Liquid crystals (LC) (**Жидкие кристаллы**)

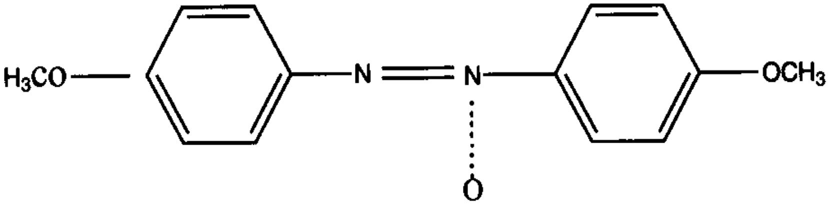
The liquid state has short-range order but no long-range order: it has the highest possible symmetry. The crystalline solid has long-range positional and rotational order; it has a much lower symmetry than the liquid and can have the lowest possible symmetry consistent with a regular filling of space. There are systems with intermediate symmetries that exhibit short-range correlations in some directions and long-range order in others.

One form of this intermediate order is orientational order.
In a periodic crystal, there is only a discrete set of directions defined by vectors between nearest neighbor particles, which occupy sites on a lattice. These directions are the same throughout the lattice and define a long-range orientational order often called bond-angle order. Remarkably, it is possible to have long-range orientational order in the absence of translational order. Among the materials that show intermediate order, the most widely studied are liquid crystals.

Some molecules forming liquid crystal (LC) phases **and their phase sequences as a function of temperature.**

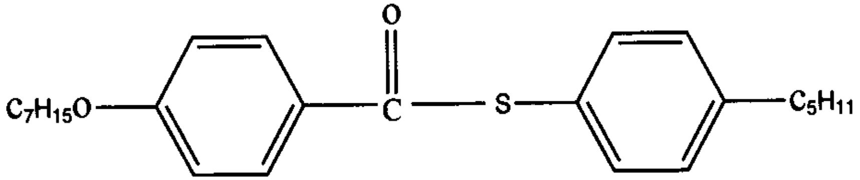
(the benzene (benzol) rings give rigidity to the molecules).

4,4' - dimethyloxyazoxybenzene (p-azoxyanisole)



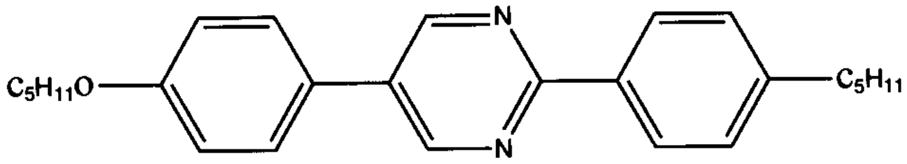
$$\text{solid} \underset{29.57\text{kJ}}{\overset{118.2\text{C}}{\rightleftarrows}} N \underset{0.57\text{kJ}}{\overset{135.3\text{C}}{\rightleftarrows}} I$$

4-*n*-pentylbenzenethio-4'-*n*-heptyloxybenzoate ($\bar{7}$S5)

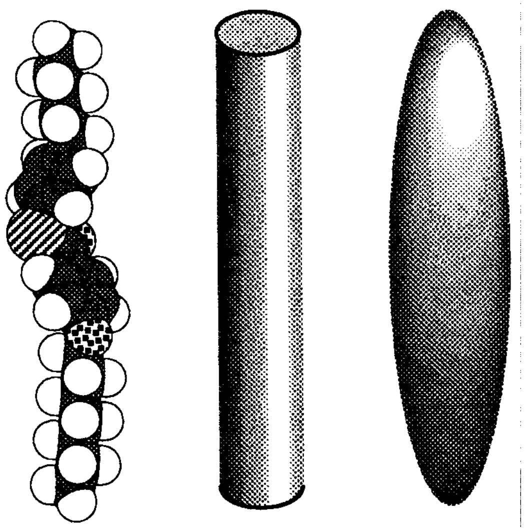


$$\text{Sm-}C \overset{37\text{C}}{\rightleftarrows} N \overset{81\text{C}}{\rightleftarrows} I$$

2-(4-*n*-pentylphenyl)-5-(4-*n*-pentyloxyphenyl)-pyrimidine



$$\text{solid} \underset{34.98\text{kJ}}{\overset{79\text{C}}{\rightleftarrows}} \text{Sm-}G \underset{0.58\text{kJ}}{\overset{102.7\text{C}}{\rightleftarrows}} \text{Sm-}F \underset{0.5\text{kJ}}{\overset{113.8\text{C}}{\rightleftarrows}} \text{Sm-}C \underset{11.45\text{kJ}}{\overset{144\text{C}}{\rightleftarrows}} \text{Sm-}A \underset{0.2\text{kJ}}{\overset{210\text{C}}{\rightleftarrows}} I$$

