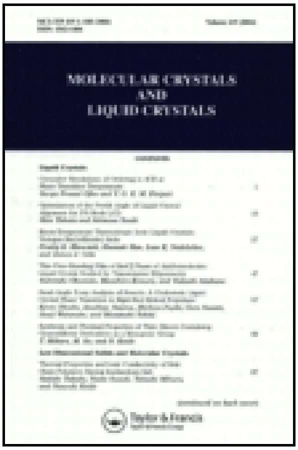

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Generalized Asymmetry of Thermotropic and Lyotropic Mesogens

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GENERALIZED ASYMMETRY OF THERMOTROPIC AND LYOTROPIC MESOGENS

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Abstract The multipole model of molecular asymmetry of rod-like and disc-like mesogens was developed by us earlier (1981). It included the electrical, sterical and biphilic asymmetry. That model was generalized later on (1985) by including the flexibility asymmetry as well. Accordingly, mesogens were classified as generalized multipoles: monopoles, dipoles, quadrupoles etc. Furthermore, the generalized dipoles were considered as functions of the generalized fields by introducing generalized polarizabilities. These new lines of development of the model are reviewed here. They are especially important for lyotropics and membranes.

Since 1981 a number of new mesogens corresponding to the theoretical predictions of the model were synthesized. We are applying our general classification to the following substances: cone-shaped discotics, flexible core discotics, discoidal amphiphilics, phasmids, biforked mesogens etc. Peculiarities in the structural organization of the tilted compounds are qualitatively discussed in a general framework based on the multipole-multipole interaction of generalized multipoles.

Such a framework is also very convenient for discussion of many effects connected to the molecular asymmetry (flexoelectricity, ordoelectricicty etc.), for a common description of thermotropic and lyotropic systems and for a directed molecular design of mesogens. It provides a catalogue of the asymmetric molecular structures, predicting a large number of possible combinations of generalized multipoles, only few of them being syntheticly realized at present.

INTRODUCTION

The problem of relating molecular structure to the properties of liquid crystals, thermotropic and lyotropic ones, is very complicated. These systems display practically all types of intermolecular interactions known in the condensed matter physics. The problem is additionally complicated by the large conformational freedom of mesogens and by the presence of additional molecular species (water, oil) in the lyotropic case.

In search for a sufficiently general but simple enough picture we developed an approach which may be called Generalized Molecular Asymmetry Model (GMAM). Being at present to some extent a qualitative one, this approach proved nevertheless a very useful and very instructive one, having large explanatory and predictive capabilities. Its development passed through the following stages:

The sterical molecular asymmetry concept (PD-concept) was first advanced by the present authors at Les Arcs (1975) and Halle (1976) LC Conferences with respect to the curvature elasticity and spontaneous curvature of lyotropics[1]. Somewhat analogical concept concerning sterical asymmetry of thermotropic nematics was developed even earlier[2]. The PDM-model (Petrov-Derzhanski-Mitov) evolved by a generalization of the PD-concept including saddle-splay effects[3], as reported[4] at Sunny Beach LC Conference (1977). In a report at Budapest LC Conference (1979) this concept was employed for a description of the spontaneous curvature generation (pore formation) by asymmetric wedge-like molecules[5]. At Tbilici LC Conference (1981) a general scheme of the molecular asymmetry of mesogens (multipole model) was proposed including electric, steric and biphilic asymmetry (E, S and B-asymmetry). The asymmetry effects were discussed by using a multipole expansion and corresponding generalized fields (E, S and B-fields) were defined[6]. At Bovec LC Conference the effects in mixtures of biphilic and steric dipoles were considered[7]. At Halle (1975) and Berkeley (1976) LC Conferences the multipole model was further generalized by introducing the flexibility asymmetry (F-asymmetry) of mesogens and flexibility field (F-field)[8]. Furthermore, the generalized dipoles are supposed to be dependent on the generalized fields by introducing generalized polarizabilities[8].

We shall review at first this development puting it in a general framework and then we will discuss some new results concerning newly synthesized mesogens and new macroscopic demonstrations of the molecular asymmetry like conformational flexoelectricity and ordoelectricity.

GENERALIZED MULTIPOLES

Speaking about "molecular asymmetry" we understand a deviation of a certain molecular property from the spherical (O(3)) and axial (D_∞) symmetry. We shall consider four types of molecular asymmetry: electric, steric, biphilic and flexible, using a multipole representation analogical to the electrostatics. Earlier another type of multipole repsentation was employed[9] for a description of the elastic impurity effects in smectics A using an analogy with magnetism. Later on similar to that approach was applied also for developing an elastic model of the protein-protein interaction in membranes[10].

Clearly , in some cases like molecular shape one could operate in terms of the specific symmetry of the molecule. But quite often molecules of different symmetry groups can be represented by one and the same generalized multipole i.e. they can manifest one and the same behaviour in the sense of our discussion. Taking into account exact details of the molecular structure is in many cases not possible but also not necessary. The generalized multipole model operates with an averaged molecular structure with a higher symmetry sufficient for the purpose of relating macroscopic to molecular properties.

It is well known that first requirement to the mesogens is a molecular shape markedly deviating from the spherical symmetry. Shape anisotropy leads to anisotropic molecular polarizability and to anisotropic intermolecular dispersion interaction, respectively. We are considering as basic ones the two most symmetrical mesogenic shapes: rod-like and disc-like (axial symmetry $D_{\infty h}$). They are represented at the two halves of Figure 1. These shapes are known to be sufficient for arising of an uniaxial molecular order of nematic type above a given packing density, even if intermolecular interactions are dominated by hard core repulsion only. Of course, such a hypothetical nematic will not display a number of properties inherent to nematic phases of lower symmetry molecules. However, such uniaxial order could be considered as a background, against which molecular asymmetry effects are better outlined.

