Chapter 2

Phase transitions in Antiferroelectric Liquid Crystals: A Theoretical Model

2.1 Overview

Organic compounds with rod like molecules forming liquid crystalline phases often carry permanent electric dipole moments with components parallel and/or perpendicular to the long axes of the molecules. Hence, one could expect ferroelectric properties in such liquid crystalline phases. Several theoretical considerations for the realization of a true ferroelectric liquid or the polar nematic phase have been reported. However, upto now there is no clear experimental evidence for such a polar nematic phase. On the other hand, using symmetry arguments, Meyer et al. [5] demonstrated that the $C_2$ point symmetry of the layers in the chiral smectic C (SmC*) phase allows them to be polarized in the plane of the layers. As this transversely polarized SmC* phase can have potential applications in display devices many compounds exhibiting SmC* phase have been synthesized and the properties of this phase have been extensively studied [6].

As we have mentioned in Chapter 1, Chandani et al. [7] discovered transverse antiferroelectricity in the compound 4 - (1 - methylheptyloxy carbonyl) phenyl 4' - octylcarbonyloxybiphenyl - 4 - carboxylate (MPOBC). Further detailed studies show that in addition to the antiferroelectric (SmC_A*) phase, these novel compounds exhibit a rich variety of other phases as they are cooled from the isotropic phase:
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SmA-SmC\(\alpha\)-SmC\(\beta\)-SmC\(\gamma\)-SmC\(\gamma\)-SmC\(\gamma\)-SmI\(\alpha\)-Cryst.,

where the symbol SmC\(\beta\) denotes the usual ferroelectric SmC\(\ast\) phase. The subscript \(\beta\) has been given to distinguish it from the other phases in these compounds. Though the structures of SmC\(\beta\) and SmC\(\gamma\) phases are well understood as discussed in chapter 1, the structures of SmC\(\ast\) and SmC\(\ast\) phases are not clearly elucidated. Several experimental studies using a variety of techniques have established the following facts:

- The SmC\(\gamma\) phase is ferrielectric in nature as the effective polarization in this phase is lower than that in the SmC\(\beta\) phase. Several pure compounds exhibit two ferri phases [13] whereas in some binary mixtures there are three subphases FI\(H\), SmC\(\ast\) and FI\(L\) [12].

- Optical and x-ray measurements reveal that the SmC\(\ast\) phase has a small tilt angle and a very short pitch [12, 14]. Also this phase has ferrielectric characteristics at lower temperatures but antiferroelectric characteristics close to the SmA-SmC\(\ast\) transition temperature [15, 16].

- All the tilted phases have a helical structure and it is established by optical measurements that the sense of the helix is opposite in SmC\(\beta\) and SmC\(\gamma\) phases [17].

- All the transitions between different tilted phases are weakly first order in nature as determined by differential scanning calorimetry (DSC) with heats of transition \(\approx 1\) joule/mole [18].

- SmC\(\ast\) and the ferrielectric phases are very sensitive to the optical purity of the sample. The transitions to these phases disappear if the compound is mixed even with a small fraction of its opposite handed enantiomer [12]. The range of SmC\(\ast\) phase shrinks as the nonchiral chain length is increased [18].
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- The apparent tilt angle (the angle between the effective optical axis of the field distorted structure and the layer normal) measurements on homogeneously aligned samples revealed that in the SmC_α phase, there is a step like variation of the apparent tilt angle as a function of an in-plane external static electric field \[19\]. This led to the speculation that there is a field induced devil's staircase in this phase.

- The conoscopic figures obtained from thick homeotropically aligned samples also show distinct characteristic changes as a function of an in-plane external static electric field in the ferrielectric \[20\] and SmC_α \[19\]phases. In both of these phases as the field is increased from zero, the conoscopic figure of the uniaxial medium acquires biaxial characteristics with the optic axial plane parallel to the electric field which then switches to the orthogonal direction beyond a critical field \[20, 19\].

- The ferrielectric phase has a rather turbid appearance rendering optical measurements in this phase difficult \[13, 21\].

- Studies on several homologous series have shown a prominent odd-even effect in the phase transition temperatures between the SmC_β to SmC_γ as well as SmC_γ to SmC_A phases \[18\].

- A strong transverse dipolar group attached close to the chiral center favours the formation of the SmC_A phase. However, even racemic mixtures with zero polarization \[12\] and achiral compounds \[22\] also exhibit the anticlinic phase in which successive layers have opposite tilts.

Several phenomenological theories have been developed to account for some of the above experimental observations in these compounds. In these phenomenological Landau type theories one expands the free energy density in powers of suitable order parameters to describe the transitions between the phases.
The first theory of this type for antiferroelectric liquid crystals was developed by Orihara et al. [23]. They assumed bilayer order in the ferro, ferri and antiferro phases to define the order parameters which vary continuously along the layer normal. To a first approximation, neglecting the fluctuations or inhomogeneous terms of the free energy density expansion, they obtained transitions between the ferro, ferri and antiferroelectric phases. Later Lorman et al. [24] extended this model to include the inhomogeneous terms in the free energy density expansion. However, these continuum theories do not account for the SmC* phase. Further, experimental observations [12, 21] in the ferrielectric phase appear to indicate that this phase has multi-layer order and the assumed bilayer order may not be adequate in this phase.

To improve upon this, a discrete model taking into account the configuration of each layer was first proposed by Sun et al. [25]. Later treating the configuration of each layer as an Ising variable, Yamashita et al. [26, 27] developed a model in analogy with Axial Next Nearest Neighbour Ising (ANNNI) model taking into account upto third nearest neighbour interactions. Again both these discrete models do not account for the SmC* phase. In the Ising picture, the helicoidal structures which are present in all the tilted phases have been neglected.

In order to account for the SmC* phase and the experimental observations mentioned above, we developed a discrete phenomenological model [28] for this system by including NN as well as competing NNN interactions between the layers whose origins are also discussed in Sec 2.4.1. In our theory, the configuration of each layer is described by a 2-d axial vector as in [25] and hence the resulting model is of xy-type. Our model takes into consideration the helicoidal structures of the phases and accounts for the SmC* for as well as the three ferrielectric phases often seen in these systems.

In Sec. 2.2, we will describe the continuum theories developed for this system in earlier studies which form a theoretical background to our model. In Sec. 2.3 we will
consider other models *viz.* the Ising type models often invoked for this system. In this section we will also point out the shortcomings of these models. Then in Sec. 2.4, we will discuss the discrete model developed by us. Finally the main conclusions of this chapter will be summarized in Sec. 2.5.

