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Invited Lecture

Structure and phase transitions in smectic A liquid crystals with polar and sterical asymmetry

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We review recent experimental studies of smectic A layering of asymmetric mesogens with emphasis on their relationship to phase transition physics. The formation of one and two dimensional lattices with long range order in the positions of the heads (tails) of molecules is considered as having either a polar or a steric origin. The various molecular models and phenomenological descriptions reproducing the phase behaviour of particular types of layering are evaluated. The influence of molecular factors on the delicate stability of different smectic A(C) phases is discussed in detail.

1. Introduction

Current studies of thermotropic liquid crystals reveal a considerable variety of smectic phases, distinguished by their layer structures and tilting, lying in the phase diagrams close to the classical smectic A(C) states [1,2]. The smectic A(C) phase is characterized by translational order in one dimension and liquid-like positional order in two others. In the classical monolayer smectic A_1 phase, the rod-like (or nearly rod-like) molecules are oriented randomly up and down within each layer and the one dimensional density wave has a periodicity d_1 approximately equal to the molecular length L. In the case of asymmetric molecules, such up-down orientational symmetry may be broken resulting in the formation of smectic phases in which the positions of molecular heads and tails with respect to the layers are well-defined. Several additional smectic A phases with such properties have been found for mesogenic molecules with polar and sterical asymmetry [1, 3]. They include bilayer smectics A_2 having a period of $d \simeq 2L$ and antiferroelectric ordering of permanent dipoles, and partly bilayer smectics A_d, whose layer periodicity is incommensurate with the length of individual molecules $d_2 \simeq L'$ $(L < L' < 2L)$. Among the polar mesogens, smectics A were detected in which a bilayer density wave proved to be modulated in the plane of layers—the antiphase or $\tilde{A}$ and the ribbon phase or $\tilde{C}$ [4, 5]. They differ in the symmetry of their two dimensional lattices which were reported to be centred rectangular ($\tilde{A}$) and oblique ($\tilde{C}$). Modulated phases, similar in their structures, were also detected for non-polar polymeric mesogens [6–8] and mesogens with fluorinated terminal chains [9]. Smectic A phases with incommensurate layering have also been found among non-polar compounds with complicated spatial configurations [10].

Experiments on asymmetric mesogens demonstrate a remarkable sensitivity of smectic A layering to details of molecular structure [2, 11, 12]. Hence it seems useful to describe in some detail the nature of molecular asymmetry for rod-like mesogens. Among the factors exerting their influence on the breaking of the inversion symmetry of

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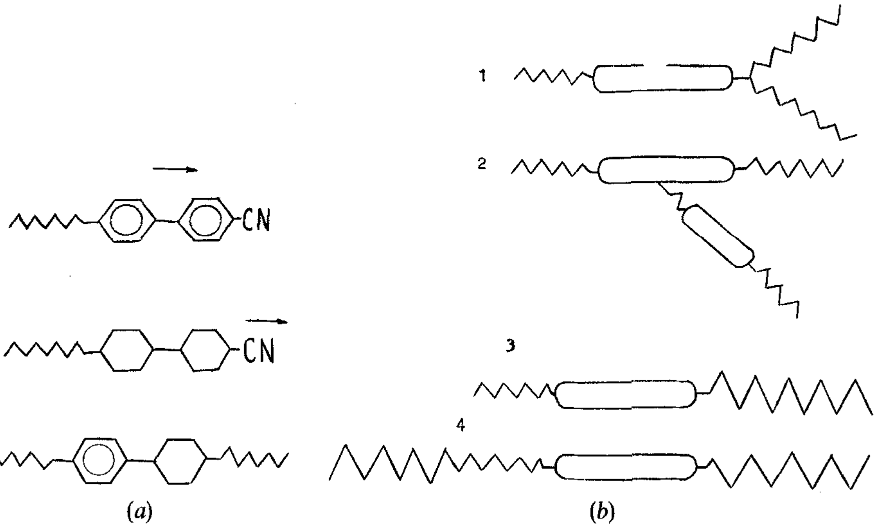
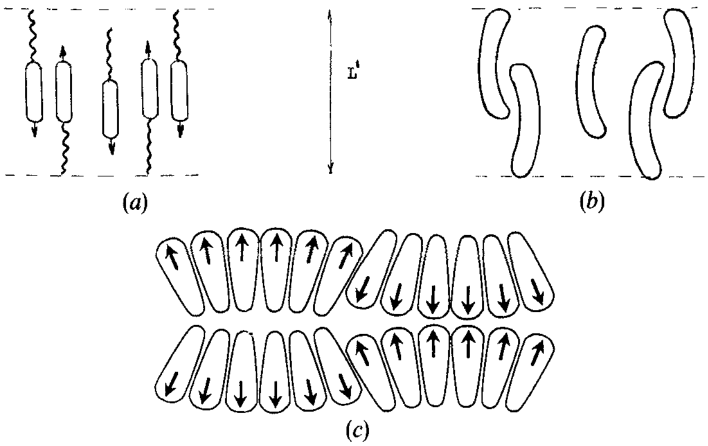


Figure 1. Schematic representation of mesogenic units with differing degrees of polar (*a*) and sterical (*b*) asymmetry. 1,2-Biforked, swallow-tailed, laterally branched [13], 3-terminally fluorinated [9], 4-polyphilic [14] mesogens.

smectic layers, both the polar and sterical asymmetry of the constituent molecules prove to be important. The polar asymmetry of mesogens may be associated with the presence of permanent dipole moments at one of the ends of the molecule, as well as with differences in the number and the type of cyclic fragments or the terminal groups in the molecules. The steric asymmetry is determined by the spatial configuration of the fragments of the rigid molecule cores, as well as by the presence of the end-groups of different nature, including the branched, biforked and polyphilic moieties (see figure 1). In terms of the multipole model of molecular asymmetry introduced by Petrov and Derzhanski [15], we can speak about longitudinal or transverse sterical dipoles and multipoles of molecules. The flexibility of the terminal alkyl chains or bridge fragments of different nature also affects the packing possibilities of molecules in the layers [16–18].

The combination of polar and steric dipoles and multipoles, together with the conformational subtleties of different moieties in the mesogenic molecules, leads to the variety of particular smectic A phases described above. How we can explain the origin of the different kinds of layering in smectics A? One of the possible answers is based on the idea suggested by Prost and co-workers [19, 20] of two incommensurate length scales competing with each other. In the case in which asymmetric molecules are present, we need not only to specify a density modulation to define the existence of layers, but also the positions of polar or steric dipoles in the molecules with respect to the layers. In this way, two characteristic lengths may be naturally involved, namely, the molecular length L and the length L' ($L < L' < 2L$) connected with the formation of spatial associates determining the repetition of the local polarization or steric states of the medium (see figure 2). This approach assumes the existence in the system of two competing interactions favouring the different periodicities. In contrast to the classical incommensurate systems (metal alloys, dielectrics, adsorbed monomolecular films [21, 22]), in smectics, it is difficult to isolate the specific interactions that are responsible for any type of periodicity. The structure of diverse smectic A phases is determined by a



(*a*) (*b*)
(*c*)

Figure 2. The formation of spatial associates of polar (*a*) and sterical (*b*) nature (arrows indicate polar heads). Idealized representation of the modulated smectic $\tilde{A}$ structure formed by molecules with strong polar and steric terminal dipoles (*c*) [2].

fine balance between attractive dispersion forces, repulsive steric forces, dipole–dipole interactions of localized or distributed dipoles of the molecules and packing entropy effects associated with the rigid and flexible molecular moieties [2]. A series of microscopic models is known from the literature which makes use of different combinations of the aforesaid interactions and gives possible explanations of the delicate stability and re-entrances in asymmetric smectic A phases [18, 23–27]. In the papers by Indekeu and Berker [25], the statistics of diverse dipole configurations in a triplet of nearest-neighbour molecules occupying discrete positions in the direction perpendicular to a smectic layer has been analysed. It was shown that these dipole clusters may or may not be frustrated, depending on the molecular close-packing conditions and the positional fluctuations occurring along the director orientation. The statistics of flexible aliphatic chains in molecules was analysed in the framework of a lattice model of smectics suggested by Dowell [18]. It was shown that under special conditions, the change in the number of *trans–gauche* and *gauche–gauche* conformers in the system may induce the transition to the re-entrant nematic phase without taking into account the polarity of molecules.

It should be noted, that in the case of liquid crystals, the division of molecular asymmetry into the polar and sterical parts is more or less artificial. Any steric difference between the head and tail of a molecule necessarily implies also its polarity. Nevertheless this approach seems to be useful for the analysis of the particular smectic A phases. The key question here will be about the relative role of steric repulsions and dipole–dipole interactions in the appearance of long range periodicity which is incommensurate with the molecular length L. In the case in which dipole correlations between asymmetric molecules play the main role, it is convenient to speak about dipolar frustrations. In the opposite case, the effects of sterical repulsions may be more pronounced (see figure 2). The effects of dipolar frustrations manifest themselves in smectic A polymorphism and multiple re-entrant behaviour (which seems to have the same origin) and are widely known [1–5]. As regards sterical frustrations, experiments that have been carried out during the past few years reveal the existence of smectic layering with incommensurate periodicities [10], re-entrant nematic behaviour [28] and modulated structures [9] occurring also among non-polar rod-like molecular systems having sterical dipoles and multipoles. An interesting situation may occur when both dipolar and sterical correlations between molecules are of equal strength. This situation was discussed earlier by Longa and de Jeu [24] and Helfrich [29]. Thus, in the case of bilayers formed by polar mesogens, the presence of a strong steric dipole at the head of a molecule may induce a local bending of the layers (see figure 2). As the size of the areas of the bent bilayers increases, an increase in the corresponding elastic energy with some critical curvature makes energetically preferable the transition from uniform bilayers into the modulated $\tilde{A}$ phase, where the areas of bilayers with opposite signs of local curvature are separated by antiphase borders (defect walls) (see figure 2).

The aim of this paper is to give an overview of the experimental situation concerning the diversity of the types of layering in liquid crystals with differing degrees of polar and sterical asymmetry. Emphasis will be on the properties of smectic A(C) phases consisting of fluid layers (neither crystalline, nor hexatic) and forming one and two dimensional structures with long range order in the positions of the heads and tails of the molecules. Our analysis deals mainly with recent X-ray studies of different smectic A(C) phases.

