

Overview of Partial Orientational and Positional Ordering in Concentrated Systems

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This paper provides an overview of the static behavior of systems with partial orientational and positional ordering of the species. The understanding of the static behavior provides the foundation needed to understand the dynamic properties of such systems, which are described in more detail in other papers in this issue. More specifically, this paper provides an overview of the fact that species of different dimensions exhibit similar types of partial ordering of the species. This paper further provides an overview of liquid crystalline (LC) phases and molecules, including discussions of types of chemical structures (both rigid and semiflexible) in LC molecules (both nonpolymeric and polymeric); thermotropic and lyotropic LCs; nematic and multiple smectic LC phases; reentrant nematic LC phases; cholesteric LC phases and blue phases; smectic crystal phases; columnar phases; micelles and lamellar LC structures; LC phase transitions; LC glasses; viscosities of LC phases; and dynamic textures and patterns in LC phases.

KEY WORDS: Liquid crystalline phases; statics; dynamics; nonpolymeric; polymeric; micelles; transitions; overview.

1. INTRODUCTION

Elsewhere in this issue are papers describing the dynamics of systems with partial ordering of species. The understanding of the dynamic properties of such systems is built on the foundation of the understanding of the static behavior of the systems.

This paper provides an overview of the static behavior of systems with partial ordering of the species.

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First of all, species of different dimensions exhibit similar types of partial ordering of the species. For example as shown in Table I, species of different dimensions can exhibit partial orientational ordering (ref. 1, pp. 3, 5) of the species.

The fact that species of different dimensions exhibit similar types of partial ordering of the species suggests a type of scaling for the ordering of structures ranging from molecular (liquid crystalline phases) to macroscopic (logs in a river, floating to a sawmill). The packing of the shapes of the structures seems to be the most important feature in the partial ordering of the structures.

It is instructive to provide an overview of the many kinds of partial ordering of different kinds of *molecules*, realizing that the ordering seen with molecules can also be seen in systems of structures of much larger dimensions.

1988 marked 100 years of liquid crystalline research.

Liquid crystalline systems are pervasive in natural and synthetic materials, such as membranes and other biological structures, fossil energy systems (oils, coals, etc.), soaps and micelles for extraction and separation purposes, partially crystalline polymers, liquid crystalline display devices (very low energy requirements in watches and calculators), etc. Some solidified backbone liquid crystalline polymers are used as stronger, lighter-weight replacements for metals, ceramics, and other materials in structural applications, such as auto and airplane parts, armor (such as in bulletproof vests, football helmets, and military tanks), etc. Some side-chain liquid crystalline polymers are used as electro-optic devices.

The liquid crystalline aspects of various biological structures are essential to their proper functioning. Consider, for example, the liquid crystalline ordering of the molecules forming the walls of a living cell. If these molecules had liquid disorder, the contents of the cell would diffuse away. If these molecules had complete crystalline order, the exchange of materials through the cell wall would be very difficult and thus too slow.

Table I. Species of Different Dimensions Can Exhibit Partial Orientational Ordering^a

Species	Dimensions
PAA molecules	$\sim 20 \text{ \AA} \times 5 \text{ \AA}$
Synthetic polypeptides	$\sim 300 \text{ \AA} \times 20 \text{ \AA}$
Tobacco mosaic virus particles	$\sim 3000 \text{ \AA} \times 200 \text{ \AA}$
Polymer fibers	$\sim 100 \text{ \mu m} \times 10 \text{ \mu m}$

^a Data from Ref. 1, pp. 3, 5. See Fig. 1 for the molecule chemical structure of PAA.

2. OVERVIEW OF LIQUID CRYSTALLINE PHASES AND MOLECULES

2.1. Types of Chemical Structures in Liquid Crystalline Molecules

Liquid crystalline (LC) molecules are molecules that form stable LC phases, that is, phases with partial ordering of the molecules. This partial ordering is intermediate between the random packing (i.e., disorder) of a liquid and the regular three-dimensional (3D) packing (i.e., order) of a crystal.

The molecules forming LC phases include nonpolymeric LC molecules and LC polymers (LCPs). Nonpolymeric LC molecules are molecules that are not polymers but that do form LC phases.

The types of LCPs include backbone LCPs, side-chain LCPs, and combined LCPs (including superstrong^(2,9) LCPs). Backbone LCPs are polymers in which the backbones (i.e., main chains) of the polymer molecules have LC ordering; there are no side chains in backbone LCPs. Side-chain LCPs are polymers in which the side chains of the molecules have LC ordering; the backbones of side-chain LCPs are semiflexible chains (such as those composed of polyethylene molecules) which do not have LC ordering. Combined LCPs are polymers in which the backbones of the molecules have LC ordering and the side chains have LC ordering. Side-chain LCPs and combined LCPs have relatively short (i.e., nonpolymeric) side chains attached to a polymer backbone.

Figure 1 shows example molecule chemical structures for a nonpolymeric LC material, a backbone LCP, and a side-chain LCP.

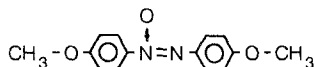
2.2. Rigid and Semiflexible Sections in LC Molecules

In this paper, we will discuss rigid sections and semiflexible sections in a molecule. There can be rigid sections and multiple semiflexible sections in a nonpolymeric molecule, in the backbone of a polymer molecule, or in the side chain of a polymer molecule.