2.2 Continuum theory of AFLC

In the uniaxial SmA phase as the long axes of the cylindrical rod like molecules orient on average along the layer normal, they can rotate freely about their long axes. But in the tilted smectic phases, the tilt order induces a hindrance to this free rotation. If the net dipole moment of such a molecule has a component perpendicular to the long axis of the molecule then one can expect the layers to become transversely polarized. However, in the SmC phase made of *achiral* molecules, the symmetry $C_{2h}$ of the layers contain a mirror plane perpendicular to the $C_2$ axis and the above rotational bias can only produce quadrupolar order within the layers. But, if the molecules are *chiral*, this mirror plane perpendicular to the $C_2$ axis is removed and the layers in the resulting SmC* phase become transversely polarized. As this transverse polarization is a consequence of the tilt order of the layers, the latter is taken as the primary order parameter whereas the former is a secondary order parameter [6] in the theories described below.

2.2.1 Order parameters

A complete prescription of the "order" in one of the tilted smectic phases involves many elements: (a) The orientational order of the rod like molecules implicitly assumed to be perfect and represented only by the director $\hat{n}$. (b) The one dimensional translational order which can be described by the density wave $\psi = |\psi| \exp[i(\mathbf{k} \cdot \mathbf{r} + \alpha)]$, where $|\psi|$ is the amplitude, $\alpha$ is an arbitrary initial phase and $\mathbf{k}$ is the wave vector. Again $|\psi|$ is implicitly assumed to be a constant and in effect only the magnitude of $\mathbf{k}$ which is coupled to the tilted orientation of the
molecules within the layers is taken into account. (c) The tilt order of the director $\hat{n}_i$ in the i-th layer which can be described by an axial vector $\vec{\xi}_i$ defined as

$$\vec{\xi}_i = (\hat{n}_i \cdot \hat{k})(\hat{n}_i \times \hat{k}).$$  \hspace{1cm} (2.1)$$

Note that the definition is consistent with the apolar nature of the director $\hat{n}$. Assuming that the wave vector $\vec{k}$ is parallel to the z-axis, the order parameter to within an arbitrary constant is then

$$\vec{\xi}_i = (n_{iy} n_{iz}, -n_{ix} n_{iz}) \equiv \frac{\sin 2\theta_i}{2} (\sin \phi_i, -\cos \phi_i),$$  \hspace{1cm} (2.2)$$

where $n_{iz}, n_{iy}$ and $n_{ix}$ are the Cartesian components of $\hat{n}_i$. Note that $\vec{\xi}_i$ is perpendicular to the c-vector $\vec{c}_i$ of the i-th layer as shown in Fig. 2.1. In the ferroelectric phase $\vec{\xi}_i$ and the corresponding $\vec{P}_i$ are the only order parameters which are assumed to be continuous functions of $z$. Detailed theoretical models using these order parameters have been developed to account for the various physical properties of this phase [6].

In the antiferroelectric phase the angle between the c-directors of successive layers is close to $\pi$ and it is convenient to define two primary order parameters $\vec{\xi}_a$
and $\xi_f$ as

$$\tilde{\xi}_a = (\xi_1 - \xi_2)/2 \tag{2.3}$$
$$\tilde{\xi}_f = (\xi_1 + \xi_2)/2, \tag{2.4}$$

where $\xi_1$ represents the orientations of the molecules in the odd-numbered layers and $\xi_2$ those for the nearest neighbour even-numbered layers along the positive $z$-axis. The subscripts "a" and "f" represent antiferroelectric and ferroelectric order respectively. Similarly the secondary order parameters $\tilde{P}_a$ and $\tilde{P}_f$ are defined as

$$\tilde{P}_a = (P_1 - P_2)/2 \tag{2.5}$$
$$\tilde{P}_f = (P_1 + P_2)/2, \tag{2.6}$$

where $P_1$ and $P_2$ are the polarizations in the neighbouring layers as defined above. These order parameters are assumed to vary sufficiently slowly along the layer normal to treat them as continuous functions of $z$.

Though all these variables transform like vectors under all rotations of the symmetry group $D_{\infty}$, the antiferroelectric and ferroelectric variables transform in different ways under translation. $\tilde{P}_a$ changes sign under a translation parallel to the layer normal by a layer spacing while $\tilde{P}_f$ does not change. Hence, if the smectic liquid crystal is regarded as a one dimensional crystal, then $\tilde{P}_f$ and $\tilde{P}_a$ are the zone center and zone boundary modes respectively.

Neglecting the in-plane fluctuation of the order parameters the free energy density can now be expanded in terms of these order parameters and their derivatives along the $z$-axis. In Sec. 2.2.2 we will consider the homogeneous case neglecting the terms involving the derivatives of the order parameters following the discussion by Orihara et al. [23]. The inhomogeneous case including the derivative terms will be discussed in Sec. 2.2.3 as was first considered by Lorman et al. [24].
2.2.2 Homogeneous case

The homogeneous part of the free energy density consistent with the symmetry (viz. $D_\infty$) of the high temperature SmA phase can be expanded as

$$
\mathcal{F}_{\text{hom}} = \frac{\alpha_a}{2} \xi_a^2 + \frac{\alpha_f}{2} \xi_f^2 + \frac{\beta_a}{4} \xi_a^4 + \frac{\beta_f}{4} \xi_f^4 + \frac{\gamma_1}{2} \xi_a^2 \xi_f^2 + \frac{\gamma_2}{2} (\xi_a \cdot \xi_f)^2 - \lambda_a \xi_a \cdot \vec{P}_a - \lambda_f \xi_f \cdot \vec{P}_f + \frac{1}{2\chi_a} \vec{P}_a^2 + \frac{1}{2\chi_f} \vec{P}_f^2 - \vec{E} \cdot \vec{P}_f,
$$

(2.7)

where $\xi_{a(f)} = |\vec{\xi}_{a(f)}|$ and $\vec{E}$ is the external field. Terms upto 4-th order in the primary order parameters $\vec{\xi}_{a(f)}$ and upto 2nd order in secondary order parameters $\vec{P}_{a(f)}$ are retained in the expansion. As is usual in a Landau theory one can assume that the coefficients $\alpha_a$ and $\alpha_f$ are temperature dependent with $\alpha_a = A(T - T_c)$ and $\alpha_f = \alpha_a + b$. The terms with coefficients $\lambda_a$ and $\lambda_f$ are called electroclinic terms which are analogous to the piezoelectric terms in solid state physics. These two terms are pseudo scalar and are allowed only in a chiral medium. The terms with $\chi_a$ and $\chi_f$ are of entropic origin arising from the rotational degrees of freedom of the tilted molecules about their long axes [6]. The last term is the coupling of electric field with the polarizations of the layers.