Electric asymmetry

Quantitative expression of E-asymmetry are various multipoles describing the distribution of electric charge along the molecule and its deviation from the spheric

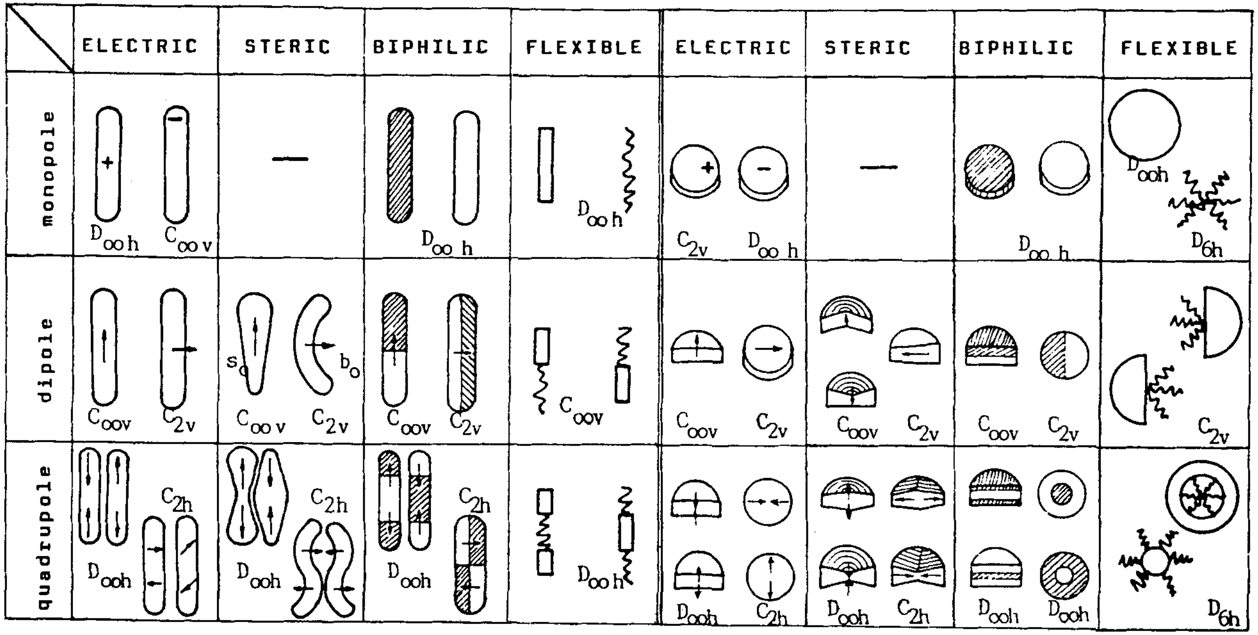

FIGURE 1. Electric, steric, biphilic and flexible multipoles with the two basic shapes of the mesogenic molecules: rod-like and disc-like. Hatched area in the biphilic case marks the hydrophobic portions of the molecules. The groups of molecular symmetry are also given. Note that different symmetry groups belong to the same generalized multipole type. This table is a catalogue of various asymmetric mesogens with only one type of asymmetry. Combinations in text.

asymmetry. We restrict our discussion to the first three terms of the multipole expansion: charge, dipole and quadrupole moment of the molecule. Their definition in the classical and in the quantum case is well known. The total electric charge of a molecule (electric monopole) can be positive, negative and zero. It is zero as a rule for thermotropics but for ionic detergents is nonzero. Electric monopole does not change the symmetry of the rod or the disc ($D_{\infty h}$), if the centre of charge coincides with the centre of mass (Fig. 1). With an off-centre situated monopole the symmetry can be reduced to $C_{\infty v}$ for rods or to C_{2v} for discs.

Total dipole moment can be longitudinal reducing the symmetry to $C_{\infty v}$ (Fig. 1) or transversal (symmetry C_{2v}) or can have both longitudinal and transversal components (symmetry C_s).

Quadrupole moment offers more possibilities. Some of them can be represented as combinations of antiparallel longitudinal dipoles preserving $D_{\infty h}$ symmetry or transversal ones reducing the symmetry to C_{2h} (Fig. 1). But there are also quadrupolar charge distributions not representable in this way e.g. a positive core surrounded by a negative axially deformed shell (symmetry $D_{\infty h}$).

Steric asymmetry

We are considering S-asymmetry in connection to the orientational elasticity of the mesophases demonstrated in splay and bend deformation of nematics, layer curvature (corresponding to a splay of the director field) in smectics and lyotropics and bending of columns (corresponding to a bend of the director field) in columnar discotic phases. This makes our case different from that of Ref. 9 dealing with the compression elasticity of layer displacement. It turned out that in our case a steric monopole could not be consistently defined[6], so that corresponding places of Fig. 1 are left empty and the multipole representation starts from the dipoles.

Longitudinal sterical dipole $\underline{s}_o$ (symmetry $C_{\infty v}$) is ascribed to molecules having a cone-like asymmetry with respect to the cylindrical[11] or discoidal[6] shape (Fig. 1). Transversal sterical dipole $\underline{b}_o$ in the case of rods is ascribed to banana-like molecules[11] while in the case of discs it is ascribed to wedge-like molecules[6] (symmetry C_{2v}). Molecular shape can combine these two asymmetries, then the sterical dipole will have the both components (symmetry C_s).