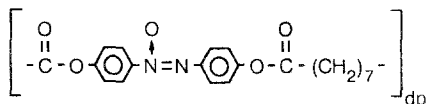
A rigid section is formed by a sequence of conjugated aromatic, heterocyclic aromatic, double, and triple bonds in the molecule. Conjugation means that the aromatic rings, heterocyclic aromatic rings, double bonds, and triple bonds are not separated by more than one single bond. The overlap of π orbitals in the aromatic, double, and triple bonds in the section makes it difficult to make rotations about bonds in the section and thus leads to the rigidity of the section.

A semiflexible (i.e., partially flexible) section is a section in which there

PAA: (nonpolymeric LC material):



B1: (backbone LCP):



PMS(4)-OCH₃: (side-chain LCP):

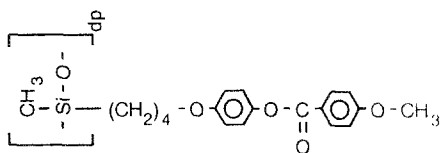


Fig. 1. Example molecule chemical structures for a nonpolymeric LC molecule, a backbone LCP, and a side-chain LCP.

are finite, but easily achievable energies to make rotations about some of the bonds in the section. A semiflexible section is frequently formed by an *n*-alkyl [i.e., $(-\text{CH}_2-)_x$] chain section, in which the rotations about any carbon-carbon bond between methylene (CH_2) units in a given chain section are of particular interest.

LC materials have rigid sections that are the source of orientational ordering. LC materials can also have semiflexible sections. Nonpolymeric LC molecules can have one or two semiflexible tail chains.

The shape of a rigid section stays more or less constant as temperature *T* and pressure *P* change, whereas the shape of a semiflexible section can vary as a function of *T* and *P*.

2.3. Thermotropic and Lyotropic LCs

Thermotropic LCs are molecules (such as PAA in Table I) that form stable LC phases in the pure state as *T* (and/or also *P*) is varied.

Lyotropic LCs are materials (such as the tobacco mosaic virus particles in Table I) that form stable LC phases when in solution.

2.4. Nematic and Smectic LC Phases

In the nematic (*N*) LC phase, there is partial orientational ordering or alignment of the long axes of the molecules parallel to a preferred axis in

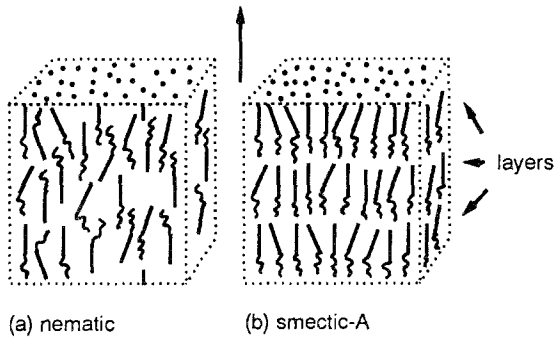


Fig. 2. Illustration of molecular packing of nonpolymeric LC molecules in (a) a nematic LC phase and (b) a smectic A LC phase. In this figure, each rigid section in a molecule is represented by a straight line, and each semiflexible section by a wavy line.

the system. See Fig. 2 for schematics of the ordering of the long axes of nonpolymeric molecules in the *N* LC phase. See also Fig. 3 for the schematics of the ordering of the long axes of rigid sections in the backbones of LCP molecules in the *N* LC phase. Experimentally, rigid sections are required for *N* phases; the molecules can also (but are not required to) have semiflexible sections.

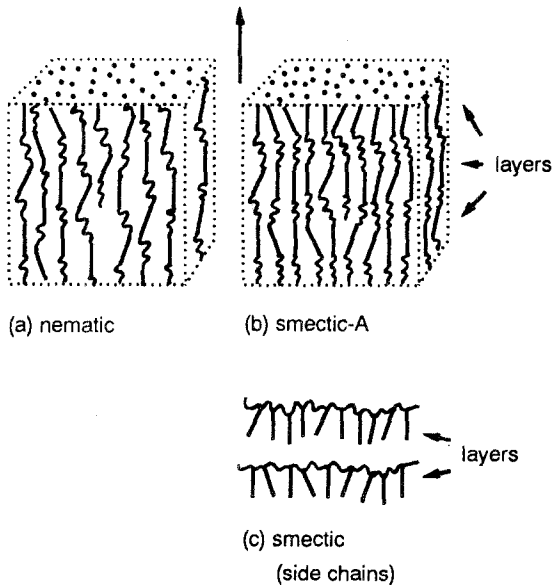


Fig. 3. Illustrations of molecular packing of backbone LCPs in (a) a nematic LC phase and (b) a smectic A LC phase. (c) Illustration of smectic LC ordering by the side chains of side-chain LCPs.

Orientational order in N phases can be understood as follows: As the volume V of a system decreases, the long axes of the rigid sections tend to align parallel to a preferred axis in order to be able to pack into the system V . This orientational ordering is reminiscent of the familiar childhood example of aligning the long axes of pencils in order to fit them into a pencil box.