Minimization of Eq. 2.7 with respect to $\vec{P}_a$ and $\vec{P}_f$ and eliminating the two, the free energy density using polar coordinates can be written as

$$
\mathcal{F}_{\text{hom}} = \frac{\alpha_a}{2} \xi_a^2 + \frac{\alpha_f}{2} \xi_f^2 + \frac{\beta_a}{4} \xi_a^4 + \frac{\beta_f}{4} \xi_f^4 + \frac{\gamma_1}{2} \xi_a^2 \xi_f^2 + \frac{\gamma_2}{2} \xi_a^2 \xi_f^2 \cos^2 \Phi - E' \xi_f \cos \Psi,
$$

(2.8)

where $\Phi$ is the angle between $\vec{\xi}_a$ and $\vec{\xi}_f$ and $\Psi$ is angle between $\vec{E}$ and $\vec{\xi}_f$. The equilibrium and stability conditions for $\Phi$ and $\Psi$ are

$$
\frac{\partial \mathcal{F}_{\text{hom}}}{\partial \Phi} = -\frac{\gamma_2}{2} \xi_a \xi_f \cos 2\Phi = 0,
$$

(2.9)

$$
\frac{\partial \mathcal{F}_{\text{hom}}}{\partial \Psi} = E' \xi_f \sin \Psi = 0,
$$

(2.10)

$$
\frac{\partial^2 \mathcal{F}_{\text{hom}}}{\partial \Phi^2} = -\gamma_2 \xi_a^2 \xi_f^2 \cos 2\Phi > 0,
$$

(2.11)
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Fig 2.2: The bilayer structures of different phases predicted by homogeneous model.

$$\frac{\partial^2 \mathcal{F}_{\text{hom}}}{\partial \Psi^2} = E' \xi_f \cos \Psi > 0. \quad (2.12)$$

From Eqs. 2.9-2.12 stable equilibrium solutions are $\Phi = 0$ or $\pi$ if $\gamma_2 < 0$ and $\Phi = \pi/2$ if $\gamma_2 > 0$, and $\xi_f$ is always parallel to $\vec{E}$ i.e., $\Psi = 0$.

Now Eq. 2.8 can be expressed in terms of the amplitudes $\xi_a$ and $\xi_f$ as

$$\mathcal{F}_{\text{hom}} = \frac{\alpha_a}{2} \xi_a^2 + \frac{\alpha_f}{2} \xi_f^2 + \frac{\beta_a}{4} \xi_a^4 + \frac{\beta_f}{4} \xi_f^4 + \frac{\gamma}{2} \xi_a^2 \xi_f^2 - E' \xi_f, \quad (2.13)$$

where $\gamma = \gamma_1 + \gamma_2 \cos^2 \Phi$ and $\Phi$ can take values (0 or $\pi$) or $\pi/2$ depending on the sign of $\gamma_2$. Minimization of Eq. 2.13 with respect to $\xi_a$ and $\xi_f$ in absence of the external electric field stabilize the five low symmetry phases. These are defined by the following equilibrium values of the order parameters

I. $\xi_a = 0, \xi_f^2 = -\frac{\alpha_f}{\beta_f}$;

II. $\xi_a^2 = -\frac{\alpha_f}{\beta_a}, \xi_f = 0$;

III and IV. $\xi_a^2 = -\frac{\alpha_a \beta_f + \gamma a_f}{\beta_a \beta_f - \gamma^2}, \xi_f^2 = -\frac{\alpha_f \beta_a + \gamma a_f}{\beta_a \beta_f - \gamma^2}, \Phi = 0$ or $\pi$;

V. $\xi_a^2 = -\frac{\alpha_a \beta_f + \gamma a_f}{\beta_a \beta_f - \gamma^2}, \xi_f^2 = -\frac{\alpha_f \beta_a + \gamma a_f}{\beta_a \beta_f - \gamma^2}, \Phi = \pi/2$;

The smectic ordering corresponding to the preceding equilibrium values of the order parameter are represented in Fig. 2.2. One can see that three types of dipolar orders are possible. Fig. 2.2a represents the ferroelectric mono-layer ordering with
the polarizations ($\vec{P}$) remaining parallel in successive layers. Fig. 2.2b corresponds to an antiferroelectric bilayer ordering, with an antiparallel orientation for adjacent $\vec{P}$ vectors. Fig. 2.2c-2.2e represent the three types of ferrielectric ordering, which can be distinguished by their tilt and azimuthal angles. Thus Fig. 2.2c & 2.2d represent ferrielectric structures in which two adjacent layers possess different tilt angles and the difference in azimuthal angle is 0 and $\pi$ respectively. In the structure shown in Fig. 2.2e the molecules in successive layers have the same tilt angles but different arbitrary azimuthal angles. As one can guess the structures shown in Fig. 2.2c and 2.2d for the ferrielectric phase involve changes in the layer spacing from layer to layer and are energetically not favoured. In fact x-ray studies have not found any evidence for these structures in the ferrielectric phase. Orihara et al. [23] have constructed the phase diagram representing the various types of phase sequences predicted by their model in the $\beta_a - \beta_f$ plane without going into the detailed structure of the ferrielectric phase.

2.2.3 Inhomogeneous case

In Sec. 2.2.2 only a homogeneous form of the free energy density was considered. Taking into account the influence of the chiral symmetry of the molecules to produce a helicoidal structure along the $z$-axis the total free energy density $F$ is a sum of two parts

$$F = F_{\text{hom}} + F_{\text{inh}}$$

(2.14)

where the $F_{\text{hom}}$ is given by Eq. 2.7 and $F_{\text{inh}}$ is the inhomogeneous part of the free energy density. Assuming that there is no variation of the orientational order parameters within the smectic layers, extending the method used for ferroelectric liquid crystals [6], $F_{\text{inh}}$ can be written as [23]

$$F_{\text{inh}} = \delta_a \left( \xi_{ax} \frac{d\xi_{ay}}{dz} - \xi_{ay} \frac{d\xi_{ax}}{dz} \right) + \delta_f \left( \xi_{fx} \frac{d\xi_{fy}}{dz} - \xi_{fy} \frac{d\xi_{fx}}{dz} \right) + \mu_a \left( P_{ax} \frac{d\xi_{ay}}{dz} - P_{ay} \frac{d\xi_{ax}}{dz} \right) + \mu_f \left( P_{fx} \frac{d\xi_{fy}}{dz} - P_{fy} \frac{d\xi_{fx}}{dz} \right)$$
\[
\frac{\kappa_a}{2} \left( \frac{d\xi_a}{dz} \right)^2 + \frac{\kappa_f}{2} \left( \frac{d\xi_f}{dz} \right)^2
\]  
\tag{2.15}
\]

where the first two terms with coefficient \( \delta_a \) and \( \delta_f \) are the lowest order Lifshitz invariants allowed by the chiral symmetry of the medium. The terms with coefficients \( \mu_a \) and \( \mu_f \) are the flexoelectric terms and the last two are the usual elastic energies associated with the distortions of the director.

