

## Chapter 2

# Brief Review of Liquid Crystals

**Abstract** Examined and summarized the types of liquid crystals. Analyzed structural characteristics of smectic, nematic and cholesteric liquid crystals. It is noted that cholesteric liquid crystals are helically twisted structure, the pitch of the helix which is temperature dependent and individual chemical properties of liquid-crystalline compounds of cholesterol. Results on the influence of temperature on rheological properties of cholesteric liquid crystals are presents.

This chapter describes briefly main ideas of liquid crystals, their structure and properties. Such approach seems reasonable since it does not require searching corresponding publications.

### 2.1 Liquid-Crystal State of Matter and Kinds of Liquid Crystals

There are three phase states of the matter, namely crystalline, liquid, and gaseous. In each of them a given substance has certain characteristics typical only for this substance. For crystalline substances these characteristics are the temperature and heat of melting, for liquids—the boiling temperature and the heat of vaporization. These and other characteristics of substances in different phase states are used to identify them.

#### 2.1.1 *History of Liquid Crystal Discovery*

At the end of the 19th century Austrian scientist Fridrich Reinitzer from the Institute of Plant Physiology studied two substances extracted from carrot, namely light-colored hydrocarotin and dark-red carotin. He knew from publications that hydrocarotin was similar to cholesterol; at least they had like compositions and chemical properties. However, Reinitzer did not decide to consider hydrocarotin as

pure cholesterol without a thorough study of its chemical and physical properties. Most probably, hydrocarotin was a mixture of cholesterol compounds or one of cholesterol derivatives, as Reinitzer believed. To clarify the situation, he decided to study some pure cholesterol derivatives especially as their physical and chemical properties were studied poorly. Moreover, the chemical formula of cholesterol had not been determined certainly. Reinitzer hoped to solve this problem at the same time. If all or almost all would be known about cholesterol it would be easier to identify components extracted from hydrocarotin at least by comparison.

This work took one and a half year. Reinitzer used industrial cholesterol. He refined it thoroughly and determined its physical and chemical properties. Using element analysis methods he derived the precise chemical formula of cholesterol— $C_{27}H_{46}O$ .

This result was a great achievement in the chemistry of natural substances. Reinitzer also described in detail cholesterol derivatives. In addition to cholesterol acetate and bromeacetate, he synthesized and studied nitrocholesterol and cholesterolbenzoate. Two esters, namely cholesterolacetate and cholesterolbenzoate, were of special interest.

Both substances in the solid phase are white fine-crystalline powders. When Reinitzer determined the melting temperature by melting in glass capillaries he saw that they became colored. At that time nobody understood that strange fact of coloring of colorless compounds in melting. Reinitzer described the coloring of cholesterolacetate as follows: “When cooling melted cholesterolacetate one is surprised by very nice color appeared before cholesterolacetate thickens. This phenomenon is seen in long capillaries used to determine the melting temperature, yet it is better if the substance is melted between a table and cover glasses. In reflected light bright emerald color appears in some areas which is rapidly spread over the whole specimen bulk and then transforms to blue-green, in places to dark-blue, then to yellow-green, orange, red, and, finally, dark-red”.

Cholesterolbenzoate demonstrated slightly different behavior: two colored areas appeared in it, one of them was one-color and the other—multicolor just as in case of cholesterolacetate. It appeared at lower temperatures. No such effect was observed up that time.

Another interesting phenomenon also was not observed. Reinitzer found two melting points of cholesterolbenzoate.

Many chemists, Reinitzer's contemporaries, studied cholesterol derivatives encountered serious difficulties when determining their melting points. The researchers failed to determine the melting point of cholesterol derivatives and established the presence of an amorphous, tar-like phase. Reinitzer observed just this amorphous tar-like phase appearing in cholesterolbenzoate melting. But unlike his colleagues, Reinitzer studied it more thoroughly. He managed to find that at a temperature of  $145.5^{\circ}\text{C}$  the white fine cholesterolbenzoate powder transformed into a turbid, hardly transparent liquid. Initially he attributed turbidity to the presence of impurities but additional studies shown no impurities. As cholesterolbenzoate was heated further, the turbidity disappeared suddenly. This occurred at  $178.5^{\circ}\text{C}$ .

Reinitzer was first who found that a new turbid phase appeared between the solid phase and the usual melt in cholesterolbenzoate melting. The color of that phase depended on the temperature and vanished in transition to the usual melt but sometimes it remained in the solid phase if the latter was rapidly overcooled.

Reinitzer was not only a chemist, he was also proficient in technical microscopy. For this reason he used an opportunity to examine the colored phase with common and polarizing microscopes. He observed a very interesting phenomenon. The turbid phase appeared from the transparent melt as drops with jagged edges seen at a great magnification. This gave Reinitzer cause to call the drops star-like aggregates. In further cooling of the substance the star-like aggregates expanded and a multiphase system formed. Brooklets of a liquid flew over a brightly colored background and played. Reinitzer called them “oily grooves”.

The oily grooves became transparent if the polarizers were crossed, i.e. they shown marked double refraction. The colored background rotated the light polarization plane. In other words, it possessed optical activity. The rotation angle of the polarization plane was very high and depended on the light wavelength.

All these facts arrived Reinitzer to a conclusion that in case of cholesterolacetate and cholesterolbenzoate he dealt with a rare variety of physical isomerism when several substances of the same chemical composition had different structures and physical properties.

Reinitzer attempted to separate these two isomers but he failed. Then he decided to send the substances to Professor Otto Leman being a famous researcher in physical methods of crystal study. He was a skilful experimenter got excellent training in experimental physics and crystallography at the Strasbourg University and examined the growth and solution of crystals with a polarizing microscope.

The samples were sent on March 14, 1888. At that time Leman studied unusual mechanical properties of silver iodide. At temperatures above 146 °C this cubic crystal did not cleave and crumble to small pieces in compression. It changed its shape easily like melted sealing-wax or rosin. It could be rolled into a thin sheet by the slight touch of a common needle.

