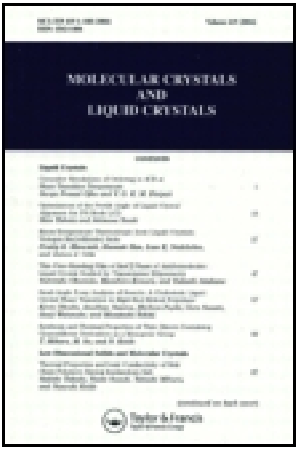


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Multipole Model of the Molecular Asymmetry in Thermotropic and Lyotropic Liquid Crystals. Volume and Surface Effects

A. Derzhanski [a] & A. G. Petrov [a]

[a] Liquid Crystal Group, Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, 1184, Bulgaria

Version of record first published: 13 Dec 2006.

To cite this article: A. Derzhanski & A. G. Petrov (1982): Multipole Model of the Molecular Asymmetry in Thermotropic and Lyotropic Liquid Crystals. Volume and Surface Effects, Molecular Crystals and Liquid Crystals, 89:1-4, 339-358

To link to this article: http://dx.doi.org/10.1080/00268948208074489

Mol. Cryst. Liq. Cryst., 1982, Vol. 89, pp. 339-358
0026-8941/82/8904-0339$06.50/0

Printed in the United States of America

Multipole Model of the Molecular Asymmetry in Thermotropic and Lyotropic Liquid Crystals. Volume and Surface Effects†

A. DERZHANSKI and A. G. PETROV

Liquid Crystal Group, Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia 1184, Bulgaria

(*Received December 16, 1981; in final form April 30, 1982*)

The molecular asymmetry of mesogenic molecules is defined as a deviation of the corresponding molecular property from spherical and axial symmetry. Three types of asymmetry—electrical, steric and biphilic, are considered using a multipole representation. Two basic molecular shapes are included—rod-like and plate-like. The first three multipoles—monopole, dipole, and quadrupole, are involved. In the steric case a monopole does not exist. The effective shape of a molecule includes not only steric, but also electrical intermolecular repulsive interactions. The biphilic asymmetry is determined by the distribution of the hydrophilic and hydrophobic groups along the molecule.

Three types of generalized fields—electrical, deformational, and biphilic, are also defined and their volume and surface sources are discussed.

The effects of the molecular asymmetry on the intermolecular interactions in thermotropic (rod-like and disc-like) and lyotropic liquid crystals are qualitatively discussed in an analogy to the electrical case. The possible pure and mixed asymmetry effects under the action of volume and surface induced generalized fields are also revealed. Some of these effects (like flexoelectricity) may have an equivalent macroscopic demonstration, but their molecular origin can be very different. Besides well known effects, there are several new effects predicted and classified. Their experimental registration may prove the effectiveness of the proposed classification.

This classification is also very useful for the common description of thermotropic and lyotropic liquid crystals.

---

† Lecture, presented at the Fourth LC Conference of Socialist Countries, Tbilisi, USSR, 5-8 October, 1981, Abstracts, A-IV.

I. QUALITATIVE DESCRIPTION OF MOLECULAR ASYMMETRY BY GENERALIZED MULTIPOLES

The notion of molecular asymmetry was used by some authors in the theory of flexoelectricity, dielectric properties of liquid crystals, elasticity, cholesteric and smectic ordering, and so on.[1-7] Many symmetry aspects, on the macroscopic and molecular level, have recently been discussed with respect to new liquid crystalline phases.[8]

Here we first systematize existing knowledge about molecular asymmetry, introducing some parameters which characterize it qualitatively and looking for some relationships between them.

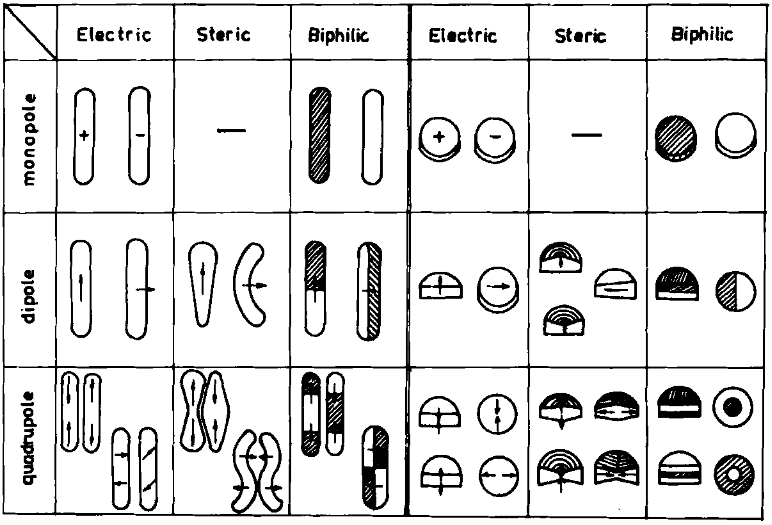
We will call "molecular asymmetry" the deviation of a corresponding molecular property from spherical and axial symmetry. Three types of asymmetry will be considered—electrical, sterical and biphilic (see below), using a multipole representation. Previously, a multipole representation was used for description of the impurity effects on smectics A, i.e., the effects of the shape of an impurity in an analogy to magnetism.[9] The discussion will be given with respect to two basic shapes of the mesogenic molecule—rod-like and plate-like. The latter molecular shape is characteristic for the recently discovered discotic mesogens.[10]

Let us start with electrical asymmetry. Its quantitative expression involves different multipoles, describing the molecular charge distribution and its deviation from spherical symmetry. Most important are the first three multipoles: the charge, dipolar, and quadrupolar moment of the molecule. The charge can be positive or negative (and most often zero), the dipolar moment—longitudinal and transverse, while for the quadrupolar moment more possibilities exist. Some of them, which are representable as combinations of antiparallel, longitudinal and transverse dipoles, are given in Table I. But there are also quadrupolar charge distributions, which cannot be represented in this way, e.g. a positively charged core surrounded by a negatively charged elongated shell.