Lorman et al. [24] assumed that the tilt order of the smectic is homogeneous (i.e., \( \theta \) is independent of \( z \)). This is a reasonable approximation in tilted smectic liquid crystals far from the SmA-SmC transition point and in the absence of an external field. The distortions in the tilt angle (the so called soft mode) which involves changes in layer spacing is energetically less favoured compared to distortions in the azimuthal angle (the Goldstone mode). Then from Eq. 2.2-2.4, the order parameters \( \xi_a \) and \( \xi_f \) become

\[
\xi_a = \xi_o (-\sin \psi \sin \phi, \sin \psi \cos \phi),  
\tag{2.16}
\]
\[
\xi_f = \xi_o (-\cos \psi \cos \phi, \cos \psi \sin \phi),  
\tag{2.17}
\]

where the variables \( \xi_o, \phi \) and \( \psi \) are given by

\[
\xi_o = \frac{\sin 2\theta}{2}, \quad \phi = \frac{\phi_2 + \phi_1}{2}, \quad \psi = \frac{\phi_2 - \phi_1}{2}.  
\tag{2.18}
\]

Now using the expressions for \( \xi_a \) and \( \xi_f \) from Eq. 2.16 and Eq. 2.17 and including \( \xi_o \) in the phenomenological coefficients, the free energy per unit area in the absence of electric field takes the form

\[
F = \int \left[ \frac{1}{2} \left( \frac{d\phi}{dz} \right)^2 (\kappa^+ + \kappa^- \cos 2\psi) + \frac{1}{2} \left( \frac{d\psi}{dz} \right)^2 (\kappa^+ - \kappa^- \cos 2\psi) - \right.
\]
\[
\left. \left( \frac{d\phi}{dz} \right) (\delta^+ + \delta^- \cos 2\psi) + \frac{a_1}{2} \cos 2\psi + \frac{b_1}{4} \cos^2 2\psi \right] dz
\tag{2.19}
\]

where \( \kappa^+ = (\kappa_f + \kappa_a)/2, \quad \kappa^- = (\kappa_f - \kappa_a)/2, \quad \delta^+ = -(\delta_f + \delta_a)/2 - (\lambda_f \chi_f \mu_f + \lambda_a \chi_a \mu_a)/2, \quad \delta^- = -(\delta_f - \delta_a)/2 - (\lambda_f \chi_f \mu_f - \lambda_a \chi_a \mu_a)/2, \quad a_1 = \alpha_f/2 - \alpha_a/2 + \beta_f/4 - \beta_a/4 \) and \( b_1 = \beta_f/4 + \beta_a/4 - \gamma_1/8 \). Note that there is a linear term in \( d\phi/dz \) in Eq. 2.19 which
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stabilizes a spontaneous helicoidal structure. This term vanishes in a non-chiral medium as $\delta^+$ and $\delta^-$ are zero in such a medium.

From the Euler-Lagrange equations corresponding to the variation of $\phi$ and $\psi$ in the free energy functional Eq. 2.19, we get

\[(\kappa^+ + \kappa^- \cos 2\psi) \frac{d\phi}{dz} - (\delta^+ + \delta^- \cos 2\psi) = C, \quad (2.20)\]

\[(\kappa^+ - \kappa^- \cos 2\psi) \frac{d^2\psi}{dz^2} = \kappa^- \sin 2\psi \left(\frac{d\phi}{dz}\right)^2 - \kappa^- \sin 2\psi \left(\frac{d\psi}{dz}\right)^2 + 2\delta^- \sin 2\psi \frac{d\phi}{dz} - a_1 \sin 2\psi - b_1 \sin 2\psi \cos 2\psi, \quad (2.21)\]

where $C$ is the first integral value that depends on the external parameters. It is easy to see that a stable solution of Eq. 2.20 and Eq. 2.21 corresponds to a uniform helicoidal structure with

\[\phi = kz, \quad \psi = \text{const.}, \quad (2.22)\]

where $k$ is the wave vector of the helix. $k$ and $\psi$ do not depend on $z$ but vary with the external variables. In other words, one obtains an in-phase azimuthal angle $\phi$ that depends linearly on $z$, whereas the azimuthal anti-phase angle $\psi$ is independent of the $z$ variable.

Substituting the stable solutions Eq. 2.22 in the Landau-Ginzburg potential Eq. 2.19, one gets by integrating with respect to the $z$ variable,

\[F(k, \psi) = \left[\frac{k^2}{2} (\kappa^+ + \kappa^- \cos 2\psi) + k(\delta^+ + \delta^- \cos 2\psi) + \frac{a_1}{2} \cos 2\psi + \frac{b_1}{4} \cos^2 2\psi\right], \quad (2.23)\]

which is a simple algebraic expression. The different phases correspond to different values of the anti-phase azimuthal angle $\psi$.

According to this model, in the ferrielectric SmC$^*$ phase, the difference in azimuthal angles between a pair of near neighbour layers i.e., $\psi$ is fixed at a value
between 0 and $\pi$, such pairs in turn having a helical arrangement. The two limiting angles correspond to ferro- and antiferro- phases respectively. The phase diagrams corresponding to different values of the phenomenological coefficients have been calculated in Ref. [24]. Note that both the ferro- and antiferroelectric phases predicted by this model are different from the experimentally exhibited structures as $\psi$ within a unit cell is exactly 0 and $\pi$ in the two predicted phases respectively. Further, the field induced structural changes can not be studied using this approximation. It has been pointed out by Gorecka et al. [20] that this type of model can not explain the conoscopic observations in the ferrielectric phase in the presence of a field (see chapter 4 for details).

2.3 Other relevant models

From the switching current measurements in the SmC$_{\alpha}$ phase, Takanishi et al. [16] found that this phase has antiferroelectric characteristics close to the SmA - SmC$_{\alpha}$ transition temperature but acquires ferrielectric characteristics with decreasing temperature. Hiraoka et al. [19] performed apparent tilt angle measurements in the SmC$_{\alpha}$ phase as a function of the applied dc field. They found step like variation of the apparent tilt angle with increasing dc field. From these observations, they speculated the existence of a temperature induced as well as field induced devil's staircases in the SmC$_{\alpha}$ phase. Further, in the ferrielectric range, the apparent tilt angle measurements show a plateau at one third of the tilt angle at intermediate fields. This plateau indicates a field induced 1:2 structure (/$\backslash\backslash\cdot\cdots\cdot$) in this phase. Conoscopic observations by Gorecka et al. [20] also indicate this field induced structure in the ferrielectric range. Later from conoscopic observations, Isozaki et al. [29, 30] have speculated that a temperature induced devil's staircase can be invoked in the ferrielectric range of AFLC also. Such a devil's staircase has been predicted using some Ising models. Bak et al. [31] have shown that the ground state of a sys-
tem of Ising spins arranged in a 1-d lattice can exhibit a complete devil’s staircase as a function of the field provided the interaction between the spins is long range and convex. The devil’s staircase obtained by Bak et al. [31] for an antiferromagnetic inverse square interaction \( \text{viz. } J(i) = i^{-2} \) is shown in Fig. 2.3. \( q \) along the y-axis represents the fraction of up spins in a period. It can be noted that there is a wide plateau corresponding to antiferroelectric structures i.e., \( q = 0.5 \) in this staircase.

Fig 2.3: Field induced devil’s staircase exhibited by 1-d Ising model with long range convex interactions \( (J(i) = i^{-2}) \). After Ref. [31].