2. X-ray diffraction on periodic structures of smectic A liquid crystals

2.1. *Geometry of X-ray scattering*

In this section, we will summarize the well-known results for X-ray diffraction by different smectic A(C) phases, which will serve as a reference point for the later discussion. In a perfectly oriented, classical smectic A_1 phase, the reciprocal space is the nodal line with spacing equal to $q_1 = 2\pi/d_1$ $(d_1 \simeq L)$ along the layer normal and a diffuse spot in the perpendicular direction at $q_\perp \simeq 2\pi/4{\cdot}5\,\text{Å} \simeq 1{\cdot}4\,\text{Å}^{-1}$ that reflects the short range order within the layers. The presence of the diffuse peak with the wave vector $q_2 = 2\pi/L'$ corresponding to a periodicity which is incommensurate with the molecular length $(L < L' < 2L)$ distinguishes liquid crystals with asymmetric molecules from the symmetrical type (see figure 3). A bilayer smectic A_2 phase exhibits two Bragg peaks at

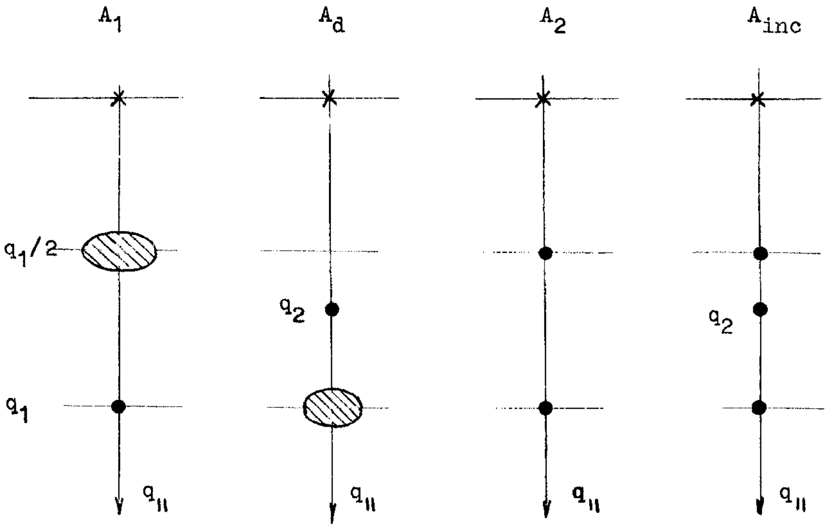


Figure 3. X-ray diffraction patterns of smectic A phases with collinear modulations. The wave vector component $q_\parallel$ is parallel to the director **n**, the cross denotes the direct beam, the solid points are Bragg reflections, the hatched areas are the diffuse scattering regions.

the points q_1 and $q_1/2$. The partially bilayer (overlapped) A_d phase is characterized by a Bragg peak at $q_2 = 2\pi/L$ and a diffuse peak at the reciprocal space points q_1 or $q_1/2$. In the incommensurate, one dimensional A_{inc} phase, which in principle can exist among the asymmetric smectics [19, 20], two collinear modulations of incommensurate wavelength are simultaneously condensed, producing sharp diffraction peaks at $q_1$and q_2 (or q_1; $q_1/2$; q_2), the ratio q_1/q_2 being irrational. Additionally, Prost and Barois [20] have predicted the existence of a strongly coupled incommensurate phase consisting of a periodic array of defect walls or solitons, which will give diffraction spots at integral sums and differences of q_1 and q_2. The commensurate antiphases ($\tilde{A}$ and $\tilde{C}$) are identified by the appearance of off-axis reflections, indicative of the additional translational order in the plane of the layers, such that two vectors $\mathbf{q}_2$ sum to form $\mathbf{q}_1$ (see figures 4 and 5).

The emergence of reflexes from the meridional plane of an X-ray pattern is a definite indicator of density modulation in the plane of smectic layers [21, 22]. However, very different variants of the periodic change in the position of smectic layers are possible. The purely sinusoidal modulation of the initial lattice represents the simplest model. In the case of the harmonic modulation of the main basis of the vectors of the reciprocal lattice, $\mathbf{q}_0$, by the perturbing potential, with the wave vector $\mathbf{q}_m$, the diffraction pattern is changed by the appearance of additional modulation peaks (satellites) at the reciprocal-space points $\mathbf{q} = n\mathbf{q}_0 + \mathbf{q}_m$: $S(\mathbf{q}) \sim \Sigma_{n,m} J_m^2(\mathbf{q}\mathbf{A})\,\delta(\mathbf{q} - n\mathbf{q}_0 - \mathbf{q}_m)$, where $J_m(\mathbf{q}\mathbf{A})$ is the Bessel function of the order m and $\mathbf{A}$ is the vector of the modulation amplitude.

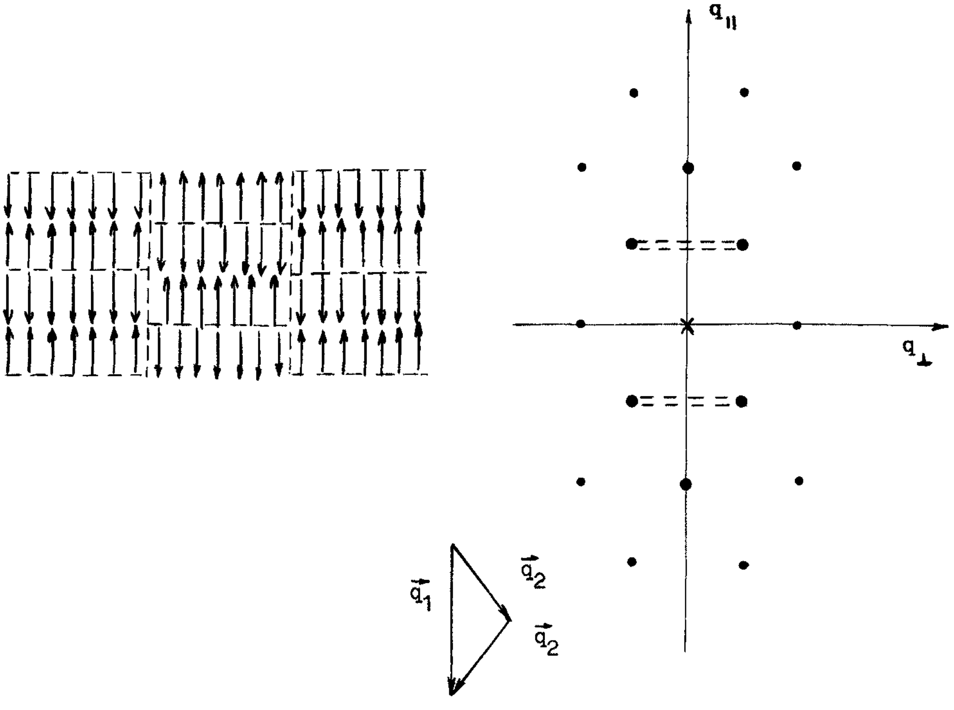


Figure 4. Real-space model of the smectic $\tilde{A}$ phase depicted with the rectangular unit cell. The reciprocal space of the smectic $\tilde{A}$. Two dimensional matching of incommensurate wave vectors is shown. Degeneration of the direction of modulation in the smectic planes leads to the appearance of the ring of scattering at $\mathbf{q} = \mathbf{q}_{\tilde{A}}$.

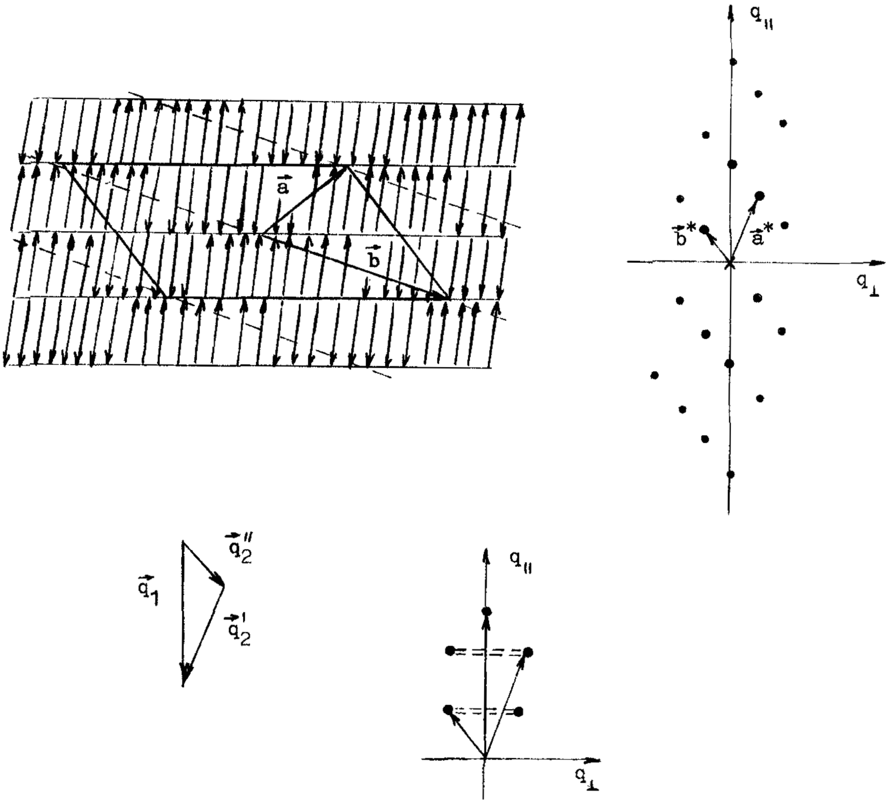


Figure 5. Real-space model of the smectic $\tilde{C}$ phase depicted with an oblique two dimensional unit cell. Solid lines indicate the average positions of the molecules and show the locations of constant phase in the density modulation. Broken lines indicate lines of constant phase in the polarization modulation. The unit cell vectors **a** and **b** and the reciprocal vectors **a*** and **b*** are defined and indexed as shown. Two dimensional matching of incommensurate wavevectors is also shown. The degeneration of the direction of modulation in the smectic planes or a mosaic average of the crystal about the magnetic field duplicates the three primary peaks.

Both the geometry of diffraction and the intensity of satellites depend upon the mutual arrangement of vectors $\mathbf{q}_0$, $\mathbf{q}_m$ and $\mathbf{A}$ [21, 22]. In the case of the periodic modulation of the general type, the additional satellites appear in the vicinity of main reflexes, whose position and intensity determine the modulation Fourier spectrum. A distinctive feature of this model is the conservation of main peaks, $n\mathbf{q}_0$, and the absence of equatorial reflexes on the X-ray pattern. In the smectic $\tilde{A}$ and $\tilde{C}$ phases, the position of the antiparallel polar or steric dipoles of molecules in bilayers changes periodically from one layer to the other in the plane of layers, thereby forming a density wave which is modulated in the xz plane (see figures 4 and 5). An obvious shortcoming of the aforesaid model when applied to $\tilde{A}$ and $\tilde{C}$ phases is the absence of the fundamental bilayer reflex at the point $(0, 0, q_1/2)$. A more realistic model of the structure of smectics $\tilde{A}$ and $\tilde{C}$ is a representation in which the regions of bilayers are located at the nodes of plane-centred rectangular ($\tilde{A}$) or oblique ($\tilde{C}$) elementary cells (see figures 4 and 5).