In the smectic (S) LC phases, there is partial orientational ordering (as in the N phase) and there is also partial positional ordering of the centers of mass of the molecules into layers. This positional ordering in S phases leads to layer structures, such that similar parts of the molecules tend to pack with each other. For example, rigid sections tend to pack with other rigid sections, and semiflexible sections tend to pack with other semiflexible sections.

Positional ordering in S phases can be understood as follows: The semiflexible sections bend and twist well around each other, but do not pack as well with the rigid sections. As the V decreases even further, rigid sections must pack with rigid sections (and semiflexible sections must pack with other semiflexible sections) in order to be able to fit in the system V .

The simplest S phase is a smectic A (SA) phase, in which there is one-dimensional (1D) positional ordering of the centers of mass of the molecules along the preferred axis of orientation for the molecules, but liquidlike disorder along the other two orthogonal axes of the system, i.e., liquidlike disorder within a layer.

See Figs. 2 and 3 for schematic illustrations of molecular packing in SA phases formed by nonpolymeric LC molecules and by backbone LCPs, respectively. See Fig. 3 for a schematic illustration of S LC ordering by the side chains of side-chain LCPs.

Except for two or three materials,^(10, 11) virtually all of the thousands of molecules⁽¹⁰⁻¹³⁾ that form S LC phases (including SA phases) in their pure states have one or more semiflexible sections. As these semiflexible sections are shortened, the S phases disappear. In these experimental cases, the rigid sections (and hence, any dipoles in the rigid sections) are *not* sufficient—without the semiflexible sections—to stabilize S phases for molecules in their pure states. In some T ranges, the packing of the semiflexible sections provides enough entropy (disorder) to keep the rigid sections from forming 3D crystals and thus allows the existence of *partial* positional order in S phases.

The formation of S phases in the pure states of the few molecules that do not have semiflexible sections seems to involve differences in the packing of different rigid parts of the molecules (somewhat similar to the differences in packing the heads of hockey sticks and the shafts of hockey sticks). It should be noted that for the series of molecules $H-(\phi)_n-H$

(where ϕ is a *para*-bonded phenyl ring), only the molecules with $n = 6$ form an *S* phase (specifically, an SA phase). To date, there has been no experimental or theoretical explanation of this SA phase. One possible suggested explanation⁽¹⁴⁾—which needs to be explored by both theoretical and experimental studies—is as follows: The existence of this SA phase might be attributable to differences in the packing of different planes of phenyl rings in the molecules. Such different planes of phenyl rings could occur in one molecule if a sequence of three of the phenyl rings packs in one plane, while the remaining sequence of three phenyl rings packs in another plane.

Experimentally, the side chains of a polymer molecule can form *S* layers if there is positional alignment of the side chains with each other and thus with respect to the plane containing the backbone. Such positional alignment defines *S* layers and thus does not require the segregated packing of rigid sections and semiflexible sections to define the layers.

Refs. 3, 6, 9, and 15–18 contain theories that predict, reproduce, and explain the above experimental results for *S* phases. See these references for

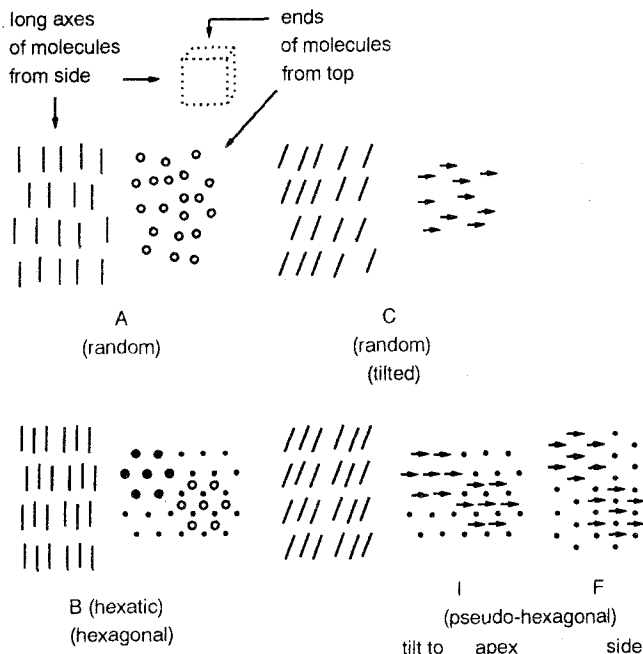


Fig. 4. Schematic illustrations of the ordering of the molecules in various smectic LC phases. In the smectic A and smectic C LC phases, there is free rotation of each molecule about its long axis. In the smectic B, smectic I, and smectic F LC phases, there is a sixfold coordinated rotation of each molecule about its long axis. Information from refs. 19 and 20.

theoretical predictions for these phases and for additional molecule systems to form these phases. See also these references for comparisons with experimental data for these theories.

2.5. More Smectic Phases

S phases involve 1D or 2D positional ordering of the molecules.

Figure 4 shows schematic illustrations of the ordering of the molecules in different kinds of *S* LC phases.^(19,20) *S* LC phases involve either random placement of the molecules with regard to crystal lattice sites in a layer or some disorder in the placement of the molecules with regard to crystal lattice sites in a layer.