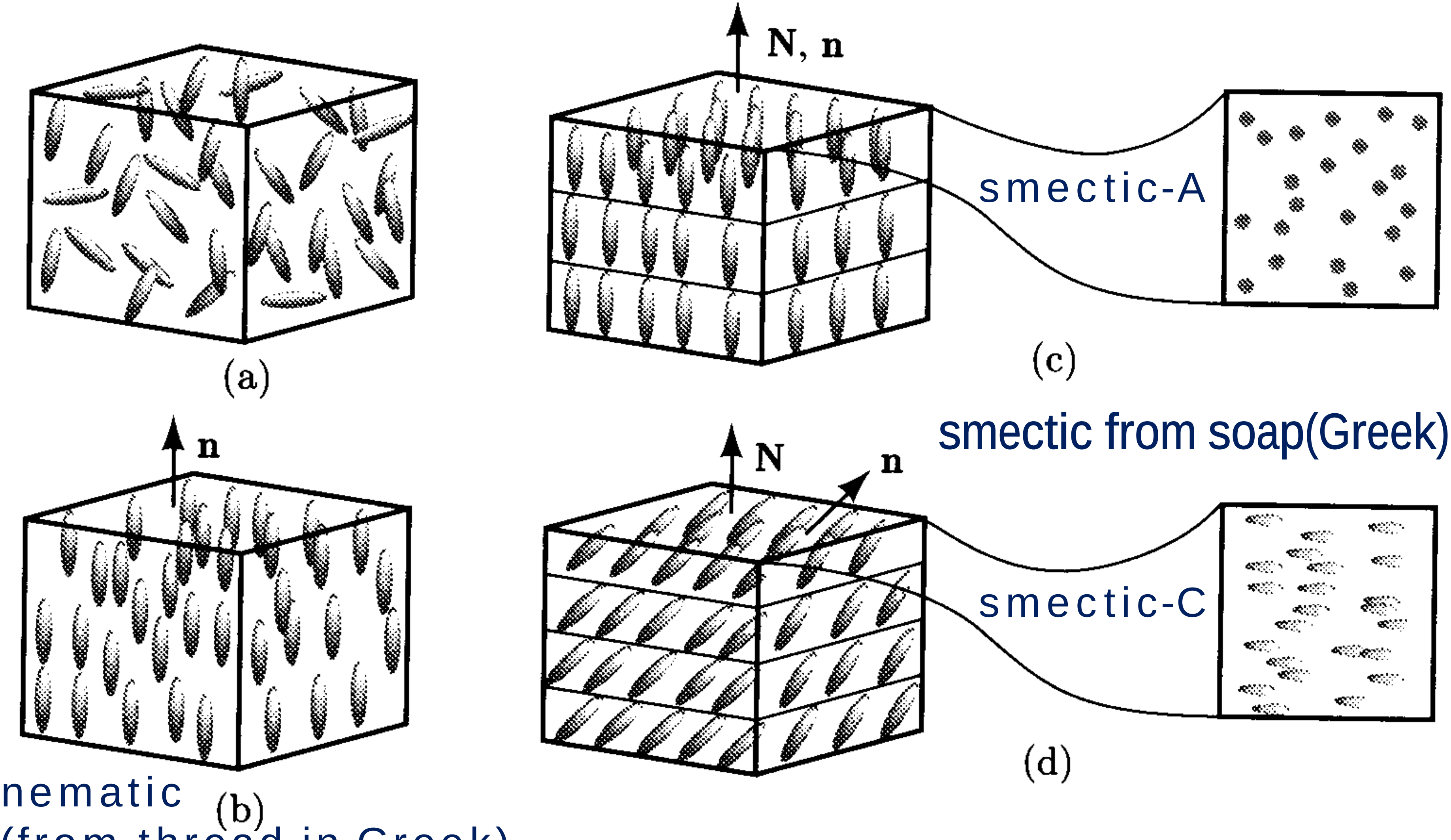


Molecule 7S5 and its model as a rigid rod or ellipsoid.

Notations of LC phases:

N – nematic; Sm – smectic; I - irregular

Schematic representation of the position and orientation of anisotropic molecules in (a) isotropic, (b) nematic, (c) smectic-A, and (d) smectic-C phases.



smectic-A

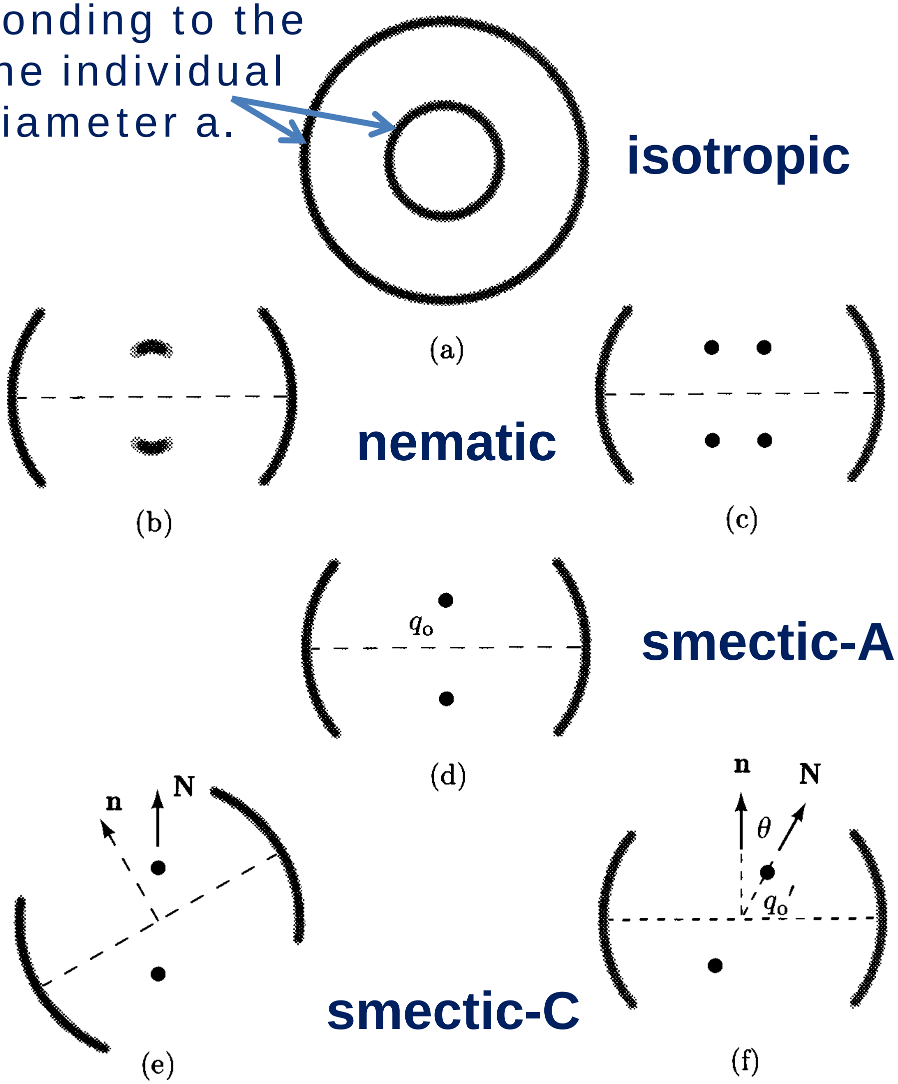
smectic from soap(Greek)