The translational vector in the $\tilde{A}$ phase has the form $\mathbf{r}_{\tilde{A}} = (a/2; 0; d/2)$, where $a \simeq 100$–500 Å [1, 30] is a period of modulation and $d \simeq 2L$. The vectors of reciprocal lattice $\mathbf{q}_{\tilde{A}}$

lie in the xz plane and give rise to reflections of the (hk) type, $h+k=2n$, n being an integer (see figure 4). The 2D monoclinic unit cell of the C phase may be characterized by the translational vectors **a**, **b** and the angle between them γ. These vectors can be inverted to give reciprocal lattice vectors $a^*=1/a \sin\gamma$ and $b^*=1/b \sin\gamma$, lying in the xz plane (see figure 5). Moreover in the $\tilde{\mathrm{C}}$ phase, the molecules are tilted relative to the wave vector of the density wave $\mathbf{q}_1$. Then the $\tilde{\mathrm{C}}$ structure gives rise to (10), (01) and combined reflections of the (hk) type, where h and k are integers. There is a continuous degeneracy of directions for the spatial modulations of the $\tilde{\mathrm{A}}$ and $\tilde{\mathrm{C}}$ phases in the xy plane which is perpendicular to the director. As a result, reciprocal lattice vectors being azimuthally averaged, give rise to rings of diffraction in reciprocal space (see figures 4 and 5). These rings intersect the Ewald sphere in two points, which explain the fact of the simultaneous appearance of different (hk) reflections on the X-ray patterns. However, under special conditions, monodomain samples of $\tilde{\mathrm{A}}$ or $\tilde{\mathrm{C}}$ phases may be prepared [31].

From the point of view of symmetry, $\tilde{\mathrm{A}}$ and $\tilde{\mathrm{C}}$ phases belong more to columnar phases than to smectics—they are both periodic in two dimensions. However, comparison between the experimental and theoretical diffraction schemes indicates a limited number of reflections and the absence of equatorial diffraction spots on the X-ray patterns of $\tilde{\mathrm{A}}$ and $\tilde{\mathrm{C}}$ phases in the small angle region [1, 31, 32]. This means that the non-uniformity of the electron density is substantially less along a layer than across it. This circumstance makes possible the consideration of $\tilde{\mathrm{A}}$ and $\tilde{\mathrm{C}}$ phases together with one dimensional smectic phases A_1, A_2, A_d, etc. However, a possibility cannot be excluded that the situation might be different for other mesogens giving $\tilde{\mathrm{A}}$ and $\tilde{\mathrm{C}}$ phases. In particular, polarization or a sterical 'lattice' in different compounds may change from being purely sinusoidal to one having sharp antiphase boundaries. In other cases, the conditions of dipole compensation, as well as the purely steric causes might lead to periodic condensation and rarefaction of the electron density in the plane of the layers. Under these conditions, other reflections allowed by the symmetry of the smectic $\tilde{\mathrm{A}}$ and $\tilde{\mathrm{C}}$ phases might show up.

2.2. *Effects of quasi-long range order on smectic layering*

Smectic A phases belong to systems with reduced dimensionality of the translational order and consequently, according to the Landau–Peierls theorem, long wavelength fluctuations of the positions of layers wash out long range translational order. This means that the mean-square fluctuations

$$\langle u^2(\mathbf{r})\rangle=\frac{k_\mathrm{B}T}{4\pi\sqrt{(KB)}}\ln\frac{R}{d} \tag{1}$$

diverge in an infinitely large sample ($R\rightarrow\infty$) [33]. Here K and B are the moduli for comparison and curvature of the layers, respectively, and d is a smectic layer spacing. However, the logarithmic growth of the fluctuations with the size, R, of the homogeneous regions of smectics A ($R<10^5$ Å [34, 35]) is so slow that it is necessary to use a highly refined X-ray technique [36] to observe the destruction of the long range smectic order. For typical values of parameters cited in equation (1), $\sqrt{(KB)}=7\times10^{-5}\,\mathrm{N\,cm^{-1}}$, $d=30$ Å and $R=10^4$–10^5 Å, the corresponding layer displacement amplitude $\sigma=\langle u^2(\mathbf{r})\rangle^{1/2}\simeq5$–$7$ Å. Since these fluctuations are smaller than the layer periodicity, the smectic layers are still well-defined. This fact reflects the presence of the quasi-long range order in the system, which is characteristic of two dimensional (2D) crystals and smectics A. It is distinguished from true long range order where the positional correlations continue indefinitely, by the power-law behaviour of the interlayer density–density correlation function $G(z)\sim z^{-\eta_1}$, where $\eta_1=k_BTq_0^2/8\pi\sqrt{(kB)}$ is a small exponent (z is the direction parallel to the layer normals, $q_0=2\pi/d$). Typically η_1 is of the order 0·1 and can even by much smaller for lyotropic smectic crystals [37]. As was shown by Caille [38], this slow algebraic decay of the correlation function leads to strong diffuse scattering in the vicinity of reciprocal lattice points $q_n=nq_0$:

$$S(q_z)\sim(g_z-q_n)^{-2+\eta_n}, \tag{2}$$

where q_z is the momentum transfer in the z direction and $\eta_n=n^2\eta_1$. Such singular behaviour of the structure factor of the infinite smectic A system distinguishes it from the Bragg peaks which are characteristic of the true long range order in conventional three dimensional crystals. In 3D crystals, $S(q)$ consists of a set of Bragg peaks whose positions are determined by the reciprocal lattice vectors and a certain diffuse background. Thermal vibrations in three dimensional systems reduce the intensities of the Bragg peaks owing to the Debye–Waller factor: $\exp(-2W)$, but introduce no line broadening. The situation is different in systems with partial translational order. Thus in the infinite smectics A, the Bragg peaks are absent due to the divergence of the Debye–Waller factor

$$\exp(-2W_n)=\exp[-q_n^2\langle u^2(\mathbf{r})\rangle]\sim(R/d)^{-2\eta_n} \tag{3}$$

replacing by the power-law singularities (see equation (2)). For smectic samples with a finite size, the X-ray intensity consists of the thermal diffuse scattering given by equation (2) and a true, albeit weakened, Bragg peak, since the Debye–Waller factor for such a system is not divergent [39, 40]. The shape factor of domains of dimension R leads to a Bragg peak of width $\simeq R^{-1}$ the contribution of which to the total intensity is proportional to the Debye–Waller factor (see equation (3)). It is important to note the very marked dependence of equation (3) on the exponent η_n (on the layer fluctuation amplitude $\langle u^2(\mathbf{r})\rangle\sim\eta_1$) and on the domain size R leading to a considerable reduction in the intensity of higher order reflections from the smectic layers [41]. For a typical value $\eta_1\simeq\langle u^2(\mathbf{r})\rangle/d^2\simeq0{\cdot}1$ (far from the transition temperature to the nematic phase T_{S_AN}) in a sample with a domain size $R\simeq10\,\mu$k, the contribution of the Bragg peak to the total intensity in the vicinity of a (001) reflection is about $(R/d)^{-2\eta_1}\simeq10^{-0{\cdot}7}\simeq2\times10^{-1}$. In the neighbourhood of the next reciprocal lattice point (002), $\eta_2=4\eta_1\simeq0{\cdot}4$ and the Bragg peak is hardly observable, amounting only to about $(R/d)^{-2\eta_2}\simeq10^{-3}$. The remaining intensity is transferred to the power-law tails. The X-ray patterns for the smectic A phase in low molecular mass thermotropic mesogens really display only the lowest order reflection (001), the intensity of second and third orders being less by three to five orders of magnitude [36, 42]. The intensity of different diffraction peaks allowed by the symmetry of the medium depends not only on the character of positional correlations and thermal motions, but also on the details of the local molecular structure. The latter is determined by a q dependence of the molecular form factor $F_M(\mathbf{q})$. The function $F_M(\mathbf{q})$ has a maximum value close to $q=0$ and non-monotonically decays as the value of q increases. However, $F_M(\mathbf{q})$, calculated on the basis of reasonable molecular models, is as a rule not so sharply peaked as to make the higher order peaks in smectics A unobservable [43, 44].

Unlike low molecular mass thermotropic smectics A, in the lyotropic lamellar L_α phase [35, 37] and certain polymeric smectics [45], high order reflections may be quite intense. We can point out at least two factors which can substantially change the relative intensity of Bragg peaks in these systems. First is the relatively small values of the layer displacement amplitude and hence the exponent $\eta_1 \simeq 10^{-2}$ in lyotropic smectic liquid crystals [37] and in some polymeric mesophases [46]. The second is the imperfections of the layer structure of smectic materials characterized by small domain sizes, $R < 10^3$ Å, as happens in some polymeric smectics [47, 48]. Both factors are favourable for higher order reflections due to the η_n and R dependences of the Debye–Waller factor (see equation (3)). Additionally the molecular form factor may be more favourable for higher harmonics in the case of the bilayer structure of lyotropics and for polymeric materials with side-chain groups.

So far we have considered the peculiarities of X-ray diffraction caused by the restrictions of long-range positional order in smectics. In many cases, we can forget that a medium with 1D translational order is not strictly periodic and describe the smectic layering by a simple electron density distribution $\rho(z)$. The function $\rho(z)$ for a smectic domain of finite size may be represented in the form:

$$\rho(z) = \rho_M(z) * f(z) * T(z) \cdot S(z), \tag{4}$$

where $\rho_M(z)$ is the z projection of the electron density profile of the molecules in their most probable configuration averaged in accordance with an up-down distribution of molecules in the layers; $f(z)$ is the molecular centre of mass distribution within the layers which may be expressed as a normalized gaussian distribution of width σ; $T(z)$ is a function which describes the set of points of a one dimensional lattice; $S(z)$ is the domain shape function and the asterisk denotes the convolution operation. Using the Fourier transform of expression (4) and the convolution theorem, we arrive at the following expression for the scattering intensity:

$$S(q_z) = F_M^2(q_z) \exp(-\sigma^2 q_z^2) \Sigma \delta(q_z - q_n) * \frac{\sin^2 Rq_z/2}{(q_z/2)^2}. \tag{5}$$

If the positions of the centres of mass of molecules in layers are strictly determined ($\sigma \to 0$), then a large number of spots are observed at the reciprocal space points q_n, reflecting the Fourier spectrum of individual molecules. In the opposite case, the intensities of high order reflections will be reduced by a factor $\exp(-\sigma^2 q_z^2)$ analogous to the Debye–Waller factor of equation (3). The number of observed layer reflections gives a good guide to the sharpness of the distribution function $f(z)$. Comparison of equations (5) and (3) clearly indicates that any other mechanism, provided it gives rise to a broadening of the gaussian distribution function $f(z)$, will manifest itself in the diffraction spectrum in the same way as long wavelength layer fluctuations [49]. In addition to layer fluctuations corresponding to collective motions of molecules and existing on a time scale of 10^{-6} s [50], there are individual motions of molecules having a liquid-like random diffusive nature with characteristic times of 10^{-11} s [43, 51] and static displacements of layers caused by the elastic fields of defects [52]. Following Holyst and co-workers [48], we can include the aforesaid contributions in the expression for the combined displacement amplitude

$$\sigma^2 = \sigma_{lw}^2 + \sigma_i^2 + \sigma_d^2, \tag{6}$$

where σ_{lw} is given by equation (1) (usually $\sigma_{lw} \simeq 5$–7 Å) and the amplitudes of individual molecular motions and those induced by defects are defined respectively as σ_i and σ_d, The value of σ_i was determined by Leadbetter and co-workers [43, 51] using quasi-elastic neutron scattering to be $\sigma_i \simeq 1$–2 Å depending on the model used for data interpretation. Point defects (for example impurities) cause two effects in the X-ray scattering: shifting of Bragg peaks and an additional contribution to the index of algebraic decay $\eta = \eta_1 + \nu$. Calculations fulfilled for reasonable concentrations of point defects in smectics lead to a quite small value of exponent $\nu \simeq 5 \times 10^{-3}$ [53]. However, the index ν can be effectively extended if the impurities gather into clusters [53]. The aforesaid estimations clearly indicate that the long wavelength contribution normally dominates in the total displacement amplitude of smectic layers.