We will consider steric asymmetry mainly with respect to the nematic-like elasticity of the liquid crystal. Unlike Ref. 9, it turned out that steric monopoles cannot be consistently defined in such a case. That is why the corresponding positions in Table I are left empty. A longitudinal steric dipole is ascribed to molecules having conical asymmetry of shape with respect to the basic rod-like[5] or plate-like shape (Table I). A transverse steric dipole, in the case of elongated molecules, is ascribed to those having banana-like asymmetry of shape, while in the case of plate-like molecules—to those having wedge-like asymmetry (Table I).

TABLE I

Schematic representation of the electric, steric, and biphilic multipoles with respect to the two basic shapes of mesogenic molecules—rod-like (left) and disc-like (right). Hatched areas in biphilic case mark the hydrophilic portions of the molecules. Different dipoles are depicted by arrows.



Concerning steric quadrupoles, some of them may be analogously represented by antiparallel combinations of longitudinal or transverse steric dipoles—see Table I.

Let us stress here that the effective shape of a molecule is a result not only of the steric (hard core) repulsive interactions, but also of the electrical intermolecular interactions. A relationship between electrical and steric dipolar asymmetry having the form of exact proportionality, was postulated by Prost and Marcerou.[10] Another relationship involving the charge is extremely important in the determination of the effective size of the head and resultant conical asymmetry of biphilic mesogens[12,13] with charged or non-charged head groups[11] (see below).

Finally let us introduce some ideas for biphilic asymmetry. This asymmetry is determined by the distribution of the hydrophilic or hydrophobic groups along or across the molecule. A positive "biphilic charge" will characterize high solubility of the molecule as a whole in water, while negative "biphilic charge" will characterize its high solubility in oil (positive charge is represented by hatched areas in Table I). Hydrophilicity is mainly connected with the presence of charged or polar groups and especially groups capable of hydrogen bond formation. A "biphilic dipole" can be ascribed to molecules, one half of which (in the longitudinal or transverse direction) is hydrophilic and another part is hydrophobic. "Amphiphilic quadrupoles," we will ascribe, e.g., to molecules with a hydrophilic middle part and hydrophobic tails or hydrophobic periphery (discotic mesogens) or *vice versa.* Let us stress, however, a characteristic feature of amphiphilic charges—oppositely to the electrical case, attraction takes place between equal and repulsion between opposite "amphiphilic charges." Consequently, the analogy must take this point into account.

Summarizing, we can say that although these three types of asymmetry are not completely independent and relations between the last two of them and the electrical asymmetry exist, as mentioned above, it does not seem possible at present to express all of them in terms of asymmetry of charge distribution.

We will see in what follows that the separate introduction of three types of asymmetry of mesogenic molecules and consideration of combinations of them is very convenient for the common discussion of many effects in thermotropic and lyotropic liquid crystals.

II. GENERALIZED FIELDS AND POTENTIALS

To continue our discussion, it is necessary to introduce generalized fields with which generalized multipoles interact. These fields can be considered as acting in the volume of the liquid crystal or at its surface.

In the electrical case, it is the electrical field **E** as a gradient of the scalar potential U that acts upon the electrical multipoles of the molecules at any point of the liquid crystal.

In the steric case it is natural to employ the invariant vectorial expressions[1] of the two basic deformations in a nematic liquid crystals (splay **S** and bend **B**) as generalized steric fields:

$$\mathbf{S} = \mathbf{n} \operatorname{div} \mathbf{n} \tag{1}$$

$$\mathbf{B} = -\mathbf{n} \times \operatorname{rot} \mathbf{n} \tag{2}$$

(**n** is the director). Note that two separate fields should be considered in this case. They cannot be, in general, represented as gradients of one scalar field, so that a steric potential will not be introduced. This is consonant with the non-introduction of a steric monopole. In the case of smectics A or lyotropics, it is only the splay field **S** which comes into play.

For the introduction of biphilic potential and biphilic field by analogy with electricity, one should use a standard biphilic charge (e.g., a H_2O molecule) and look for its standard free energy in different zones of the liquid crystal—lyotropic or thermotropic. Steep changes in the standard free energy take place at various interfaces, such as oil–water, air–water, liquid crystal–air, and at the interfaces between hydrophobic and hydrophilic zones in lyotropics. These are just the planes where strong biphilic fields **A** will be considered to act. There are also examples of gradual intermixing of two liquids e.g., the H_2O-nitrobenzene contact zone. In this case the biphilic field will be weaker but extended over a substantial distance (Figure 1). The quantitative definition of the biphilic potential makes use of the expression for the

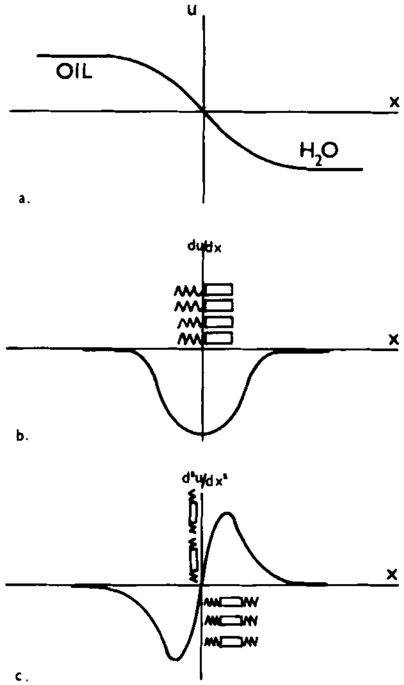


FIGURE 1 Distribution of the biphilic potential and its derivatives at an oil–water interface.