Such behavior of silver iodide crystals was beyond concepts of those days. The ductility of metals was explained by their polycrystalline structure but in that case a monocrystal was considered whose lattice could not deform so greatly, as it was believed.

Attempting to answer the questions arisen Leman received the samples from Reinitzer. The study of properties of the substances sharpened still more the issues of a high ductility of the compounds showing the crystal-like behavior. The thorough investigation of cholesterolbenzoate properties with exchange of opinions concerning different aspects of the problem with Reinitzer and other specialists and the discovery of some nitrooxyphenol esters by Hatterman with properties similar to those of cholesterolbenzoate gave rise to new ideas on the behavior of crystals. Their essence was expressed in the Leman’s letter to Reinitzer: “Physicists always show great interest to the fact that there are crystals whose ductility allows one to call them liquid crystals”. However, Leman avoided using this term in his papers. He gingerly called cholesterol compounds fluid crystals and nitrooxide compounds—drop-liquid

crystals. The latter definition resulted from the fact that these compounds had a less viscosity and were shaped as spherical drops in mixtures with fluids.

Analyzing the situation with silver iodide, cholesterolbenzoate, and nitrooxide compounds Leman supposed that if such ductile crystals as silver iodide existed which hardly retained their weight why crystals totally incapable of retaining their shape should not exist? They will run into a fluid while their physical properties should be anisotropic like those of other crystals and they should grow from oversaturated solutions. Cholesterolbenzoate was undoubtedly one of such liquid crystals.

That reasoning of Leman resulted in the discovery of liquid crystals. Solid crystals having a right spatial arrangement and totally disordered isotropic liquids were bridged by viscous-fluid and absolutely liquid drop-fluid crystals. Leman believed that the solid crystals retained well their weight that caused their polyhedral shapes. Liquid crystals of silver iodide, cholesterolacetate, and cholesterolbenzoate hardly retained their weight and for this reason sometimes they had a polyhedral shape while smoothed and deformed. Finally, drop-fluid crystals of nitrooxide compounds were absolutely incapable of retaining their weight and their equilibrium shape was a spherical drop.

This Leman's understanding formed finally in 1890.

Leman really considered both liquid and drop-fluid crystals as crystals while realizing clearly that these substances differed from solid crystals in their structure. Anisotropy and homogeneity are the main attributes of real crystals. Anisotropy is the dependence of crystal properties on the direction. It results in optical anisotropy appearing as double refraction. Homogeneity implies equal properties along parallel directions. It causes a geometrically right, periodical arrangement of particles making up the crystal, i.e. the existence of a lattice.

Liquid crystals are anisotropic but their fluidity is incompatible with the existence of the lattice. For this reason Leman supposed that those phenomena (anisotropy and fluidity) could be explained satisfactory if the right spatial arrangement of molecules was considered as a minor factor, as a mode of stacking implemented only in slow crystallization. This stacking mode can be disordered by an enough high deforming force but this does not affect the nature of crystal. According to Leman, the essence of crystal is the anisotropy resulted from the anisotropy of molecules themselves. Leman wrote: "The proper anisotropy of molecules which produces indirectly the right structure of a body is an essential and main attribute of crystal rather than the right arrangement of the molecules in the right system of points".

Another equally important feature of crystal is its ability to grow in oversaturated solutions. As Leman noted, both non-deformed and deformed (without a lattice) crystals grow with the same rates while amorphous bodies do not grow.

Afterwards this view of Leman arrived him to some erroneous conclusions which luckily did not influence scientific progress but hampered the recognition of liquid crystals.

Reinitzer's and Leman's results introduced new, revolutionary ideas in science which encountered a suspicious reaction of most physicists and chemists rather than

made a sensation in the scientific community. The discovery of liquid crystals followed by a long period of their study and recognition.

This is a brief history of the discovery of liquid crystals. The development of liquid crystal research is described in more detail in book [1] specially devoted to this problem.

It took more than two decades to recognize the existence of the liquid-crystal state of the matter. This is not surprising since, according to the understanding of many physicists and chemists of the beginning of the 20th century, the phrase “liquid crystals” was nonsensical. This is Leman’s blame. It was he who proposed the expression “liquid crystal” unfortunate at that time.

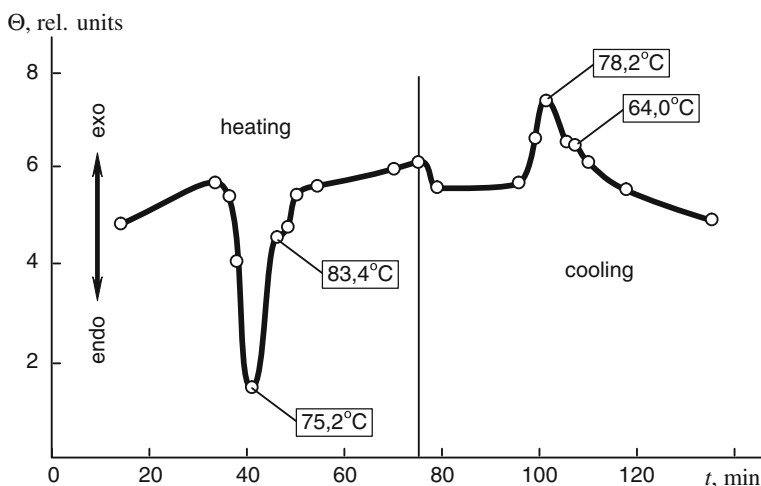
Afterwards French physicist Fridel corrected Leman’s mistake and proposed the term “mesomorphous state” as a synonym of the term “liquid-crystal state” formed from the Greek word “mezos” meaning intermediate. Indeed, the liquid-crystal state is the fourth phase state of the matter and takes an intermediate position between the crystalline and liquid states.