The traditional approach to the description of the properties of smectic layers consists in expanding the distribution function $f(z)$ into a Fourier series

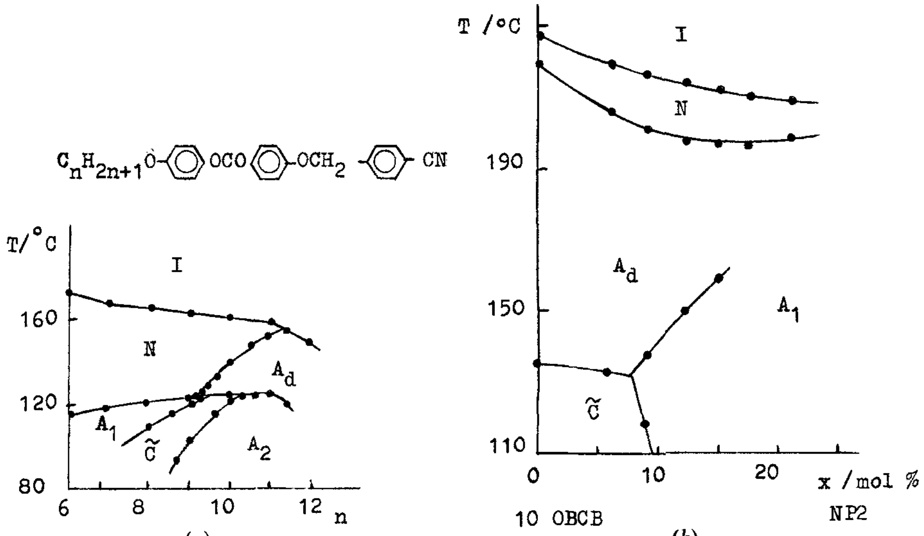
$$f(z) = \sum_n \psi_n \cos(nq_0z), \tag{7}$$

where coefficients ψ_n are the de Gennes translational order parameters of the smectic A phase. In view of equations (4) and (7), the intensities of the (00n) reflections from the smectic layers are directly proportional to the square of the order parameter ψ_n: $I_n \sim F_m^2(q_n)\psi_n^2$. In accordance with equation (5), $\psi_n \sim \exp(-\sigma^2 q_n^2/2)$ and hence the absence of higher order peaks and the absence of higher order Fourier components in the density expansion in equation (7) have the same origin, i.e. the extended long wavelength fluctuations of the smectic A layers. For typical values of $F(2q_0)/F(q_0) \simeq 1$–10^{-1} and $I_{002}/I_{001} = 10^{-3}$–$10^{-4}$, the corresponding ratio of the first two translational order parameters is $\psi_2/\psi_1 \lesssim 10^{-1}$. These estimations indicate that low molecular mass thermotropic smectics are, as a rule, essentially 'soft' layered systems with a nearly sinusoidal density wave $\rho(z)$. However, for particular types of layering, the ratio ψ_2/ψ_1 may be much higher, leading to the necessity of taking into account the higher order terms in equation (7).

3. Smectic A polymorphism in terminally polar mesogens (dipolar frustrations)

3.1. *Experimental phase diagrams: phenomenological description*

Let us restrict ourselves now to the peculiarities of smectic A layering affected mainly by the polar asymmetry of the constituent molecules. A large variety of smectic A phases with a broken up-down symmetry has been detected among mesogens possessing strongly polar cyano or nitro end groups [1, 3–5] (see figure 6). The smectic phases A_1, A_d and A_2 have the same macroscopic symmetry, differing from each other in the wavelength of the spacing. Hence it should be possible to go from A_1 to A_d or from A_d to A_2 by only varying the layer periodicity. Usually this can be made in a discontinuous way through first order transitions with a jump in the layer spacing d. Smectic A transition lines of such first order changes may terminate at critical points where the differences between the wave vectors of the smectic A phases vanish, providing a continuous evolution of A_1 or A_2 from A_d [56]. The situation is more delicate in the case of $\tilde{A}$ and $\tilde{C}$ phases due to the two dimensional character of their periodicities [57]. To understand the peculiarities of polar smectics A phase diagrams, it is necessary to consider more closely the way the one dimensional layers that are trying to condense at two incommensurate length scales may be in agreement with each other. A similar problem is known to exist in classical incommensurate systems, such as metal alloys, dielectrics, magnetic crystals and adsorbed monomolecular films [21, 22]. Thus, for a monolayer of krypton on graphite, the dispersion interaction between the noble gas atoms favours the period which is incommensurate with the graphite lattice parameters. With decreasing temperature, we can observe in this system the transition from a commensurate to an incommensurate phase with an intermediate melted state [58]. In spite of the different origin of incommensurability, smectics A and monolayers



(*a*) (*b*)

Figure 6. Typical experimental phase diagrams with N, S_{A_1}, S_{A_d}, S_{A_2} and $S_{\tilde{C}}$ phases. (*a*) [54], (*b*) [55].

have the common feature of large scale layer fluctuations of competing periodicities which is characteristic of systems with reduced dimensionality of translational order.

The phenomenological theory which describes the formation of diverse periodicities in terminally polar smectic A phases was suggesteed by Prost and Barois [19, 20]. This theory defines the free energy of the system in terms of two order parameters ψ and Φ, which are characteristic of the modulation of density and the local polarization states P of smectics, respectively. The free energy density involves harmonic and quartic terms in both ψ and Φ, as well as the coupling term $F_{\psi\Phi}$. Depending on the parameters of the model, one or both order parameters may condense. The competition between the elastic terms, which favours the natural wavelength ($q_1 = 2\pi/L$, and $q_2 = 2\pi/L'$, $L < L' < 2L$) and the coupling term which favours commensurate lock-in of $\mathbf{q}_1$ and $\mathbf{q}_2$ vectors leads to formation of diverse smectic A phases ($A_1, A_2, \tilde{C}$, etc.). In the case in which the coupling term $F_{\psi\Phi} \simeq -\mathrm{Re}(\psi^*\Phi^2)$ dominates in the free energy density, the commensurate phases are stabilized. On integration over the macroscopic volume, F proves to be proportional to the delta function

$$\int \psi^*\Phi^2 d^3r \sim \sum_{\mathbf{q}_1;\mathbf{q}_2;\mathbf{q}_2} \psi(\mathbf{q}_1)\Phi(\mathbf{q}'_2)\Phi(\mathbf{q}''_2)\delta(\mathbf{q}_1-\mathbf{q}'_2-\mathbf{q}''_2)$$

which corresponds to the formation of the layers, whose inverse lattice vectors satisfy the condition

$$\mathbf{q}_1 = \mathbf{q}'_2 + \mathbf{q}''_2. \tag{8}$$

The law of conservation of these vectors allows the existence of a bilayer A_2 phase ($\mathbf{q}_1 = 2\mathbf{q}_2$), as well as smectic $\tilde{A}$ and $\tilde{C}$ phases, in which the structural vectors $\mathbf{q}'_2$ and $\mathbf{q}''_2$ are not collinear with $\mathbf{q}_1$ (see figures 3–5).

The inclusion of additional mechanisms of one dimensional melting makes the problem of smectic A_1 and A_d layering coexistance more complicated. For instance, the dislocation loop melting theory of Prost and Toner [59] predicts different ways in which the A_1–A_d phase boundary may terminate. In the mean field approximation, the theory predicts the existence of a A_1–A_d critical point. However, when the effect of fluctuations is considered, several topological possibilities appear, including the A_1–A_d termination as a critical point or as a nematic island. This nematic island can merge with the main area of the nematic phase resulting in smectic A–nematic boundaries with complicated topological features, including multiple re-entrances [59].

On the experimental side, Cladis and Brand [60] and Hardouin *et al.* [61] have detected the cholesteric (nematic) island surrounded by a smectic A phase at the end of the A_1–A_d phase transition line in binary mixtures of terminally polar mesogens. Beyond this island, the layer spacing evolves continuously from the A_d to the monolayer value which is characteristic of the upper critical region. It was also shown that, by varying the chain length of the components of mixtures, the nematic island can merge with the main area of nematic [55]. The smectic layer compression elastic constant B has a minimum value at the A_1–A_d critical point [59]. Hence, local fluctuations of the q_1 density wave in the A_d phase, or of the q_2 density wave in the A_1 phase may be large enough (see equation (1)) to blur the smectic phase and induce the nematic gap in between the regions of stability of smectic A_1 and A_d phases (see figure 7). One of the possible ways to escape frustration is to go over to two dimensional smectic $\tilde{A}$ or $\tilde{C}$ phases which effectively reduce the free energy of the system owing to the coupling term. It is not surprising therefore that those phases occupy a position in phase diagrams intermediate between the regions of stability of A_1 and A_d phases (see figure 6). The situation where the nematic phase directly transforms into a two dimensional $\tilde{C}$ phase is also possible [31] (see figure 8). Another way to escape frustration is to go over to an incommensurate A_{inc} phase. A few years ago Ratna *et al.* [63] reported the existence of such a smectic A phase in binary mixtures of polar mesogens. It was argued that the temperature and concentration evolution of the wavelengths distinguishes this new phase from a simple coexistence of A_2 and A_d

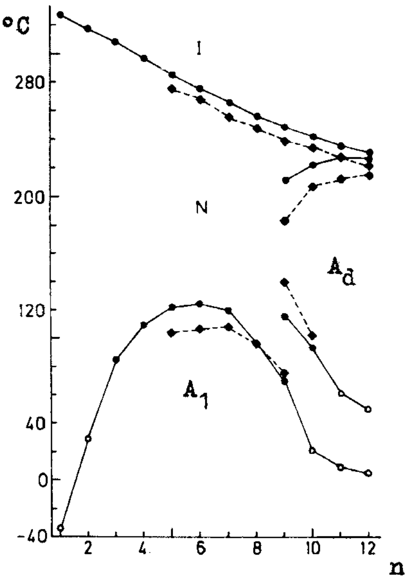


Figure 7. Typical experimental phase diagram with the nematic gap in between the smectic A_1 and A_d phases [62].