Another model which exhibits temperature induced devil’s staircase is the Axial Next Nearest Neighbour Ising or ANNNI model [32, 33]. In the 3D version of the model, Ising spins lying in a certain plane are coupled ferromagnetically to its \( z_o \) nearest neighbours \( (J_o > 0) \) while spins lying in different planes interact through nearest \( (J_1) \) and next nearest \( (J_2) \) neighbour competing interactions. The mean field phase diagram of the 3-d ANNNI model for \( J_1 > 0 \) is shown in Fig. 2.4. The structures \( <k_1k_2\cdots k_n> \) represent the k-bands present in a period. A k-band is defined as the number of layers with parallel spins separated on both sides by oppositely oriented spins. Thus \( <2> \) represents \( \uparrow\downarrow\downarrow \cdots \) structure, \( <12> \) represents \( \uparrow\uparrow\downarrow \cdots \) structure etc. The stable structures corresponding to negative \( J_1 \) can be
obtained from that of positive $J_1$ by reversing every alternate spin. The structure $<3>$ corresponding to positive $J_1$ becomes $<12>$ for negative $J_1$. With this transformation, the phase diagram corresponding to negative $J_1$ is the same as that for positive $J_1$ (see Selke [33] for a review). Thus the stability range of $<3>$ phase for positive $J_1$ corresponds to the stability range of the $<12>$ phase for negative $J_1$. From the phase diagram, apart from ferro and antiferro phases we see three 'broad' phases namely $<3>$ and $<2>$ for $J_1 > 0$, $<2>$ and $<12>$ for $J_1 < 0$. Among these the stability range of $<2>$ phase is rather wide as $J_1$ is varied.

The extension of the ANNNI model including a third neighbour interaction which was specifically used for describing liquid crystalline phases also exhibits similar structures. The mean field phase diagram of this model with $J_1 < 0$ is shown in Fig. 2.5. This model appears to widen the $<12>$ range compared to that in Fig. 2.4.

Coming back to the AFLC system, to qualitatively account for the devil’s staircase in the SmC$_a$ phase, Takanishi et al. [16] invoked the Ising model developed by Bak et al. [31] treating the configuration of each layer as an Ising variable. Later to account for the temperature devil’s staircase in the ferrielectric range, Yamashita et al. [26] (mistakenly) stated that the ANNNI model is not sufficient in this case as it does not stabilize the $<12>$ (equivalent of 1:2 structure) which is seen in the
presence of field. Therefore they extended the ANNNI model with third neighbour interaction, as stated above.

In the magnetic systems crystal fields confine the spins to specific orientations. In liquid crystals the polarization vectors are associated with liquid layers and indeed can align along any azimuthal direction to minimize the energy. As such, we believe that the Ising models are highly inappropriate for AFLC. This is further corroborated by the following facts:

1. From the conoscopic observations it is unequivocally established that all the tilted phases in the absence of field have helicoidal structures of \( \hat{n} \) along the layer normal. The assumption of the Ising character of the orientational order parameter is contrary to this helicoidal structure.

2. It is well known from the theory of ferroelectric phase (which is also a sub-phase exhibited by AFLC) that the order parameter is a 2-d vector in the plane of the layers, thus indicating xy- rather than Ising-character of the order parameters.
3. Both dielectric and electrooptic measurements detect modes with the relaxation frequencies typical of the Goldstone mode (involving the phase fluctuation of the orientation order parameter). This indicates an xy-type behaviour of the orientational order parameter in these phases.

4. Further even if we take the ANNNI models seriously, it can be seen from the phase diagram of these models (Fig. 2.4 and 2.5) that as $J_1$ varies from large positive values in the ferroelectric phase to zero and to large negative values in the antiferroelectric phase, the $<22>$ structure has a large range of stability. However, experimentally this phase is not found in most of the pure compounds and even if it is found in some binary mixtures, it has very short temperature range of stability [12].

None of the above models i.e., both xy- and Ising- models account for the entire sequence of phases, particularly the SmC* phase. We therefore developed an xy-type model taking into account the correct symmetry of the SmC* layers. The pitch in some phases is found to be extremely short. Further, a field induced structure in the ferrielectric phase indicates a 3-layer periodicity. In contrast to the models described in Sec. 2.2, we do not assume a continuous variation of the order parameter along the layer normal and instead, we develop a discrete model. In the following, we will describe the model which accounts for the entire sequence of phases exhibited by AFLC.

2.4 Discrete model of AFLC

The experimental observations [14] of very short pitch in SmC* phase indicate that the assumption of sufficiently slowly varying order parameters along the layer normal may not be appropriate. Therefore a model with the free energy density depending on the configuration of each layer is more relevant. Cepic et al. [34] first pointed out that second neighbour competing antiferroelectric coupling can lead to small pitch
values as seen in the SmC* phase in such a model.

This type of discrete model was first studied by Sun et al. [25]. However, they neglected the helicoidal structure which is present in all the tilted phases and assumed that in the SmC* phase, successive layers have opposite tilts of different magnitudes. But x-ray investigations in this phase have not found any evidence for this structure.

For molecules within a layer the anisotropic intermolecular dispersion interactions between the cores and end groups of the molecules as well as the packing considerations favour them to be parallel to one another. This gives rise to a strong ferroelectric coupling within the layers. On the other hand, for molecules in different layers, the interactions are mainly through end groups of the molecules or some long range interactions and are expected to be relatively weak. Therefore in the discrete model, we will assume that the tilt order within the smectic layers arise due to intra-layer interactions and such tilted layers are coupled weakly through nearest neighbour (NN) and next nearest neighbour (NNN) interactions.

In the following, we will consider different possible origins of such inter-layer interactions on the basis of which we will construct the free energy density expression of our model.

### 2.4.1 Origin of inter-layer interactions

As the layers are polarized, the most obvious candidate to give rise to an antiferroelectric NN interaction may seem to be dipolar coupling between the layers. However, Bruinsma et al. [35] pointed out that the dipolar coupling between i-th and j-th layers $V_{dp}(i - j)$, can be computed by treating each layer as a two dimensional liquid of dipoles. The interaction between two such layers seperated by a distance $d$ is

$$V_{dp}(i - j)/A = S_i S_j \frac{P^2}{2\epsilon} \int d^2\rho \left[ \frac{1}{(\rho^2 + d^2(i - j)^2)^{3/2}} - 3 \frac{(\vec{\rho} \cdot \vec{y})^2}{(\rho^2 + d^2(i - j)^2)^{5/2}} \right]$$
where $A$ is the area of the layer and $S_i P$ is the dipole moment per unit area of the $i$-th layer (along the y-axis). The cancelation is strict only in the thermodynamic limit of infinite $A$ and is a consequence of Maxwell’s law that an infinite slab of material, which is uniformly polarized perpendicular to the surface normal, has no electrical field outside the surface.

Therefore the antiferroelectric configuration is often thought to arise from dipolar interactions between a pair of molecules in adjacent layers [12]. However a simple calculation shows that this energy is much lower than the thermal energy and such pairs are unlikely to be important for the stability of the $SmCA$ phase.