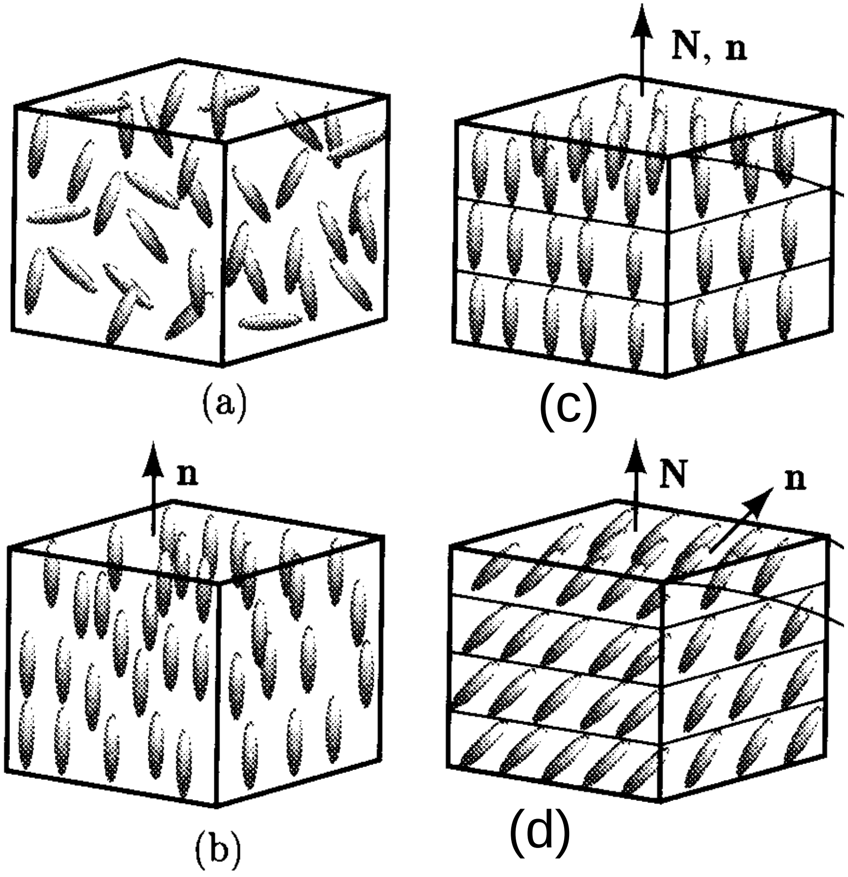
smectic-C

nematic
(from thread in Greek)

Schematic representation of X-ray scattering intensities profiles from (a) isotropic, (b)&(c) nematic, (d) smectic-A and (e)&(f) smectic-C phases.

The structure factor is isotropic but shows rings at wave numbers corresponding to the two characteristic lengths of the individual molecules - their length l and diameter a.

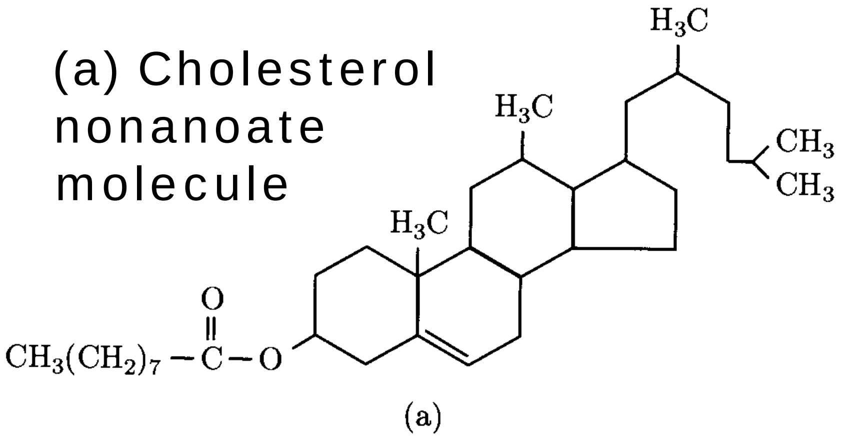


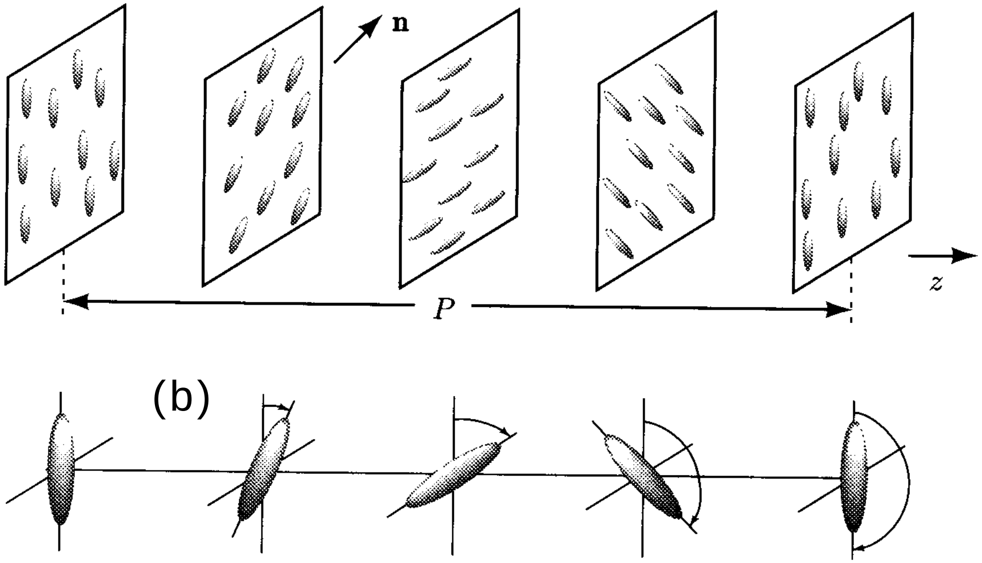


Cholesteric state of liquid crystal (LC)

Chiral molecules (such as cholesterol nonanoate) are molecules with no mirror plane. When such molecules are added to a nematic liquid crystal, a twisted or chiral nematic (N*) state results. This state is often referred to as the cholesteric state. In this state, the direction of average molecular alignment rotates in a helical pattern. The pitch (distance between equivalent planes) depends on the concentration and degree of chirality of the chiral molecules and typically of order several thousand angstroms. This means that cholesterics Bragg scatter visible light. Their X-ray scattering intensity is, however, generally similar to that of a nematic.