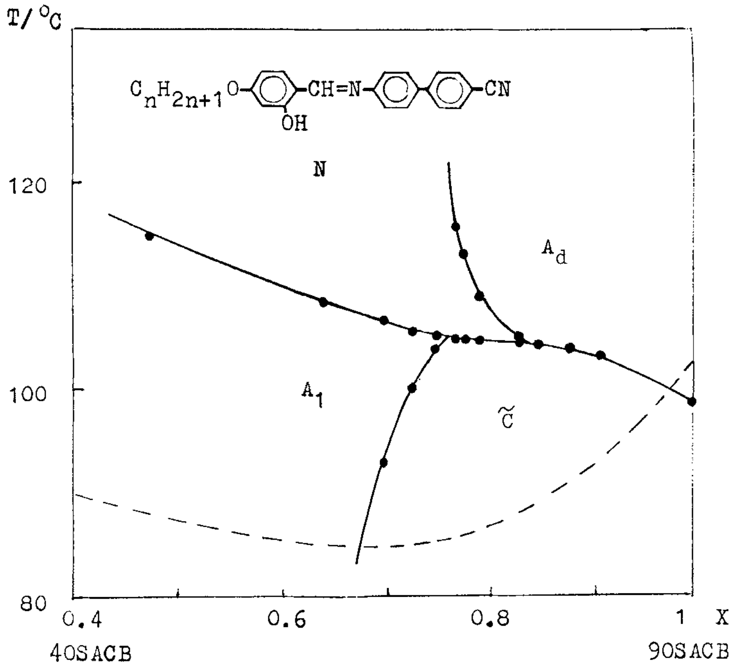


Figure 8. Phase diagram for the 4OSACB–9OSACB mixture with the N, S_{A_1}, S_{A_d} and $S_{\tilde{C}}$ phases [31].

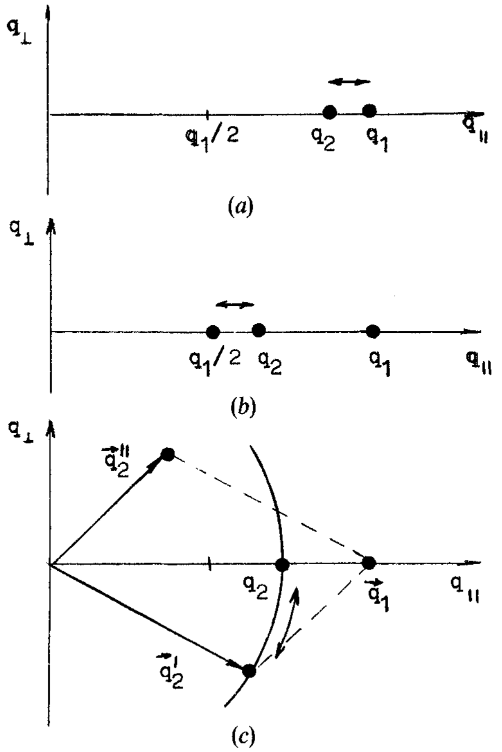


Figure 9. Reciprocal-space representation of competing smectic periodicities: (a) strong overlap limit ($q_1/q_2 \gtrsim 1$); (b) weak overlap limit ($q_1/q_2 \lesssim 2$); (c) intermediate case $q_1/q_2 \simeq 1{\cdot}5$.

phases [64]. However, recent high resolution X-ray diffraction [65] and calorimetry [66] measurements have presented evidence that the A_{inc} phase is actually the phase coexistence of the A_2 and A_d phases at a first order transition between them. In the light of these results the problem of the experimental observation of the A_{inc} phase is still an open question.

Experimental studies of terminally polar mesogens clearly indicate the strong dependence of the topology of A_d–A_1 (A_2) phase diagrams on the ratio q_1/q_2 ($1 \lesssim q_1/q_2 \lesssim 2$). This point is more convenient to discuss by using the reciprocal space representation of competing periodicities (see figure 9). For small $q_1/q_2 \gtrsim 1$ the reciprocal space vector of A_d periodicity q_2 may vary from the monolayer q_1 value in a continuous way or through a weak first order transition. In the case where $q_1/q_2 \lesssim 2$ the q_2 vector varies smoothly to the bilayer value $q_1/2$ (see figure 9). For the wavelength ratio $q_1/q_2 \simeq 1{\cdot}5$ (significantly different from two or one), the direct transition from one 'soft' point q_2 to another q_1 ($q_1/2$), through a strong first order transition A_d–A_1 (A_d–A_2), may cost a lot of energy. The formation of the smectic $\tilde{C}$ phase may be more advantageous from the energetical stand-point, if by chance one of the fundamental structure vectors of this phase $\mathbf{q}'_2$ lies on the same sphere in the q space as the vector q_2 of the A_d spacing. The position of another structural vector $\mathbf{q}''_2$ will be determined by the vector conservation law in equation (8). Indeed, X-ray experiments confirm such a scenario of formation of the commensurate two dimensional $\tilde{C}$ phase. For example, in the mixture of terminally polar mesogens 9OSACB–4OSACB studied by Lobko *et al.* [31] (see figure 8), the reciprocal lattice vector q_2 corresponding to A_d periodicity varies continuously with decreasing temperature and transforms without any jump into the structure vector, q'_2, of the $\tilde{C}$ phase at the A_d–$\tilde{C}$ phase transition point (see figure 10). Accordingly, the intensity of the $\mathbf{q}'_2$ Bragg peak is much higher than that of the low q side reflex $\mathbf{q}''_2$.

The topology of the phase diagram observed for the 9OSACB–4OSACB mixture (see figure 8), includes two particular $N_{re}A_d\tilde{C}$ and $N_{re}A_1\tilde{C}$ points. These could be common triple points with additional complications due to fluctuation effects, or real multicritical points. Mean field theory predicts for A_1–$\tilde{C}$ and A_d–$\tilde{C}$ a transition fairly similar to A_1–A_2, which seems to belong to the 3D Ising universality class [67]. However, since the bilayer order parameter fluctuations occur on a cone in q space, it should, following the arguments of Brazovskii [68], like the N–C transition, be first order. The N–$\tilde{C}$ transition is first order for the same reasons. The N–A_1 and N–A_d transition lines may be of second or first order with the tri-critical points induced by the proximity to a $\tilde{C}$ phase. Clearly, high resolution X-ray and calorimetry studies are required for an understanding of the nature of $N_{re}A_1\tilde{C}$ and $N_{re}A_d\tilde{C}$ points.

3.2. *Microscopic aspects of smectic A layering*

Considering the effective interaction leading to the appearance of a periodicity $d = L'$, which is incommensurate with the molecular length, it would be natural to relate it to some structural element of the medium. A pair of overlapping antiparallel molecules (dimer) would represent the simplest cluster (see figure 2). However, it is not necessary to think that each molecule interacts predominantly only with its neighbour. The value of L' is a result of a statistical averaging over the possible dipole and steric configurations rather than the length of some static object [25]. Nevertheless, this simplified notion proves to be very useful, and is widely used by different authors for data interpretation and microscopic modelling.

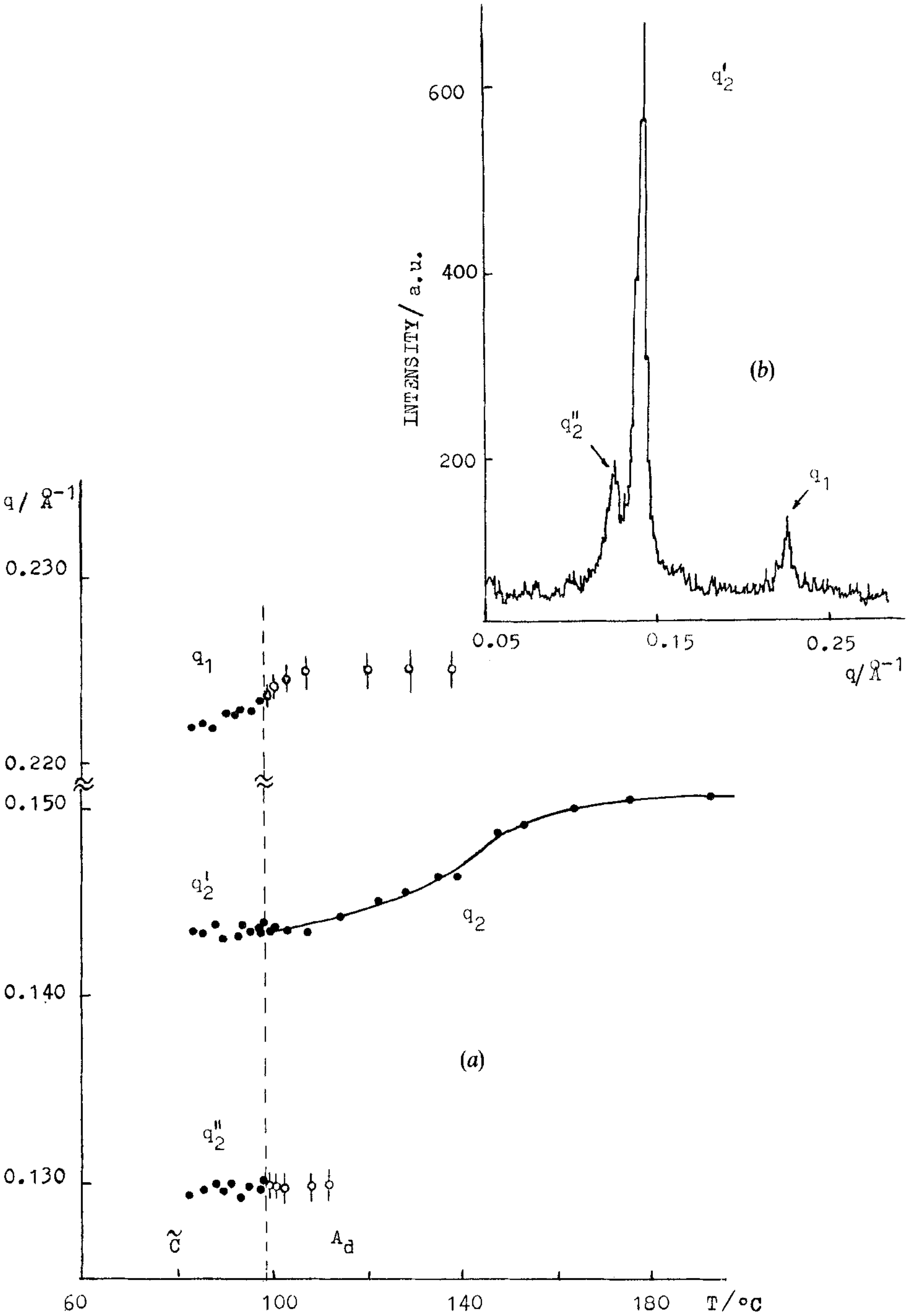


Figure 10. (*a*) X-ray diffraction profiles demonstrating the simultaneous existence of three fundamental peaks in the $S_{\tilde{C}}$ phase for 9OSACB liquid crystal; (*b*) magnitudes of the $\mathbf{q}_1$, $\mathbf{q}_2$, $\mathbf{q}'_2$ and $\mathbf{q}''_2$ diffraction vectors as a function of temperature. Filled circles indicate resolution-limited peaks, open circles diffuse maxima [31].