The anisotropic dispersion interaction between tilted molecules in adjacent layers is minimized when the molecules in the two layers are in one plane. This gives rise to the two-fold anisotropic $J_2$ term in Eq. 2.30 below. Further, the dispersion interaction between the end chains of a pair of molecules in adjacent layers in ferroelectric and antiferroelectric configurations can be written as

$$
\frac{V_{dis}^{f(a)}}{k_B T} \propto \int_{L_a}^{L_a + L_c} dl_1 c \int_0^{L_c} dl_2 c \alpha_c^2 \frac{1}{\left[\left(x \pm (l_2c + l_1c) \sin \theta\right)^2 + (g + l_2c - l_1c)^2 \cos^2 \theta\right]^3}
$$

where $\alpha_c$ is the polarizability per unit length of the end chain of length $L_c$. $L_a$ is the length of the aromatic core. As shown in Fig. 2.6, $\theta$ and $x$ denote the tilt angle and horizontal separation of the molecules in the neighbouring layers respectively. We have assumed a small gap $g$ between the smectic layers. The superscript “$f(a)$” denotes the interaction for ferroelectric (antiferroelectric) configurations with the upper sign corresponding to the ferroelectric configuration. The interaction energies calculated from Eq. 2.25 are shown in Fig. 2.7. The antiferroelectric configuration has a lower energy minimum compared to the ferroelectric configuration. However, it is clear from Fig. 2.7 that the energy difference between the two minima for one pair of molecules is also much less than $k_B T$. But, as the molecules are already
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Chapter 2.

Fig 2.6: The geometry for the calculation of dispersion interaction between the molecules.

Fig 2.7: The dispersion interaction $V_{\text{dis}}$ between two molecules in adjacent layers as a function of the lateral separation $x$ between them. The calculation has been done assuming $\theta = 0.5$ rad, $\alpha_c = 1.6$, $L_a = 10\,\text{Å}$, $L_c = 8\,\text{Å}$ and $g = 2\,\text{Å}$. 
ordered in each layer and they can move in unison, the relevant quantity is the energy difference between the two configurations per unit area which is of course quite substantial and far exceeds $k_BT$.

Further, this mechanism works for racemic mixtures as well as for achiral systems without any further assumptions. Also, as the angle made by the last C-C bond of the alkyl chain with the layer plane varies substantially between the odd and even members of a homologous series, the strong odd-even effect mentioned earlier can be understood from this mechanism (see Fig. 2.11).

However, the ferroelectric configuration allows a relatively free translational motion of the molecules between adjacent layers, and is favoured entropically at higher temperatures. Therefore the nearest neighbour inter layer interaction is expected to be temperature dependent and should change sign to favour ferroelectric configuration at higher temperatures and antiferroelectric configuration at lower temperatures. The simplest assumption is to take $J_1 = j(T_{AF} - T)$, where $J_1$ is defined in Eq. 2.30.

Bruinsma et al. [35] also analyzed different types of interactions between the polarized smectic layers to account for the second and higher neighbour interactions. They have shown that the van der Waals and the elastic forces are weak compared to the forces which arise due to the correlated thermal fluctuation of polarization of the layers. By perturbative calculations, they found that the fluctuation force between the i-th and j-th layer is

$$V_{fluc}(i - j) \approx \Gamma \frac{S_i S_j}{|i - j|^2}$$

where $\Gamma$ is given by

$$\Gamma = \frac{P_0^2}{4ed} \frac{k_BT}{\sqrt{K_||K_\perp}} \left(1 + \sqrt{\frac{K_||}{K_\perp}}\right)^2$$

where $P_0$ is the polarization per unit area of the layers and $K_||, K_\perp$ are the appropriate anisotropic curvature elastic constants parallel and perpendicular to the
layers. Since polarization $P_0 \propto \theta$ and $K_{\parallel}, K_{\perp}$ vary as $\theta^2$ with the tilt angle $\theta$, it is clear from Eq. 2.27 that $\Gamma$ is independent of $\theta$. This fact leads to the next nearest neighbour (NNN) $J_3$ term in Eq. 2.30.

Chiral intermolecular interactions can be quite complex. A well known and simple expression for the twist interaction between two rod like molecules $i$ and $j$ is [4]

$$H_{\text{twist}} = -\frac{1}{2} \sum_{ij} K(r_{ij})(\hat{a}_i \cdot \hat{a}_j)(\hat{a}_i \times \hat{a}_j \cdot r_{ij}),$$

(2.28)

where $\hat{a}_i$ denotes the unit vector along the long axis of the $i$-th molecule and $r_{ij}$ is the intermolecular distance between the $i$-th and $j$-th molecules. After replacing $\hat{a}_i$ by its average $\hat{n}_i$ within the layer, this interaction in the tilted smectic phases takes the form [4]

$$f_{\text{twist}} = y_1 \sin 2\theta_1 \sin 2\theta_2 \sin(\phi_j - \phi_i) + y_2 \sin^2 \theta_1 \sin^2 \theta_2 \sin 2(\phi_j - \phi_i).$$

(2.29)

This form is consistent with the apolar nature of $\hat{n}$ and gives rise to the $Y_1$ and $Y_2$ terms in Eq. 2.30 below. In analogy with the non-chiral NNN interaction, we introduced an NNN chiral $Y_3$ term in Eq. 2.30. This can be expected to be more important than a higher order ($\propto \theta^6$) first neighbour chiral interaction. As these chiral interactions can have many contributions we cannot guess the relative signs of the $Y$ coefficients. For any given set, a reversal of the signs of all the coefficients would correspond to the opposite enantiomer.

### 2.4.2 The discrete model

In view of above observations we introduce a second neighbour antiferroelectric interaction which is independent of the tilt angle $\theta$. Experimental observations clearly indicate that polarized layers are necessary for the occurrence of ferrielectric and SmC$\alpha$ phases and hence by implication, for the second neighbour antiferroelectric interaction. Using the order parameter defined in Eq. 2.2, we write the following
phenomenological free energy per unit area for an $N$-layer system:

$$\mathcal{F}^{(N)} = \sum_{i=1}^{N} \left[ \frac{A'}{2} |\vec{\xi}_i|^2 + \frac{B}{4} |\vec{\xi}_i|^4 - \lambda \vec{\xi}_i \cdot \vec{P}_i + \frac{1}{2\chi} P^2 + J_1 (\vec{\xi}_i \cdot \vec{\xi}_{i+1}) - \frac{J_2}{2} (\vec{\xi}_i \cdot \vec{\xi}_{i+1})^2 + J_3 (\vec{\xi}_i \cdot \vec{\xi}_{i+2}) + Y_1 (\vec{\xi}_i \times \vec{\xi}_{i+1}) + Y_2 (\vec{\xi}_i \times \vec{\xi}_{i+1}) (\vec{\xi}_i \times \vec{\xi}_{i+2}) + Y_3 (\vec{\xi}_i \times \vec{\xi}_{i+2}) - \vec{E} \cdot \vec{P}_i \right],$$

(2.30)

where $A'$ and $B$ are the usual Landau coefficients describing the second order SmA to SmC transition, with $A' = \alpha(T - T_{AC})$, $T_{AC}$ being the SmA-SmC transition temperature, and arise from intra-layer interactions. $J_1 = j(T_{AF} - T)$, where $T_{AF}$ is the temperature at which $J_1$ changes sign to favour ferroelectric interaction at higher temperatures.