With respect to the sterical quadrupoles, some of them could also be represented as antiparallel combinations of longitudinal ($D_{\infty h}$) or transversal (C_{2h}) sterical dipoles both in the rod-like and disc-like case (Fig. 1).

We want to stress explicitly that the effective molecular shape is determined not only by the hard-core repulsive steric interactions but also by the electric intermolecular interactions. A relationship between electric and steric dipolar asymmetry was postulated[12] having the character of an exact proportionality. The possible relation between induced electric asymmetry in polarizable symmetric molecules in an electric field and their induced steric asymmetry was also noted[13]. Other relationships[14] including the charge of a lipid polar head or its longitudinal dipole moment could be useful in determining the effective size of the lipid head of an ionic or zwitterionic lipid i.e. in determining its resulting conical asymmetry[1].

Biphilic asymmetry

B-asymmetry is relatively rarely used as a concept. One could say that its applicability is limited to the lyotropics only. However, this concept can be useful in thermotropics as well[6,15]. B-asymmetry is determined by the distribution of hydrophilic and hydrophobic groups along or across the long molecular axis. A "positive" biphilic monopole is supposed to characterize the solubility of the molecule in water as a whole, this monopole having the higher value the better this solubility is. Analogically, a good solubility in oil as a whole is characterized by a "negative" B-monopole. The B-charge is a property, attributed to the molecular surface[6], following the ideas of Frenkel[16]. On Fig. 1 the positive charge is denoted by hatching the corresponding area. Biphilic mesogens (soaps, lipids etc.) display a different water solubility of both halves of the molecule. Such molecules are described by B-dipoles: longitudinal ($C_{\infty v}$ symmetry) and transversal (C_{2v} symmetry). B-quadrupoles represent α, ω - amphiphiles with two hydrophilic groups at the two ends of an alkyl chain, integral membrane proteins spaning the whole membrane, or also disc-like mesogens with hydrophopic core and hydrophilic periphery or vice versa (all belonging to $D_{\infty h}$ symmetry).

B-monopole could be defined as proportional to its surface times a specific value of a surface energy depending on the oil/water ration in the environment[6]. B-dipole could be described by the monopole value times the vector between the centers of mass of the opposite monopoles, etc.

Let us specially stress a basic property of B-monopoles[6]: contrary to the electric case here equal monopoles attract each other while opposite repel. This is in fact a basic property of the hydrophobic effect leading to a decrease of the free energy of the system when alike associates to alike. According to this point the analogy with electrostatics should take into account the inversion of the sign of the interaction, e.g. adjacent parallel dipoles will attract each other while antiparallel will repel. This is not the case with S-asymmetry: there the analogy with elecrostatics is complete.

To sum up, we can say that although the three types of asymmetry considered up to now are not completely independent one from another and the last two are somehow connected to the electric asymmetry, for the time being it does not seem possible to express all of them in terms of electric charge distribution. The separate introduction of three types of asymmetry of mesogens and the consideration of combinations between them proved very convenient for a joint discussion of many effects in thermotropics and lyotropics[6].

Flexibility asymmetry

The motivation to introduce F-asymmetry as a forth type of generalized asymmetry came from the works of Dowel[17-19]. In these papers by means of an exact calculation of the statistical sum of a lattice model the tendency for space separation of rigid and flexible molecular segments in smectic phases was demonstrated in such a way that flexible packs with flexible and rigid with rigid.

In our language rigid and flexible segments (e.g. cholesterol skeleton and its alkyl tail) could be called F-monopoles. They can be combined together in F-dipoles, F-quadrupoles etc. Some examples with respect to rod-like and disc-like mesogens are shown on Fig. 1.

Let us note that flexible segments are often hydrophobic as well, so that in many cases F-monopoles and B-monopoles coincide. But in nonionic surfactants the hydrophilic parts are also flexible. F-asymmetry and B-asymmetry are similar in that in both cases equal monopoles atract, while opposite repel. In the case of F-asymmetry this is due to the fact that a rigid segment in a flexible environment restricts the conformational freedom of adjacent flexible segments, reduces their entropy and increases the free energy of the system being as a result expeled from this environment. Analogical is the situation with a flexible segment in a rigid environment, this time its own free energy being increased (Fig. 2 a.). The similarity of B- and S-asymmetry will further be revealed later on.

F-monopoles could be assigned a value proportional to their length. F-dipoles could be defined as equal to the monopole value times the vector between the centre of mass of the opposite monopoles, etc.

Generally speaking, all types of molecular asymmetry discussed above could be dynamic characteristics of mesogenic molecules. This is especially valid for the biphilic mesogens possessing a substantial conformational freedom. Molecular asymmetry can be changed by variations of temperature, polar head hydration, pH, ionic strength etc. Most typical is the temperature influence on F-multipoles: at a specific temperature depending on the packing density and alkyl chain length the flexible segments become all-trans and rigid. The mesogenic molecule loses its character of a F-quadrupole or F-dipole becoming an entirely rigid monopole. It was shown[19] that in the case of smectics A such a rigidification can destroy the one-dimensional smectic periodicity thus explaining the transition to a re-entrant nematic phase at decreasing the temperature. Effects of rigidification of the hydrophilic and hydrophobic segments are also taking place in lyotropics below the liquid crystal - gel transition temperature. Eventually, it might be possible to trace a relationship between the molecular symmetry change under the influence of the abovementioned factors and the change of the symmetry of the various liquid crystal and gel phases as well as the order of the phase transitions for the complicated lipid polymorphism at lower temperature and degree of hydration[20] following the general method of Landau[21] and its development for the smectic polymorphism[22,23].