### 2.1.2 *Classes of Liquid Crystals*

At present *thermotropic* and *liotropic* liquid crystals are distinguished. The class of *thermotropic* liquid crystals is formed by the substances which transit to the liquid-crystal state with elevating temperature. In this case the following *phase transitions* are considered: solid–liquid crystal–*isotropic liquid*. They are phase transitions of the first kind and can be successfully registered by the differential thermometry method (Fig. 2.1). When the isotropic liquid is cooled down the phase transitions are repeated in the reverse sequence.

The temperature of the transition solid–liquid crystal is called the *melting temperature*  $T_m$ . The temperature of the transition liquid crystal–isotropic liquid is called the *elucidation temperature*  $T_e$ . The term results from the fact that many crystals in the mesophase are turbid liquids scattering light considerably. The scattering disappears and the melt becomes transparent in transition to the isotropic liquid.

Liotropic liquid crystals are the substances which form the liquid-crystal phase when dissolving them in water or other solvents. As a rule, the phase appears within a strictly certain range of the concentration of the substance being dissolved in the solvent. Potassium *n*-alconate soap is a typical example of liotropic liquid crystals. Nowadays liotropic liquid crystals are very attractive for researchers. This is due to the fact that liotropic liquid-crystal phases are typical for more materials than thermotropic ones and to a great role of liotropic liquid crystals in biology. Note that myosin being an albumen contained in the contracting substance of the muscular tissue, desoxyribose nucleic acid playing a leading role in the transfer of heritable data, many polypeptides, ferments and other substances of biological origin are capable of forming the liotropic liquid-crystal phase [2, 3]. It is also found that liquid crystals are of great importance in metabolic processes in living organisms.



**Fig. 2.1** Phase transition temperatures of cholesterolpelargonate

Like solid crystals, liquid crystals show the *anisotropy of properties* which is always closely related to the *anisotropy of the matter structure* [4]. Apparently, proceeding from this fact German chemist Vorländer supposed that liquid crystals were formed mainly from the organic compounds whose molecules had an elongated cigar-like shape, i.e. shown the anisotropy of the structure. His predictions had come true. It should be noted that earlier Leman assumed the structure of molecules of liquid-crystal substances to be anisotropic.

It is found that the substances with flat *disc-shaped molecules* also form the liquid-crystal phase. Such substances are called *discotic liquid crystals* or *discotics*.

Elongated cigar-shaped molecules of the liquid crystal are always in thermal motion. The direction of their major axes continuously changes relatively to a certain direction. To mark the direction of predominant orientation the unit vector  $n$  is used which is called “*director*”. The director characterizes phenomenologically the long-range order of molecules.

Because of the thermodynamic least free energy principle the elongated or disc-shaped structure of liquid crystal molecules a certain arrangement of the molecules appears in the mesophase. The pattern of the arrangement is governed by both the structure of the liquid crystal molecules and thermodynamic conditions.

## 2.2 Classification and Structure of Liquid Crystals

The classification of liquid crystals was proposed by French physicist Frédel in the beginning of the 19th century and is based on molecular arrangement. Like Reinitzer and Leman, he examined microscopically thin layers of liquid crystals formed on a table glass in melting. He found that irrespective of the chemical structure of the

compounds liquid crystals formed a limited number of kinds of optical pictures. Fridel related the kind of the optical picture observed with the arrangement of molecules in the samples and proposed the classification of liquid crystals on this basis.

He divided liquid crystals into *smectic* (from the Greek word “smegma” meaning soap) and *nematic* (from the Greek word “nema” meaning thread) crystals. Nematic liquid crystals are divided into properly nematic and *cholesteric* crystals. Two following facts resulted in such division. The first fact was that no mesogens were found passing consecutively the nematic and cholesteric mesophases. The second fact was that it was possible to transform a properly nematic liquid crystal into a cholesteric one and vice versa by external effects such as mechanical deformation, electric and magnetic fields.

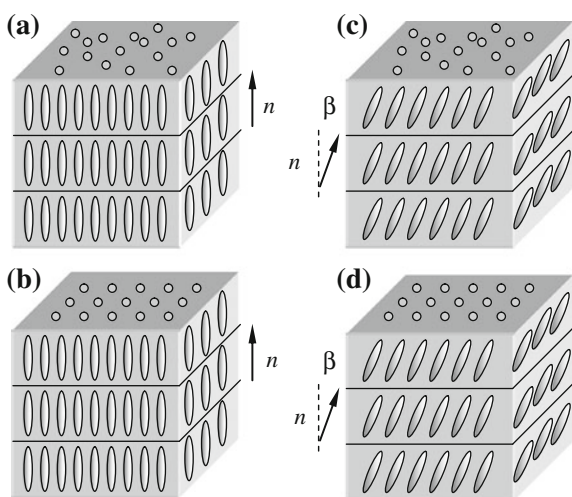
In smectic liquid crystals molecules are arranged so that their major axes are parallel and their centers of mass lie in one plane. Major axes of the smectic molecules or the director  $n$  form an angle  $\beta$  with the normal to this plane (Fig. 2.2).

The location of the centers of mass of the molecules results in the formation of *smectic layers*. It is apparently that the thickness of the layers depends on the molecule length and the angle between the director  $n$  and the location plane of the centers of mass.

By the pattern of arrangement in the layers smectic liquid crystals are divided into two groups: with *structured* and *non-structured* layers. In smectic crystals with structured layers the centers of mass of the molecules form a two-dimensional lattice in the layer. The director can be oriented relatively to the layer both normally (Fig. 2.2a, b) and at an angle (Fig. 2.2c, d). Smectic crystals with structured layers are ordered better than crystals with non-structured layers. In smectic crystals of both groups the mutual slip of layers can occur and in most cases the rotation of molecules about their major axes is possible.

In non-structured layers molecules of the smectic crystal are distributed chaotically (Fig. 2.2a, c). This group consists of several subgroups of smectic crystals which differ in the angle of director orientation relatively to the normal to the layer.