Model calculations performed by the Monte Carlo method [69] indicate that for a smectic A phase to appear there are no specific intermolecular interactions required—it can be formed as a result of just the steric repulsions of strongly anisotropic molecules. Of course, in real smectics A, attraction forces are substantial, and the formation of smectic layers with a broken up-down symmetry is extremely sensitive to the details of the molecular structure. For instance, a reversal of the sign of a dipole moment in one of the bridge fragments of a mesogenic molecule can radically change the type of the smectic A phase [1, 2]. Quantum chemical calculations by Tokita *et al.* [70] indicate that the polar component of the energy of asymmetric mesogenic molecules in which one of the benzene rings is replaced by a cyclohexane ring has the same order of magnitude as the dispersion interaction energy determining the transition into the nematic phase. The interaction energy of the permanent dipoles of molecules may also be fairly large: $U_{\mathrm{dip}} \simeq p^2/a^3 \simeq kT/3$ for two neighbouring molecules, at distances $a \simeq 5$ Å, having a longitudinal dipole moment $P \simeq 4D$. In spite of a considerable value for the polar interaction in mesogens, it does not give a direct contribution to the molecular field of a system with a non-polar symmetry [71]. However, it might lead to strong dipole correlations between molecules, including the formation of dimers, trimers, etc. [25].

As distinct from classical polar dielectrics, not only the value and position of the dipole moment of the molecules, but also the spatial distribution of charges due to conjugation between molecular fragments play their role in the formation of associates. Most bridge and many end-fragments of mesogenic molecules contain double and triple bonds, and, consequently, they are able to realize π-electron conjugation with one another or with the non-saturated cyclic moieties of the core, for example, benzene rings [2, 72, 73]. As a result, delocalization of π-electrons and polarization in a molecule over the entire conjugated system can arise. The properties of polarized molecules strongly depend not only on the terminal dipoles, but also on the intensity and direction of the secondary molecular dipoles associated with the different bridging groups and the oxygen of alkoxy chains in the molecules. Reversal of the bridge groups in mesogens affects the character and length of conjugated molecular dipoles and can change the type of smectic A phase [1, 2].

On the formation of an associate, the polarized molecules tend to be arranged in such a way that the opposite charges of neighbouring molecules are located at a minimum distance, which corresponds to the formation of an $\mathrm{A_d}$ phase. Purely steric factors are substantial, too. The transverse dimension of the central parts of molecules in the associated state considerably exceeds that of alkyl chains due to acoplanarity of phenyl rings and the planes of bridge fragments. This leads to an unfavourable decrease in the entropy of packing and restricts the discrete set of points at which the mesogenic molecules can overlap with one another.

The molecular origin of diverse modifications of the smectic A phase has been considered by a number of investigators [18, 23–27]. As the reference point for the latter discussion we will use the theories based on the McMillan model [74, 75]. These theories successfully describe the properties and the phase behaviour of symmetrical mesogens consisting of molecules with two hydrocarbon chains. A mean field, single particle potential describing the appearance in the system of a one dimensional density wave can be expressed in the McMillan model in terms of a Fourier series: $V_1(z) = -\alpha\psi_1 \cos q_0 z - \ldots$, where ψ_1 is the translational order parameter introduced by equation (7). The parameter $\alpha = 2\exp[-(\pi r_0/d)^2]$ depends on the relationship between the length of the central (aromatic) cores of the molecules, r_0, where the attractive intermolecular interactions are localized, and that of whole molecules, including the aliphatic chains $d \simeq L$. In accordance with the expression for $V_1(z)$, the stability of the smectic A phase in homologous series increases with the length of the hydrocarbon chains. These predictions, however, markedly contradict the phase diagrams of mesogens consisting of asymmetric molecules, where the stability of the smectic A phases often increases as the homologous number n decreases [1, 9, 62] (see figures 7 and 8). This obvious restriction of the McMillan model stems from neglecting the effects of variation of the packing entropy of the molecules, effects which may be very large in the case of asymmetrical molecules having a tendency to spatial association or having a very specific geometry of rigid or flexible moieties.

Attempts have been made to apply McMillan's theory to liquid crystals forming dimers [23, 76]. Longa and de Jeu have noted that an increase in the number of dimers in the system stabilises the A_d phase owing to a more favourable ratio between r_0 and $d = L'$ in dimers, compared with monomers [23]. This allows us to consider the nematic–smectic A_d transition as a transformation of the percolation type, occurring at a certain concentration of dimers. The direct reason for the re-entrant behaviour is an unfavourable decrease in the packing entropy with the increasing quantity of dimers in the system at lower temperatures. Any other mechanism resulting in the unfavourable packing of molecules or their moieties in smectic layers causes the same effect. If more than one type of dimer with different degrees of overlap can exist, we could expect more than one A_d phase, each separated by the nematic phase (multiple re-entrance).

A possible molecular origin of the A_d, $\tilde{A}_2$ and $\tilde{A}$ phases has been discussed by Longa and de Jeu [24]. The regions of stability of diverse smectic A phases were obtained considering competition between dispersive and dipolar interactions in conjunction with steric repulsions. It was found from estimates of these interactions that the ferroelectric smectic A phase with non-zero macroscopic polarization is strongly destabilized almost independently of the position of the molecular dipoles. In contrast, the dipole repulsions become quite small in the bilayer A_2 phase, provided the dipoles are located at the end of molecules [24]. This favours the formation of the A_2 phase for mesogenic molecules with terminally localized dipoles (not conjugated). In combination with the optimal packing, this makes the A_2 phase (and also $\tilde{A}$ and $\tilde{C}$ phases where local bilayer ordering occurs) the lowest temperature smectic A phase, as observed experimentally (see figures 6 and 8).

In the papers of Indekeu and Berker [25], the statistics of diverse dipole configurations in the lattice model of smectics A have been analysed. Because of the corrugated architecture of the rigid parts and the alkyl chains, the nearest neighbour molecules have a discrete set ($n = 4$ and 5) of energetically preferred positions of mutual penetrations determining the effective length of the nieghbouring molecules. Of great importance is the consideration of stable groups of three molecules creating a zero field at the positions of the surrounding molecules. These triplets evidently stabilize different types of smectic A layering. In the framework of a theory, the multipole re-entrant phenomenon, including the appearance of four and six re-entrant phases, has been successfully described [25]. For example, the transition from smectic A to the nematic phase corresponds to the nearest neighbour configuration in which two molecules form an antiparallel dimer; a lone neighbouring molecule interacts only very weakly with that dimer and obtains a greater freedom in its shifting perpendicular to the layer, thus disturbing the smectic order. At the same time, the regions of thermal stability of different smectic A phases are determined by the competition between the local ferroelectric and antiferroelectric order. In the latest version of the theory [77], in addition to frustrated dipolar interactions, the van der Waals and benzene ring steric hindrance interactions were included, yielding the appearance of smectic A and C phases with in-plane domain formation resembling that of $\tilde{A}$ and $\tilde{C}$ phases.

Parallel with dipolar frustrations, the statistics of flexible aliphatic chains of molecules is of great significance for the stability of smectic layers. Additional conformational entropy connected with the aliphatic chains prevents the full crystallization of rigid parts of molecules in smectic layers, thus expanding the range of existence of the smectic A phase. The conformational versatility of the alkyl chains of mesogenic molecules is explained by the fact that the energy required for *trans–gauche* and *gauche–gauche* rotations about C–C bonds is of the order of kT [16, 17]. This means that there is an appreciable fraction of *gauche* bonds in *n*-alkyl end chains. The presence of molecules with different chain configurations (conformers) in the system may stabilize certain smectic phases due to the denser packing of molecules in the layers. With decreasing temperature, the tails become less flexible, thus decreasing the packing differences between cores and tails. In turn, this can induce the transition to the phase where the packing entropy requirements are not so strict. Recently, a lattice model of smectics A, formed by molecules with flexible chains, was suggested by Dowell [18]. It was found that differences in the steric (hard repulsive) packing of rigid cores and flexible tails as a function of tail chain flexibility can stabilize smectic A_1, A_d and low temperature nematic (re-entrant nematic) phases. Thus, it is not necessary to take into account the dipolar interactions to stabilize these phases. Of course, it is hardly to be expected that the changes in flexibility of the tails of molecules could be the universal mechanism of layer destruction. However, it must be taken into account when constructing realistic molecular models.

The phase diagrams of known terminally polar compounds prove that the character of the smectic layering (A_1, A_2 or A_d) depends upon the length of the hydrocarbon chains [1, 9] (see figure 6–8). The size of an alkyl (alkoxy) chain does not influence the length of a conjugation length nor the value of the dipole moments of a molecule [12, 72, 73]. Hence, its effect can show up only through the effects of packing of the molecules in smectic layers. The response of the layered system to an unfavourable packing situation of molecules in the A_d phase might be very different. This may involve the orientational melting of the end links of aliphatic chains that diminish the energy of the orientational interaction in smectics [78]. It may lead also to the appearance of an additional number of tail chain conformers effectively increasing the entropy of the system. The probability of the formation of *gauche* conformers is higher for mesogenic molecules with long tails. Therefore, higher homologues can give a denser packing in the A_d phase even at a higher concentration of dimers. As the temperature is lowered or on passing to a homologue with a short tail, when the molecules predominantly adopt an all-*trans* configuration, the entropy-unfavourable packing of the end chains of molecules can induce the transition to either the smectic $A_1(A_2)$ or the re-entrant nematic phase. It is interesting to note that the characteristic size of the hydrocarbon chain, which divides the states with predominantly A_1 or A_d layering is $n = 6$–8 (see figures 6, 8 and 9), and is of the same order of magnitude as the persistence length in linear hydro-carbon polymers [79].

In closing this section, we will make some remarks concerning the various types of tilted smectic phases occurring among asymmetric mesogens. The formation of the smectic $\tilde{C}$ phase is associated not only with the appearance of a two dimensional polarization lattice, but also with tilting of molecules (see figure 5). From the purely steric point of view, the tilting of molecules in smectic layers is a disadvantage, since in this case the average area per molecule increases, and, hence, the entropy of packing diminishes. In accordance with the mechanism proposed by van der Meer and Vertogen [80], a decrease in entropy can be compensated due to the additional induction interaction of the permanent transverse dipoles of molecules with polarizable cores of nearest neighbours. Therefore, the formation of tilted analogues of smectic phases, i.e. C_1, C_2 and $\tilde{C}$, is possible for asymmetric molecules with large transverse dipoles. However, up to now no tilted analogues of the A_d phase (i.e. C_d) have been detected. This is, of course, not accidental. On the one hand, the dimers in the A_d phase possess not one, but two oppositely directed transverse dipole moments and this increases the induction contribution to the interaction energy. However, the existence of the smectic A_d phase is unfavourable from the packing entropy standpoint. Therefore, an additional decrease in entropy connected with the tilting of molecules is very difficult to compensate for by any additional interaction.