GENERALIZED POTENTIALS AND FIELDS

The concept of generalized multipoles is inherently coupled to the concept of generalized potentials and fields. Each type of multipole interacts with a corresponding type of field listed below. Examples of mixed interactions are also possible[8].

Electric field

The case of E-multipoles is most simple. Here a generalized field is the electric field $\underline{E}$ itself as a gradient of the scalar electric potential U: $\underline{E} = -\mathrm{grad}\ U$. E-monopoles experience a force $\underline{F}$ proportional to the field $\underline{E}$ and E-dipoles to the gradient of field $\mathrm{grad}\,|\underline{E}|$. On the other hand dipoles experience a torque $\underline{M}$ equal to their vectorial product with the field vector $\underline{E}$ while quadrupoles' torque is equal to the vectorial product of the quadrupole tensor with the vector-gradient of the field $\mathrm{Grad}\underline{E}$.

For a moment we are considering electric and other multipoles as field-independent i.e. with zero polarizability of their own. General case will be considered below.

Steric field

As we have shown[6] natural generalized fields in the steric case are splay vector $\underline{S} = \underline{n}\ \mathrm{div}\underline{n}$ and bend vector $\underline{B} = -\underline{n} \times \mathrm{rot}\underline{n}$, where $\underline{n}$ is the director (Fig. 4). We noted that in this case two separate fields have to be considered and they can not in general be represented as gradients of a potential field. That was a reason not to introduce S-monopoles and potentials.

Consequently, the lowest order forces proportional to the fields are absent and first nonzero influences on steric dipoles are torques. Expressions for the energy of S-dipoles in deformed nematics were given earlier[11,24]. These expressions contain, like electrostatics, scalar products $\underline{s}_o.\underline{S}$ and $\underline{b}_o.\underline{B}$, where steric dipoles $\underline{s}_o$ and $\underline{b}_o$ are suitably defined[25]. In the general case of nonideally oriented nematics crossed terms $\underline{s}_o.\underline{B}$ and $\underline{b}_o.\underline{B}$ arise as well[26]. These results easily yield expressions for the torques upon S-dipoles.

In the case of smectics A and lyotropics bend deformation does not exist and only splay field $\underline{S}$ is active. In that case the steric dipole of lipids was shown to be equal to the spontaneous curvature of a monolayer of lipid molecules which can be expressed e.g. via the parameters of the PDM model[1,8]:

$$c_o = (1/\delta)\ (H - C)/A_o \quad , \qquad (1)$$

where H and C are the effective cross sections of the head and chain(s) resp. , A_o is the equilibrium area per molecule (being a weighted average of H and C) and δ is the distance between the two effective planes over which the head and chain interaction is considered to be concentrated ($\delta \simeq h/2$, where h is the length of the alkyl chain). Some possibilities and examples for evaluating H and C via Monte Carlo method were discussed[14]. Eq.(1) permits qualitative conclusions concerning the effects of: the increase of the head group's charge which in turn depends on pH (increasing H), the increase of the ionic strength (decreasing H), the presence of bivalent ions (decreasing H), the temperature rise (increasing C), the presence of double bonds (increasing C), the enzymatic cleavage of lipid chains (decreasing C) etc.

From the point of view of the spontaneous curvature and its molecular interpretation according to (1) the following classification of the lyotropic phases can be done in terms of the steric asymmetry of the molecule:

$c_o \simeq 2/\delta$ i.e. $H \simeq 3C$ - micellar phase
$c_o \simeq 1/\delta$ i.e. $H \simeq 2C$ - hexagonal phase
$c_o \simeq 0$ i.e. $H \simeq C$ - lamellar phase
$c_o \simeq -1/\delta$ i.e. $H \simeq C/2$ - inversed hexagonal phase
$c_o \simeq -2/\delta$ i.e. $H \simeq C/3$ - inversed micellar phase

With steric asymmetries having intermediate values between those listed above defect phases can be realized, the defects having a structure of the next possible phase. Cubic phases with saddle curvature require a positive saddle curvature elasticity $\bar{K}$, which is also connected to the sign of molecular asymmetry ($H - C < 0$) according to the PDM-model[3].

Biphilic field

The way of introducing biphilic field and biphilic potential by using the standard free energy of a probe biphilic monopole (H_2O, CH_4) was discussed in details earlier[6]. Steep variations of the biphilic potential can be observed at various interfaces like water/oil, water/air, liquid crystal/air and also the interfaces between the hydrophilic and hydrophobic regions in lyotropics. Those are just the surfaces where strong biphilic fields $\underline{B}$ are considered to act along their normals. Charvolin[27] used a similar notion of "anisotropic field of the interface" exerting orienting action upon the alkyl chains.

Our concept of biphilic multipoles can be compared to the well known concept of hydrophilic-lipophilic balance[28,29]. Pure biphilic dipoles will be amphiphiles of HLB = 20. When HLB < 20 the amphiphile can be considered as a combination of a lipophilic monopole and biphilic dipole and when HLB > 20 it can be considered as biphilic dipole plus hydrophilic monopole. Obviously, the presence of a non-zero biphilic monopole will influence the localization of the molecule in the contact zone attracting it towards the polar or non-polar region in accordance to the sign of the monopole. This could explain the behaviour of detergents with various values of the empirical HLB number. However, the biphilic dipole is a more detailed characteristic than HLB because to B-dipoles differing in value and length could correspond one and the same HLB number calculated according to Davies' rule[29].