a. Biphilic potential shown as a free energy of transfer of a water molecule across the interfacial region.

b. Biphilic field **A** as a first derivative of the biphilic potential and the corresponding orientation of biphilic dipoles at the interface.

c. Gradient of the biphilic field **A** as a second derivative of the biphilic potential and the corresponding orientations of biphilic quadrupoles at both sides of the interface.

chemical potential μ of a standard molecule (e.g., H_2O or CH_4) across the interfacial region, which must have a constant value in equilibrium:

$$\mu = u(x) + kT \ln c(x)$$

where $c(x)$ is the molar concentration of the water (oil) molecules at the point x, and $u(x)$—the standard free energy (free energy of transfer) of the water (oil) molecule at the point x.

The simultaneous definition of biphilic charge and biphilic potential could be achieved by a model in which $u(x)$ is proportional to the product of the surface area of the molecule a and a specific surface energy $\gamma(x)$ which depends on the composition of the interfacial region at the point x:

$$u(x) = \alpha a \gamma(x)$$

The coefficient α takes the value $+1$ for a completely hydrophilic molecular surface (H_2O) and -1 for a completely hydrophobic one (CH_4). For bigger and more complex molecules (e.g., glycerol, benzene) it may take intermediate values. Now αa is the biphilic charge of the molecule. (Biphilic dipoles would be characterized by dividing their surface into two parts with respect to biphilic charges $\alpha_1 a_1$ and $\alpha_2 a_2$, where sign $\alpha_1 = -\text{sign } \alpha_2$ etc).

$\gamma(x)$ is the biphilic potential, which has the meaning of a position dependent surface tension. For convenience its zero value could be taken at the point of maximal slope $d\gamma/dx$ (i.e., the point of maximal biphilic field—Figure 1). For an oil-water interface the difference between the asymptotic values of $\gamma(x)$ in the oil and in the water should be equal to the oil-water interfacial tension i.e., $\gamma(-\infty) - \gamma(+\infty) = 50$ erg/cm^2.

From the condition of constancy of the chemical potential $\mu = \text{const}$, one gets at equilibrium:

$$c(x) = c_0 \exp\left(-\frac{\alpha a \gamma(x)}{kT}\right),$$

i.e., the well known formula for the concentration distribution of charged molecules in an external field.

The distance dependence of the concentration of one type of molecule in a critical binary liquid mixture (AB) in contact with a wall has been studied by Fisher and de Gennes.[41] When molecules of type A are preferentially adsorbed onto the wall and the mixture is far above its critical point T_c the concentration profile is of the type $c(x) \sim$

$\exp(-x/\zeta)$, where x is the distance from the wall and ζ is the correlation length of the density fluctuations:

$$\zeta = \zeta_0\left(\frac{T - T_c}{T_c}\right)^{-\nu}$$

$\nu = 0.63$ is the critical exponent.

For our purpose, one can imagine a hydrophilic wall in contact with oil containing a small amount of water (or other hydrophilic molecules) or a hydrophobic wall in contact with water containing a small amount of oil.

If a critical binary mixture approaches its critical temperature from above, the exponentially decaying concentration profile is replaced at distances $x < \zeta$ with the power dependence $c(x) \sim x^{-1/2}$, i.e., the spatial extension of the wall-induced perturbation becomes much longer.[41] Such critical behavior of the concentration profile has very recently been experimentally established in the critical mixture nitrobenzene-*n*-hexane, where nitrobenzene is strongly adsorbed onto a silica wall.[42] From our point of view this is an example of a surface-induced biphilic field near a hydrophilic surface.

The attractive interaction of two parallel identical plates with a distance D between them when immersed in a binary liquid mixture has also been considered.[41] Due to the preferential adsorption of the type A molecules and the deviation of their concentration near the walls from the unperturbed value, an extra term in the free energy of the system arises. Far from T_c this coupling energy term is $U_{12} \approx -kT/\zeta_0^2 \exp(-D/\zeta)$. In the limit $T \rightarrow T_c$ (or $D < \zeta$) a power law is predicted: $U_{12} \approx -kT/D^2$.

These general results can be directly applied with our concept of biphilic interactions. In the language proposed above, we can say that from a biphilic field between two identical surfaces (hydrophilic or hydrophobic) an *attraction* between them arises. The distance dependence of the interaction energy far from the critical point resembles the screened Coulomb interaction of two (oppositely) charged plates in an electrolyte, the role of Debye screening length being played by the correlation length ζ, which in this case is of the order of one molecular length. This points out that in general, biphilic multipoles would interact *via* a screened Coulomb-type biphilic potential. That means that in most cases biphilic interactions are rather short range. Possibilities for long range interactions exist, according to the results of Fisher and de Gennes, in critical oil-water mixtures.

The biphilic interactions we considered above as due to the perturbation of the local *concentrations* in binary mixtures are not to be confused with the hydration[43] or solvation[44] forces in pure liquids due to the perturbation of the local *order* of the liquid (orientation, density etc.). For comparison, hydration forces (short ranged too) between two identical surfaces are *repulsive.*[43]

III. ASYMMETRY OF THE SOLID SUBSTRATES

The asymmetry of various types of solid substrate can be considered as the origin of surface-induced generalized fields:

1. Electrical case—charged or dipolar surfaces.
2. Steric case—specific "dipolar" microtopography of the surface (Figure 2a & b).