**Fig. 2.2** Structure diagram of smectic liquid crystals with non-structured (a) and structured (b) layers



Smectic crystals for which  $\beta = 0$  (Fig. 2.2a) belong to the first subgroup. Therefore, in these crystals major axes of the molecules are perpendicular to smectic layers. Such crystals are commonly called *smectics A*. They are most widespread among smectic crystals.

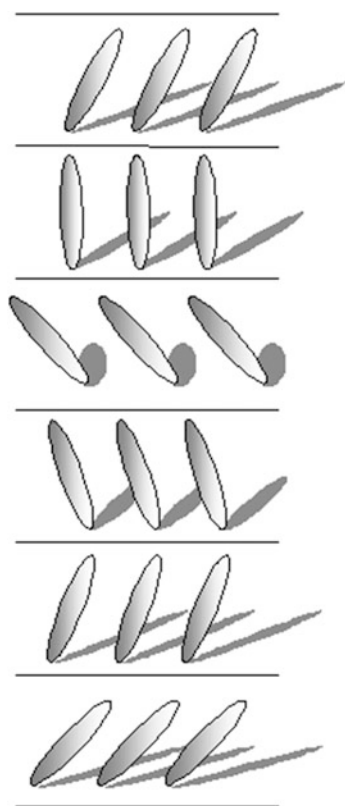
The second subgroup consists of non-structured smectic crystals for which  $\beta \neq 0$ . They are called *smectics C* (Fig. 2.2c). Among them are smectics *C* with a small ( $\beta < 30^\circ$ ) and great ( $\beta \approx 45^\circ$ ) angle between the director and the normal to the layer. With elevating temperature smectics *C* with the small slope angle transform into smectics *A*. However, the smectics *C* are known for which the angle  $\beta$  depends on the temperature within a certain temperature range and can decrease down to zero while other smectics with the small slope angle show no temperature dependence of the slope angle  $\beta$ .

Smectics *C* with the great angle  $\beta$  do not transform into smectics *A* and their angle  $\beta$  is independent of the temperature.

If molecules of the smectic substance are chiral, i.e. twisted about their major axes, the twisted *smectic mesophase*  $C^*$  is formed (Fig. 2.3).

In such smectics the director rotates along the taper generatrix when passing from one layer to another.

**Fig. 2.3** Smectic  $C^*$  mesophase





In *smectics B* centers of mass of molecules in layers are located at points of the hexagonal lattice and the director is perpendicular to layers (Fig. 2.4).

A similar location of centers of mass is typical for *smectics H* but the director  $n$  is inclined to layers (Fig. 2.5).

If the smectic *H* forms a compound with chiral molecules the quasi-hexagonal arrangement remains but when passing from layer to layer the director rotates along the taper generatrix as in case of the smectic  $C^*$ . This smectic is called *smectic H*<sup>\*</sup>.

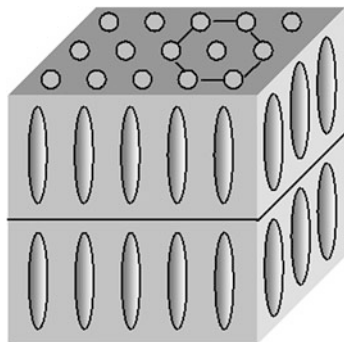
The quasi-hexagonal arrangement of centers of mass of molecules in layers is also typical for *smectics E* but unlike other smectics with structured layers the rotation of the molecules about their major axes is hampered. As the director is perpendicular to the layers, rhombic arrangement occurs (Fig. 2.6).

In *smectics G* the arrangement of centers of mass of molecules and the hampering of rotation about major axes are the same as in smectics *E* but the director is inclined to the layer plane (Fig. 2.7).

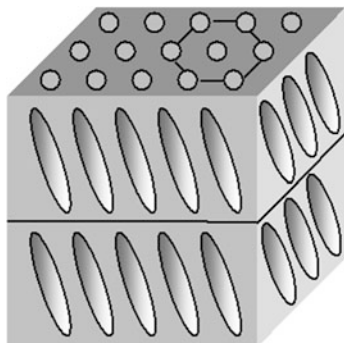
*Smectics D* have the cubic body-centered structure (Fig. 2.8).

It consists of structure units containing many molecules; they are called micelles (from the Greek word *mica* meaning grain). In nematic liquid crystals molecules are parallel to each other and their centers of mass are arranged chaotically unlike smectic crystals (Fig. 2.9).

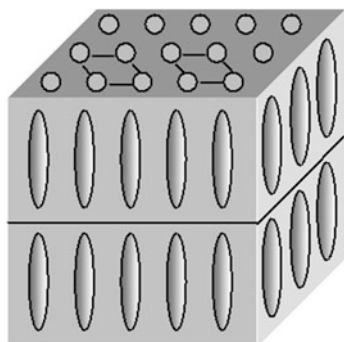
**Fig. 2.4** Smectic *B* mesophase



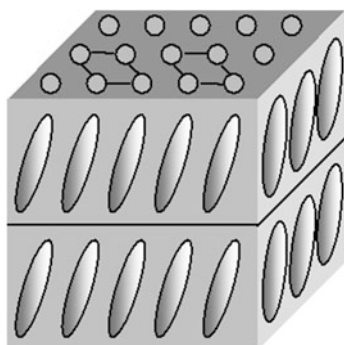
**Fig. 2.5** Smectic *H* mesophase



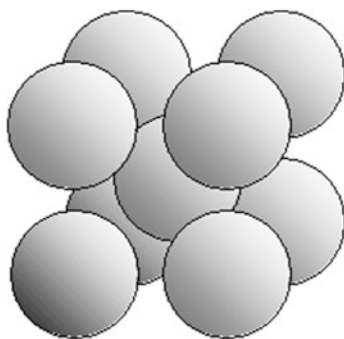
**Fig. 2.6** Smectic  
*E* mesophase



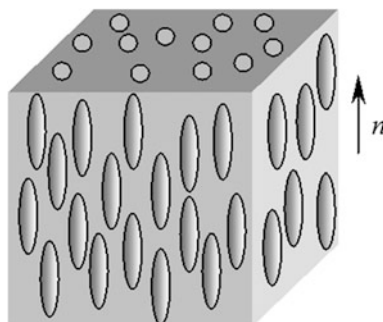
**Fig. 2.7** Smectic  
*G* mesophase



**Fig. 2.8** Smectic  
*D* mesophase



**Fig. 2.9** Structure diagram of  
nematic liquid crystal



In this case layers typical for smectics are not formed and long-range order exists only in respect to the orientation of major axes of the nematic crystal.