4. Specific features of smectic A layering affected by the sterical asymmetry of mesogens

4.1. *Examples of sterical frustrations*

So far we have considered the diversity of the types of smectic A ordering as being due mainly to dipolar origins. Now we will focus our attention on the effects of sterical repulsions, in combination with the conformational mobility of the constituent molecules. It has already been noted that incommensurate layering, modulated structures and re-entrant nematic behaviour may be detected not only among terminally polar mesogens, but also in non-polar compounds having sterical dipoles and multipoles. For example, re-entrant nematic behaviour has been found by Pelzl *et al.* [28] in binary mixtures of mesogens without polar end groups. Instead, however, at least one of the components of the mixture was strongly sterically asymmetric. Evidently the smectic A layering in such a system can occur only at the expense of packing which is less favourable than that in the nematic phase. The driving force for the re-entrant nematic transition, in accordance with the mechanism proposed by Dowell [18], is the change in the packing differences between the cores (or tails) of different nature, that cannot be compensated at low temperatures by the flexibility of aliphatic chains.

The particular types of smectic layering resulting from exceptionally asymmetric molecular shape have been found among the swallow-tailed compounds studied by the Halle group [10, 81, 82] (see figure 11). Thus, the X-ray diffraction patterns of oriented samples for compounds with one branched terminal group show a Bragg spot corresponding to the monolayer periodicity $d_1 \cong L$ and diffuse scattering in the vicinity of the reciprocal space point $q_2 = 2\pi/L'$ ($L < L' < 2L$), corresponding to uncorrelated strings of interdigitated molecules [81] (see figure 11). In the case of swallow-tailed compounds with two terminal branched chains, the formation of the monolayer smectic A_1 phase from the purely steric point of view is a disadvantage due to the appearance of an excess of free volume in the region of the rigid cores. A denser packing may be obtained for a tilted arrangement or the partial overlap of molecules (see figure 11). However, both these variants also do not satisfy the requirements of optimal packing. As a result the bi-swallow-tailed compound usually form only the nematic phase. However, X-ray diffraction patterns of the nematic phase display a strong diffuse scattering in the small angle region corresponding to uncorrelated regions with incommensurate and tilted types of layering [82] (see figure 11). The A_d type of

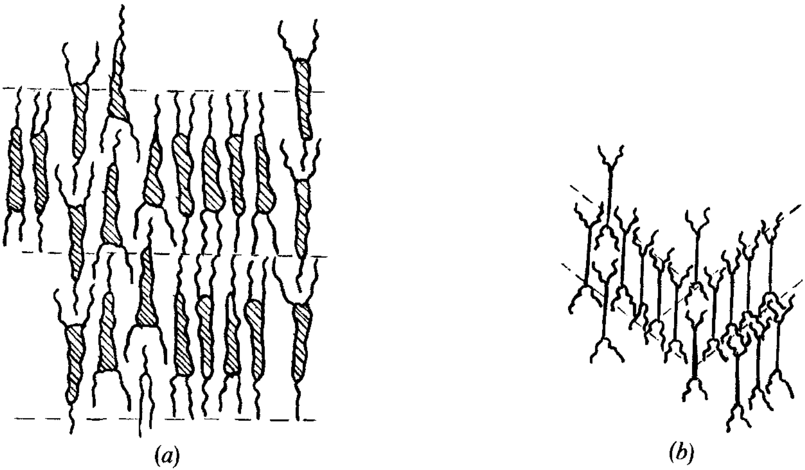


Figure 11. Examples of sterical frustrations for mesogenic compounds with one (*a*) and two (*b*) branched terminal chains [81, 82].

periodicity ($d_2L \cong 1{\cdot}1$–$1{\cdot}2$) in these compounds may be stabilized in a certain temperature–concentration range by the incorporation of shorter non-branched molecules into the free space between the bulky swallow-tailed ends of molecules (the so-called filled smectic A phase) [10, 82]. Different types of particular nematics (with strong A_d and tilted fluctuations) and smectic phases where molecules are overlapped or interdigitated have also been reported to exist for mesogenic molecules of complicated form. Among these are laterally branched compounds [83], twin molecules [84] and dimeric mesogens, where two rigid cores are linked through a flexible spacer [85].

4.2. *Smectic A layering in fluorine substituted mesogens*

The aforesaid examples do not, of course, exhaust the possibilities for imparting steric asymmetry to mesogenic units. An alternative approach consists in the partial or total substitution of fluorine atoms for hydrogen atoms at one of the end fragments of a molecule [86–89]. Now, what particular properties of perfluorinated chains may exert their influence of the smectic A layering? In the first place, the van der Waals radius of fluorine ($\cong 1{\cdot}33$ Å) considerably exceeds the corresponding value for a hydrogen atom, and fluorine atoms cover the carbon skeleton as a dense 'fur coat', Secondly, in accordance with quantum chemical calculations [88], the activation energy of *trans–gauche* and *gauche–gauche* rotations in fluorocarbons (for example decafluorobutane) is a factor of 3 to 5 times higher than that in linear hydrocarbons (for example butane). This practically excludes the possibility of the formation of *gauche*-conformers at finite temperatures. As a result, perfluorinated chains, similar to polytetrafluoroethylene units, form a rigid rod-like structure featuring a consecutive turning of the CF_2 moieties through an angle of $\cong 16°$. Such properties of perfluorinated chains diminish the packing differences between the cores and tails and introduce sterical dipoles at the end of the molecules, which can modify the character of smectic A layering. Furthermore, $-CHF_2$ and $-CF_3$ groups, as distinct from the CH_3 group, possess a fairly large longitudinal dipole moment of the order of 2–3 D [89]. This means that in perfluorinated chains comprising CF_2 moieties, the charges of opposite signs are spatially distributed along the chain in an alternating way. As a result, local dipolar repulsions between the fluorinated chains of the neighbouring molecules may arise. In turn, this can favour the shifting of molecules relative to one another in a parallel or an antiparallel configuration or affect the segregation of identical moieties.

In fact, X-ray diffraction studies of the fluoro-substituted pyridines 1Py70F7 and 1Py5F6 containing seven and six carbon atoms in the perfluorinated chain, respectively, reveal interesting features of smectic A layering [9]. Thus, the layer periodicity exceeds the molecular length: $d_2/L \cong 1{\cdot}05–1{\cdot}1$, and corresponds to the formation of an A_d phase consisting of parallel or antiparallel dimers (see figure 12). The diffraction patterns for these compounds display up to three orders of reflection resulting from smectic A layering. The ratio of the second harmonic intensity to the first was found to be about $I(2q_0)I(q_0) \cong 10^{-1}$, i.e. two orders of magnitude higher than that in conventional smectics A. In order to relate these data to the characteristics of smectic layering, it is necessary to calculate the wavelength dependence of the molecular form factor $F_M(q)$ using a reasonable model for layer organization (see figure 12). This is complicated generally, by orientational disorder and the many equivalent tail configurations of the molecules at finite temperatures [43, 44] (see also §2.2). Nevertheless, our estimations indicate that the values of $F_M(2q_0)$ and $F_M(q_0)$ in terminally fluorinated compounds are of the same order of magnitude, yielding the ratio of the first two translational order parameters $\psi_2/\psi_1 \cong 4–5 \times 10^{-1}$. These estimations indicate that in the case of terminally fluorinated mesogens, the one dimensional density wave $\rho(z)$ (see equation (4)) is far from being purely sinusoidal and the distribution function $f(z)$ of the positions of the molecules within the layers is more narrow than in conventional smectics A. These estimates are in good agreement with recent studies of the thickness dependence of the layer displacement fluctuations for the perfluorinated mesogen F_{11} [90]. The value of the exponent $\eta_1 \cong 4 \times 10^{-2}$ of algebraic decay of the interlayer density–density correlation function was determined to be approximately a factor of two less than that commonly reported for low molecular mass thermotropic smectics. The corresponding value of the layer displacement amplitude $\sigma \sim \eta_1^{1/2}$ (see equation (6)) for perfluorinated compound F_{11} does not exceed 3–4 Å instead of 5–7 Å in conventional smectics A.

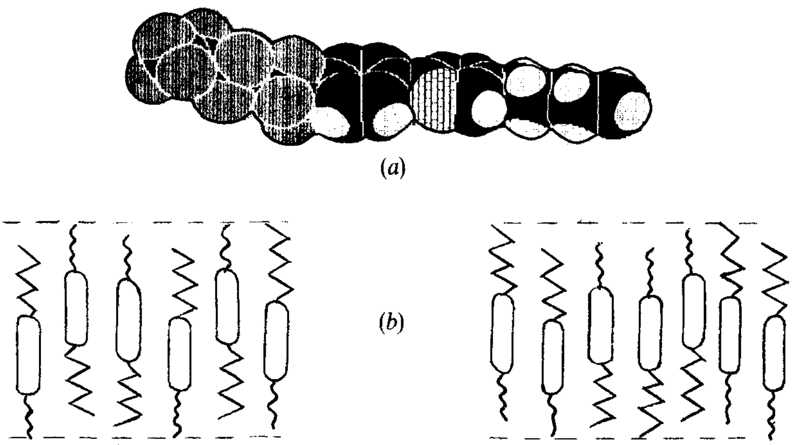


Figure 12. (*a*) Molecular model and (*b*) different types of parallel and antiparallel packings in smectic layers of terminally fluorinated mesogens.