(a) Cholesterol nonanoate molecule





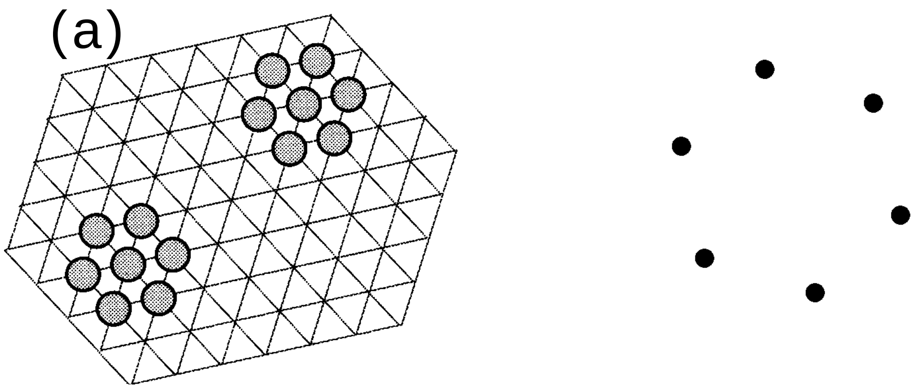
(b) Schematic representation of the molecules in the cholesteric phase. The director n rotates in a helical fashion.

Hexatic state of LC

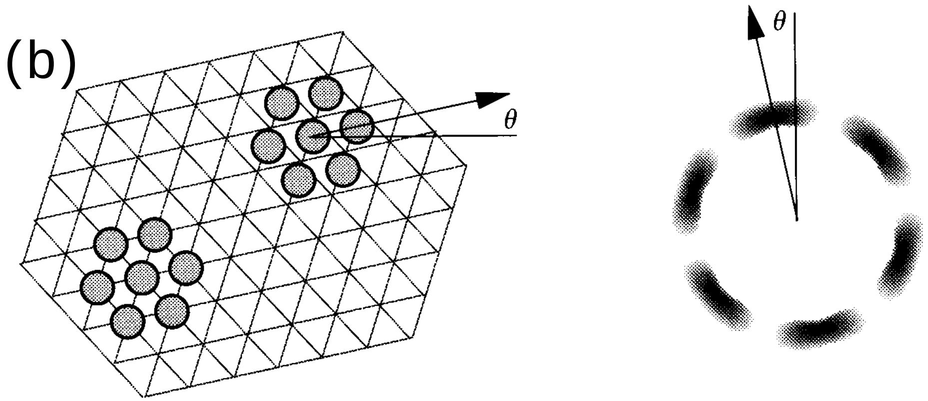
When smectic-A phases are cooled, they condense into what was historically called a smectic-B phase. It is now known that a smectic-B phase can be a crystalline-B phase with a three-dimensional crystal structure and Bragg scattering at points in a three-dimensional reciprocal lattice. In some cases, however, the smectic-B phase is not a true crystal. It has hexagonal orientational order manifested by the development of a six-fold modulation in the intensity of the diffuse ring at $q = 2\pi/a$ in the X-ray scattering intensity of the smectic-A phase. Whereas the *smectic*-A phase is invariant with respect to arbitrary rotations about n, this *hexatic*-B phase is invariant only with respect to rotations of $2\pi/6$ about n.

The existence of long-range orientational order in hexatics is quite remarkable. The breaking of rotational symmetry in the nematic phase is easy to accept. The molecules comprising the nematic phase have a rigid core produced by strong chemical bonds. Orientational order is produced by the collective alignment of rigid bar-like molecules. In hexatics, on the other hand, there is no chemical bond between neighboring molecules, and orientational order is a reflection of the long-range alignment of the position vectors connecting nearest neighbor molecules. In fact the hexatic-bond-angle order can be viewed as resulting from the loss of long-range positional but not orientational order of a hexagonal crystal.

Hexatic state of liquid crystal (LC)



(a) hexagonal crystal



(b) hexatic phase of LC

(a) Separated groups of nearest neighbor atoms in a hexagonal crystalline phase. Atoms occupy lattice sites on a triangular lattice, indicated by grid lines. Each atom has six nearest neighbors forming a hexagon. There is both long-range translational and orienta-tional order. The figure at the side shows the hexagonal pattern of Bragg peaks in the X-ray scattering intensity at the shortest reciprocal lattice vectors,

(b) Separated groups of atoms in a hexatic phase. Each atom has six nearest neighbors forming a local hexagon. Distant hexagons have the same orientation relative to some fixed axis. Atoms do not, however, occupy sites of a triangular lattice. There is long-range orientational but no long-range positional order. The X-ray scattering intensity from a hexatic phase has a six-fold symmetry but no Bragg peaks.

Discotic state of liquid crystal (LC)

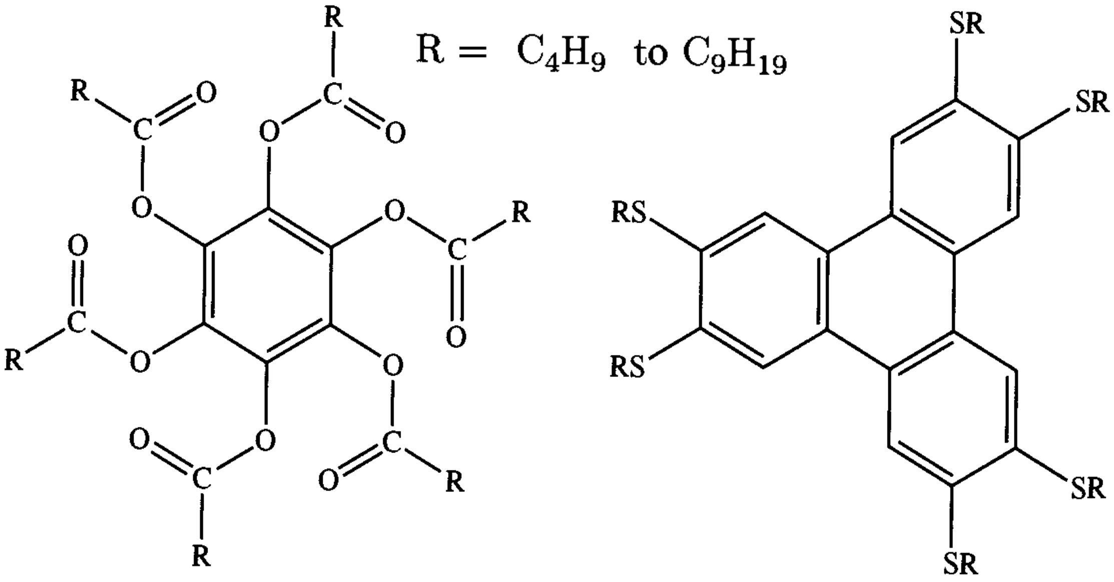


Fig. 1. Some plate-like molecules forming discotic liquid crystalline phases.