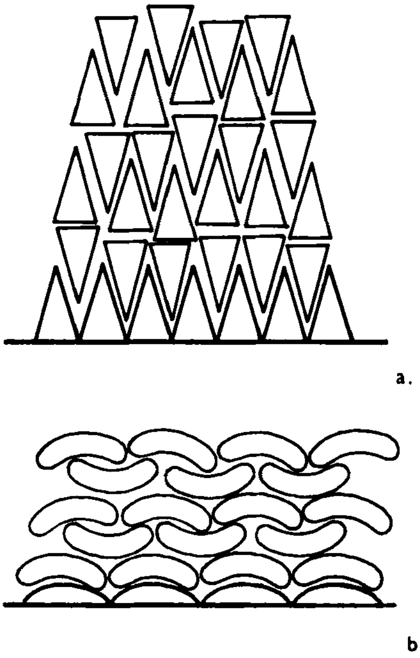


FIGURE 2 Steric-dipolar microtopography of a substrate surface and the corresponding surface orientation of the steric dipoles.
a. homeotropic case—longitudinal steric dipoles.
b. planar case—transverse steric dipoles.

3. Biphilic case—hydrophilic or hydrophobic surfaces. Some combinations can also be considered. The usual way to get hydrophobic surfaces is by adsorption of monolayers of surfactants onto glass plates. But recently, a deeper insight into the orienting mechanism of adsorbed lecithin monolayers on MBBA was given.[14,15] Their homeotropic orienting action turned out to be connected not only with the hydrophobic interactions with the butyl tails of MBBA, but also mainly with the presence of vacancies (holes), since condensed monolayers with no holes strikingly lose their orienting action. Such a hydrophobic surface with molecular holes is an example of a combination of steric and biphilic asymmetry of the surface.

Adsorption of ionic or zwitterionic surfactants provides us with examples of the combination of electrical and biphilic asymmetry. As above, the biphilic field is localized in the close vicinity of the substrate. An idea of its spatial variation is given by the corresponding halves of Figure 1b.

IV. MOLECULAR ASYMMETRY, INTERMOLECULAR INTERACTIONS AND STRUCTURE OF THE LC

To begin our discussion of the influence of molecular asymmetry on the intermolecular interaction and the structure of liquid crystals, let us stress that molecular asymmetry is not a basic prerequisite for liquid crystal ordering. Historically, the attempt of M. Born to describe nematic order as a result of the interaction of electrical dipoles was not in accordance with the experimental situation of non-polar molecular order. On the contrary successful theoretical models of the uniaxial ordering which is a basic characteristic of the liquid crystal state suffice to use cylindrically symmetrical hard rods or plates (Onsager model)[16,17] or the anisotropy of the electronic polarizability (Maier–Saupe model[18]) which is intrinsically inherent to such symmetrical shapes. So we will look upon the effect of molecular asymmetry against the background of the uniaxial ordering provided by basic rod-like or plate-like shapes. We will try to explain qualitatively details on the molecular order in different mesophases such as deviations from this background ordering caused by a given type of molecular asymmetry or a combination of them.

First we will discuss the effects of the molecular asymmetry in the absence of generalized fields, i.e., the consequences of each type of molecular asymmetry on the intermolecular interactions and the structure of liquid crystals, and the possibility of a unique description of these consequences based on our systematics. Then we will look for some combined effects.

IV.1. Electrical asymmetry

IV.1.1. Monopoles: The influence of electrical charges upon intermolecular interactions in thermotropics is usually negligible because of their small volume density and the essentially non-orientational character of these interactions. Important exceptions are charge-transfer complexes in mixtures of donor and acceptor mesogens.[19] In lyotropics, the charges of the hydrophilic head groups determine to a great extent the effective size of the head (steric asymmetry) and in this way the structure of the lyotropic phase (lamellar, cubic, hexagonal, nematic I, nematic II, or micellar). Many possibilities for changing the charge and consequently the structure of the phase exist in lyotropics (pH, ionic strength etc.) The transition from nematic I (rod-like micelles) to nematic II (plate-like micelles) with a small increase in the ionic strength[20] can be discussed on such a basis. Another example of this kind is the formation of lamellar structures from molecular solutions of single chain ionic amphiphiles (acids) by titration, when the charge of the head group is neutralized.[21]

IV.1.2. Dipoles: The electrostatic interaction of permanent dipoles often leads to a compensation of the dipolar asymmetry of the mesogenic molecules by suitable mutual orientation of neighbors so that the resulting mesophase is nonpolar, i.e., with higher symmetry than the constituent molecules. In nematics, antiparallel orientation of dipolar moments giving rise to antiferroelectric short range order is well known. It is reflected in the sudden decrease of the mean dielectric permittivity of the nematic phase with respect to the permittivity of the isotropic phase at the phase transition isotropic–nematic. Such antiferroelectric short-range order may be not only electrically determined (see the theory[22] including longitudinal moments only), but also sterically determined (see below).

Examples of true ferroelectric ordering due to dipole–dipole interaction have not been found up to now in liquid crystals. We are able to predict that in discotic phases, the combination of columnar order and a longitudinal dipole can result in a permanent polarization along the column axis.

