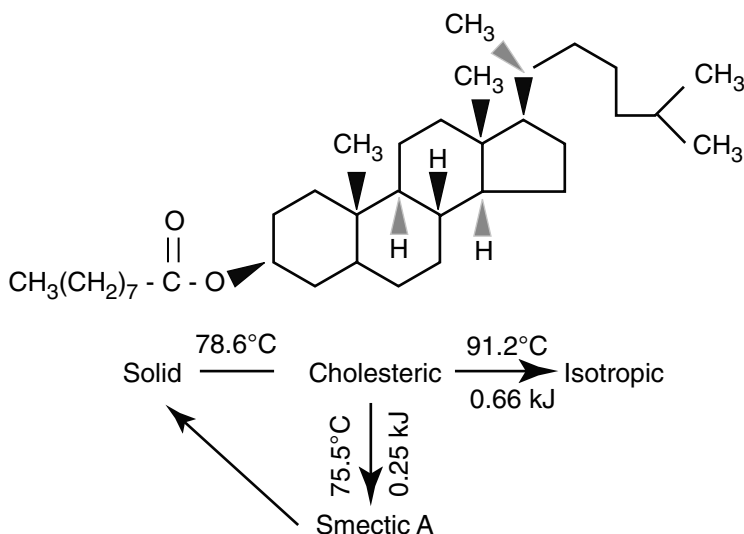


Fig. A.I.6 Molecular structure of cholesteryl nonanoate and its phase transitions. The structures of the cholesteric and smectic phases will be described in the following chapter.

In particular, Reinitzer knew of Otto Lehmann for his work on crystal growth and the changes of crystalline structure induced, for instance, by temperature (crystalline polymorphism). That is why, in 1888, he sent Lehmann a 16-page letter, presenting in detail his surprising observations on the properties of cholesteryl esters. Here is an excerpt:

*“The two substances (cholesteryl esters) hold such beautiful and peculiar phenomena that I hope they will be of the greatest interest to you.(...) **The substance (cholesteryl benzoate) has two melting points, if one may say so.** At about 145.5°C it melts, forming a turbid, but completely fluid liquid, that suddenly becomes completely clear at about 178.5°C. On cooling it, blue and violet colors appear that rapidly get dim, leaving the substance opaque but still fluid. If one cools it further, one sees the blue and violet colors reappear and, immediately afterwards, the substance solidifies forming a white crystalline mass (...) The turbidity that appears upon heating is not due to crystals, but rather to the liquid forming oily streaks.”*

I.4 Fließende Kristalle or “the flowing crystals” of Otto Lehmann

The physicist and the biologist started corresponding. After confirming Reinitzer’s findings with his own observations, Lehmann published in 1889 in the *Zeitschrift für Physikalische Chemie* a paper entitled “Über fließende Kristalle,” thus coining the name “liquid crystals” [6]. What surprised Lehmann the most was that Reinitzer’s substance, although fluid, was birefringent, one of the features of solid crystals. The way he put it was:

“If one trusts the interpretation of the experimental observations, this is so far the only case when a crystalline substance, showing considerable birefringence, has such a weak mechanical strength that it can hardly resist the action of its own weight.”

The publication of Lehmann’s paper was immediately followed by the observation of a similar combination of birefringence and fluidity in other substances, such as *para*-azoxyanisole (PAA) synthesized and studied in Heidelberg by Gattermann, who communicated his results to Lehmann right away. Emphasizing that the viscosity of this new substance was much lower than in cholesteryl esters, Lehmann introduced in 1890 another designation: “Kristalline Flüssigkeiten” or crystalline liquids.

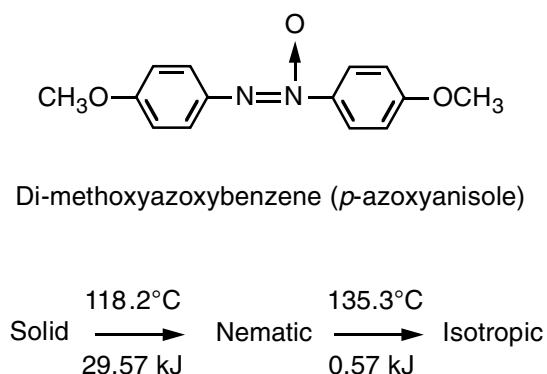


Fig. A.I.7 Molecular structure and sequence of phase transitions for PAA (*para*-azoxyanisole).

The years following the seminal works of Lehmann saw an increasing volume of similar observations, and the question of the real molecular structure of “liquid crystals” or “crystalline liquids” became more and more important. Heated debates opposed those that pleaded for chemically and physically homogeneous phases to the ones holding that the optical turbidity was a result of either demixing impure substances or incomplete melting of the crystalline

phase. And even for those considering the phases homogeneous, the question was if they were to be classified among (flowing) crystals or, on the contrary, in a category of their own.

It is in this state of conceptual and terminological confusion that Georges Friedel came up with the idea that these phases were **distinct states of matter whose molecular structures were intermediary (*mesomorphic*) between the crystals and ordinary liquids**. At the same time, he proposed a classification of mesomorphic states which is still in use today and that will be described (in its modern form) in the next chapter.

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Chapter A.II

Modern classification of liquid crystals

We begin this chapter with a brief summary of the principles used by Georges Friedel to classify liquid crystals (section II.1). As will be seen, this classification is not complete and it can be extended by employing the very general notion of broken symmetry (section II.2). We then return to the classification of smectic and columnar phases (sections II.3 and II.4, respectively).

II.1 The terminology introduced by Georges Friedel

II.1.a) Polymorphism and mesomorphic states

As stated in the previous chapter, Friedel was the first to speak of “mesomorphic states.” By this designation of liquid crystalline phases, Friedel intended, on the one hand, to avoid the semantic controversies triggered by the discrepancy of the terms “crystalline” and “liquid” and, on the other hand, to point out that they were genuine states of matter whose molecular properties are intermediary (*meso*-morphic) between those of crystals and those of ordinary liquids. By reading certain passages of his 1922 treatise (see the previous chapter), one notices that, by speaking of mesomorphic *states*, in the plural, Friedel already knew that at least two structures could combine crystalline anisotropy and fluidity. Perhaps his idea of mesomorphic polymorphism was an analogy with the crystalline polymorphism, a notion well established by that time. As a matter of fact, Friedel knew very well that the same substance could display different crystalline structures depending on the temperature or pressure. In his other work, “Lessons in crystallography,” Friedel actually gave a complete overview of the 230 space groups allowing for

the classification of all possible crystalline structures in three dimensions [1a]. However, since he only knew two mesomorphic structures, Friedel's idea of mesomorphic polymorphism was a jump ahead. The future proved him right, as the number of mesophases with different symmetries known today is large, with the count still ongoing.