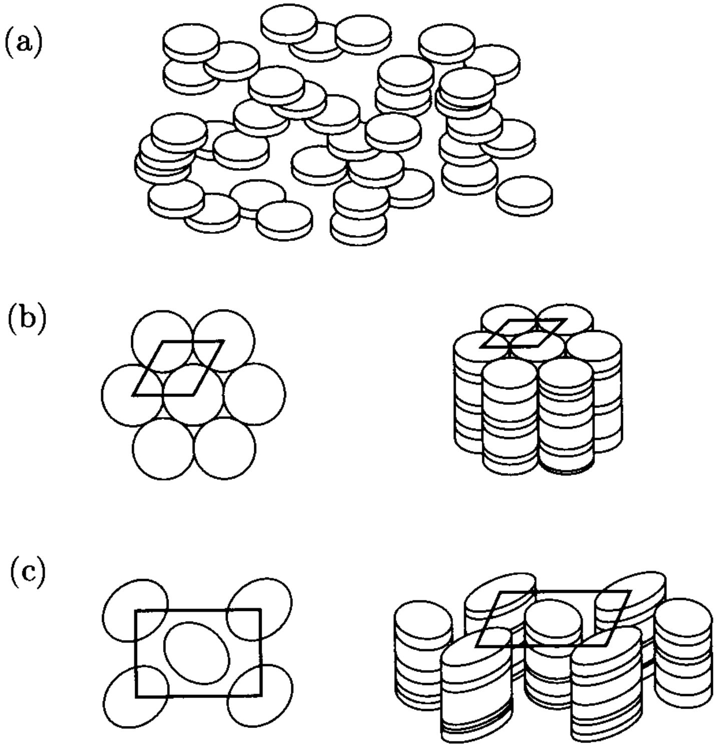


Fig. 2. Plate-like molecules in (a) discotic nematic, (b) hexagonal columnar discotic, and (c) a rectangular columnar discotic.

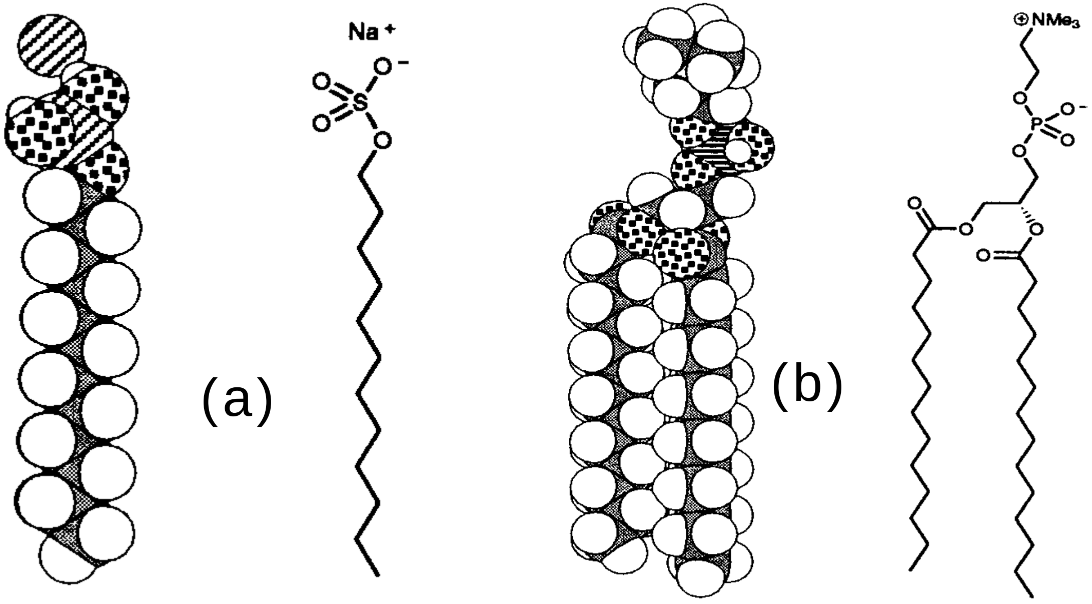
Plate-like molecules can form *discotic nematic phases*, in which the plate normals are aligned, and phases with crystalline order in two dimensions and liquid-like order in the third direction (called columnar) .

The plate-like molecules segregate into columns with the plate normals either parallel to or tilted at an angle to the columnar axes. There is no long-range positional order within a column. The columns themselves form any of the two-dimensional crystals.

Lyotropic liquid crystals and microemulsions

In the preceding discussion, we have focused on liquid crystals whose phases change in response to changes in the temperature. They are called ***thermotropic*** liquid crystals. Liquid crystalline phases also appear in response to changes in concentrations of water, oil, surfactants, or other species in a wide variety of molecular mixtures. These are called ***lyotropic*** liquid crystals and are generally formed by amphiphilic molecules consisting of two parts that repel each other and/or are soluble in different solvents.