Considerations in Ref. 6 have shown that biphilic multipoles interact in general via biphilic potentials of a screened Coulomb type i.e in most cases they are short-range. Possibilities for long-range interactions exist in critical binary liquid mixtures[30]. Biphilic interactions are considered to be produced by local concentration variations in binary oil-water systems and they should not be confused with the hydration or solvation forces in pure liquids due to variations of the local translational or orientational order of the liquid. For a comparison, biphilic forces between two hydrophilic surfaces should be attractive (if one follows the reasoning in [30]) while hydration forces between them are repulsive[31].

Flexibility field

F-potential and F-field could be defined in layered mesomorphic states where spacial separation into rigid and flexible regions is realized[8]. F-potential of a flexible monopole could be identified with its standard free energy having low value in a flexible environment and a higher value in a rigid one due to entropy reasons discussed above. Interfaces between flexible and rigid regions are just the places where strong F-fields are considered to act in normal direction (Fig. 2). F-field is the first derivative of the F-potential and determines the force acting upon a F-monopole (Fig. 2 a.) and the torque upon a F-dipole. The force acting upon a F-dipole (Fig. 2 b.) is equal to the first derivative of the F-field i.e. to the second derivative of the F-potential[8], etc.

The flexibility asymmetry notion can be of importance in discussing smectic induction in mixtures of nematic mesogens. This notion tells us that F-dipoles should be more effective in the smectic induction than F-quadrupoles. This is so because the longitudinal force acting upon F-dipoles becomes zero just at the interface. In comparison, the force acting upon the quadrupoles being proportional to the second derivative of F-field becomes zero below and above the interface (Fig. 2 c.). Consequently, the maxima of density wave describing one-dimensional translational smectic

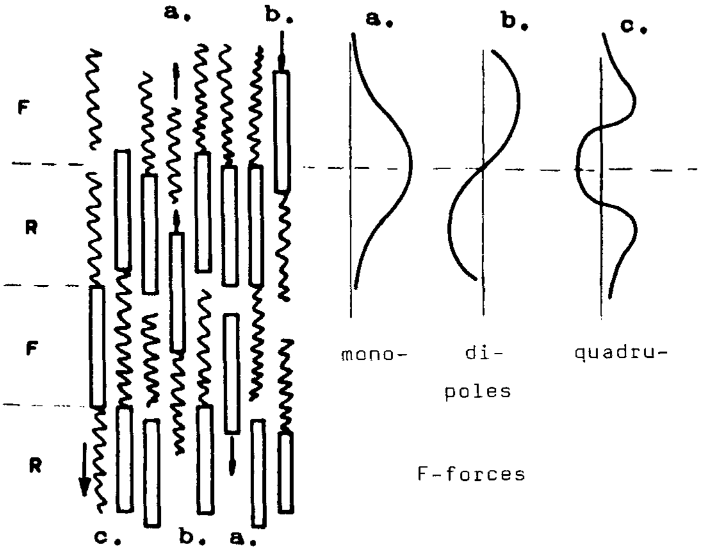

FIGURE 2. Distribution of the flexibility field and its derivatives. Forces, acting upon F-multipoles in a layered mesophase with flexible (F) and rigid (R) layers: a) Forces upon monopoles b) Forces upon dipoles c) Forces upon quadrupoles.

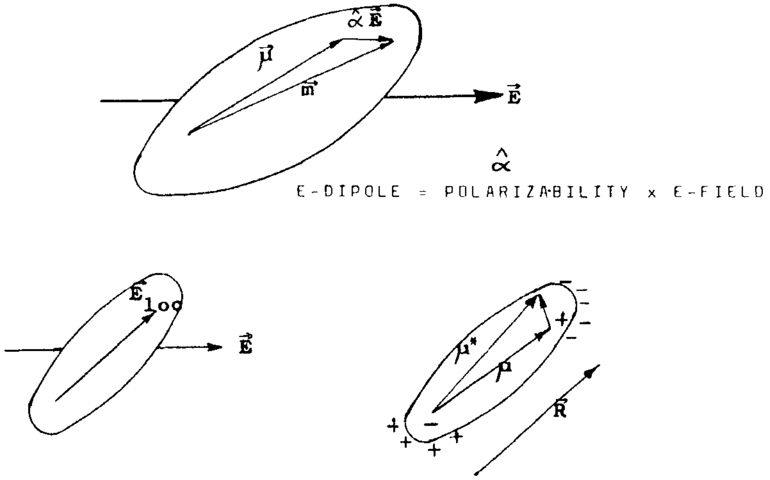

FIGURE 3. Polarization of electric dipoles in an electric field; local field E_{loc} and reaction field R.

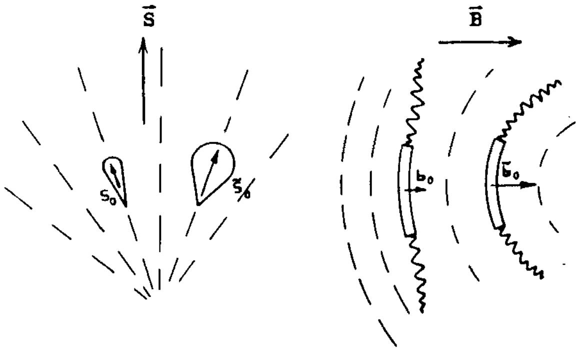

FIGURE 4. "Sterization" of steric dipoles in a steric field: conformational flexoelectricity.