The effects of sterical repulsions influenced by terminal fluorination are much more pronounced in the case of lateral substitution of a fluorine atom for a hydrogen atom in the benzene ring adjacent to the perfluorinated chain [9] (see figure 13). Thus, X-ray diffraction patterns of oriented samples of PF7OF8B in the smectic phase show a Bragg-like peak at wave vector $2q_1$ corresponding to the periodicity $d \simeq L/2$, and diffuse off-axis spots corresponding to fluctuations of a monolayer density wave modulated in the plane of layers (see figure 13). The period of modulation $d = 2\pi/q_{\perp_0} \simeq 50$ Å corresponds to a group of approximately ten molecules in a layer. Comparison of the X-ray diffraction pattern (see figure 13) with the type for the reciprocal-space smectic $\tilde{\text{A}}$ (see figure 4) allows us to propose a structural model of the smectic phase, as represented in figure 13. In accordance with the model, the regions of monolayers are shifted relative to one another by a half of the molecular length, thereby forming an alternating structure of a chequer-board type. Taking into account the diffuse character of the modulation peaks, we can conclude that in the case of perfluorinated PF7OF8B we have to deal with a strongly defective modulated structure of the smectic $\tilde{\text{A}}$ type, where the positions or the areas of shifted layers are not correlated in space. Similar types of defective layer structures were reported earlier for certain comb-like liquid crystalline polymers [6, 7]. If we consider a stereo-model for the PF7OF8B molecule, than it is readily seen that a fluorine atom in the lateral position in the benzene ring prevents the perfluorinated tail from rotating about the C–O bond, thereby setting the rigid chain in a strictly fixed position relative to the plane of the

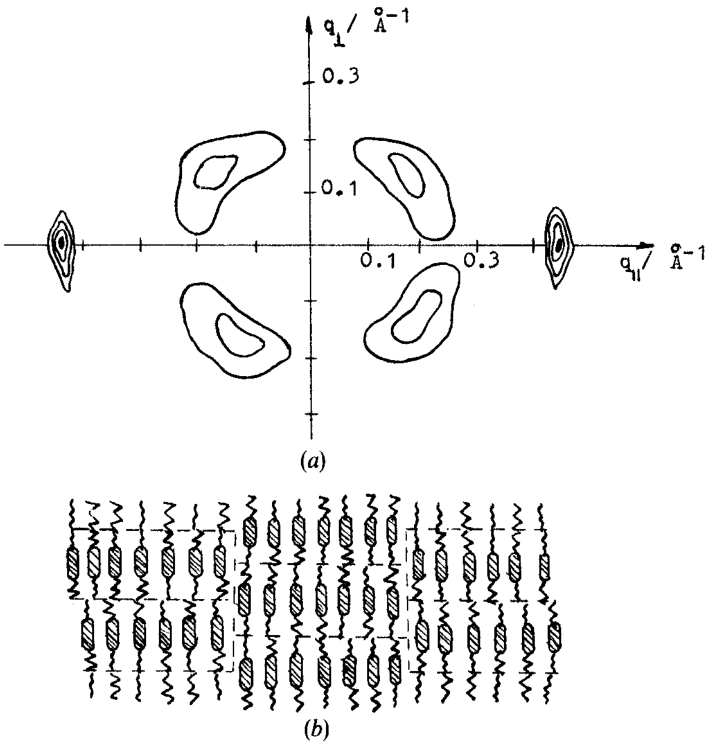
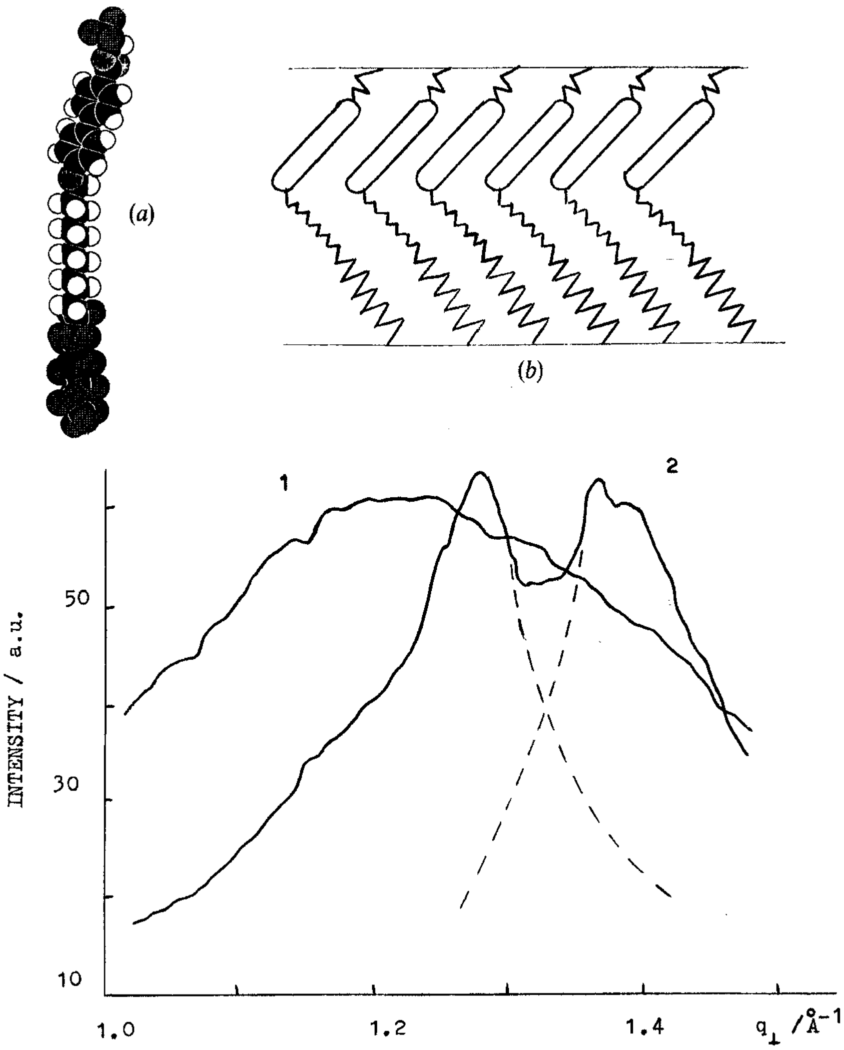


Figure 13. (*a*) The intensity contours of X-ray scattering in the $q_\parallel$–$q_\perp$ plane in the smectic A phase of the perfluorinated PF7OF8B liquid crystal; (*b*) the real-space model of the smectic phase [9].

phenyl ring. This corresponds to the appearance of a strong sterical dipole at the end of the molecule. Taking into account the tendency of perfluorinated compounds to form parallel or antiparallel dimers (see figure 12), the presence of such a sterical dipole may induce the bending of layers and the formation of a modulated Ã phase according to the mechanism suggested by Longa and de Jeu [24] and Helfrich [29].

Before finishing this section, it is relevant to consider the peculiarities of smectic A layering for a new class of mesogenic compounds containing perfluorinated chains, so-called polyphilic molecules, originally synthesized by Tournilhac and Simon [14]. These molecules are made up of a sequence of chemical moieties differing in their properties, for example, rigid perfluoroalkyl chain, flexible hydrocarbon chain, rigid biaryl core and again a perfluoroalkyl chain (see figure 14). The basic idea that stimulated the



(c)

Figure 14. (a) Molecular model of the polyphilic compound; (b) structure of the smectic C layers with the tilted molecules in the zig-zag conformation; (c) X-ray diffraction profiles in the wide scattering angle region: (1) smectic A_1 phase, (2) smectic X′ phase [93].

synthesis of these compounds was that in polyphilic mesogens three or more chemically different fragments could segregate in a special way, resulting in the formation of particular types of layering, including the non-centrosymmetric arrangement with a non-zero macroscopic polarization (see also [91]). Indeed, the possibility of reversing the sign of polarization was demonstrated recently by several methods for binary mixtures of polyphilic compounds differing in the direction of the longitudinal dipoles [92]. These results are apparently the first examples of the observation of polarity in non-chiral smectic media. The polyphilic mesogens, on cooling down from the isotropic phase display a monolayer smectic A_1 phase with the interlayer spacing d_1 equal to the length of the fully extended molecule. The diffraction patterns, in common with those of other mesogens having perfluorinated chains, show up to three orders of resolution limited peaks resulting from smectic order. At lower temperatures, we observe the particular smectic phases (X and X′) in which the macroscopic polar properties have been detected [92, 93]. X-ray diffraction patterns for the X and X′ phases show different combinations of spots, including off-axis reflections, that are characteristic of modulated structures. All peaks are not resolution limited with the correlation length in the direction parallel to the director $\xi_{\parallel} \lesssim 300$ Å. This corresponds to the formation of strongly defective periodic structure with alternating packing of the molecular moieties of different nature. With dependence on concentration, diverse types of layering can be observed for mixtures of polyphilic compounds. In the $S_{X'}$ phase, lamellar ordering is of the smectic C type, in which molecules in a complicated zig-zag conformation are tilted relative to the layer normals (see figure 14). In the S_X phase, two types of layering coexist, namely the modulated structure in which the smectic C layers are periodically shifted relative to one another by a half of the interlayer spacing and the monolayers of the A_1 type.

The intensity distribution in the wide scattering angle region in the A_1 phase show a broad liquid-like peak centred at the point in q space corresponding to an average intermolecular distance of ≈ 5 Å in the smectic planes (see figure 14). The angular width of the peak corresponds to interlayer positional correlations of length $\xi_{\perp} \lesssim 12$–16 Å. In the smectic X′ phase, this broad peak splits into two peaks, which may be fitted by a sum of two lorentzians, yielding the intermolecular distances $d_1 = 4{\cdot}9$ Å and $d_2 = 4{\cdot}5$ Å and intralayer positional correlations $\xi_{\perp 1,2} \lesssim 40$ Å. The values of d_1 and d_2 could be related to the typical average distances between the two perfluorinated and the two hydrocarbon chains respectively [94]. These observations indicate that the X′ phase still consists of fluid layers with two types of preferential nearest neighbour contacts, which most likely correspond to segregation of perfluorinated and hydrocarbon moieties. It is still unclear in what way the particular structures of the smectic X and X′ phases can give rise to the observed polar behaviour of polyphilic mixtures. Further studies are necessary to understand this point.

5. Final remarks

In this paper, a review has been given of particular types of layering in low molecular weight thermotropic liquid crystals with differing degrees of polar and sterical asymmetry. It has been shown that a combination of polar and sterical dipoles and multipoles, together with conformational mobility of different moieties in the mesogenic molecules, leads to a variety of smectic phases wth a broken up-down symmetry. In special cases, the formation of strongly defective layers with an alternating packing of molecular fragments of a different nature has been detected. Of course, the aforesaid examples do not exhaust the total possible variety of one dimensional and two dimensional layered structures. We have not discussed here the specific features of layering for disc-shaped, bowl-like and plate-like mesogenic molecules, as well as the properties of thin smectic films obtained by different methods and of the surface state of smectics A.

Practically, all the smectic A phases identified in low molecular weight asymmetric mesogens have been found among thermotropic, comb-like, liquid crystalline polymers [95, 96]. Side chain polymers possess additional possibilities for dipole compensation and the inclusion of new flexibility mechanisms associated with changes in the relative arrangement of the basic polymeric chain, the mesogenic groups, and the spacers between them. For example, the modulated smectic $\tilde{A}$ phase has been detected by Endres *et al.* [8] for combined main chain/side chain polymers containing no terminal dipoles, but with repeating units similar to laterally branched mesogens. These observations confirm our present view that frustrated types of layering may be obtained without any dipolar coupling, but only by an appropriate design of the mesogenic molecules. We may expect that the role of steric repulsions associated with asymmetry of form will increase for mesogenic molecules occupying the marginal states between the very different types of liquid crystalline order. Among these are phasmids, which bridge the gap between rod-like and disc-like mesogens [97], compounds with tetrahedral symmetry, filling the space between monomeric rod-like mesogens and side chain polymers [98], and rod-like molecules with extended lengths of the hydrocarbon chains forming three dimensional cubic lattices resembling the types of layering in amphiphile–water systems [29, 99, 100].

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