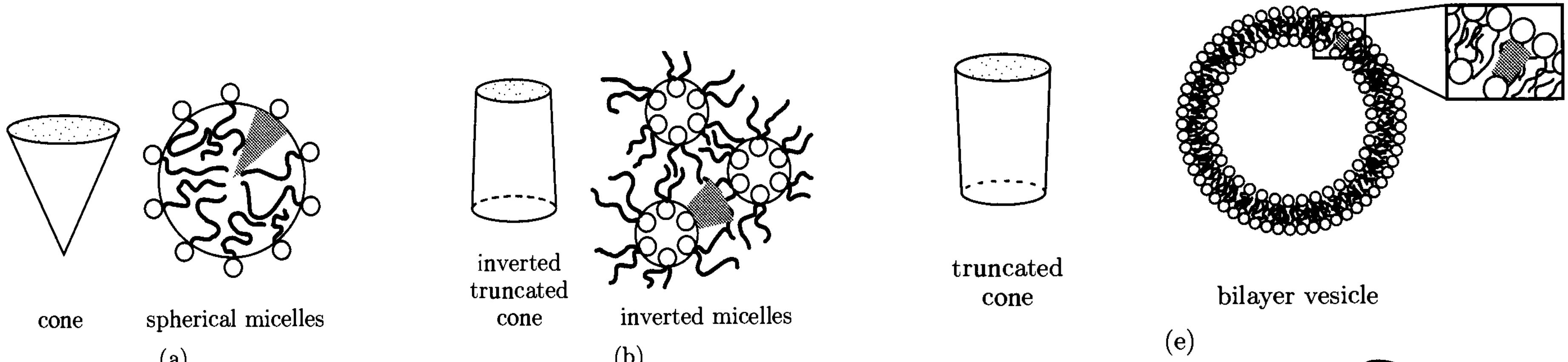
For example, lipids with hydrophilic (water "liking") and hydrophobic (water "fearing") parts. The hydrophobic part consists of one or two hydrocarbon chains containing 8 to 20 carbon atoms. The hydrophilic group generally has a charge or a dipole moment.

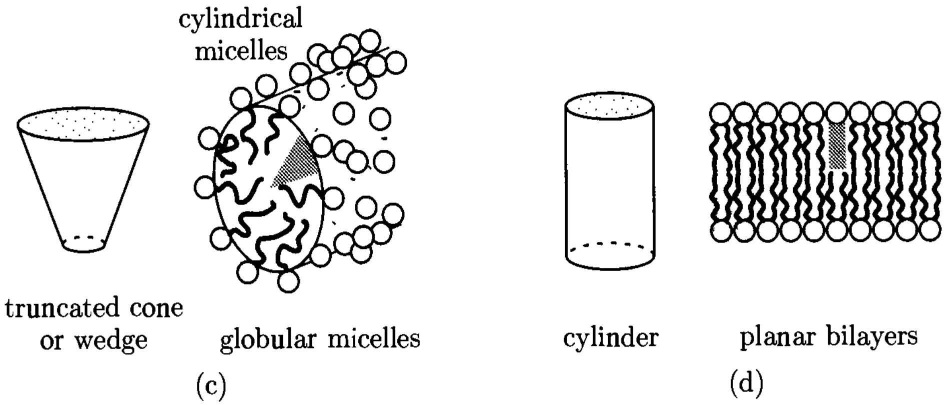


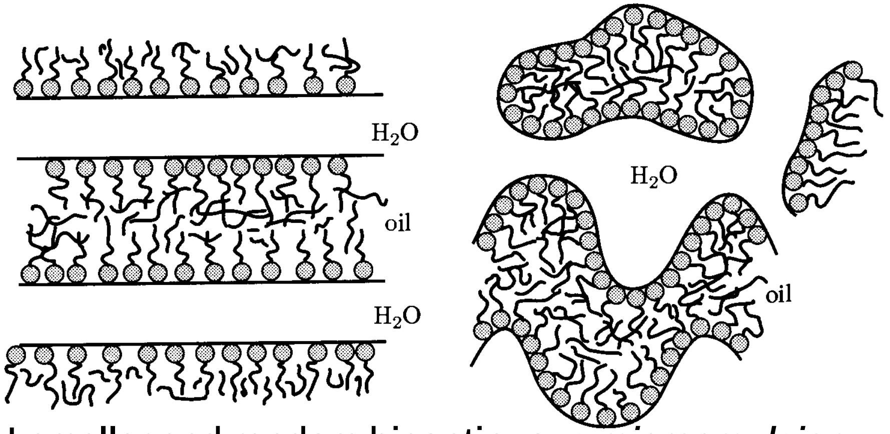
Examples of lipids: (a) SDS, a soap with a single tail, and (b) DMPC, a phospholipid with two tails.

Lyotropic liquid crystals and microemulsions

When in contact with water, lipids will self-organize into structures in which hydrophobic tails are shielded from contact with water. Common structures include spherical and cylindrical micelles, inverted micelles, bilayer sheets, vesicles. The origin of these geometrical structures can be understood in terms of the packing of lipids of different shapes.