Figure 5 shows schematic illustrations of the ordering of the molecules in different kinds of *S* crystal phases.^(19,20) *S* crystal phases involve regular placement of molecules on crystal lattice sites within a layer. The ordering *within* one layer of an *S* crystal phase appears to be crystalline. However, the correlation of the ordering *between* layers in *S* crystal phases does not persist beyond about five layers and is thus not long range. Thus, *S* crystals

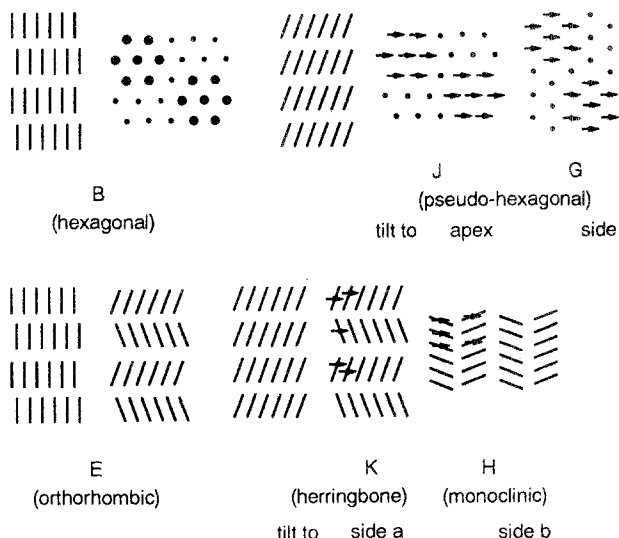


Fig. 5. Schematic illustrations of the ordering of the molecules in various smectic crystal phases. The correlation of the ordering *between* layers in smectic crystal phases does not persist beyond about five layers and is thus not long range. In the smectic B, smectic J, and smectic G crystal phases, there is a sixfold coordinated rotation of each molecule about its long axis. In the smectic E, smectic K, and smectic H crystal phases, each molecule oscillates through 180° about its long axis. Information from refs. 19 and 20.

lack the long-range 3D ordering of a true 3D crystal phase. As in *S* LC phases (see discussion earlier), the packing of the semiflexible sections in *S* crystal phases provides enough entropy (disorder) to keep the rigid sections from forming 3D crystals.

It should be noted that the conformationally disordered (“condis”) phases of polymers studied by B. Wunderlich would appear to correspond to *S* crystal phases.

2.6. Nematic, Cholesteric, and Blue Phases

Figure 6 shows schematic illustrations of the partial ordering of the long axes of the molecules parallel to a preferred axis in the *N* LC phase

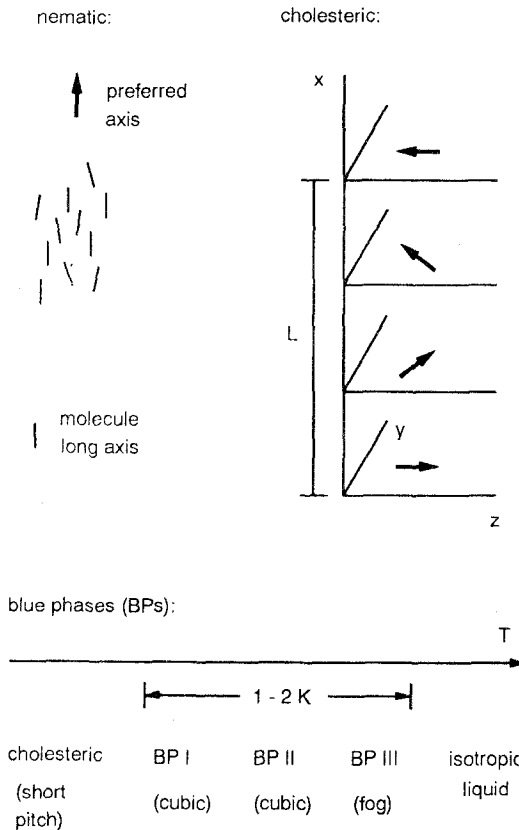


Fig. 6. Schematic illustrations for nematic and cholesteric LC phases and for blue phases. For the cholesteric phase, *L* is one-half the pitch and is typically of the order of $\sim 3000 \text{ \AA}$. Information on cholesteric phases from ref. 1, pp. 9-13.

and in the cholesteric LC phase. As seen in Fig. 6, the director (i.e., preferred axis for orientational ordering) twists through space in a cholesteric phase, forming a helical structure. Cholesteric phases are formed by molecules which are chiral (i.e., the molecule cannot be superimposed on its mirror image). For more discussion of cholesteric phases, see Ref. 1, pp. 9–13, and references therein.

In some systems of chiral molecules with a short pitch, there are stable blue phases in T ranges of about 1–2 K between the cholesteric phase and the isotropic I liquid phase. See Fig. 6. Thus far, two cubic blue phases (BP I and BP II) and a blue phase “fog” (BP III) have been identified experimentally. The cubic blue phases have been interpreted as involving bicontinuous cubic structures of surfaces. There is still considerable discussion about the nature of the different blue phases. For more discussion of blue phases, see refs. 21–23.