II.1.b) Nematic and cholesteric phases

If the term “mesomorphic” and the concept of mesomorphic polymorphism stood the test of time, one can wonder if Friedel's other terminological proposals were equally correct. The last passage from Friedel's treatise cited in the previous chapter shows that the choice of the name “nematic” was based on microscope observations of “linear discontinuities” (thread-like texture shown in figure A.II.1). Polarized light observations allowed Friedel to deduce the configuration of the optical axes around these lines and to characterize them as orientational singularities of the optical axis (similar observations had also been made by Lehmann and, later, by Grandjean).

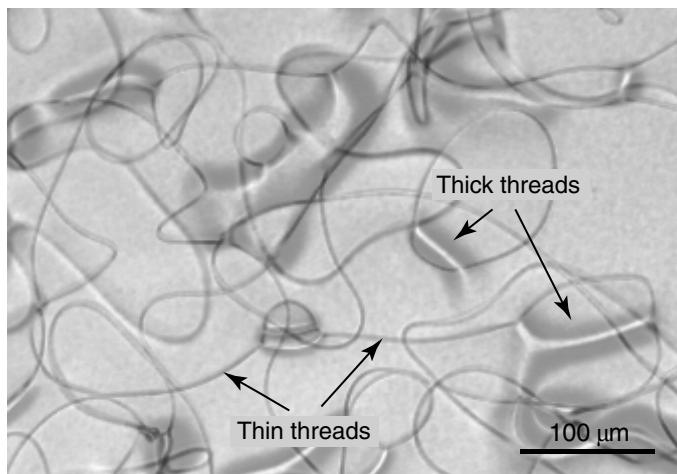


Fig. A.II.1 Thread-like texture observed in a free drop of uniaxial nematic liquid crystal. Thin and thick threads correspond to two different kinds of line defects.

Was Friedel right in speaking of line defects? One might doubt it, since today condensed phases are classified by the type of symmetry breaking they present with respect to the liquid isotropic phase. We shall see that, according to these criteria, a “nematic” is a phase whose only broken symmetry is orientational and whose order parameter is quadrupolar. Yet we shall also find out that the line defects observed by Friedel are nothing other than topological defects (nowadays termed disclinations) of the nematic order

parameter. These defects are a distinctive mark of uniaxial quadrupolar orientational long-range order. Once again, Friedel's choice of terms was accurate, although one must note that the quadrupolar moment can be uniaxial or biaxial. A corresponding distinction should therefore be made between uniaxial and biaxial nematics. In most of the cases, the nematic phase is uniaxial. It took half a century to find the first examples of a biaxial nematic phase that imposed a revision of Friedel's nomenclature. We will return to this topic in the chapter on nematics.

Friedel was also right to consider that the cholesteric phase (see figure A.II.5) was only a particular (chiral) type of nematic phase. This is how he describes it in his treatise:

"Two important conclusions seem to emerge from this series of observations: 1. Cholesteric bodies are nothing more than a very special type of nematic bodies. Upon the gradual disappearance of rotatory power and of the related structural properties: (e.g., Grandjean planes, commas, etc.) what remains is a nematic proper. There is a continuous passage between the cholesteric and the nematic types..."

Finally, he explains that:

"The transition from the right-handed to the left-handed body or vice versa is done by changing the sign of structure twist. This twist takes place about the normal to the preparation plane when the layered structure is uniform; it is undergone by a positive uniaxial nematic body whose optical axis is parallel to the preparation plane and hence it takes place about the normal to its optical axis, thereby giving rise to a negative uniaxial arrangement. It is this twist that, together with the negative uniaxiality, determines the rotatory power."

Friedel was once again right, as we will show in chapter B.VII, dedicated to the cholesteric phase.

II.1.c) Smectic phases

Polarized light observations led Friedel to the conclusion that in the second type of mesophases molecules are arranged in layers. Although their thickness is fixed, these layers can bend and give rise to textures that exhibit singular lines in the shape of "focal conics" (Fig. A.II.2).

These geometrical objects were invented by Dupin, a mathematician from the early 19th century (see the chapter on defects in smectic phases). Instead of trying to coin a term inspired by focal conics, Friedel put forward the term "smectics," as this layered molecular structure is very frequent in aqueous solutions of soaps. In order to confirm his conclusions on the structure of the smectic mesophase, Friedel considered the use of X-rays [1b]:

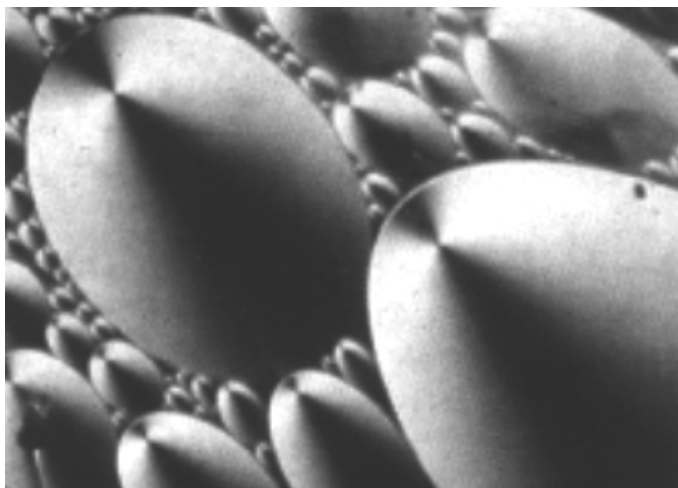


Fig. A.II.2 Focal conics texture observed in a free smectic A drop placed on a glass plate.

“Let us point out that the measurements of Perrin and Wells on soaps are in principle sufficient to validate the structural hypothesis suggested by so many facts. There is however another way of revealing the equidistant planes in all smectic bodies and to measure their distances in pure bodies, better defined than those used by Perrin, namely the use of X-rays. (...) The repeat distance is probably of the order of several tens of Angstroms so that, in order to have a satisfying reflexion angle, long wavelength X-rays should be employed.”

According to broken symmetry criteria, nowadays one calls smectic a phase where molecules are organized in layers, the translational symmetry being broken in **at least** one direction in space.