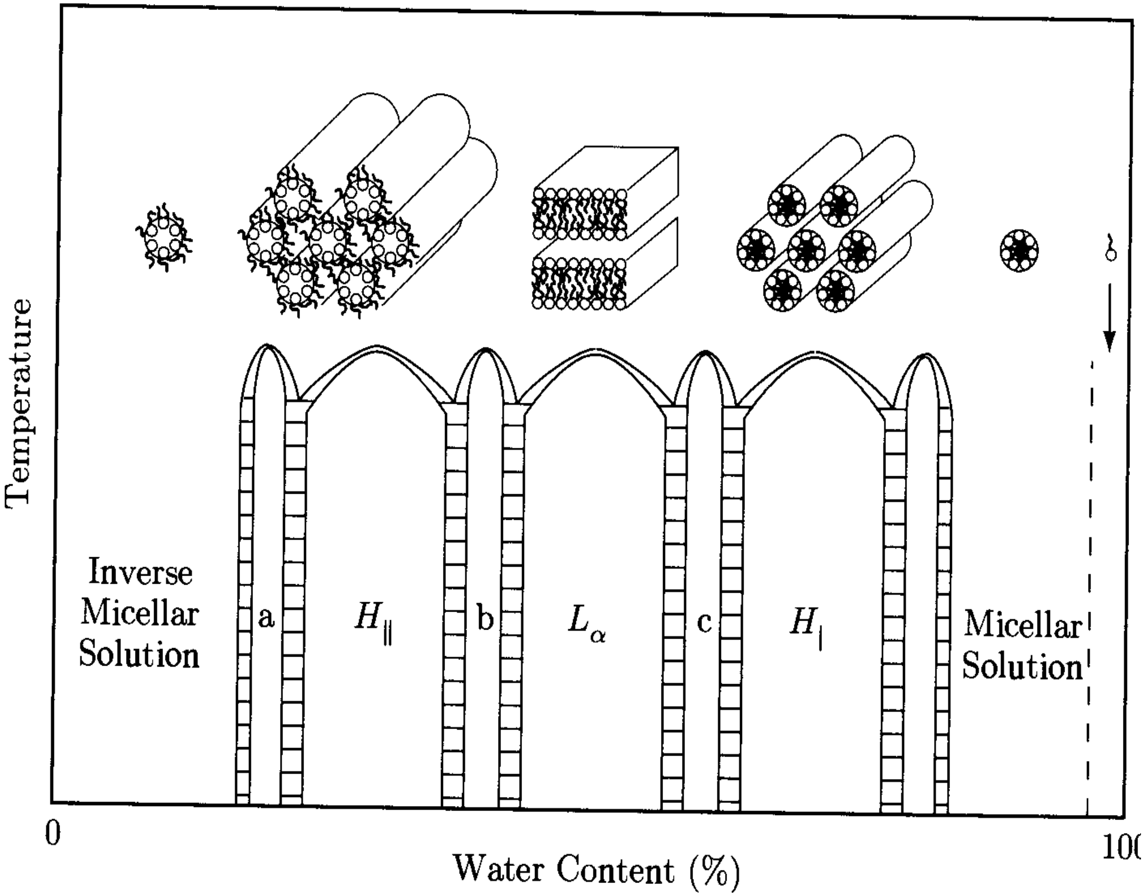




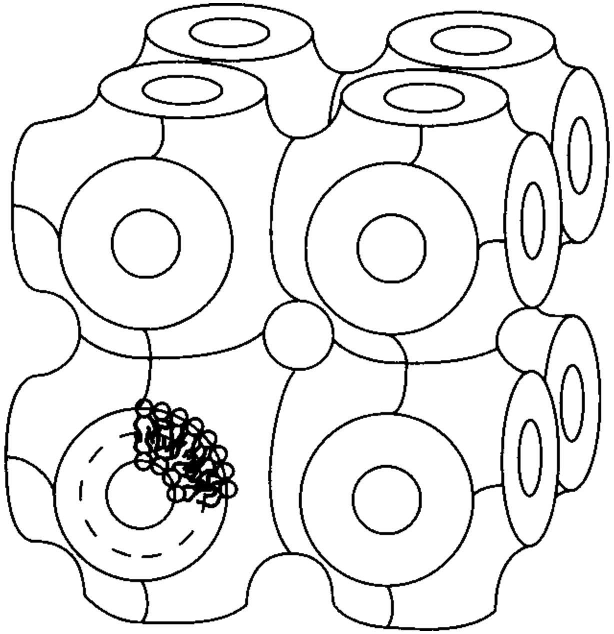
Lamellar and random bicontinuous *microemulsion* phases with water, oil, and surfactant layers.

Lyotropic liquid crystals and microemulsions

These structures can arrange into arrays of equilibrium phases, including nematic, lamellar (smectic), and columnar phases.



Phase diagram and schematic representation of phases of aliphatic chains in water showing micellar solutions: lamellar (L_a), and hexagonal columnar $H_{||}$ and $H_|$ phases.



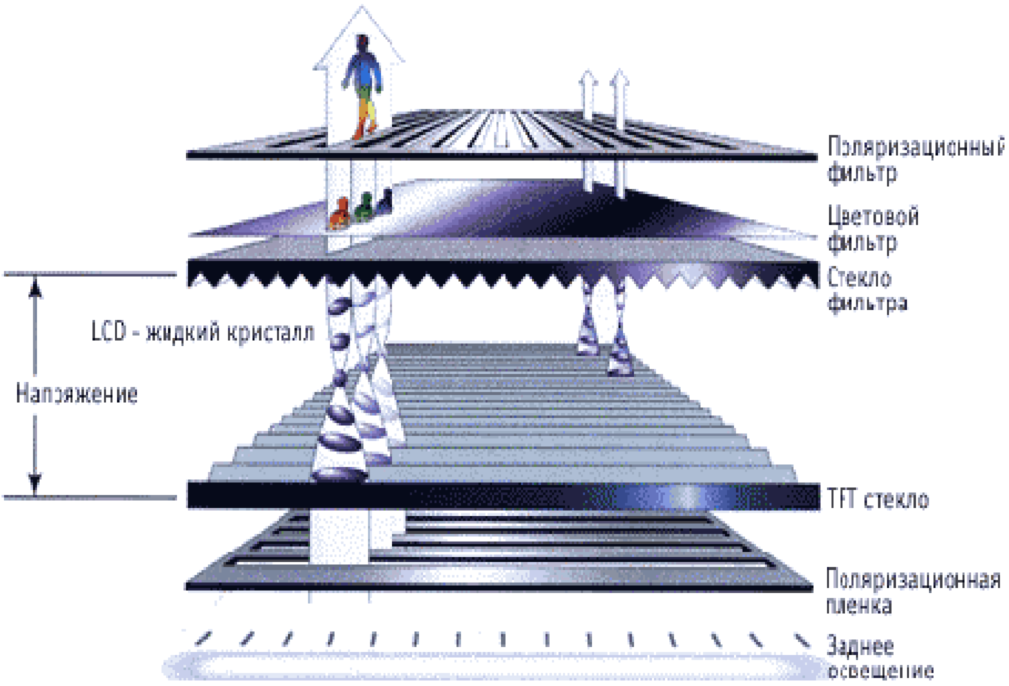
Schematic representation of a surfactant surface in the triply periodic phase "plumber's nightmare“, having cubic symmetry.

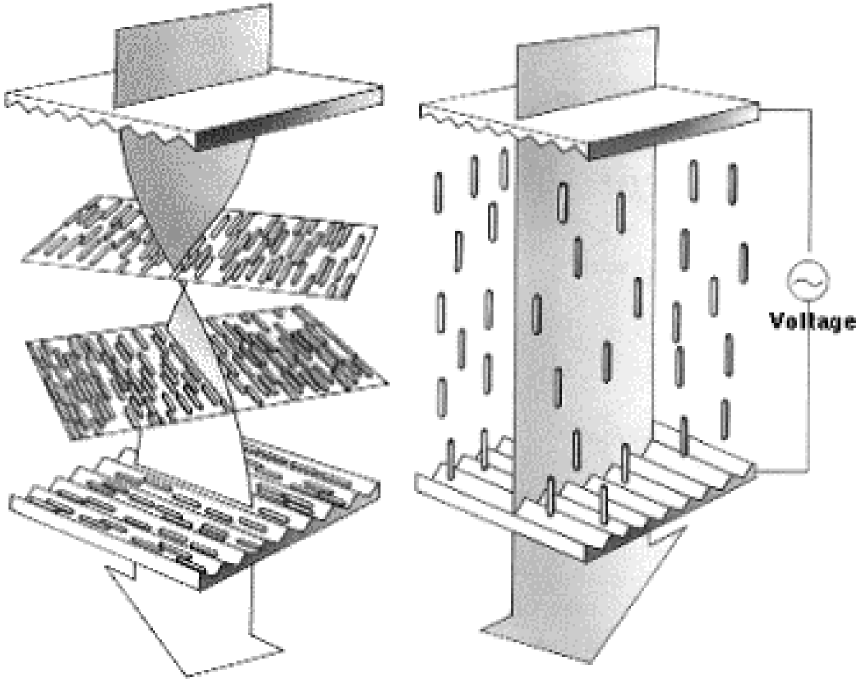
LCD-мониторы. История.