S-dipole = "sterizability" x S-field

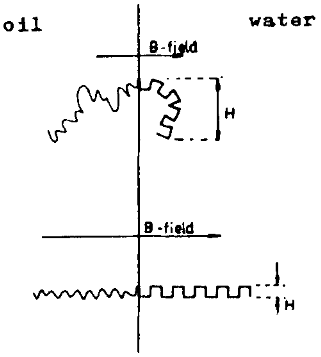

FIGURE 5. "Biphilization" of biphilic dipoles in a biphilic field: inverted phase formation.

B-dipole = "biphilizability" x B-field

ordering should be sharper in the case of F-dipoles. Bigger efficiency of F-dipoles in comparison to the F-quadrupoles was demonstrated in the thorough studies of smectic induction by Szabon[31]. The flexibility asymmetry concept could be related to the concept of condis crystals[32] as well.

The simultaneous introduction of biphilic and flexibility asymmetry is very convenient for a common description of thermotropic and lyotropic systems in the framework of our GMA-model. In thermotropics the role of B-field is lominated by the F-field. From the discussion above a close analogy between these two fields can be established. Consequently, existence in both systems of lamellar, cubic and columnar type of ordering appears quite natural, being determined by analogical combinations of B and S-asymmetry in lyotropics resp. F and S-asymmetry in thermotropics.

GENERALIZED POLARIZABILITIES

Our discussion of the molecular asymmetry is essentially based upon the analogy with electrostatics. Here we will again use as a starting point the case of electric asymmetry.

E-polarizability

Electric polarizability $\underline{\underline{\alpha}}$ is an expression of the dependence of E-dipole on the E-field. If it is non-zero and the mesogenic molecule is subjected to the action of an external E-field its total dipole moment $\underline{m}$ will contain a constant and a field-dependent term (Fig. 3):

$$\underline{m} = \underline{\mu} + \underline{\underline{\alpha}} \cdot \underline{E} \qquad (2)$$

Two problems should be mentioned with respect to the further discussion:

i. The problem of local field: with non-zero dielectric susceptibility of the liquid crystal medium the electric field $\underline{E}$ in (2) must actually be replaced by its local value $\underline{E}_{loc} \neq \underline{E}$. Otherwise $\underline{\underline{\alpha}}$ should take a corrected value $\underline{\underline{\alpha}}^*$.

ii. The problem of reaction field: even in the absence of an external E-field the permanent electric dipole of a molecule by virtue of polarizing the surrounding medium will create a reaction field acting upon itself and getting a higher effective value $\underline{\mu}^* > \underline{\mu}$.

S-polarizability

Analogically to (2) one can write for a steric asymmetry of dipolar type a relationship in the form:

S-dipole = const + "sterizability" x S-field (3)

In nematics two linear relationships for the two components of the steric dipole (s_o and b_o) and the two steric fields (S and B) can be written[8] with two principle sterizabilities α_s and α_b (Fig. 3) and two cross terms α_{sb} and α_{bs}. In layered or columnar systems these two relationships reduce to one for the splay or bend field resp.

Unlike electric polarizabilities originating mainly from the displacement of the easily susceptible electronic cloud, the sterizabilities will require conformational changes in the molecular skeleton (displacement of the location of the nuclei), so that their values will be nearly zero in the case of rigid mesogens and will be demonstrated only with long, flexible substituents (e.g. alkyl chains). Thus, sterizability is in a sense coupled to the flexibility asymmetry. The sterizability, combined with conformational changes of the intramolecular electric dipole will give rise to the phenomenon of "conformational flexoelectricity", a term introduced by Durand et al.[33] for description of the flexoelectric behaviour of mesogens with long-chain alkoxy substituents. Similar considerations were earlier used by us in discussing the contribution of different conformers to the bend flexoelectric coefficient of PAA[34,35].

The problem of local S-field and reaction S-field could be formulated like above and would lead to analogical consequences.

In lyotropics this concept should be even more effective. Both hydrophilic and hydrophobic portions of a lyotropic mesogen of zwitterionic or nonionic type are characterized by a substantial degree of flexibility, i.e. they possess a great number of conformations with very similar values of the intramolecular conformational energy. With a strong monolayer curvature the packing of head groups and chains can be substantially different from that in a planar monolayer (the reference state for definition of the effectve cross sections H and C, see Eq. 1). Consequently, both H and C could be changed as a result of the deformation and their difference defining the steric asymmetry according to (1) could be considered as deformation dependent. But it is possible in this case that the sterizability may differ depending on the sign of monolayer curvature.

B-polarizability

B-polarizability could be defined by a relationship of the type (Fig. 5):

$$\text{B-dipole} = \text{const} + \text{"biphilizability"} \times \text{B-field} \qquad (4)$$

B-field is defined as a gradient of the biphilic potential (see above) i.e. the free energy of transfer of a small probe molecule (water or methane) across a hydrophilic/hydrophobic interface (or in the vicinity of a specific surface) as a function of the position. In thermotropics a possible way to induce a varying B-field is to make a contact e.g. of a nematic having a B-asymmetry in the end substituents (like MBBA) and a solid surface with varying hydrophilicity or hydrophobicity (by adsorbing different substances over it).

In lyotropics the usual way to vary the biphilic field is by variation of the water (or oil) concentration. Of course, substantial variations could be realized in the limit of low water (oil) content: when e.g. the number of water molecules per hydrophilic head is lower than the full hydration limit. In the case of lecithin these are about 11 H_2O molecules per polar head; with nonionics this number depends on the polyoxyethylene chain length. Above the limit of full hydration when free water appears in the system the biphilic field reaches a saturation. Another way is to vary the temperature, especially in the vicinity of clouding point of non-ionics, when the polyoxyethylene chains become dehydrated.