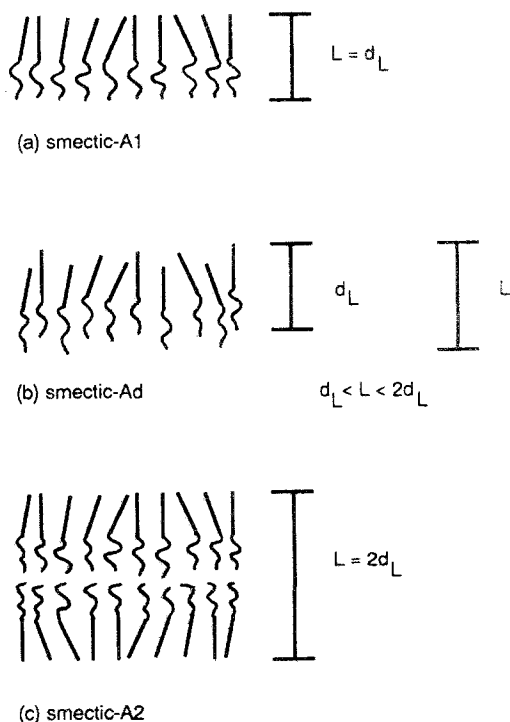


Fig. 7. Illustration of the packing of the molecules in smectic A1, smectic Ad, and smectic A2 LC phases. For these phases, d_L is the actual length of the molecule at a given T and P , and L is the thickness of the smectic layer.

2.7. Different Smectic A LC Phases

There are multiple smectic A phases. Figure 7 shows schematic illustrations of the packing of nonpolymeric molecules in smectic A1 (SA1), smectic Ad (SAd), and smectic A2 (SA2) LC phases.

Figure 8 shows schematic illustrations of the packing of the long axes of backbones and side chains in noninterdigitated SA1, interdigitated SA1, and SAd LC phases and in different kinds of SA2 LC phases.

SAd LC phases have partial 1D positional alignment of the molecules, while SA1 and SA2 phases have full 1D positional alignment of the molecules.

Refs. 3, 6, 9, and 15–18 contain theories that predict, reproduce, and explain these different SA phases formed from nonpolymeric molecules and polymeric molecules. In fact, these theories predict the existence of these phases in various systems, especially in polymeric systems. See these references for theoretical predictions for these phases and for additional molecule systems to form these phases. See also these references for comparisons with experimental data for these theories.

See Moussa *et al.*,⁽²⁴⁾ elsewhere in this issue, for neutron scattering results for SA and *N* LC phases of side-chain LCPs.

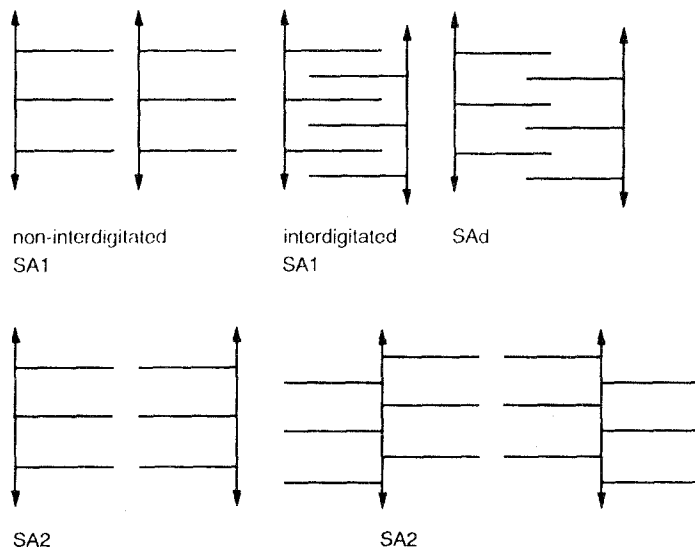


Fig. 8. Schematic illustration of the packing of the long axes of backbones and side chains in noninterdigitated SA1, interdigitated SA1, and SAd LC phases and in different kinds of SA2 LC phases. The backbones and side chains can contain both rigid and semiflexible sections. The arrows indicate the continuation of the polymer backbones.

2.8. Reentrant Nematic Phase

Figure 9 shows schematic illustrations of the packing of molecules in an N LC phase, an SA LC phase, and a reentrant nematic (NR) LC phase as T decreases. [A reentrant phase occurs when a phase appears in one T range, disappears in a lower T range, and then reappears (reenters) in an even lower T range.]

Steric (i.e., hard, or infinitely large) repulsions are sufficient to generate^(9,15 18) the N , SA, and NR LC phases illustrated in Fig. 9 (as well as multiple SA LC phases). The appearance of the stable N phase as the system V decreases (as T decreases) has been discussed in an earlier section of this paper. Attractive forces (including dipolar forces) are not necessary^(9,15 18) to generate these phases.