When intermolecular interactions of the biphilic type lead to liquid crystal structures with a high degree of parallel molecular order of neighbors, like different lyotropic phases, the orientation of the dipolar moment of the head group in zwitterionic amphiphiles contributes substantially to the effective cross section of the head, i.e., the steric asymmetry of the molecule. Longitudinal dipolar moments, of which reorientation around the short molecular axis is forbidden, lead to a higher equilibrium area per head group due to electrostatic repulsion, while transverse dipoles, for which rotation around the long molecular axis is free, attract each other and lead to a smaller equilibrium area per head.

IV.1.3. Quadrupoles: The role of electrical quadrupoles in thermotropics is relatively well understood.[7] Interaction between adjacent quadrupoles composed of two antiparallel longitudinal dipoles favors, by means of longitudinal displacement, relative two-molecular correlations of the type middle–end, i.e., a nematic phase or a smectic C phase with large tilt (Cabib and Benguigui model[23]). On the other hand the interaction between adjacent transverse quadrupoles favors middle–middle correlations, i.e., smectic A phase or smectic C phase with low tilt, when some longitudinal components of the antiparallel dipoles are also present (McMillan model[24]).

In disc-like mesogens, transverse quadrupoles will favor relative positions involving center-periphery, i.e., a tilted columnar phase. Longitudinal quadrupoles should prevent formation of columnar phases and lead to a nematic phase.

IV.2. Steric asymmetry

IV.2.1. Monopoles: no effects.

IV.2.2. Dipoles: In macroscopically non-deformed structures, the steric dipoles of adjacent molecules are often antiparallel in order to compensate for the steric asymmetry of the single molecule. This corresponds to a minimum in the elastic energy of the medium. Because of the coupling between the electrical and steric dipoles, this also leads to an antiferroelectric short-range order in nematics, which is, however sterically determined. This leads again to a decrease of the mean permittivity of the nematic phase by a decrease of both its components ($\epsilon_{\parallel}$ and $\epsilon_{\perp}$).[2]

In disc-like mesogens, longitudinal steric dipoles should, in general, prevent formation of columnar phases—such steric asymmetry at the condition of dense packing can be best compensated in a discotic nematic phase.

IV.2.3. Quadrupoles: The steric interaction of longitudinal steric quadrupoles also favors middle–end relative positioning, i.e., a nematic phase or a smectic C with large tilt (Van der Meer model),[7] while the interaction of adjacent transverse quadrupoles—middle–middle and end–end position, i.e., smectic A or smectic C phase with low tilt (zig-zag model).[25]

In disc-like mesogens, transverse quadrupoles will again favor center-periphery positioning, leading to a tilted columnar phase. Longitudinal quadrupoles should prevent formation of columnar phases.

IV.3. Biphilic asymmetry

IV.3.1. Monopoles: these determine the hydrophilicity of the liquid crystal as a whole and its solubility properties—for polar and nonpolar additives.

IV.3.2. Dipoles: As a consequence of the basic property of biphilic charges (attraction of equal, repulsion of opposite), the favorable orientation of longitudinal biphilic dipoles is already parallel for lateral neighbors and antiparallel for neighbors in the longitudinal direction. Such interactions probably lead to formation of bilayer smectics A when a strong polar group is situated at one end of the molecule,[26] i.e., a hydrophilic and hydrophobic portion of the smectogenic molecule can be distinguished. This bilayer structure is at the same time antiferroelectric.

An example of the second type—antiparallel orientation of longitudinal neighbors—is provided by the dimer formation in alkoxybenzoic acids. The hydrophilic parts of these acids (—COOH groups) are connected in dimers by means of hydrogen bonding.[27] This is a typical hydrophilic interaction. The dimer formation can be considered as a manifestation of the tendency for the compensation of longitudinal biphilic dipoles. The dimer itself can be already described by a biphilic quadrupole.

IV.3.3. Quadrupoles: The association between longitudinal biphilic quadrupoles is already of the type middle–middle/end–end, and favors the formation of smectic structures of the monolayer type. This is in agreement with the behavior of mesogens with polar groups (hydrophilic part) situated in the middle of the molecule. It is manifested best when the biphilic quadrupole is big enough, i.e., at sufficient length of the hydrophobic end substituents (alkyl chains), as is observed experimentally in homologous series of rod-like mesogens.[28]

All disc-like mesogens synthesized up to now are characterized by a hydrophobic periphery (alkyl chain substituents) and a more hydrophilic central part. It means that the formation of columnar phases (center–center association) implies the interaction of biphilic quadrupoles as an important part of the intermolecular interaction. For this interaction to be strong enough, a sufficient chain length is again necessary.

IV.4. Some combined effects

The combination of electrical charge and biphilic dipole is important for determination of the steric asymmetry of amphiphiles (see above). The same is valid for the combination of the electrical and biphilic dipole. This combination is also responsible for the formation of antiferroelectric bilayer smectics A.

The combined action of electrical and steric dipoles giving rise to antiferroelectric short-range order in nematics was also considered above.

If the non-polar part of a smectogenic molecule is rather bulky (a combination of biphilic and steric dipole), formation of an inverted cubic phase (smectic D)[29,30] and eventually an inverted hexagonal phase (in mixtures) can be expected.

A combination of biphilic dipole and quadrupole effects may explain the formation of a smectic phase on mixing a "dipolar" and a "quadrupolar" nematic, as in Ref. 40. To make an analogy with lyotropic lamellar phases, "quadrupolar" molecules could be considered as a hydrophobic solvent in which biphilic dipoles associate to form lamellar structures.

Finally, let us consider the combined influence of the quadrupoles. As we have already explained the longitudinal amphiphilic quadrupoles by association of the type middle–middle and end–end favor smectic A formation. This is enhanced by the transverse electrical quadrupoles, eventually leading to a smectic C transition.[24] Alternatively or simultaneously, transverse steric quadrupoles lead to the same effect—the so called "zig-zag" model[25] of the smectic C phase.