Cholesteric liquid crystals are formed by cholesterol derivatives (esters), yet they may contain substances of other classes.

Cholesteric liquid crystals typically consist of molecular layers; each of them demonstrates the molecular arrangement specific for nematics when centers of mass lie in the molecular plane chaotically. The director also lies in the layer plane [5]. The thickness of the molecular layer called also a quasi-nematic layer [6] is 0.5–0.6 nm. In transition from one molecular layer to another the director rotates by a small angle relatively to the director of the underlying layer. This angular shift accumulates in the sequence of the layers and, generally, ends of the molecules or the director end move along a spiral (Fig. 2.10). Apparently, the lead  $P$  of the spiral is

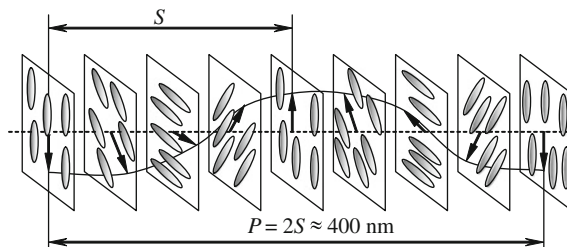
$$P = \frac{2\pi}{\alpha} d \quad (2.1)$$

where  $\alpha$  is the shift (twist) angle of the director in transition from layer to layer;  $d$  is the thickness of the molecular layer of the cholesteric crystal.

According to the results reported in [7], the angular shift of the director in transition from layer to layer in cholesteric crystals is 15 angular minutes on the average. Other authors give the value of about  $0.5^\circ$  [8]. Further thorough studies have shown that the twist angle  $\alpha$  depends on both the temperature and the molecular structure of the cholesteric liquid crystal as well as some other factors [9–11].

Taking  $\alpha = 0.5^\circ$  and  $d = 0.6$  nm we obtain that the lead of the cholesteric spiral is 400 nm.

It is apparently that in the molecular layers corresponding to the director twist angles of  $0^\circ$ ,  $\pi$ , and  $2\pi$  the major axes of liquid crystal molecules have the same orientation (Fig. 2.10) that makes the layers indistinguishable. Then the distance  $S = P/2$  is the period of the specific lattice of the cholesteric liquid crystal. It is easy to note that in cholesteric crystals the molecular orientation is repeated at a distance equal to the period  $S$ . However, the molecules can move freely and exchange their positions in each molecular layer but their spiral arrangement with the period  $S$  remains unchanged.



**Fig. 2.10** Structure diagram of cholesteric liquid crystal

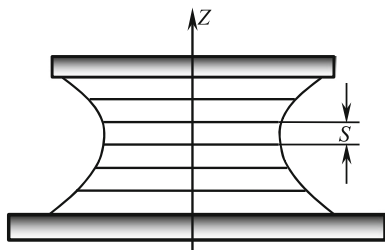
*Macrolayers* consisting of many molecular or *quasi-nematic* layers in which the spiral arrangement is retained along the certain direction at a distance of one or more lattice periods are called monocrystal layers of cholesteric liquid crystals (Fig. 2.11). Such layers can be formed between bearing surfaces.

We presented in general outline the classification of liquid crystals. Apparently, it is far from the total scientific classification whose main attribute is predictability. The presented classification does not possess predictability and is mainly of the descriptive character. Therefore, often it may occur that newly synthesized liquid crystals show mesophases which can not be classified according to this scheme. Such mesophases are called exotic. Future studies will allow researchers to refer many of them to the already known kinds and groups. Yet, the possibility of appearing new arrangement modes among exotic mesophases can not be ruled out.

This substance forms the *discotic mesophase* within the temperature range 81.2–87 °C. One of these new arrangement modes has been found recently. It appears in the so-called disc-shape crystals or *discotics* (Fig. 2.12). Their molecules have the symmetric branched formula which can be approximated by a flat disc. For example, benzol-hexa-*n*-heptanoate contains such molecules.

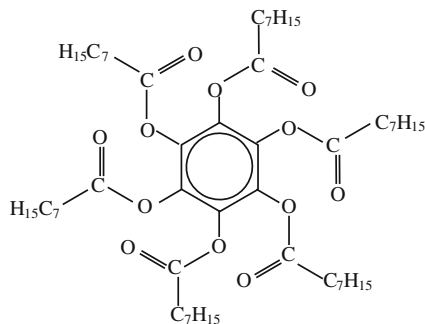
Discotics demonstrate the layered molecular arrangement like smectic crystals [3, 12]. Their molecules lie in the layer planes forming close hexagonal packing shown in Fig. 2.13.

The classification presented above shows that though some liquid crystals have the solely mesophase typical only for the given crystal in many liquid crystals



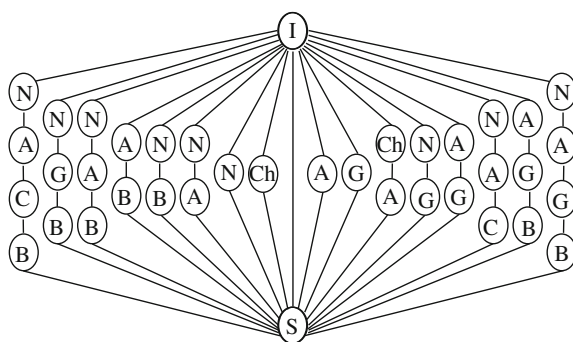
**Fig. 2.11** Monocrystal layers of cholesteric liquid crystal between bearing surfaces

**Fig. 2.12** The molecule of disc-shape crystals





**Fig. 2.13** Discotic mesophase



**Fig. 2.14** Some cases of polymesomorphism of liquid crystals: *I* isotropic fluid, *S* solid crystal, *N* nematic, *A*, *B*, *C*, and *G* corresponding smectics, *Ch* cholesteric

different phase transformations occur with varying temperature and several mesophases change consecutively. As experiments have shown, there are certain regularities of changing mesophases. Figure 2.14 illustrates some cases of the *polymesomorphism* of liquid crystals known presently.