As T and thus V decrease even further, the SA phase becomes stable for the following reasons: In the SA phase, the differences in the steric

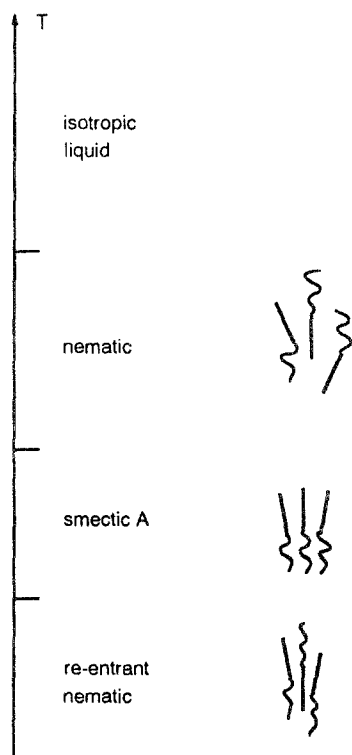


Fig. 9. Schematic illustration of isotropic liquid phase and nematic, smectic A, and reentrant nematic LC phases as a function of decreasing T .

packing of the rigid sections and the semiflexible sections are large enough that orientationally oriented molecules tend to positionally order such that rigid sections tend to pack with other rigid sections while semiflexible sections tend to pack with other semiflexible sections. Thus, the coupling of orientational ordering and positional ordering of the molecules arises naturally from the packing of the molecules. The semiflexible sections tend to bend and twist around each other, but do not pack as well with the oriented rigid sections.

As T decreases, the semiflexible sections become less flexible, and the packing differences between the rigid sections and the semiflexible sections decrease. Thus, the need for segregated packing of rigid sections with rigid sections (and semiflexible sections with semiflexible sections) is overcome by the entropy of unsegregated packing, leading to the disappearance of the SA phase and thus the appearance of a low- T N phase.

Refs. 9 and 15–18 contain theories that predict, reproduce, and explain these NR phases. See these references for theoretical predictions for these phases and for additional molecule systems to form these phases. See also these references for comparisons with experimental data for these theories. In addition, see refs. 25 and 26 for review articles about both theories and experiment for SA and NR phases.

2.9. LC Phases Formed by Molecules with Rigid Discs

Figure 10 shows the molecule chemical structure of an example molecule⁽²⁷⁾ with a rigid disc that forms LC phases.

Molecules with rigid discs can form⁽²⁷⁾ an N LC phase and multiple columnar LC phases (both ordered and disordered). See Fig. 11 for schematic illustrations of these phases. The columnar phases for molecules with rigid discs are somewhat reminiscent of smectic phases for molecules

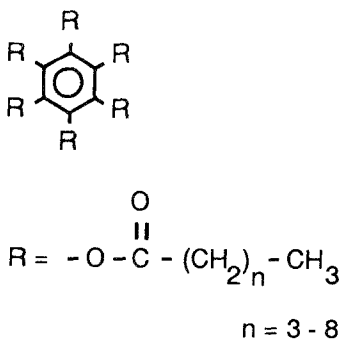


Fig. 10. Example molecule chemical structure⁽²⁷⁾ for an LC molecule with a rigid disc.

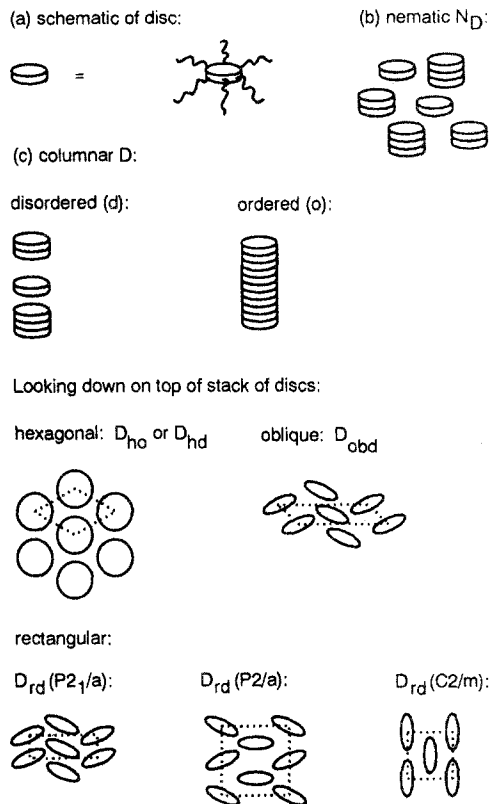


Fig. 11. Schematic illustration of the packing of molecules containing rigid discs into LC phases. Information from ref. 27.

with rigid rodlike sections. Experimentally, semiflexible sections seem to be necessary in molecules with rigid discs to have stable columnar phases in pure systems.

2.10. Micelle and Lamellar LC Structures

In the preceding sections of this paper, we discussed stable LC phases formed by molecules with rigid sections and semiflexible sections.

In this section of the paper, we shall discuss LC ordering by molecules composed of a polar head (replacing the rigid section discussed earlier) and a nonpolar tail (semiflexible section).