In both these models of the C phase, molecular reorientations around the long axis are strongly hindered.

However, both electrical and steric longitudinal quadrupoles will counterbalance the smectic A arrangement, as we have already discussed. This will result in a smectic C with free reorientations around the long molecular axis or a nematic phase.

V. MULTIPOLES IN THE PRESENCE OF GENERALIZED FIELDS

As we have already noted, the fields of interest may be volume-induced or surface-induced. Let us consider first the interaction of each type of multipole with its corresponding field.

V.1. Electrical asymmetry and electric field

i. Charged molecules (ions) experience a force proportional to the electric field **E**.

ii. Dipoles experience a force proportional to the gradient of the electric field [grad $|\mathbf{E}|$] and a torque proportional to the field.

iii. The presence of a dipolar moment leads to a difference between the static and the high-frequency dielectric permittivity of the mesophase ($\epsilon_{ii}^{0} \neq \epsilon_{ii}^{\infty}$).

iv. Quadrupoles experience a torque proportional to the gradient of the field (Grad **E**).

v. The jump in the quadrupolar density of uniaxially oriented quadrupoles at the surfaces of the liquid crystal is equivalent to a surface dipolar moment, which, under the action of an electric field **E**, gives rise to a surface torque.

V.2. Steric asymmetry and steric field

i. Monopoles do not exist.

ii. Steric dipoles must be oriented in a deforming field, as qualitatively suggested by R. Meyer (1969) and should experience a force if this field is not homogeneous.

iii. Analogously to the electric case, the energy of steric quadrupoles should depend on the derivatives of the deforming field, e.g., div **S**. But it means that steric quadrupoles contribute to the non-linear elasticity described by the term K_{13} div ($\mathbf{n}$ div$\cdot\mathbf{n}$).

iv. The presence of a "steric dipole" leads to a difference between static and dynamic elastic constants ($K_{ii}^{0} \neq K_{ii}^{\infty}$).

v. In favor of the above-mentioned conclusion concerning K_{13} is also the next analogy with electrical quadrupoles—the density jump of steric quadrupoles should lead to a surface density of oriented steric dipoles. This is illustrated by Figure 3. The latter density, however, should lead to surface orientational strains and in definite cases to a spontaneous deformation of the free surface, due to the absence of steric compensation. This is also typical to the non-linear elasticity; because of its divergent character, it influences the boundary conditions only. Spontaneous deformations at the free surface have already been observed.[36]

V.3. Biphilic asymmetry and biphilic field

i. In the presence of a gradient in the potential of the amphiphilic field (e.g., at an oil–water interface), the "biphilic charges" will move towards the water or oil phase in accordance with their sign. This property is demonstrated, for example, in the distribution of different molecules in lyotropic liquid crystal phases and in the solubilization phenomenon.

ii. The "biphilic dipoles" will be localized just at the interface and oriented normally to it (Figure 1b).

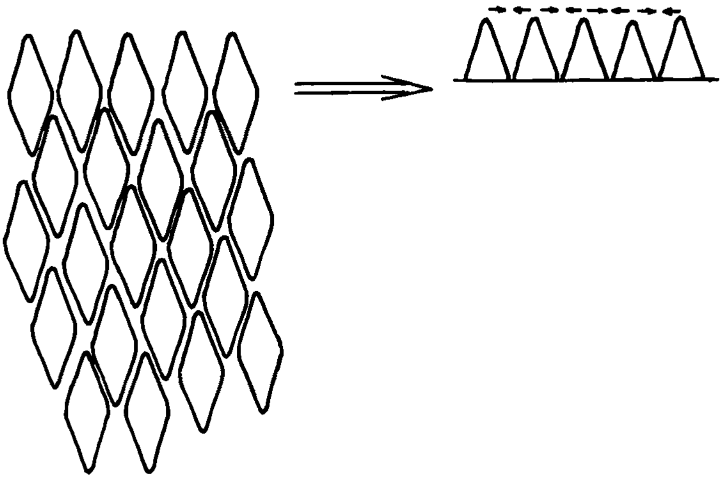


FIGURE 3 Jump in the density of the oriented steric quadrupoles at a free surface and the equivalent surface density of steric dipoles leading to orientational strains.

iii. "Quadrupoles" will also experience an orientating action, but according to the sign of the "quadrupole," they will orient tangentially or normally to the interface (Figure 1c).

These properties (ii and iii) are demonstrated by the building-up of two-dimensional liquid crystals—monolayers with an oil–water or air-water interface,[31] by the building up of volumes of lyotropics,[32] and also by the orientation of thermotropic mesogenic molecules at a free surface and, with respect to hydrophilic or hydrophobic supports, with both possibilities—homeotropic (the "dipoles") and planar or homeotropic (the "quadrupoles"). It is interesting to note that according to the space variation of the first derivative of the biphilic field (i.e., the second derivative of the biphilic potential) (Figure 1), biphilic quadrupoles should be localized not just at the interface (like dipoles), but also at one or another side of it. At one of these two positions, the orientation of the quadrupole will be normal to the interface (homeotropic) while at the other it will be parallel (planar). An example of the planar orientation of biphilic quadrupoles is the observation of Grandjean textures of cholesteric esters (hydrophilic middle part) at hydrophilic substrates and of focal-conic textures at hydrophobic substrates.[33] In the last case of solid supports, the corresponding half of Figure 1c is relevant.

iv. To discuss further the effect of biphilic dipoles, a corresponding response function like ϵ or K describing the biphilization of the liquid crystal in the presence of a biphilic field should be introduced.

v. The surface jump in the density of oriented biphilic quadrupoles will be equivalent to a surface biphilic dipolar moment.