It is natural to expect that by changing the degree of hydration the conformation of the polar head could change. Similar changes were postulated in lamellar lecithin-water phases with varying water content at 4 H_2O molecules per head. The B-dipole being defined as biphilic charge times distance will be clearly dependent on the B-field (Fig. 5), perhaps in a non-linear way.

Quite important structural consequences could be connected to the problem of reaction field, coupling a single B-dipole to its environment. The simultaneous changes of the S- and E-dipoles coupled to the B-dipole could throw additional light to the inverted phases appearing in the limit of low water.

By decreasing the water content the polyoxyethylene chain, being unable to participate in a sufficicent number of hydrogen bonds, will most probably assume a random coil conformation instead of a more extended one (decrease of B-field would decrease the B-dipole). But in view of the simultaneous increase of the effective head group area H (Fig. 5) the S-dipole of the nonionic amphiphile will simultaneously attain a larger positive value thus resisting the negative monolayer curvature necessary for inverted phases' formation. The conclusion is that inverted phases appear only at short hydrophilic chain amphiphiles. This is in accordance to the experiment.

F-polarizability

Using all the same analogy F-polarizability should be defined by a relationship:

F-dipole = const + "flexibilizability" x F-field (5)

This relationship could be applied for shorter F-dipoles introduced in a matrix of longer F-dipoles or F-quadrupoles (stronger F-field at flexible/rigid interfaces). Another case of variation of the F-field where Eq. (5) may be of use is the case of temperature variation: increase of temperature should in general increase the flexibility gradient (F-field) while for temperature decrease the opposite is true.

SOME APPLICATIONS OF G M A - MODEL

Ordoelectricity in lyotropics and smectics

Ordoelectricity is a phenomenon suggested[37] by Barbero et al. in nematics having a free surface or a nematic/isotropic interface or near disclination lines . A nematic should present an order electric polarization associated with the gradient of order parameter, in addition to the flexoelectric polarization associated with the gradient of orientation. Both dipolar and quadrupolar mechanism are shown to contribute to the ordoelectric coefficients, these being of the same order as the flexoelectric ones.

One contribution to the molecular mechanism of this effect in nematics can be immediately extracted from our GMA-model: in a case of mesogenic molecules being a combination of F-dipole and E-dipole the F-field at the nematic/isotropic interface will orient F-dipoles in such a way that flexible segments will be nearer to the isotropic phase than the rigid ones, thus orienting simultaneously the longitudinal E-dipoles giving rise to ordoelectricity. In a second case of F-quadrupolar type of mesogens our previous result about B-quadrupoles[6] could be applied in view of the close analogy between F- and B-asymmetry: within the interface zone two sublayers of F-quadrupoles could be identified, those nearer to the nematic phase being oriented normally to the interface, while those nearer to the isotropic phase being tangential to it (compare to Fig. 1 of Ref.6). This is due to the fact that F-quadrupoles experience a torque proportional to the second derivative of the F-potential (here supposed to be proportional to the order parameter profile S(z)), this derivative changing its sign on both sides of the point of steepest variation of S (the point of maximal F-field). Due to the orientational elasticity of the nematic phase most probably a smooth transition between the two orientations will take place. This will results in an inclined orientation of the director and both longitudinal and transversal component of E-dipole will contribute to the order polarization (cf.[37]).

Here we want to explore this effect in layered or columnar mesomorphic systems with long alkyl chain residues where substantial flexibility gradient exist. In this case order polarization will provide us with an example of a mixed influence of the F-field upon E-quadrupoles. Gradient of the order parameter S along alkyl chains in smectics and lyotropics is well documented by many experiments e.g. by using deuterated chains and it is also theoretically interpreted by mean-field and other methods. CH_2 groups possess a small quadrupole moment anisotropy Θ_a of the order of 2.10^{-26} esu. According to the quadrupolar mechanism of flexoelectricity[38] the order parameter gradient coupled to the quadrupole moment gradient will produce an electric polarization. In bilayer lyotropics order parameter distribution[39] is characterized by two plateaus near the head groups and two drops of about 0,1 along a distance of 3 Å to a lower common plateau in the central zone of the bilayer. The tensor of the quadrupole moment per unit volume is given by:

$$\Theta_{ij} = N \Theta_a Q_{ij}, \qquad (6)$$

where N is the number of CH_2 groups per unit volume,

$$Q_{ij} = S (n_i n_j - \delta_{ij}/3) \qquad (7)$$

is the tensorial order parameter and n_i are the components of the director. For the polarization in z-direction it holds:

$$P_z = (1/3)\, d\Theta_{zz}/dz = (2/9)\, N \Theta_a\, dS/dz \qquad (8)$$

If one represents this polarization in a form

$$P_z = N\,\tilde{\mu} \quad ,$$

where $\tilde{\mu}$ is an effective dipole per CH_2 group, one gets

$$\tilde{\mu} = (2/9)\Theta_a dS/dz = (2/9).2.10^{-26}.0,1/3.10^{-8} \simeq 0,01\ D$$

Having in mind that about 3 - 5 CH_2-groups are situated in the region of the drop of S the order polarization per chain is estimated of the order of 0,05 debye, which is a rather low value. In any respect, however, this results means that the hydrophobic core of lipid bilayers and also flexible regions in layered smectics are weak antiferroelectrics. With respect to columnar phases one can conclude that they are weakly polarized in radial direction of each column.