This definition does not specify the way molecules are set up inside the layers, or define the type of stacking, or the shape of the layers, which need not be flat. Hence, there is a very large number of distinct smectic phases. Their names are formed by adding one or several letters to the name proposed by Friedel. We provide some examples later.

II.2 Modern definition of mesophases; broken symmetries; short- and long-distance order

Boundaries between different liquid crystalline phases are not always easily determined. Sometimes it is even hard to say if one is dealing with a mesophase or not. One of the possible criteria involves the concept of broken

symmetry. As explained by Anderson [2a], this idea, stemming from the work of P. Curie on magnetism [2b] and from that of L. Landau on second-order phase transitions [2c], is based upon the fact that the symmetry of a system of particles can be lower than that of the interaction hamiltonian.

In a homogeneous and isotropic space, the hamiltonian for a system of interacting particles must be invariant with respect to the elements of the group G [3]:

$$G = \mathbf{t} \times \text{SO}_3^{(L)} \quad (\text{A.II.1})$$

comprising the following symmetries:

$\mathbf{t}$ – the group of 3D translations; it consists of all the translations $\mathbf{t} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$ with x, y, z real;

$\text{SO}_3^{(L)}$ – the group of space rotations; its elements are the matrices $\underline{R}$ fulfilling $\det(\underline{R}) = \pm 1$.

Put another way:

$$\text{for all } \mathbf{g} \in G \text{ one must have } \mathbf{gH} = \mathbf{H} \quad (\text{A.II.2})$$

with H being the hamiltonian. Remarkably, in spite of this interaction symmetry G , all thermodynamic equilibrium states, except for the gas and the isotropic liquid, have lower symmetries G' such that:

$$G' \in G \quad (\text{A.II.3})$$

where G' is a sub-group of G . This lowering of hamiltonian symmetry is termed symmetry breaking. Here, “symmetry of the system states” refers, for instance, to the symmetry of density distribution, molecular orientation, or dipolar magnetic or multipolar electric moments, etc.

In the gas or the isotropic liquid phases, there is no symmetry breaking. In periodic 3D crystals, both translational and orientational symmetries are broken, as the mass (or charge) density

$$\langle \rho(\mathbf{r}) \rangle = \rho_o + \sum \rho(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}) \quad (\text{A.II.4})$$

is only invariant with respect to the elements of one of the 230 space groups, rather than with respect to all translations $\mathbf{t}$ and all rotations $\underline{R}$. In particular, simple translations belonging to these space groups are discrete and define the Bravais lattices well known to crystallographers.

By definition, symmetry breaking is *less important* in mesophases than in 3D crystals; these phases can therefore be seen as *intermediaries* between 3D crystals and the liquid isotropic phase.

From now on, whenever it is called for, we shall analyze the symmetry breaking characteristic to the phase studied. To provide an idea of liquid crystalline diversity, figure A.II.3 presents a simplified diagram of mesophase classification. This diagram merits some comments:

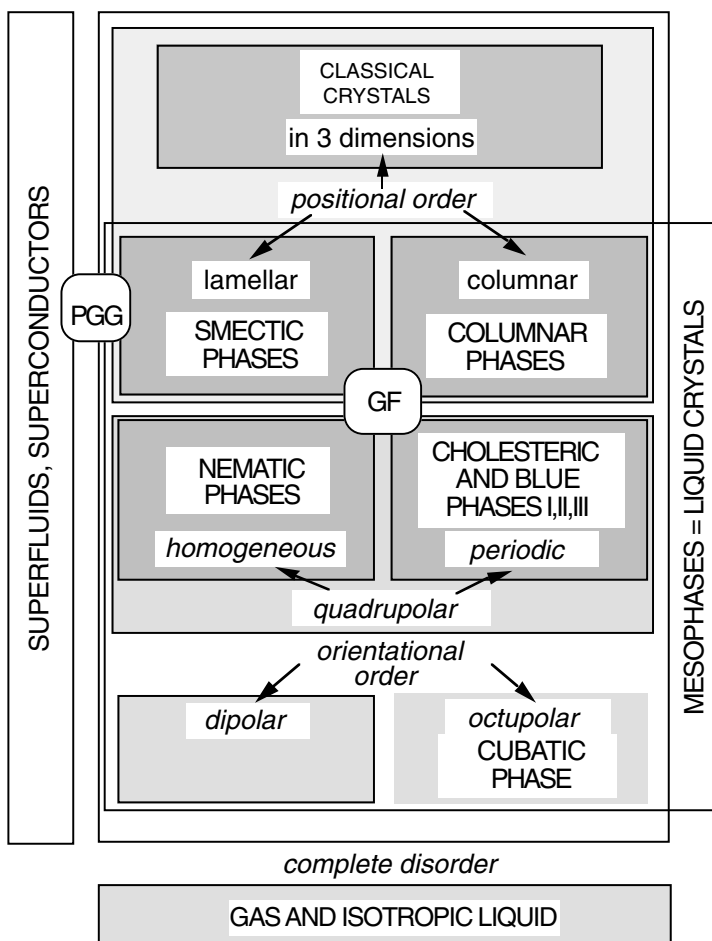


Fig. A.II.3 Mesophase classification diagram. PGG indicates the analogy established by P.-G. de Gennes between quantum liquids and smectics (see chapter C.I). GF denotes the terminology proposed by G. Friedel.

– All classification of condensed matter phases only in terms of symmetries is incomplete, as a system can exhibit two distinct phases of the same symmetry, separated by a discontinuous phase transition. The classic example is that of the liquid-gas transition. To understand the difference between these two phases one must look at the nature of the local order and calculate the correlation functions of the corresponding order parameter. Similar transitions exist in liquid crystals, such as those between smectic phases with the same symmetry, but with locally different molecular arrangements (for instance, the smectic A_1 -smectic A_2 transition [4]).

– In this diagram, nematic phases belong to the family of mesophases presenting only orientational long-range order. This order is quadrupolar (the

concept will be rigorously defined in chapter B.I) and spatially homogeneous. When the mesogenic material is composed of chiral molecules, quadrupolar order is spatially modulated, which does not imply the appearance of long-distance positional order. Cholesteryl esters present such phases, one of which was termed “cholesteric” by Friedel. In this particular case, the modulation appears along one space direction. We know now that, between the isotropic and the cholesteric phases, these materials also exhibit the so-called “Blue Phases” (I, II, and III), where quadrupolar order varies periodically in the three space directions. It is even probable that they are responsible for the blue and violet colors mentioned by Reinitzer in his letter to Lehmann (see the previous chapter). However, as these phases only exist in a very narrow temperature range ($\approx 3^\circ\text{C}$), they were only identified in the late 1970s.