Note that only up to quadratic terms in the secondary order parameter $\vec{P}$ have been taken into account as the higher order terms are expected to be small. Also the terms with $(\vec{P}_{i+1} \cdot \vec{P}_i)$ are not taken into account as these are identically zero in the limit of infinite area as discussed in Sec. 2.4.1.

The $Y$ coefficients correspond to chiral interactions between the layers. The term with coefficient $\lambda$ is called electroclinic term in analogy with the piezoelectric term in solid state physics as it couples the polarization with the tilt angle. This term as well as the $Y$-terms are allowed only in the chiral medium.

Minimization of Eq. 2.30 with respect to $\vec{P}_i$ as in the continuous case yields

$$\vec{P}_i = \chi (\lambda \vec{\xi}_i - \vec{E})$$

(2.31)

Elimination of $\vec{P}_i$ from Eq. 2.30 using Eq. 2.31 gives

$$\mathcal{F}^{(N)} = \sum_{i=1}^{N} \left[ \frac{A}{2} |\vec{\xi}_i|^2 + \frac{B}{4} |\vec{\xi}_i|^4 - J_1 (\vec{\xi}_i \cdot \vec{\xi}_{i+1}) - \frac{J_2}{2} (\vec{\xi}_i \cdot \vec{\xi}_{i+1})^2 + J_3 (\vec{\xi}_i \cdot \vec{\xi}_{i+2}) + Y_1 (\vec{\xi}_i \times \vec{\xi}_{i+1}) + Y_2 (\vec{\xi}_i \times \vec{\xi}_{i+1}) (\vec{\xi}_i \times \vec{\xi}_{i+2}) + Y_3 (\vec{\xi}_i \times \vec{\xi}_{i+2}) - C (\vec{E} \cdot \vec{\xi}_i) \right]$$

(2.32)

where $A = A' - \chi \lambda^2$ and $C = \lambda \chi$. To study the phase transition in the absence of electric field, we assume that the energy associated with the soft mode is much higher
than that for Goldstone mode and hence the tilt angle of the layers is homogeneous i.e., independent of $i$. X-ray studies on antiferroelectric liquid crystals appear to justify this assumption. With this assumption and using Eq. 2.2, the free energy Eq. 2.32 can be rewritten as

$$F^{(N)} = \sum_{i=1}^{N} \left[ \frac{A}{2} \xi_{o}^{2} + \frac{B}{4} \xi_{o}^{4} + J_{1} \xi_{o}^{2} \cos(\phi_{i} - \phi_{i+1}) - \frac{J_{2}}{2} \xi_{o}^{4} \cos^{2}(\phi_{i+1} - \phi_{i}) + J_{3} \cos(\phi_{i} - \phi_{i+2}) + Y_{1} \xi_{o}^{2} \sin(\phi_{i} - \phi_{i+1}) + Y_{2} \xi_{o}^{4} \cos(\phi_{i} - \phi_{i+1}) \sin(\phi_{i+1} - \phi_{i}) + Y_{3} \xi_{o}^{6} \sin(\phi_{i} - \phi_{i+1}) \right],$$

(2.33)

where $\xi_{o} = \sin(\theta/2)$ and $\theta$ is the tilt angle. To obtain the equilibrium configuration the free energy in Eq. 2.33 has to be numerically minimized as discussed below.

### 2.4.3 Calculations

The free energy given by Eq. 2.33 is minimized numerically using a multidimensional conjugate gradient method [36]. Starting from an initial guess this method in successive iterations minimizes the function along "non-interfering" or so called conjugate directions with the special property that minimization along one direction is not "spoiled" by subsequent minimization along another direction.

To make conjugate directions mathematically more explicit, first note that if we minimize a function along some direction $u$, then the gradient of the function must be either zero or perpendicular to $u$ at the line minimum. Next consider some point $P$ as the origin of the coordinate system with coordinates $x$. Then any function can be approximated by its Taylor series

$$f(x) = f(P) + \sum_{i} \frac{\partial f}{\partial x_{i}} x_{i} + \frac{1}{2} \sum_{i,j} \frac{\partial^{2} f}{\partial x_{i} \partial x_{j}} x_{i} x_{j} + \cdots$$

$$\approx c - b \cdot x + \frac{1}{2} x \cdot A \cdot x,$$

(2.34)

where

$$c \equiv f(P) \quad b \equiv -\nabla f \mid_{P} \quad A_{ij} \equiv \frac{\partial^{2} f}{\partial x_{i} \partial x_{j}} \mid_{P},$$

(2.35)
The matrix $A$ whose components are the second partial derivatives of the function is called the Hessian matrix of the function at $P$. In the approximation of Eq. 2.34, the gradient of $f$ is easily calculated as
\[
\nabla f = A \cdot x - b
\]  
(2.36)

Therefore the change in $\nabla f$ as we move along some direction is evidently
\[
\delta(\nabla f) = A \cdot (\delta x).
\]  
(2.37)

Suppose that we have moved along some direction $u$ to a minimum and now propose to move along some new direction $v$. The condition that the motion along $v$ not "spoil" our minimization along $u$ is just that the gradient stays perpendicular to $u$, i.e., that the change in gradient be perpendicular to $u$. By Eq. 2.37 this is just
\[
0 = u \cdot \delta(\nabla f) = u \cdot A \cdot v
\]  
(2.38)

When Eq. 2.38 holds for two vectors $u$ and $v$, they are said to be conjugate. When the relation holds pairwise for all members of a set of vectors, they are said to be a conjugate set. If one does successive line minimization of a function along a conjugate set of directions, then there is no need to redo the minimization along any of those directions. Therefore, the algorithm reduces to finding the conjugate set and carry out successive line minimizations along those directions using an iterative procedure. We have used the Polak and Rebiere version of the algorithm (see [36] for detail) in our calculations.

Coming back to our problem, we assume that $A$ and $B$ coefficients in Eq. 2.33 are much larger than the $J$ and $Y$ coefficients, so that the magnitude $\xi_0$ varies with temperature as $\xi_0^2 \approx \alpha(T_{AC} - T)/B$ below the SmA-SmC transition temperature. A typical set of parameters used in the calculations are as follows (in cgs units): $\alpha = 0.088$, $B = 13.8$, $j = 2.18 \times 10^{-4}$, $J_2 = 3.0 \times 10^{-4}$, $J_3 = 1.2 \times 10^{-5}$, $Y_1 = 8.0 \times 10^{-6}$, $Y_2 = 4.2 \times 10^{-4}$, $Y_3 = -1.47 \times 10^{-5}$, $T_{AC} = 379K$ and $T_{AF} = 367K$ (the last two values correspond to those of C8-tolane [13]).
Fig 2.8: Schematic representation of the structures of the various phases predicted by our model. The arrows indicate the c-vectors, the projections of the director on the smectic layers. In the representations of the helical structures in the (a) SmC$^{*}_B$ (b) SmC$^{*}_A$ (c) FI$H$ (d) FI$H$ (e) FI$L$ and (f) SmC$^{*}_A$ phases, the differences in tilt angle in the different phases has been ignored.