As illustrated in Fig. 12, these molecules can align to form spherical micelles or lamellar structures in water and aqueous solutions, such that

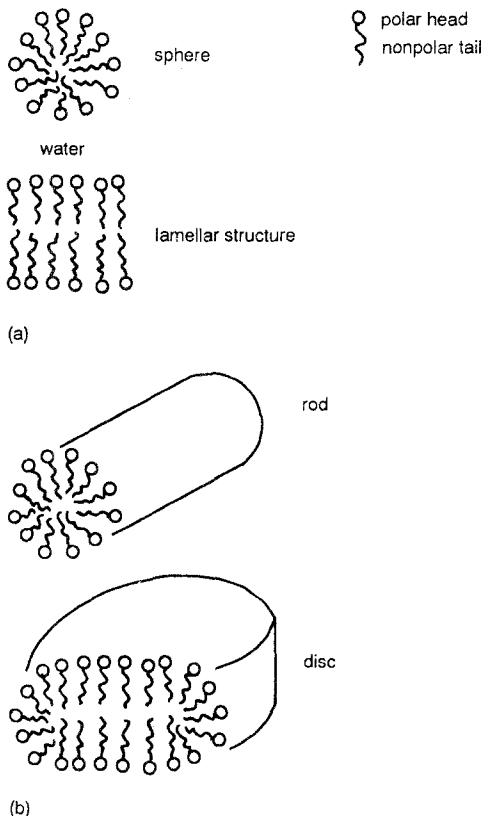


Fig. 12. Illustration of the packing of molecules with polar heads and nonpolar (semi-flexible) tails into spherical micelles and lamellar structures with smectic LC ordering. Rod-shaped and disc-shaped micelles can have large-scale LC ordering of these rods and discs.

the polar (i.e., hydrophilic) head groups of the molecules are on the outer surfaces of the structures while the nonpolar (i.e., hydrophobic) tails are in the interior of the structures. The molecular ordering in micelles and lamellar structures is reminiscent of the positional ordering of molecules in smectic phases. In an organic solvent, reverse micelles and lamellar structures would be formed, such that the nonpolar tails are on the surfaces and the polar heads are in the interior.

These spherical micelles and lamellar structures can grow by the addition of more molecules to form rod-shaped and disc-shaped micelles. These rod-shaped and disc-shaped micelles can then themselves exhibit partial ordering into LC phases similar to—but on a larger scale than—the LC phases formed by rodlike and disclike molecules discussed earlier in this paper.

2.11. Phase Transitions Involving LC Phases

The transitions involving various LC phases are of particular interest since these transitions constitute stepwise melting or freezing (i.e., stepwise progression between order and disorder of the molecules).

The transition between the *N* LC phase and the *I* liquid phase is a weakly first-order transition in 3D. That is, there are small, but finite changes in the first derivatives of the free energy (i.e., in the volume, energy, entropy, etc.) at the transition. The transition is termed *weakly* first-order, since the changes in these quantities are about an order of magnitude smaller at the *N-I* transition than at the transition between a 3D crystal and an *I* liquid phase.

The transition from an *S* LC phase and the *N* LC phase or another *S* LC phase can be very weakly first-order or can be second-order. At a second-order transition, there are no finite changes in volume, energy, entropy, etc., but there are discontinuities in their derivatives.

For a recent experimental study of the order of *S* transitions, see Cladis⁽²⁸⁾ elsewhere in this issue.

2.12. Glasses Formed from Different LC Phases

An ordinary glass is a glass state with the disorder of a stable *I* liquid frozen in. An LC glass is a glass with the LC order of a stable LC phase frozen in. Thus, there are a number of possible kinds of LC glasses.

2.13. Viscosities of LC Phases

Since the dynamics of LC phases will be affected by the viscosities of these phases, it is useful to say a few words about these viscosities. The viscosities for LC phases range from samples that can be poured [such as PAA, with a viscosity (ref. 1, p. 7) of about 0.1 P in the *N* LC phase] to samples (such as hydrocarbon waxes) that look solid, but can be deformed relatively easily. (For comparison, the viscosity of water at room temperature is of the order of 10^{-2} P.) The greater the ordering of the molecules in the LC phase, then the greater the overall viscosity of the phase.

2.14. Dynamic Textures and Patterns

Molecules in LC phases can form various dynamic textures and patterns. For example, Fig. 13 shows a schematic illustration of a convective roll of molecules in an *N* LC phase between electrically charged plates.

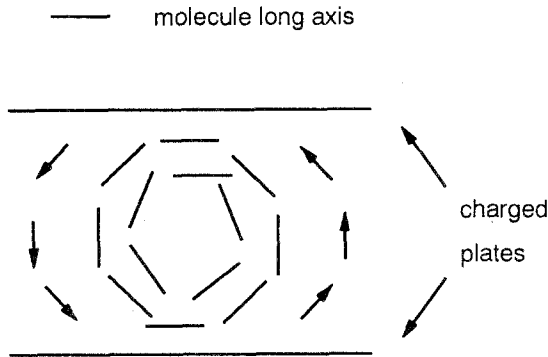


Fig. 13. Schematic illustration of a convective roll formed by nematic LC molecules between two electrically charged plates. The arrows indicate the direction of the convection.

See, for example, refs. 1 (pp. 187–200) and 29 and references therein for more details of dynamic textures and patterns formed by molecules in LC phases under various conditions.

2.15. Additional Studies and References

For more experimental studies of LCPs, see also Jaffe⁽³⁰⁾ and Berry *et al.*⁽³¹⁾ elsewhere in this issue.

Some additional general references for nonpolymeric and polymeric LC systems include refs. 32–41.