- The diagram also contains a fourth phase, not present in the Friedel classification, called columnar or canonic (the last denomination proposed by Sir Charles Frank). In this type of mesophase, the molecules (usually discoidal or cone shaped) are stacked in one-dimensional columns that can present various spatial arrangements.

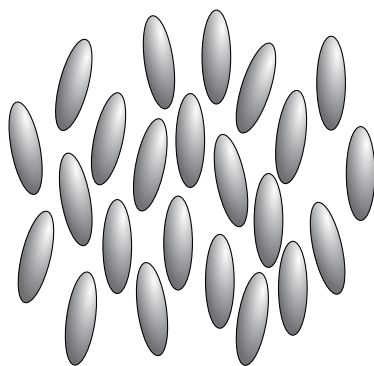


Fig. A.II.4 Schematic representation of the nematic uniaxial phase.

- Note that order is sometimes intermediate between short and long range. This is the case for two-dimensional systems where correlation functions can algebraically decay with the distance r (say $1/r^n$). The resulting behavior is in between exponential decay (defining short-range order) and convergence towards a finite value for $r \rightarrow \infty$ (characteristic of long-range order). As an example one can consider hexatic phases, predicted by Kosterlitz and Thouless [5], and subsequently discovered in smectics (chapter C.V).

- Finally, phases of dipolar or octupolar orientational order have never been experimentally observed.

Figure A.II.4 depicts the nematic uniaxial phase. Every molecule is represented by a prolate spheroid. This rendering is suggestive of the fact that

molecules can rotate freely about their major axes. One should notice that the three-dimensional orientational order is long range.

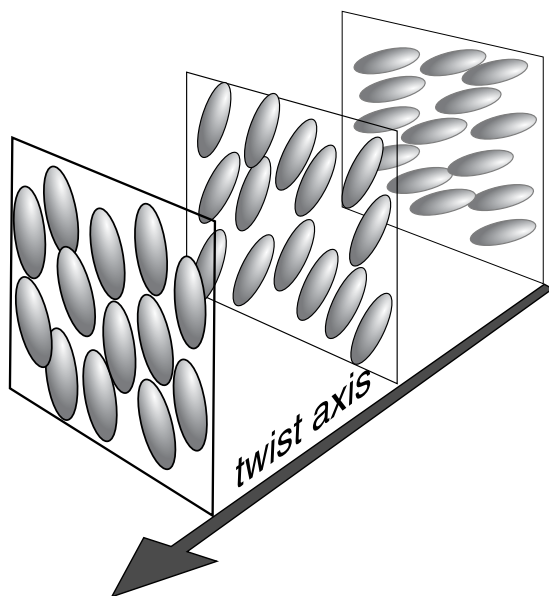


Fig. A.II.5 Schematic representation of the cholesteric phase. The planes have no real existence, the centers of mass of the molecules being randomly distributed.

In the cholesteric phase, the average molecular orientation turns about a space direction called the helicoidal axis. This twisted chiral phase is shown in figure A.II.5.

These two phases are fluid, the centers of mass of the molecules being randomly distributed. The molecular arrangement in Blue Phases is more complicated and will be described in chapter B.VIII. In the two following sections we shall thoroughly explain the classification of smectic and columnar phases.

II.3 Classification of smectic phases

These phases are distinguished by the different molecular positioning in the layers and in the transverse direction. In particular, rod-like molecules (see the following chapter on molecular architecture) can be parallel or tilted with respect to the layer's normal axis [6]. The figure A.II.6 table summarizes the primary smectic phases.

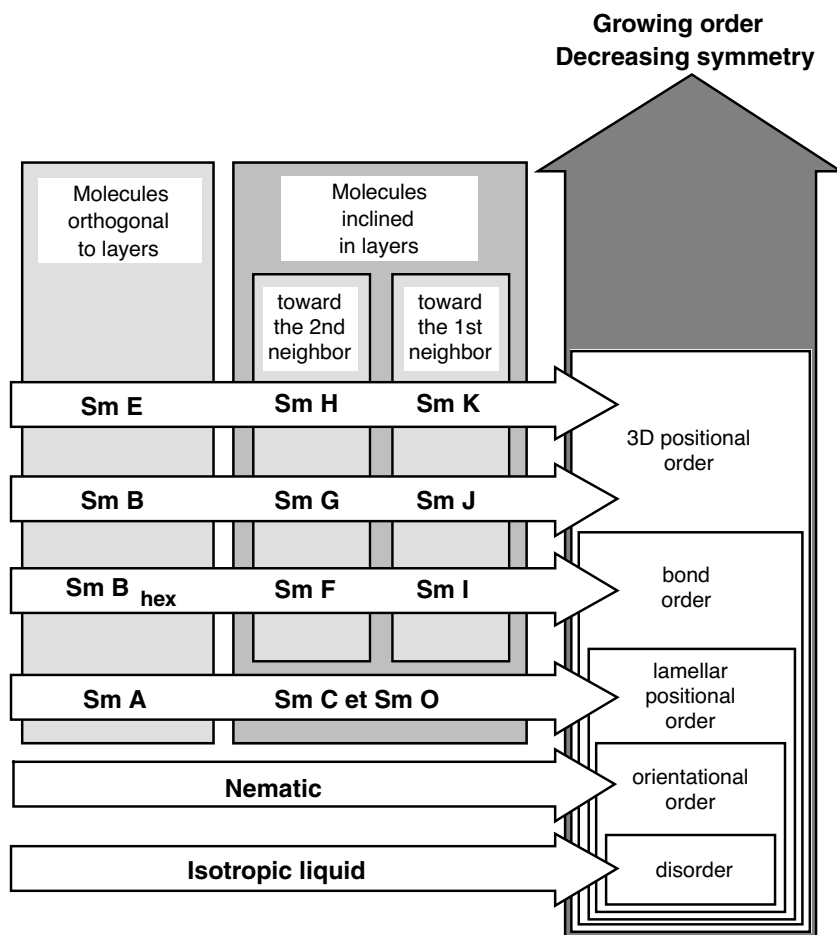


Fig. A.II.6 Classification of the main smectic phases.