In addition to the ferroelectric and antiferroelectric phases, this model gives rise to other stable uniform helical phases and a nonuniformly modulated phase. The profile of the c-vector in different layers for these structures are shown in Fig. 2.8. The transition points between different phases are obtained by comparing the appropriate free energies.

2.4.4 Results and discussion

In the absence of chirality, and if $J_2 = 0$ it is easy to see from Eq. 2.33 that ferroelectric ($J_1 < 0$) and antiferroelectric ($J_1 > 0$) phases are stable when $|J_1|\xi^2_0 > 4J_3$. Otherwise there is a second order transition to an intermediate uniform helical structure with $\delta \phi = J_1\xi^2_0/4J_3$. Since there is no chirality the right handed and left handed structures are degenerate in this case.

The chiral terms in our model lift this degeneracy and drive these second order transitions from SmC$^{*}_B$ to FI$H$ ($-\pi/2 < \delta \phi < 0$) and SmC$^{*}_A$ to FI$L$ ($-\pi < \delta \phi < -\pi/2$), to first order. When $J_2 > 0$ and is sufficiently large, another ferrielectric phase FI$I$ develops. It is characterized by a nonuniform modulation with $\delta \phi_1$ be-
Fig 2.9: Theoretical temperature variation of $\delta \phi$, the difference in azimuthal angles between successive layers for the parameters given in the text. $\delta \phi$ characterize the helical structure which is uniform in all the tilted phases except in the FI$_I$ phase giving rise to the splitting of $\delta \phi$ in this phase.

Between one pair of neighbours being different from $\delta \phi_2$ of an adjacent pair (see Fig. 2.8 and 2.9). In addition, when $T$ approaches $T_{AC}$, $|J_1|\xi_0^2$ again becomes smaller than $4J_3$ and another ferriphase (SmC$_{\alpha}^*$) is stabilized. Further, as first pointed out by Cepic et al. [34] close to $T_{AC}$, $\delta \phi$ in the SmC$_{\alpha}^*$ phase approaches $\pi/2$ which explains the antiferroelectric character in the high temperature ranges of SmC$_{\alpha}^*$ phase seen experimentally [16].

Ignoring the tilt angle $\theta$ of the layers, the order parameter of the FI$_I$ phase is related to the difference ($\delta \phi_1 - \delta \phi_2$). In the other uniformly modulated phases, the order parameter is related to $\delta \phi (= \delta \phi_1 = \delta \phi_2)$ which changes in sign and magnitude across the different phase transitions. The global symmetry of all the uniform phases with a helical twist is the same and the phase transitions between them can only be 1st order in nature. These transitions involve jumps in $\delta \phi$, which do not cost too much energy. The entropy $S = -\partial F/\partial T$, and the heat of transition $T\Delta S$ between two phases is $(Tj\xi_0^2\Delta(\cos \delta \phi))$ which is typically $\sim 1$ joule/mole in broad agreement.
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Fig 2.10: (a) Temperature--$J_2$ phase diagram and (b) Temperature--$J_3$ phase diagram. Note the tricritical points in the phase boundary involving FI$_I$ phase, and the critical points in the SmC$_\alpha^*$-FI$_H$ and FI$_L$-SmC$_\alpha^*$ phase boundaries. $J_3$ can be expected to decrease with chain length in a homologous series.

with the experimentally measured values [13].

The detailed phase diagrams when $J_2$ and $J_3$ are varied, keeping all the other parameters fixed, are shown in Fig. 2.10. In the $J_2$-temperature phase diagram the phase boundary involving the FI$_I$ phase has a parabolic shape which is characteristic of reentrant phenomenon. Also in part of the phase boundary (shown by dashed line) the transition between the nonuniform and uniform structures is second order in character. There are two tricritical points on this boundary beyond which the transition becomes first order in nature. Both SmC$_\alpha^*$-FI$_H$ and SmC$_\alpha^*$-FI$_L$ transition lines end in critical points as $J_2$ is increased as a consequence of the same global symmetry of the phases involved in these transitions. Depending on the value of $J_2$ we can have either one or three ferriphases (Fig. 2.10).

As $J_3$ arises from the fluctuations in the polarization of the layers, we can expect that it decreases for higher homologs in which the nonchiral end chain length
Fig 2.11: Phase diagram as a function of the nonchiral end chain length in a homologous (nFF) series. $J_3$ can be expected to decrease with chain length in a homologous series. Note the odd-even effect on the transition temperatures involving the ferroelectric, SmC*$_b$ and SmC*$_a$ phases but not the transition temperature between the SmA and SmC*$_a$ phases. After Ref. [18].

is increased. As can be seen in Fig. 2.10, the ranges of both the SmC*$_a$ phase and the ferriphases are reduced as $J_3$ is decreased. This trend has been seen in many homologous series [18] as shown in Fig. 2.11. If an enantiomer of opposite chirality is added to an originally pure compound, the polarization of the layers is lowered. In this case both the $J_3$ and $Y$ coefficients are reduced leading to a disappearance of the SmC*$_a$ and ferriphases as seen experimentally [12]. Both SmC*$_b$-FI$_H$ and SmC*$_a$-FI$_L$ transitions exhibit critical points as $J_3$ is lowered. In Fig. 2.10, the finite width of the FI$_I$ phase even when $J_3 = 0$ arises from the second neighbour chiral interaction $Y_3$.

2.5 Conclusions

The discrete chiral ANNNXY model developed by us for the antiferroelectric liquid crystals incorporating the correct symmetry of the tilted smectic layers accounts for
the first time the entire sequence of phase transitions often seen in experiments. The very weak first order transitions between many of these phases arise from abrupt changes in $\delta \phi$ values, which are brought about by chiral interactions. In racemic mixtures the NNN $J_3$-term arising from the fluctuations of the polarizations as well as the chiral $Y$-terms will be zero and the ferrielectric phases will be absent as observed experimentally. Further, we will see in Chapter 3 and Chapter 4 that the various optical properties of the system in the presence and absence of a static field predicted by the model are in good agreement with the experimental observations.

The SmC$^\ast_\alpha$ phase has a very short pitch, and further, at higher temperatures, the $\delta \phi$ value approaches $\pi/2$, which will lead to antiferroelectric properties as seen in some experiments [16]. The $\delta \phi$ values vary rapidly with temperature in the ferri as well as SmC$^\ast_\alpha$ phases. Indeed there are strong visible fluctuations in these phases [21], which are also seen in ellipsometric measurements on relatively thick films [37] caused by the strong dependence of the pitch on temperature.