It is seen in the figure that in transition from the solid crystal to isotropic liquid through different mesophases a sequence of the mesophases occurs with decreasing ordering degree: the smectic, cholesteric, and nematic mesophases.

The same regularity is typical for the smectic mesophase. If the solid crystal melts initially the smectic crystals appear with structured layers and only at higher temperatures the smectics with non-structured layers are formed.

The smectic *C* always exists at lower temperatures than the smectic *A*. As for polymesomorphism with the mesophase *G*, Fig. 2.14 shows that it behaves like the mesophase *C* and often precedes the mesophase *B* with decreasing temperature.

## 2.3 Properties of Liquid Crystals

### 2.3.1 Optical and Electrical Properties of Liquid Crystals

An original molecular architecture of monocrystalline layers of cholesteric crystals causes some specific optical properties. First of all, this is *optical activity*, i.e. the ability of the crystals to rotate the polarization plane of linearly polarized light passing the crystal layer. Alpha-quartz crystals considered quite optically active rotate the polarization plane of light by approximately  $20^\circ$  per one millimeter of the crystal thickness while the cholesteric monocrystalline layer of the same thickness rotates the polarization plane by an angle of about  $18,000^\circ$  [7]. Such gross optical activity is typical only for cholesteric liquid crystals. Nematic and smectic crystals do not possess optical activity.

However, one can give the structure of the cholesteric to the nematic by twisting it between the bearing surfaces. Additives of cholesteric liquid crystals to nematics result in the formation of the cholesteric structure.

*Circular dichroism* is another typically crystal property of cholesteric liquid crystals. It causes the division of natural white light into two components by the cholesteric crystal. The electric vector of one of the components rotates clockwise and that of the other component rotates counter-clockwise. Depending of the structure of liquid crystal molecules one of the components passes the crystal while another component reflects from it causing the certain *color of the cholesteric substance*. This phenomenon is called the selective reflection of light and results from changes in the spiral lead of cholesterics with varying temperature. It should be noted that the selective reflection of light governs the action of liquid-crystal thermoindicating films applied in medicine, engineering and life, for example, in liquid-crystal room thermometers [13, 14]. The systematic description of optical properties of cholesteric liquid crystals is presented in monograph [15].

Like cholesteric liquid crystals, nematic and smectic crystals possess double refraction. However, it occurs at a certain orientation of the director relatively to the light propagation direction.

*Double refraction* proves the anisotropy of the refractive index that is caused by the anisotropy of the permittivity of liquid crystals. There are refractive indices of the light polarized along ( $n_{\parallel}$ ) and perpendicularly to ( $n_{\perp}$ ) the director. Similarly, there are permittivities for the orientation of the director along ( $\varepsilon_{\parallel}$ ) and perpendicularly to ( $\varepsilon_{\perp}$ ) the electric field direction. The difference  $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$  is called the *dielectric anisotropy of the liquid crystal*. It can be both positive and negative. The dielectric anisotropy results from the anisotropy of liquid crystal molecules, their structure, and the nature of atoms contained in the molecules.

Liquid crystals also possess the anisotropy of magnetic properties. The difference of the diamagnetic susceptibilities measured along major axes ( $\chi_{\parallel}$ ) of liquid crystal molecules and perpendicularly to the axes ( $\chi_{\perp}$ ) is called the *anisotropy of the diamagnetic susceptibility* ( $\Delta\chi$ ). It can be both positive and negative. For nematic

and smectic crystals  $\Delta\chi > 0$  and for pure cholesterol ethers  $\Delta\chi < 0$ . However, for some cholesterics  $\Delta\chi > 0$  [16].

The anisotropy of electrical and magnetic properties of liquid crystals provides the possibility of the orientation of their molecules under the effect of electric and magnetic fields. The direction of major axes of liquid crystal molecules in electric and magnetic fields is governed by the sign of the dielectric and diamagnetic anisotropies, respectively. If the anisotropy is positive the major axes of molecules are parallel to the field direction and if it is negative the orientation is perpendicular.

Frideriks and his colleagues observed first the effect of changes in the nematic orientation in electric field. For this reason this effect is generally called the Frideriks transition. These experiments have shown that there is a limiting thickness of the layer between the bearing surfaces, for example between flat and convex glasses, at which the re-orientation of molecules occurs under a given magnetic field strength [17]. The threshold character of the Frideriks transition is caused by a quite strong adhesion between liquid crystal molecules and the bearing surfaces. It occurs only when the magnetic field strength is enough high to overcome the adhesion of the nematic crystal to the bearing surfaces.

The orientation effect of electric field is complicated by the electric conductivity of liquid crystals. The electric conductivity is anisotropic and can cause substance motion and the redistribution of electric fields. All this induces a number of new effects such as magnetoelectricity, electrohydrodynamic instability etc. whose nature is described in papers [8, 14, 18–21].

### 2.3.2 *Peculiarities of Formation of Liquid-Crystal Layers on Solid Surfaces*

In liquid crystals the director can rotate not only in electric and magnetic fields but also under the effect of the bearing surfaces. They are, for example, the walls of a flat capillary formed by glasses.