To begin, a distinction is made in order between:

- 3D orientational order of the molecular major axis,
- orientational order of bonds between nearest neighbor molecules (in the plane of the layers) and, finally,
- positional order of the molecular center of mass in the layer plane and in the transverse direction.

In each case, one should distinguish between short-range order (S.R.O.), long-range order (L.R.O.) or intermediate (Q.L.R.O. for “quasi-long-range order”) as in hexatics. These data are gathered in the figure A.II.7 table for the primary smectic phases, which will now be described in detail.

Phases	Orientational order of the molecular major axis	Orientational order of bonds in nearest neighbor molecules	Positional order across the layers	Positional order in the layers
Smectic A (SmA)	L.R.O.	S.R.O.	L.R.O.*	S.R.O.
Smectics C and O (SmC, SmO)	L.R.O.	S.R.O.	L.R.O.*	S.R.O.
Smectic B hexatic (SmB _{hex})	L.R.O.	Q.L.R.O.	L.R.O.*	S.R.O.
Smectic F (SmF)	L.R.O.	Q.L.R.O.	L.R.O.*	S.R.O.
Smectic I (SmI)	L.R.O.	Q.L.R.O.	L.R.O.*	S.R.O.
Smectic B (SmB)	L.R.O.	L.R.O.	L.R.O.	L.R.O.
Smectic G (SmG)	L.R.O.	L.R.O.	L.R.O.	L.R.O.
Smectic J (SmJ)	L.R.O.	L.R.O.	L.R.O.	L.R.O.
Smectic E (SmE)	L.R.O.	L.R.O.	L.R.O.	L.R.O.
Smectic H (SmH)	L.R.O.	L.R.O.	L.R.O.	L.R.O.
Smectic K (SmK)	L.R.O.	L.R.O.	L.R.O.	L.R.O.

Fig. A.II.7 Types of order present in three-dimensional smectic phases. The asterisk * indicates that, strictly speaking, lamellar order in fluid layer smectics is Q.L.R. because of the Landau-Peierls instability (unbounded 1D crystals cannot exist).

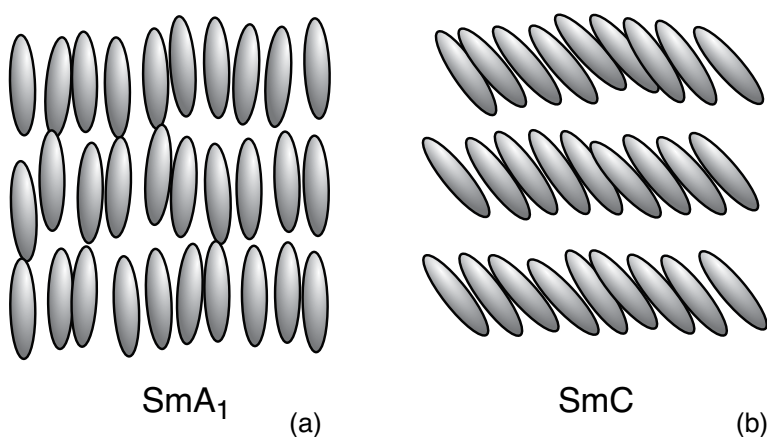


Fig. A.II.8 Schematic representation of the smectic A and smectic C phases.

In the smectic A phase (Fig. A.II.8a), molecules are arranged in fluid layers that can slide one with respect to the other. On average, molecules are perpendicular to the layer plane. This phase is therefore optically uniaxial, with an optical axis normal to the layers. The layer thickness d can vary with temperature and the molecular nature. It can be equal to the molecular length l ($d=l$, SmA_1), twice the molecular length ($d=2l$, SmA_2) or have an intermediate value ($d=xl$ with $1 < x < 2$, SmA_d). These different types of smectic A phases are separated by discontinuous phase transitions.

In the smectic C phase (Fig. A.II.8b), molecules are tilted with respect to the layer normal. As in the A phase, fluid layers can slide over each other. This phase is optically biaxial.

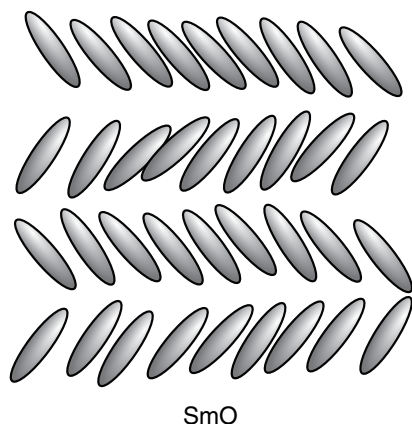


Fig. A.II.9 Schematic representation of the smectic O phase.

The smectic O phase (Fig. A.II.9) is another “tilted version” of the smectic A [7]; this time, molecules are placed in a “herringbone” pattern, alternately tilted to the left and to the right in successive layers. This phase is also optically biaxial.

Hexatic phases are more ordered than the previously discussed phases, from which they are distinguished by the existence of quasi-long-range orientational order of geometrical bonds between nearest neighbor molecules. Thus, in the hexatic B phase, the molecules are normal to the layers and locally disposed on a hexagonal lattice (Fig. A.II.10). The lattice orientation is preserved over quasi-long distances, but the positional order of the molecular center of mass is only short range due to the presence of a high density of free (i.e., very mobile) dislocations breaking the translational symmetries. One therefore speaks of hexatic order, a rather subtle concept to be discussed in chapter C.VI. The layers are fluid, as they cannot sustain shear stress without flowing, so they too slide over each other. This phase is optically uniaxial, the optical axis being normal to the layers. Smectic F and I phases are “tilted versions” of the hexatic B phase (Fig. A.II.11). However, they are optically biaxial.

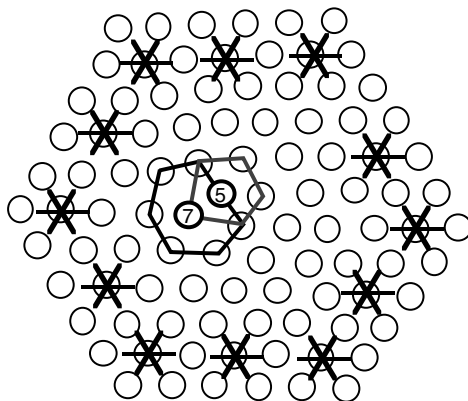


Fig. A.II.10 Locally hexagonal lattice of a hexatic phase. Although the geometrical bonds between nearest neighbor molecules exhibit quasi-long-range order, the positional order is short range due to an important density of “free dislocations” like that shown in the center of the drawing.