V.4. Mixed Interactions

Up to now, we have considered the interaction of different types of multipoles with the corresponding generalized fields. Let us look now for some examples of mixed interactions. As an example, we have the interaction of the deforming field with electrical multipoles. A direct influence of this field upon the charges and dipoles cannot be expected. However, the orientational deformation of uniaxially oriented electric quadrupoles leads to electrical polarization of the structure—the quadrupolar flexo-effect of Prost and Marcerou.[11] This polarization in turn creates a depolarizing electric field which acts on the charges and moves them, and in the case that the field is non-homogeneous, it will also move the dipoles, which are already preferentially oriented.

Analogously to this, the deformation of a liquid crystal structure with "steric quadrupoles" should lead to "steric polarization"–"sterization" of the medium. Such a sterization could act upon the steric "dipoles" analogously to that discussed above.

Finally, a deformation of amphiphilic uniaxially oriented "quadrupoles" (e.g., in a smectic A) should lead to amphiphilization" of the medium, i.e., to a gradient of its hydrophility. This last gradient, equivalent to an amphiphilic field could influence the distribution and the orientation of small amounts of hydrophilic, hydrophobic, or biphilic materials.

A direct influence of the electrical field upon the steric and amphiphilic multipoles is not to be expected. The same seems to be valid for the biphilic field with respect to electrical and steric multipoles. Why then is the deformational field more universal? The reason is that in all three cases the starting state consists of uniaxially oriented quadrupoles and the deformational field itself simply reflects the fact that this orientation is changed.

VI. COMBINATIONS OF ASYMMETRIES

Here, the effects connected with combinations of asymmetries will be considered. Best studied are the effects arising from the simultaneous presence in the mesogenic molecules of two kinds of dipolar asymmetry. The combination of an electrical and a steric dipole leads to the well known dipolar flexo-effects[1] (R. Meyer, 1969)—direct and converse. The combination between electrical and biphilic dipoles should lead to an "ampho-electrical" effect, direct as well as converse. The direct effect is in fact also well known—this is the surface polarization under the action of a biphilic field. Most often this is observed at an interface air–water for monolayers and oil–water for lyotropics. But this phenomenon also exists in thermotropics—at a free surface or at the contact with hydrophilic or hydrophobic supports[34,35] (Prost & Pershan, 1976; Petrov & Derzhanski, 1977). The converse "ampho-electrical" effect should be expressed in an "amphiphilization" of the medium, i.e., causing an amphiphilic gradient or giving a change in amphiphilic gradient under the action of an electric field.

The third combination—between steric and biphilic dipoles—leads to an "amphosteric" effect. The direct one is known—this is the presence of those orientational strains and spontaneous deformations over interfaces which orient biphilic dipoles of thermotropic liquid crystals[36] (Meyer & Pershan, 1975) and of lyotropic lamellar and hexagonal phases[12] (Petrov & Derzhanski, 1976), and the pore forming action of conical lipids[37] (Petrov, Mitov & Derzhanski, 1979). The converse effect should be expressed in an "amphiphilization" of the medium, experiencing an orientational deformation. As in the electrical case, the combination between a geometrical and a biphilic dipole gives an effect equivalent to an amphiphilic quadrupole only.

The combinations between different types of charges lead also to some known and some new effects. For example, the effect of redistribution of hydrophilic and hydrophobic ions between water and oil zones in lyotropics and membranes is known. This effect creates a surface potential and diffuse double layers, and connected with them is the electrical component of the disjoining pressure,[38] which essentially determines the stability of some two-dimensional liquid crystals, e.g., black films. Inversely, the application of an electrical field, by changing the space distribution of hydrophilic or hydrophobic ions should change the "amphiphilization" of the medium. Let us call these effects "electrobiphilic" effects.

The last combination—of a steric and electrical quadrupole—should lead to a specific surface flexo-effect—a relationship between surface polarization and surface torques. This effect, in which the essential role is played by the non-linear elasticity K_{13}, has no volume analogue.

VII. CONCLUSION

Let us summarize the situation. In principle, the eight elements of asymmetry introduced by us for each of the two chosen basic shapes, taken separately and in twos and combined with the three generalized fields, lead to

$$3.8 + 3\cdot\binom{8}{2} = 24 + 84 = 108$$

different effects. We must count separately the effects in the absence of external fields as well:

$$8 + \binom{8}{2} = 36$$

More combinations are still possible—e.g., by threes, as well as generalized tensorial fields as for the case with quadrupoles.

By including higher order multipoles (octupoles), the scheme can be used to discuss chirality effects.[39] Such a development has been made in Osipov—Pikin's theory of chiral smectics C.

To conclude, a large number of effects connected with molecular asymmetry (some known and some new) can be discussed within a general framework. We have considered here a small part of these effects and have clarified some of them as non-existing. We see that some of the effects may have an equivalent macroscopic manifestation (e.g., flexoelectricity), but their molecular origin may be very different. This of course makes it difficult to use some relationships between the macroscopically measurable parameters of mesophases (e.g., flexocoefficients) and their molecular characteristics (considered earlier as unequivocal). The experimental registration of the predicted new effects may prove the effectiveness of the proposed classification. It is also very useful for the common description of thermotropic and lyotropic liquid crystals.