Экраны LCD-мониторов (Liquid Crystal Display, жидкокристаллические мониторы) сделаны из вещества, которое находится в жидком состоянии, но при этом обладает анизотропией свойств (в частности оптических), связанных с упорядоченностью в ориентации молекул. Как ни странно, но жидкие кристаллы старше ЭЛТ почти на десять лет, первое описание этих веществ было сделано еще в 1888 г. Однако долгое время никто не знал, как их применить на практике. Жидкокристаллические материалы были открыты еще в 1888 году австрийским ученым Ф. Ренитцером, но только в 1930-м исследователи из британской корпорации Marconi получили патент на их промышленное применение. Впрочем, дальше этого дело не пошло, поскольку технологическая база в то время была еще слишком слаба. Первый настоящий прорыв совершили ученые Фергесон (Fergason) и Вильямс (Williams) из корпорации RCA (Radio Corporation of America). Один из них создал на базе жидких кристаллов термодатчик, используя их избирательный отражательный эффект, другой изучал воздействие электрического поля на нематические кристаллы. В конце 1966 г. корпорация RCA продемонстрировала прототип LCD-монитора – цифровые часы. Значительную роль в развитии LCD-технологии сыграла корпорация Sharp. Первый в мире калькулятор CS10A был произведен в 1964 г. именно в Sharp. В октябре 1975 г. уже по технологии TN LCD были изготовлены первые компактные цифровые часы. Во второй половине 70-х начался переход от восьмисегментных жидкокристаллических индикаторов к производству матриц с адресацией каждой точки. Так, в 1976 г. Sharp выпустила черно-белый телевизор с диагональю экрана 5,5 дюйма, выполненного на базе LCD-матрицы разрешением 160x120 пикселов.

Принцип работы LCD-мониторов

Работа ЖКД основана на явлении поляризации светового потока. Поляроиды способны пропускать только ту составляющую света, вектор электромагнитной индукции которой лежит в плоскости, параллельной оптической плоскости поляроида. Для оставшейся части светового потока поляроид будет непрозрачным. Данный эффект называется поляризацией света. Длинные молекулы ЖК чувствительны к электростатическому и электромагнитному полю и способны поляризовать свет, => появилась возможность управлять поляризацией. Основываясь на этом открытии и в результате дальнейших исследований, стало возможным обнаружить связь между повышением электрического напряжения и изменением ориентации молекул кристаллов для обеспечения создания изображения.



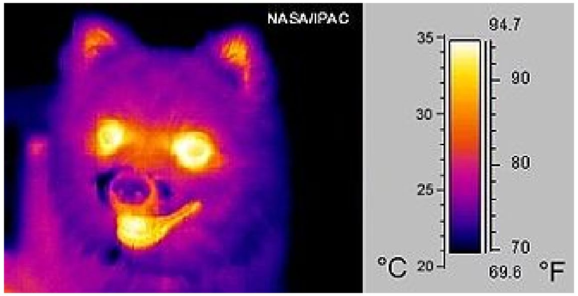


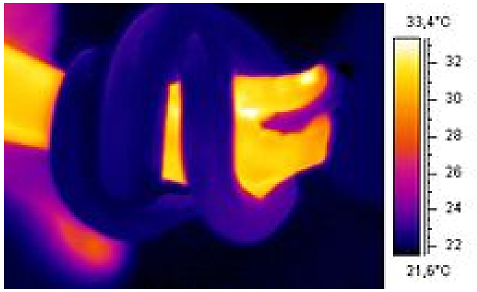
Возможные темы для курсовой

1. **Жидкие кристаллы и их применение** (общий обзор).

2. **Плеохроизм жидких кристаллов.**

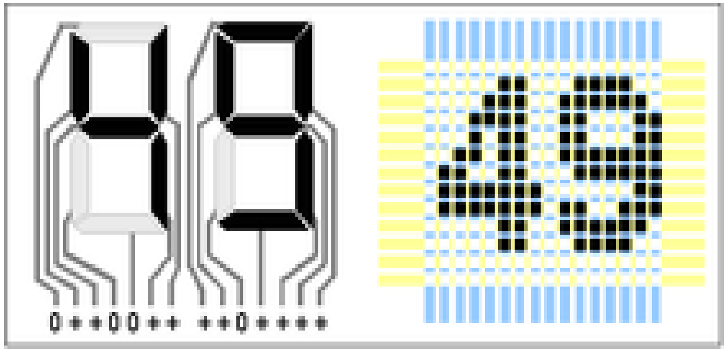
3. **Подробнее о каком-нибудь из применений жидких кристаллов** (возможны различные применения, основанные на разных физических свойствах, => несколько тем). (Пример: термография)





4. **Применение ЖК в дисплеях (принцип работы, типы)**

Сегментный и точечный ЖК-дисплей:



Тема 2: Плеохроизм жидких кристаллов.

Плеохрои́зм (от греч. pleon — более многочисленный и chroa — цвет), свойство анизотропных тел, напр. кристаллов, обнаруживать различную окраску при рассматривании их в белом свете в разных направлениях.
Обусловлен различием спектров поглощения вещества для лучей, имеющих разное направление и поляризацию. Частный случай плеохроизма — дихроизм.

Применение

(1) изготовление поляризационных фильтров (поляроидов).
(2) Для идентификации самоцветов, наряду с другими методами.

дихроизм кордиерита

Плеохроизм красного турмалина