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REFERENCES

1. P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University Press, Oxford, 1975).
2. F. Dowell, *J. Stat. Phys.*, this issue.
3. F. Dowell, *J. Chem. Phys.* **91**:1316, 1326 (1989).
4. F. Dowell, *Polymer Preprints* **30**(2):532 (1989).
5. F. Dowell, in *Industry–University Advanced Materials Conference II*, F. W. Smith, ed. (Advanced Materials Institute, Colorado School of Mines, Golden, Colorado, 1989), p. 605.
6. F. Dowell, *Mat. Res. Soc. Symp. Proc.* **134**:33, 47 (1989).
7. F. Dowell, *Nonlinear Structures in Physical Systems*, L. Lam and H. C. Morris, eds. (Springer-Verlag, New York, 1990), p. 232.

8. F. Dowell, in *Liquid Crystalline Polymers*, R. A. Weiss and C. K. Ober, eds. (American Chemical Society, Washington, D.C., 1990), p. 335.
9. F. Dowell, *Adv. Chem. Phys.* (in press).
10. D. Demus, H. Demus, and H. Zschke, *Flussige Kristalle in Tabellen* (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1974); D. Demus and H. Zschke, *Flussige Kristalle in Tabellen II* (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1984).
11. D. Coates and G. W. Gray, *J. Phys.* (Paris) **36** (Coll. 1):365 (1975); I. C. Lewis and C. A. Kovac, *Mol. Cryst. Liq. Cryst.* **51**:173 (1979).
12. E. M. Barrall II and J. F. Johnson, in *Plastic Crystals and Liquid Crystals*, Vol. 2, G. W. Gray and P. A. Winsor, eds. (Wiley, New York, 1974), p. 254.
13. G. W. Smith and Z. G. Gardlund, *J. Chem. Phys.* **59**:3214 (1973); G. W. Smith, Z. G. Gardlund, and R. J. Curtis, *Mol. Cryst. Liq. Cryst.* **19**:327 (1973); D. A. Dunmur and W. H. Miller, *J. Phys.* (Paris) **40** (Coll. 3):141 (1979).
14. F. Dowell, research to be published.
15. F. Dowell, *Phys. Rev. A* **38**:382 (1988); **36**:5046 (1987).
16. F. Dowell, *Mol. Cryst. Liq. Cryst.* **157**:203 (1988); **155**:457 (1988).
17. F. Dowell, in *Competing Interactions and Microstructures: Statics and Dynamics*, R. LeSar, A. Bishop, and R. Heffner, eds. (Springer-Verlag, Berlin, 1988), p. 177.
18. F. Dowell, *Phys. Rev. A* **31**:2464, 3214 (1985); **28**:3520, 3526 (1983).
19. G. W. Gray and J. W. G. Goodby, *Smectic Liquid Crystals: Textures and Structures* (Heyden, Philadelphia, 1984).
20. J. W. Goodby, *Mol. Cryst. Liq. Cryst. Lett.* **92**:171 (1983).
21. E. Dubois-Violette and B. Pansu, *Mol. Cryst. Liq. Cryst.* **165**:151 (1988).
22. R. M. Hornreich and S. Shtrikman, *Mol. Cryst. Liq. Cryst.* **165**:183 (1988).
23. H. Stegemeyer *et al.*, *Liq. Cryst.* **1**:3 (1986).
24. F. Moussa *et al.*, *J. Stat. Phys.*, this issue.
25. A. Nayeem and J. H. Freed, *J. Phys. Chem.* **93**:6539 (1989).
26. P. E. Cladis, *Mol. Cryst. Liq. Cryst.* **165**:85 (1988).
27. C. Destrade, *Mol. Cryst. Liq. Cryst.* **106**:121 (1984).
28. P. E. Cladis, *J. Stat. Phys.*, this issue.
29. R. Ribotta, A. Joets, and L. Lam, *Phys. Rev. Lett.* **56**:1595 (1986).
30. M. Jaffe, *J. Stat. Phys.*, this issue.
31. G. C. Berry *et al.*, *J. Stat. Phys.*, this issue.
32. G. R. Luckhurst and G. W. Gray, eds. *The Molecular Physics of Liquid Crystals* (Academic Press, New York, 1979).
33. *Physics Today* **35**(5) (1982).
34. *Mol. Cryst. Liq. Cryst.* **165** (1988).
35. W. W. Adams and R. K. Eby, *MRS Bull.* **12**(8):22 (1987).
36. A. Blumstein, ed. *Liquid Crystalline Order in Polymers* (Academic Press, New York, 1978).
37. A. Ciferri, W. R. Krigbaum, and R. B. Meyer, eds. (Academic Press, New York, 1982).
38. *Advances in Polymer Science*, Vols. 59, 60, 61: *Liquid Crystal Polymers I, II, III* (Springer-Verlag, New York, 1984).
39. L. L. Chapoy, ed. *Recent Advances in Liquid Crystalline Polymers* (Elsevier, New York, 1985).
40. A. Blumstein, ed., *Polymer Science and Technology*, Vol. 28: *Polymeric Liquid Crystals* (Plenum Press, New York, 1985).
41. G. W. Calundann and M. Jaffe, in *Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research: XXVI. Synthetic Polymers* (Robert A. Welch Foundation, Houston, Texas, 1983), p. 247.