References

1. R. B. Meyer, *Phys. Rev. Lett.*, **22**, 918 (1969).
2. A. Derzhanski and A. G. Petrov, *Phys. Lett.*, **36A**, 483 (1971).
3. W. Helfrich, *Z. Naturforsch.*, **26a**, 833 (1971).
4. W. Helfrich, *Mol. Cryst. Liq. Cryst.*, **21**, 187 (1973).
5. H. Gruler, *J. Chem. Phys.*, **61**, 5408 (1974).
6. J. P. Straley, *Phys. Rev.*, **A14**, 1835 (1976). A. Derzhanski, A. G. Petrov and I. Bivas, *Adv. in Liquid Crystal Research and Applications*, Ed: L. Bata, Pergamon Press, Oxford—Akad. Kiadó, Budapest, 1980, vol. 1, p. 505.
7. B. W. van der Meer, Thesis, Groningen University, 1979.
8. J. Prost, *Proc. Colloque Pierre Curie, Paris,* 1980.
9. P. S. Pershan and J. Prost, *J. Appl. Phys.*, **46**, 2343 (1975).
10. S. Chandrasekhar, D. K. Sadashiva and K. A. Suresh, *Pramana,* **9**, 471 (1977).
11. J. Prost and J. P. Marcerou, *J. Phys.* (*Paris*), **38**, 315 (1977).
12. A. G. Petrov and A. Derzhanski, *J. Phys.* (*Paris*) **47**, 155 (1976).
13. A. G. Petrov, S. A. Seleznev and A. Derzhanski, *Acta Phys. Polonica,* **A55**, 385 (1979).
14. K. Hiltrop and H. Stegemeier, *Ber. Bunsenges. Phys. Chem.*, **82**, 884 (1978).
15. K. Hiltrop and H. Stegemeier, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 61 (1978).
16. L. Onsager, *Ann. N.Y. Acad. Sci.*, **51**, 627 (1949).
17. P. G. de Gennes, *The Physics of Liquid Crystals,* Claredon Press, Oxford, 1974.
18. W. Maier and A. Saupe, *Z. Naturforsch.*, **14a**, 882 (1959), **15a**, 287 (1960).
19. N. K. Sharma, G. Pelzl, D. Demus and W. Weißflog, *Z. Phys. Chem., Leipzig,* **261**, 579 (1980).
20. J. Charvolin, A. M. Levelut and E. T. Samulski, *J. Phys.* (*Paris*) *Lett.*, **40**, L-587 (1979).
21. W. R. Hargreaves and D. W. Deamer, *Biochemistry,* **17**, 3759 (1978).
22. N. V. Madhusudana and S. Chandrasekhar, *Pramana, suppl.*, **1**, 57 (1973).
23. D. Cabib and L. Benguigui, *J. Phys.* (*Paris*), **38**, 419 (1977).
24. W. L. Mc Millan, *Phys. Rev.*, **A8**, 1921 (1973).
25. A. Wulf, *Phys. Rev.*, **A11**, 365 (1975).
26. P. E. Cladis, *Phys. Rev. Lett.*, **35**, 48 (1975); P. E. Cladis, R. K. Bogardus, W. B. Daniels and G. N. Taylor, *Phys. Rev. Lett.*, **39**, 720 (1977).

27. B. Deloche and B. Cabane, *Mol. Cryst. Liq. Cryst.*, **19**, 25 (1972).
28. D. Demus, H. Demus and H. Zaschke, *Flüssige Kristalle in Tabellen,* VEB Deutscher Verlag für Grundstoff-industrie, Leipzig, 1974.
29. D. Demus, G. Kunicke, J. Neelsen, and H. Sackmann, *Z. Naturforsch.*, **23a**, 84 (1968).
30. A. Tardieu and J. Billard, *J. Phys.* (*Paris*), **37**, 479 (1976).
31. G. L. Gaines, Jr., *Insoluble Monolayers at Liquid–Gas Interfaces,* Interscience, N.Y., 1966.
32. P. A. Winsor, *Chem. Rev.*, **68**, 1 (1968).
33. A. Derzhanski, S. Naydenova, and B. Taneva, *C. R. Acad. Bulg. Sci.*, **31**, 517 (1978).
34. J. Prost and P. S. Pershan, *J. Appl. Phys.*, **47**, 2298 (1976).
35. A. G. Petrov and A. Derzhanski, *Mol. Cryst. Liq. Cryst. Lett.*, **41**, 41 (1977).
36. R. B. Meyer and P. S. Pershan, *Solid State Comm.*, **13**, 989 (1973).
37. A. G. Petrov, M. D. Mitov and A. Derzhanski, *Adv. Liquid Crystal Research and Applications,* Ed: L. Bata, Pergamon Press, Oxford—Akad. Kiadó, Budapest 1980, vol. II, p. 695.
38. A. D. Scheludko, *Adv. Colloid Interface Sci.*, **1**, 391 (1967).
39. M. Osipov and S. A. Pikin, *Fourth Int. LC Conf. Soc. Countries, Tbilisi,* 1981, Abstract B-IV; *Kristallografia,* **26**, 263 (1981).
40. C. Oh, *Mol. Cryst. Liq. Cryst.*, **42**, 1 (1977).
41. M. E. Fisher and P. G. de Gennes, *C. R. Acad. Sci. Paris,* **287B**, 207 (1978).
42. D. Beysens and S. Leibler, *J. Phys.* (*Paris*) *Lett.*, **43**, L-133 (1982).
43. S. Marčelja and N. Radić, *Chem. Phys. Lett.*, **42**, 129 (1976).
44. I. K. Snook and W. van Megen, *J. Chem. Phys.*, **72**, 2907 (1980).