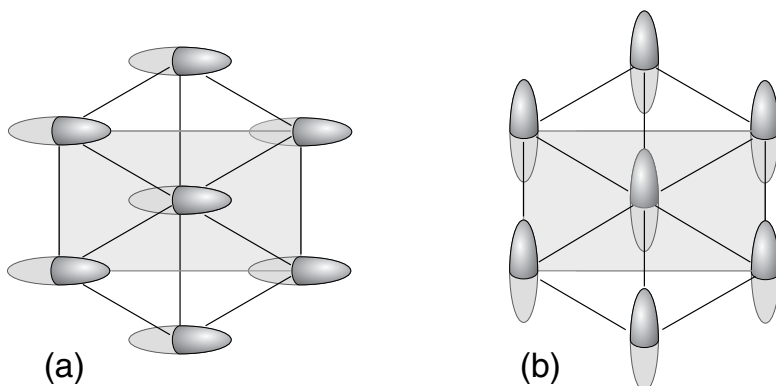


Fig. A.II.11 Local arrangement of molecules in the plane of the layers in smectic F (a) and I (b) phases. Ellipses represent molecules tilted with respect to the plane of the layers. In both phases, the hexagonal lattice is slightly deformed (in fact, it becomes rectangular).

Finally, crystalline smectics are, by definition, more ordered than hexatic smectics. In these systems, molecules are placed on the sites of a 3D lattice with positional long-range order. However, as we will see, they preserve some degrees of freedom.

Let us begin with smectics B and E. In both phases, molecules are on average normal to the layers, but their rotation about their major axes is different. Thus, in the B phase molecules are free to turn and they are placed on the sites of a hexagonal lattice. The phase is therefore optically uniaxial, the optical axis being normal to the layers. In the E phase, on the contrary, this rotation is partially hindered and the molecules exhibit herringbone stacking in the plane of the layers (Fig. A.II.12) [8]. This particular stacking

induces a slight distortion of the hexagonal lattice that becomes rectangular ($a \neq b$). The phase is therefore optically biaxial. Smectic G and J and smectic H and K phases are tilted versions of the B and E phases, respectively.

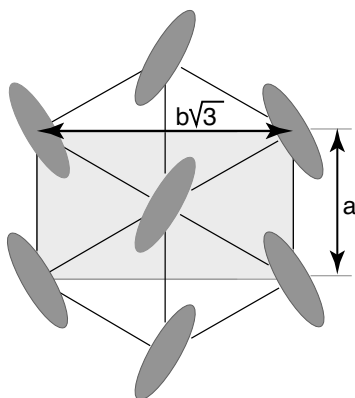


Fig. A.II.12 Herringbone molecular stacking in the smectic E phase (here the segments represent sections normal to the molecular major axis and not the tilted molecules as in Fig. A.II.11). The lattice has rectangular symmetry ($a \neq b$) and the phase is optically biaxial.

Let us emphasize that crystalline smectic phases are more properly classified among plastic crystals, as the molecules, although placed on the sites of a 3D lattice, retain a certain rotational freedom, contrary to true crystals where all rotations are frozen. Some authors drop the term smectic (Sm) for such phases, referring to them simply as B, G, K, etc. phases, or cryst. B, cryst. G, cryst. K, etc. phases.

II.4 Classification of columnar phases

In these phases, discovered in 1977 by the Chandrasekhar group in India [9], discoidal [10] or cone-like [11] molecules stack up to form “infinitely long” columns, free to slide with respect to each other (no positional correlation between columns). The molecules can be normal to the column axis or have a certain tilt angle. Strictly speaking, molecular positional order along the columns is short range, although in some cases the stacking is very regular: one speaks then of “ordered” phases, as opposed to the so-called “disordered” phases, where the distance between molecules along a column has strong fluctuations. There is however no clear-cut distinction between these two kinds of phases that must all be considered as one-dimensional fluids. On the other hand, the columns themselves are parallel and form a two-dimensional lattice that can be hexagonal (Fig. A.II.13), rectangular, or oblique. From this point of view, columnar phases are two-dimensional crystals. Figure A.II.14 shows some of the experimentally observed structures, but the list is by no means exhaustive.

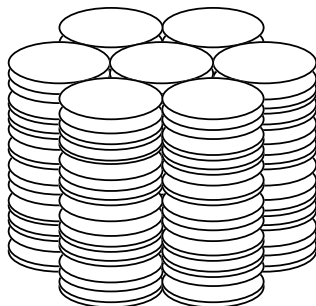


Fig. A.II.13 Hexagonal D_{hd} phase formed of discoidal molecules (sometimes misnamed discotic). The letter “D” stands for the disk-like shape of the molecules. The index “h” indicates the nature of the lattice, hexagonal in this case. The second index is optional and specifies the nature of the stacking in a column: “d” for disordered and “o” for ordered.

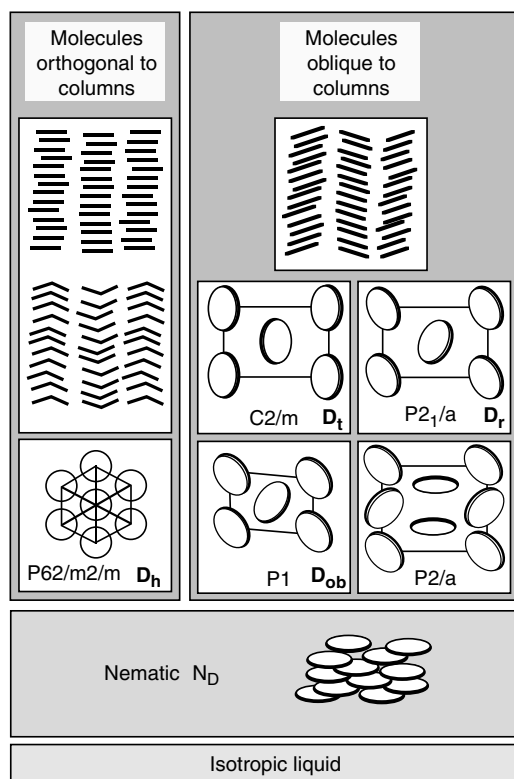


Fig. A.II.14 Some examples of columnar mesophases. In certain materials a nematic N_D phase appears between the columnar phase and the isotropic liquid. For every columnar phase the symmetry group is indicated. D_h and D_r phases are the most common. Note that the letter D stands for the shape of the molecule, while the index specifies the nature of the lattice (“h” for hexagonal, “r” for rectangular, and “ob” for oblique). A singular example of a triangular lattice with four columns per unit cell will be given in chapter C.IX [12].