Cone-shaped discotics

The possibility of non-planar, cone-shaped discotics first appeared in our report at the Tbilisi LC Conference (1981) as a part of our general classification illustrating longitudinal steric dipoles in disc-like case. Later on this classification was published (see Table 1 of Ref. 6). In 1982 the so-called bowlic liquid crystals were formally proposed by Lin[40] and extensively discussed by him at Berkeley LC Conference (1986)[41]. According to us the bow-like shape belongs to the same steric asymmetry type: longitudinal S-dipole (see Fig.1).

Recently cone-shaped[42], or pyramidic[43] discotics were synthesized (hexasubstituted tribenzocyclononane ethers or esters). They were characterized in our language as a combination of S-dipole and E-dipole along their symmetry axis (C_{3v} symmetry). This assures conditions for permanent electric polarization of the whole column of cones or pyramides piled one over another, as predicted by us earlier[6] on the basis of dipole-dipole interaction of E-dipoles which will be additionally enhanced by the presence of S-dipoles.

Flexible core discotics

This new family of discotics (octasubstituted tetrabenzocyclododecatetraene ethers and esters of sufficiently long chains) was reported very recently (1986)[44]. As not only the core, but also the substituents are flexible they could be classified as disc-like flexible monopoles according to the term, proposed by us in 1985[8](see Fig.1). They also showed enantiotropic mesophases which appeared to be columnar. From our point of view flexible monopoles should preferentially form nematic phases, so that for columnar packing some flexibility gradient in radial direction of the discs should still be present.

Discotic amphiphiles

Other molecular structures predicted by our multipole model and recently synthesized are discotic amphiphiles[45] represented by 2,3,6,7,10,11-hexa(polyethylenoxy) triphenylenes. These belong to B-quadrupoles with hydrophylic periphery made by polyoxyethylene chains (like in nonionic rod-like surfactants) and hydrophobic planar core (Fig.1). These amphiphiles in water display a lyonematic phase with remarkably broad stability range. This is because their type of molecular asymmetry does not allow formation of bilayer aggregates and the transition to lamellar phase is forbidden. At further increase of the concentration a hexagonal phase of columnar type is formed, water being situated between the columns. This is the same aggregation principle like in thermotropic discotics, but here driven by the B-field instead of the F-field.

A complicated example of lyotropic mesomorphism, not fully understood, is supplied by the "chromonic" mesogens used as antiastmatic drugs[46,47]. They form columnar nematic and hexagonal mesophases like discotic amphiphiles above but with supposed tilt of the planar molecules in the columns. Molecular asymmetry of these mesogens could be described as a combination of planar, rigid B-quadrupole of elliptical (not disc-like shape) and a large coplanar E-dipole, normal to the longer dimension of the B-quadrupole (C_s symmetry). This dipole is probably responsible for the tilted arrangement in columns, which minimizes the electrostatic interaction.

Phasmids

"Phasmids"[48] is a term for describing some hexasubstituted mesogens, like bis-(3,4,5-trialkoxybenzoyl) 4'-phenyl terephthalates. These are very interesting substances realizing in one homologous series a smooth transition between rod-like and disc-like mesogens. They have a rigid rod-like core ending with two flexible half-disc fragments. They could be classified as hybride flexible quadrupoles, shorter homologues (C_7 to C_{10}) being rod-like and showing lamello-columnar ordering while longer ones (C_{11} to C_{14}) being disc-like with typical columnar phases.

Biforked mesogens

Biforked mesogens are tetrasubstituted. Their molecular structure is intermediate between rod-like and phasmidic one[49,50]. Depending on the way of substitution biforked mesogens could be classified as predominantly disc-like flexible quadrupoles (meta, meta substituted) giving columnar phases or a combination of disc-like flexible quadrupole and rod-like steric quadrupole of zig-zag type (para, meta substituted) with a lower temperature tendency to S_C ordering, evidently due to the interaction of zig-zag S-quadrupoles.

CONCLUSION

We tried to demonstrate above that Generalized Molecular Asymmetry Model is very useful as a general framework for discussion of the peculiarities in the structural organization and macroscopic properties of a number of mesogenic compounds on the basis of multipole-multipole interaction of generalized multipoles. At present this discussion is mainly qualitative, but in some cases quantitative description is already possible. By further extension of the model including generalized octupoles chirality effects would also become tractable in its framework.

Such a framework is also very convenient for a common description of thermotropic and lyotropic systems. This is a quite unique feature of G M A - model. This becomes possible on the basis of the close analogy between biphilic field active in the organization of lyotropics and flexible field active in thermotropics. The existence in both systems of lamellar, cubic and columnar type of ordering appears quite natural now.

Our model could also be very useful in directed molecular design of mesogens. Its predictive force was demonstrated on the examples of some newly synthesized mesogens, most typical being amphiphilic discotics and cone-shaped discotics. But this does not exhaust its predictive capabilities. Fig. 1 could be considered as a catalogue of the asymmetric molecular structures of both rod-like and disc-like mesogens. At present most examples given in this catalogue can be considered as being realized, with a few exceptions. But this are so to say the pure cases: when the molecule could be classified as a single generalized multipole. Taking combinations of two multipoles yields:

$$\binom{15}{2} = 105 \text{ combinations,}$$

taking three of them yields:

$$\binom{15}{3} = 405 \text{ combinations, etc.}$$

Of course, not all of them could be meaningful, but still the vast number of possibilities is quite impressive and a systematic synthetic chemistry approach is worth trying.

Another promising field of research is offered by various new effects arising from combinations of generalized multipoles in generalized fields.

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