The bearing surfaces can orient the director parallel, normally, or at an angle to them. In the first case when major axes of molecules are parallel to the surface the orientation is called *planar* or plane. Their optical properties are similar to those of a plate of the optically positive monocrystal cut parallel to the crystal optical axis. The optical axis is the direction in the monocrystal along which light propagates without double refraction. In the second case when the major axes of molecules are perpendicular to the bearing surfaces the orientation is *homeotropic*. In its optical properties such structure is similar to a plate of the optically positive monocrystal cut perpendicularly to the optical axis.

The orientation mode on the bearing surface is governed by its nature, preparation technique, and the liquid crystal nature. Under given conditions the orientation is implemented at which the free energy of liquid crystal molecules on the bearing surface is minimal. It is apparently that the orientation effects are possible

only when liquid crystal molecules are attracted to the solid surface by certain intermolecular forces. These forces, hence the energy of interaction, are governed by a number of factors. The surface preparation technique is believed the main factor [16].

The energy of interaction between the liquid crystal and bearing surface can be: (a) comparable with the energy of intermolecular interaction in the liquid crystal; (b) much less than the intermolecular interaction energy in the crystal.

In the first case the *strong adhesion* of liquid crystal molecules to the bearing surface occurs; in the second case the adhesion is *weak*. It is difficult to predict which of the cases appears in the experiment. In practice empirical rules are used. It is found that the strong adhesion is easier to implement than the weak one.

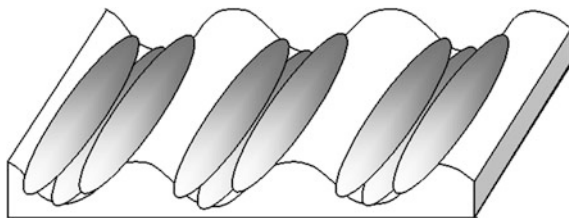
A number of methods of providing a certain orientation of liquid crystal molecules on the bearing surface have been developed. They are divided into *mechanical* and *chemical* methods. The mechanical methods involve the producing of the *orienting microrelief* on the bearing surface. This is achieved by surface machining with polishing pastes in the certain direction. The appeared microgrooves orient molecules of nematic and cholesteric crystals parallel to the surface (Fig. 2.15).

Liquid crystals are also oriented on the surfaces rubbed with soft materials like wool, paper, and leather.

The required microrelief can be also produced by *depositing* thin, about 20 nm thick, metal or oxide films onto the bearing surfaces at a certain angle. If the flow of the substance under deposition is perpendicular to the surface liquid crystal molecules are oriented mainly parallel to it. If the substance is deposited at blunt angles (more than  $80^\circ$ ) the molecule orientation is "oblique". In this case the director  $\mathbf{n}$  is inclined to the bearing surface at an angle of  $20^\circ$ .

As a rule, the mechanical methods provide a strong adhesion of liquid crystal molecules to the bearing surface. The orientation of the molecules along microrelief grooves is more profitable from the energy viewpoint that the transverse orientation.

According the results reported in [16, 22], for the sinusoidal profile with the wavelength of 20 nm and the amplitude of 1 nm the energy gain at the parallel orientation in comparison with the perpendicular one is  $8 \cdot 10^{-5} \text{ J/m}^2$ . This provides so strong adhesion that to rotate liquid crystal molecules normally to microrelief grooves it is necessary to apply electric field with the strength of  $6 \cdot 10^8 \text{ V/m}$  or magnetic field with the strength of  $6 \cdot 10^8 \text{ A/m}$ .



**Fig. 2.15** Orientation of liquid crystal molecules along microrelief grooves



As a rule, major axes of smectic liquid crystals are oriented normally to the bearing surface. In its close vicinity a smectic film copies the surface microrelief. As the distance from the bearing surface increases, the distortion of smectic films decreases and, finally, disappears at all. The thickness of the distorted smectic film on finely polished surfaces reaches 1 mm and more [14].

The *chemical methods of orientation* are based on the use of chemical compounds which are deposited onto the bearing surface or introduced directly into the liquid crystal and produce a certain surface structure because of physisorption and chemisorption on the bearing surfaces. These substances are called orientants. As a rule, their molecules contain active end groups and a hydrocarbon radical. The end groups interact with the surface and the hydrocarbon radicals are oriented either normally or parallel to the substrate depending on their length. Liquid crystal molecules are placed between the hydrocarbon radicals and oriented parallel to them. Thus, the corresponding orientation of liquid crystal molecules appears.

It should be noted that the great number of orientants providing a strong adhesion in most cases includes surfactants. The surfactants initiate the homeotropic orientation of nematic and cholesteric liquid crystals [22].







The analysis of the described orientation methods has shown that, as a rule, their application varies the energy state of the surface. Interactions on the solid–liquid interface are described phenomenologically by the surface tension. The use of this approach for the liquid crystal–solid system yielded the empirical rule according to which the homeotropic orientation occurs in the cases when the critical surface tension ( $\sigma_c$ ) of the solid is less than the surface tension of the liquid crystal ( $\sigma_{lc}$ ). If  $\sigma_c > \sigma_{lc}$  the planar orientation of liquid crystal molecules appears [22, 23]. The author of [22] proposed to call it the rule of Fridel-Kreig-Kmetz (FKK rule). Though the rule was verified by a great number of experiments it is not true in some cases.



The studies have shown that when using FKK rule one should consider the sign of the dielectric anisotropy, the nature of forces (polar or dispersion) causing the surface tension, and the pattern of the solid surface microrelief. Paper [22] summarizes the study results which are presented in Table 2.1.

Here we should mention the ability of liquid crystals to orient molecules of dissolved substances parallel to their major axes. This effect is called the “*guest-host*” effect. Dichroic dyes which absorb light depending on the molecule orientation and light polarization make the “*guest-host*” effect visible. If a small amount of the dye (the guest) is added to the nematic crystal (the host) dye molecules are oriented by nematic molecules parallel to their major axes. The nematic arrangement is retained in this case.