Note that in the hexagonal phase the molecules are not always normal to the column axis. Indeed, hexagonal symmetry is preserved if the molecules are free to rotate about this axis [12]. Finally, certain rod-like molecules, called phasmids because of their six aliphatic chains [13], can yield columnar phases of hexagonal (Φ_h) or oblique (Φ_{ob}) symmetry. Here, the letter Φ refers to the “phasmidic” nature of the molecule.

II.5 Chiral smectic phases

The preceding classification of smectic phases only applies to non-chiral substances. What happens then when the molecules are chiral? Several structures can appear. One of them, called SmC^* , is a twisted version of the SmC phase [14] and is characterized by the fact that the molecules are tilted and turn from one layer to the next with a constant angle about the layer normal. This phase can be ferroelectric after unwinding and can therefore have interesting applications. This topic will be presented in the next volume.

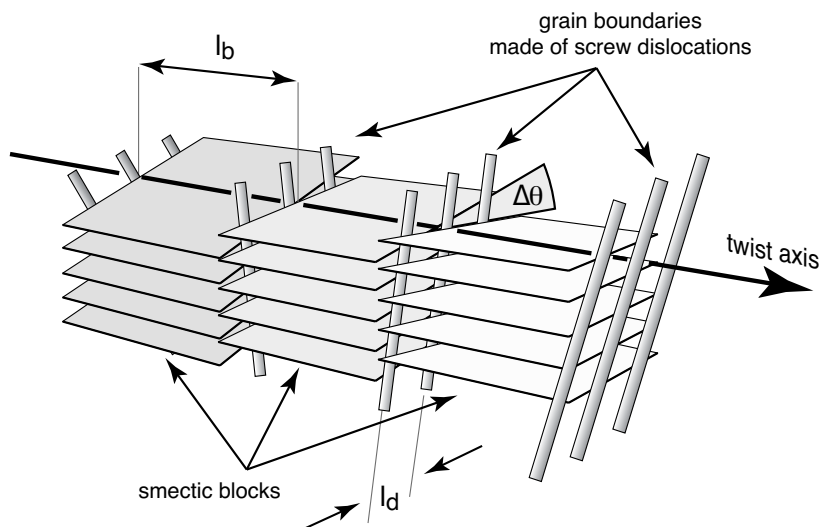


Fig. A.II.15 Renn and Lubensky model of the TGB_A phase (from “twist-grain-boundary”). In this twisted smectic phase, the smectic A layers form blocks of width l_b separated by screw dislocation walls. Inside each wall, dislocations are parallel and equidistant, but their orientation turns with an angle $\Delta\theta$ between two successive walls, so they are on the average normal to the smectic layers and therefore retain the “screw” character. Note that $\Delta\theta$ is also the angle of the layers between two successive blocks.

Another solution, theoretically predicted by de Gennes in 1973 by analogy with superconductors [15] and experimentally evidenced 25 years later

[16], is obtained by slicing the smectic A (or smectic C) phase in blocks, subsequently assembled in a helical structure. Between two neighboring blocks appears a wall of screw dislocations (Fig. A.II.15). The phase is therefore called TGB, from “twist-grain-boundary.” An entire chapter of the second volume is devoted to this phase.

Later, we shall also discuss the recent discovery of so-called Smectic Blue Phases [17,18], still under study (chapter C.V of the second volume). The next chapter discusses the materials that can exhibit mesomorphic phases.

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Chapter A.III

Mesogenic anatomy

Mesophases are found in all kinds of materials. To specify the nature of the mesogenic material one distinguishes between:

1. Thermotropic LCs (low molecular mass species)
2. Lyotropic LCs (aqueous solutions of amphiphiles)
3. Polymeric LCs (reticulated or not)
4. Colloidal LCs (suspensions of colloidal particles, the best known being the tobacco mosaic virus)

This distinction is important because, even though a mesophase always has, by definition, the same symmetries and the same laws of macroscopic behavior, its physical constants strongly depend on the chosen material. Thus, thermotropic nematics flow very easily (with viscosities ranging from that of water to that of glycerine) while polymeric (unreticulated) nematics are extremely viscous.

The rest of this chapter is devoted to describing, using concrete examples, the general architecture of mesogenic molecules. The examples are deliberately chosen from thermotropic (section III.1) and lyotropic (section III.2) liquid crystals, which constitute the main topic of this book. Special attention will be paid to the concept of molecular frustration, which is the key to mesomorphic polymorphism. At the end of the chapter, diblock copolymers (section III.3) and colloidal liquid crystals (section III.4) will be discussed briefly.

III.1 Thermotropic liquid crystals

Practically all mesogenic substances known today were obtained by synthesis [1, 2]. Their number is impressive and they are thought to account for about 5%

of the synthesized organic products. The work achieved by chemists in this regard is admirable, for they continuously design new mesogenic molecules that engender new phases.

Nowadays, new synthesis is no longer performed at random; on the contrary, it is the result of reflection based upon a considerable body of knowledge, acquired over almost a century. The essential question, which has been asked by Vorländer, Lehmann, and Friedel is the following:

“For what reason does a given substance go through mesomorphic states instead of passing directly from the crystalline solid to the isotropic liquid?”

III.1.a) Hybrid molecular form and molecular frustration

To find the first clues, let us consider the phase sequences of figure A.III.1.

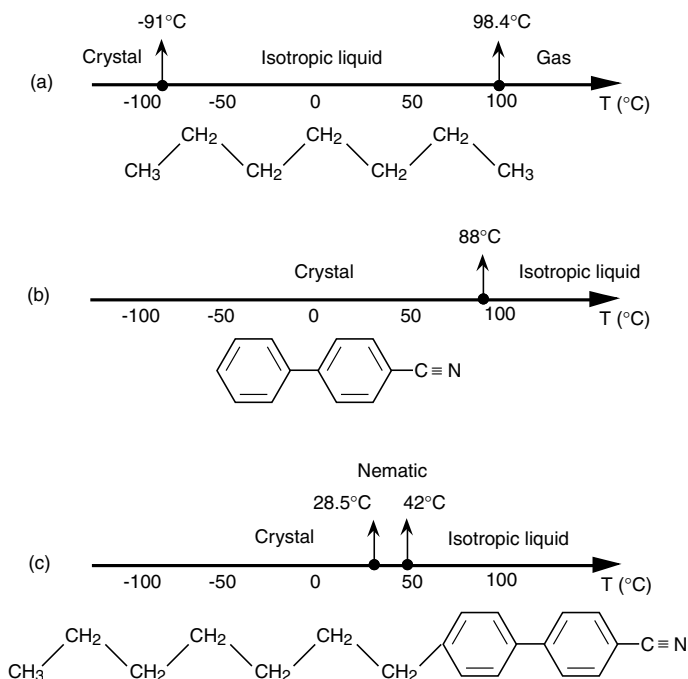


Fig. A.III.1 Phase sequence of three organic substances; the third one, known as 7CB, is mesogenic. It is obtained by covalently bonding two very dissimilar and non-mesogenic molecules, heptane (A) and 4-cyanobiphenyl (B).