If the nematic crystal with the dye additive is placed into a flat capillary the liquid crystal has certain color at the planar orientation. In electric field normal to the capillary walls the nematic changes its color. This proves that the Frideriks transition resulted in the re-orientation of both nematic and dye molecules. The behavior of the “guest” is governed by the behavior of the “host”.

**Table 2.1** Orientation possible in substrate—liquid crystal interaction substrate

Подложка		Подложка — жидкий кристалл			
Material	Microrelief pattern	$\sigma_K > \sigma_{JK}$		$\sigma_K < \sigma_{JK}$	
		$\Delta\varepsilon > 0^a$	$\Delta\varepsilon < 0$	$\Delta\varepsilon > 0$	$\Delta\varepsilon < 0$
Activated oxides and diacids (polar surface)	Smooth surface	$\perp^2$	$x^b$	Нет случаев	
	Symmetrical grooves	$\perp$	$\parallel$	Есть $\sigma_K > \sigma_{JK}$	
	Non-symmetrical grooves	 <sup>a</sup>	 <sup>a</sup>		
	3D valleys <sup>d</sup>	$\parallel$	$\perp$		
Wet oxides, polymers, and fatty acid derivatives	Smooth surface	$x$	$x$	$\perp^5$	$\perp^5$
	Symmetrical grooves	$\parallel$	$\parallel$	$\perp$	$\perp$
	Non-symmetrical grooves				
	3D valleys <sup>d</sup>	$\perp^e$	$\perp^e$	$\parallel$	$\parallel$

<sup>a</sup> $\Delta\varepsilon$  characterizes the polarity of liquid crystal<sup>b</sup>this case is poorly confirmed by experiments<sup>c</sup> $\perp$ ,  $\parallel$ , ,  homeotropic, planar, and inclined orientations<sup>d</sup>regular set of 3D alternating peaks and valleys<sup>e</sup>homeotropic orientation resulted from 3D relief independent of liquid crystal nature and appearing due to zero interactions

### 2.3.3 Rheological Properties of Liquid Crystals

The anisometric structure of molecules of liquid crystals influences their rheological behavior.

The viscosity of liquid crystals, like that of common fluids, decreases with temperature elevation. However, nematics and some cholesterics demonstrate a substantial viscosity variation at temperatures of the transition liquid crystal phase —isotropic fluid. In most cases the viscosity rises. The viscosity increment of nematics is insignificant [24–26].

Cholesteric liquid crystals are characterized by an almost jump-like viscosity rise by several orders of magnitude. According to the results of [16], the viscosity of cholesterolacetate increases by approximately six orders of magnitude at the elucidation point. However, the measurements of the viscosity of cholesterolformate with varying temperature carried out in a rotation viscometer did not show so great viscosity rise at the elucidation point (Fig. 2.16). This can result from errors of the measuring techniques or the discrete mode of temperature variation in the experiments.

There are liquid crystals whose viscosity decreases under similar conditions [1]. The described viscosity variations occur at low shear rates. The rheological nature of liquid crystals changes depending on the shear rate. According to the results of [24], at shear rates less than  $10^{-3} \text{ c}^{-1}$  the cholesteric liquid crystal shows the non-Newtonian flow mode. Within the range from 10 to  $10^3 \text{ c}^{-1}$  the hydrodynamic flow orients liquid crystal molecules and the viscosity does not depend on the shear rate similarly Newtonian fluids. The isotropic fluid of cholesteric liquid crystals behaves in the same manner as the Newtonian fluid.

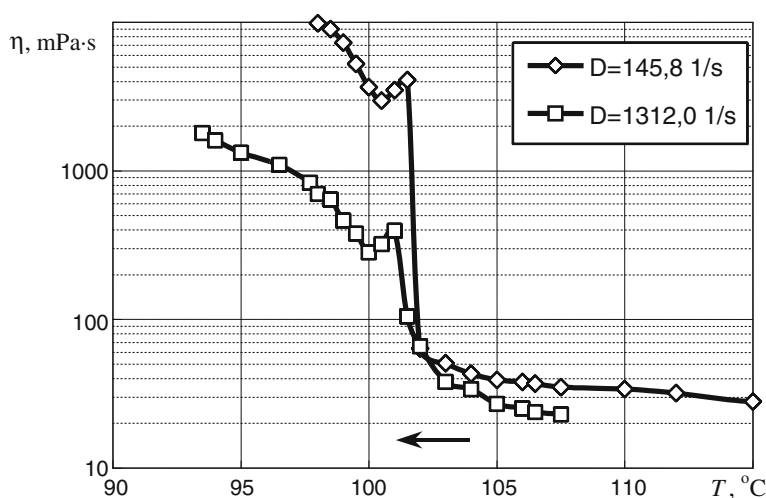


Fig. 2.16 Temperature dependence of viscosity of cholesterolforniate

In the liquid crystal phase the viscosity of liquid crystals depends on the orientation of the director relatively to the flow. Tsvetkov [24] and other researchers have shown that the orientation of nematics by magnetic field perpendicular to the axis of the capillary in which the liquid crystal flows increases the effusion time, i.e. the viscosity. If the magnetic field direction coincides with the capillary axis direction the time of liquid crystal effusion decreases. This proves that liquid crystals possess *the viscosity anisotropy*. The viscosity is less if molecules are oriented along the flow. The viscosity anisotropy of liquid crystals appears only at a slow flow velocity. Otherwise the orientation effect of magnetic or electric field is too weak since the orientation in the liquid crystal flow becomes dominating.

According to the results reported in [16, 27], the direction of major axes of nematic molecules appearing in the flow does not coincide with the flow direction. As I.Ya. Frenkel shown [27], the major axes of anisometric molecules are oriented at an angle of  $45^\circ$  to the flow direction. This angle can be less than  $45^\circ$  at high shear rates and it decreases with increasing shear rate. However, according to the calculation results from [16], the orientation angle does not depend on the shear rate but is governed by the ratio of anisotropic viscosities. Experimental verification confirmed the theoretical predictions.

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