The first two sequences belong to very dissimilar and non-mesogenic molecules, heptane (A) and 4-cyanobiphenyl (B). The third sequence is that of the substance C (A-B) obtained by chemically bonding the first two molecules.

These species were not randomly chosen; indeed, mesogenic A-B, known as 7CB, is a component of many nematic mixtures used in liquid crystal displays [3, 4].

Thermodynamically, at fixed temperature and pressure a substance chooses between two possible phases α or β the one that has the lowest chemical potential $\mu_{\alpha,\beta}(T,p)$. For a given pressure, μ is a function of temperature and depends on the phase α or β of the system. For heptane and 4-cyanobiphenyl, the solid crystalline phase S is in competition with the liquid phase L. The S-L transition takes place at the temperature at which the curves $\mu_L(T)$ and $\mu_S(T)$ cross.

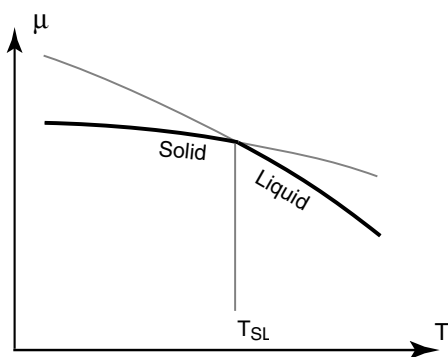


Fig. A.III.2 Chemical potential variation close to a first-order transition between the solid crystalline phase (S) and the liquid phase (L).

In order to understand better the microscopic nature of this transition, one should recall that the chemical potential μ is the Gibbs free energy G per molecule:

$$\mu = G / N \quad \text{with} \quad G = U - TS + pV \quad (\text{A.III.1})$$

where G is the thermodynamic potential to be minimized at fixed T and p .

In a three-dimensional crystal, molecules are placed on the sites of a crystalline lattice. When $T = 0$, they are optimally stacked in order to minimize the potential energy U of intermolecular attraction. At constant pressure p , let the temperature increase up to $T \geq T_{SL}$. At the melting point T_{SL} , the entropy $\Delta S = S_L - S_S$, gained as the molecules quit their fixed positions, exactly balances the increase $\Delta U = U_L - U_S$ in internal energy due to this transformation and the work $p\Delta V = p(V_L - V_S)$ necessary for dilating the system. Consequently, melting takes place when:

$$\Delta G_{SL} = \Delta U - T\Delta S + p\Delta V = 0 \quad (\text{A.III.2})$$

Hence, when the attraction between the molecules is stronger, it is more difficult for the substance to melt, so the melting temperature is higher.

The attraction between two organic molecules can be due to:

1. Direct interaction between their permanent electric dipoles – this interaction is attractive for certain positions of the molecules;
2. Permanent dipole-induced dipole interaction – this interaction depends on the molecular polarizability;
3. Induced dipole-induced dipole interaction named after van der Waals – this interaction also depends on the molecular polarizability.

In alkanes such as heptane, the first two kinds of interaction do not exist, because the molecule bears no permanent dipole; moreover, dispersion forces are weak due to the low polarizability of these molecules which have no double bond. Therefore, it is not surprising that at ambient pressure, heptane melts at a temperature as low as $T_{SLA} = -91^{\circ}\text{C}$ [5] (and boils at 98.4°C).

On the other hand, 4-cyanobiphenyl melts at a much higher temperature, around $T_{SLB} = 88^{\circ}\text{C}$. The height of the melting point is due to the presence of the cyano group $-\text{C}\equiv\text{N}$, which has a strong dipolar moment, and to the high polarizability of the aromatic rings. In conclusion, the 7CB molecule consists of two parts, each of them having a classical phase sequence but with very different melting temperatures.

Let us now see how mesophases are created. As shown in figure A.III.3, merely mixing the two substances is not enough. Indeed, the phase diagram of the binary mixture (A+B) is altogether classical, comprising a liquid isotropic phase and two crystalline phases of almost pure A or B (the phase diagram for the case of a diluted binary mixture will be discussed in detail in chapter B.IX).

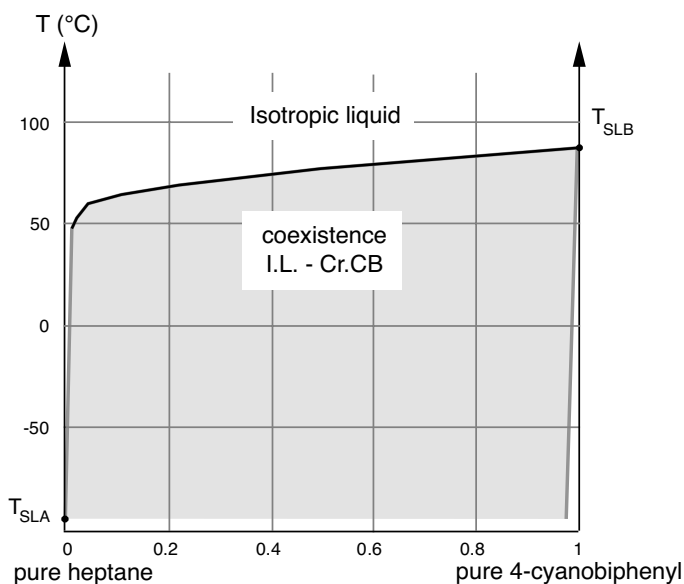


Fig. A.III.3 Phase diagram of the binary mixture heptane / 4-cyanobiphenyl. The thick line corresponds to measurements performed on mixtures of 1.9%, 4.9%, and 50% molar concentration. Thin lines are hypothetical and have been included for clarity.