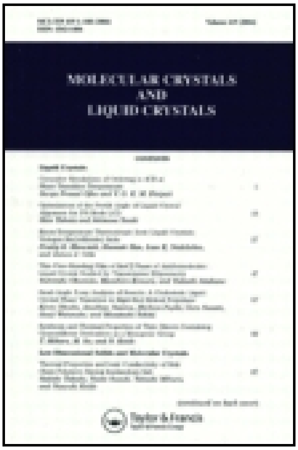

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Phase Transitions and Solitons in Liquid Crystals

M. Yamashita [a] & H. Kimura [a]
[a] Department of Applied Physics, Faculty of Engineering, Nagoya University, Nagoya, 464, Japan
Version of record first published: 03 Jan 2007.

To cite this article: M. Yamashita & H. Kimura (1988): Phase Transitions and Solitons in Liquid Crystals, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 165:1, 213-232

To link to this article: http://dx.doi.org/10.1080/00268948808082202

Mol. Cryst. Liq. Cryst., 1988, Vol. 165, pp. 213–232
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Phase Transitions and Solitons in Liquid Crystals

M. YAMASHITA and H. KIMURA

Department of Applied Physics, Faculty of Engineering, Nagoya University, Nagoya 464, Japan

(Received November 13, 1987; in final form February 23, 1988)

Phase transitions occurring in liquid crystals are reviewed from a viewpoint of solitons. First, cholesteric–nematic phase transition is explained as a condensation process of solitons. This mechanism of phase transition is common to the so-called commensurate-incommensurate phase transition. In the next place, not only liquid crystals such as chiral smectic C and smectic A phases but also ferroelectrics and some other systems belonging to this category and its generalized versions are introduced, and discussed especially in relation to an order of phase transition, where a symmetry of periodic phases on an order parameter space gives the basis of the consideration.

1. INTRODUCTION

An interesting aspect of liquid crystals is that many kinds of phases appear and accordingly various phase transitions occur between them. Some of these phase transitions are known to be accompanied by soliton excitations, or localized excitations generally, where a referred phase becomes unstable with respect to such excitations. We can name the phenomena by softening with respect to the soliton excitation,[1] after a terminology softening at usual phase transitions accompanied by soft modes.[2] Those are named by de Gennes[3] as phase transitions of nucleation type, while these latter ones are as phase transitions of instability type. The commensurate-incommensurate phase transitions familiar in ferroelectrics[4] and charge density waves[5,6] in two-dimensional metal dichalcogenides are examples of the former.[7]

In cases of phase transitions of nucleation type as well, there appear both the first order transitions and the second order ones. Phases appearing as the result of the softening with respect to solitons mentioned above have generally periodic structures. Consequently such phase transitions can be studied by analyzing how the periodic phases change to uniform, or another periodic phase.[8-10] We classify the phase transitions on the basis of the symmetry of the periodic phases on an order parameter space, and in the next place phase transitions occurring in liquid crystals and also in some other systems are reviewed in relation to such arguments.

As a typical example of phase transition of nucleation type, a cholesteric-nematic phase transition in a magnetic field[11,12] is first explained in section 2 as the softening with respect to soliton. As a generalization of this phenomenon, studies on the classification of various phase transitions occurring at periodic phases, and especially on the order of such transitions are developed on the order parameter space in section 3, where it is shown that two cases of continuous phase transitions are possible. In one case the wave number of the periodic structure vanishes. The cholesteric-nematic transition belongs to this. Even in this category, both of the nucleation and instability types of phase transitions are shown to occur.[10] The other one is realized by contracting a circle representing the periodic phase on the order parameter space continuously to a point representing the uniform one. This type of continuous phase transition is observed in ferroelectric smectics in an electric field[8,13] and in some ferroelectrics.[14] One more kind of periodic state called the rippled phase has been shown to appear in a certain model system.[15] Phase transitions including this rippled phase[9,15-17] belong also to this latter type. In the two sections that follow such phase transitions in liquid crystals and ferroelectrics are explained in connection with the order of phase transition. Finally, in section 6 a summary is given.

2. SOFTENING WITH RESPECT TO SOLITON

First, in this section, the cholesteric-nematic phase transition driven by the magnetic field is explained as a condensation process of solitons.[12] A periodical structure of the cholesteric phase is unwound by the magnetic field H due to an anisotropy of magnetic susceptibility and at a certain critical value of the magnetic field H_c the cholesteric-nematic phase transition occurs.[11]

A free energy F of this system is expressed with an angle ϕ of the director field in a plane perpendicular to the helical axis as

$$F = \frac{K_2}{2} \int \left[\left(\frac{d\phi}{dz} - q_0 \right)^2 - \xi^{-2} \sin^2\phi \right] dz, \quad (1)$$

where the helical axis is assumed in the direction of the z-axis, the magnetic field in the plane, K_2 denotes an elastic constant of twist deformation, q_0 the inverse of pitch p_0 free from the field multiplied by 2π and ξ a magnetic coherence length given with positive anisotropy of diamagnetic susceptibility χ_a by

$$\xi = (K_2/\chi_a)^{1/2} H^{-1}. \quad (2)$$

An equilibrium state minimizing F is determined from a solution of the Euler-Langrange equation derived from (1) as

$$\frac{d^2(2\phi)}{dz^2} + \xi^{-2} \sin 2\phi = 0, \quad (3)$$

which is no other than a time-independent sine-Gordon equation. Uniform solutions, $\phi = (m + 1/2)\pi$ with integer m, represent the nematic phase. As soliton solutions to Eq. (3) with boundary conditions $\phi = \pi/2$ (or $-\pi/2$) at $z = \infty$ and $\phi = -\pi/2$ (or $\pi/2$) at $z = -\infty$, we obtain

$$\phi = 2\tan^{-1}\exp(\pm z/\xi) - \pi/2, \quad (4)$$

where the plus and minus signs at the exponent correspond to the soliton and anti-soliton, respectively. By substituting (4) into (1), an excitation energy ΔF of such solitons at the nematic phase is calculated as

$$\Delta F = 2(K_2\chi_a)^{1/2}(H \mp H_c), \quad (5)$$

in which H_c is given by

$$H_c = \frac{\pi}{2} \left(\frac{K_2}{\chi_a} \right)^{1/2} q_0. \quad (6)$$

The equation (5) shows that the excitation energy of soliton becomes small as H decreases and vanishes at $H = H_c$, that is, the softening of nematic phase with respect to soliton excitation occurs.

For $H < H_c$, ΔF turns to negative and many solitons are excited and consequently the cholesteric phase appears.

On the other hand, a periodic solution to Eq. (3) representing the cholesteric phase is given by

$$\phi = \sin^{-1}\mathrm{sn}(z/\kappa\xi), \tag{7}$$

where sn is Jacobi's sn-function. By the minimum condition of F, a modulus κ coming from the integration constant is determined from the following equation with the complete elliptic integral of second kind $E(\kappa)$ as

$$E(\kappa)/\kappa = \pi q_0\xi/2. \tag{8}$$

From the solution (7) the pitch p of the helical structure is given by

$$p = 4\xi\kappa K(\kappa), \tag{9}$$

where $K(\kappa)$ denotes the complete elliptic integral of first kind. By using Eqs. (2), (8) and (9) we can show that the pitch increases as H does and diverges at $H = H_c$, where $\kappa = 1$. In this limit, the solution (7) is reduced to (4) with a plus sign. Thus, the cholestric-nematic phase transition is shown to occur continuously at $H = H_c$ and for $H < H_c$ the condensed solitons are located regularly with spacing p. This periodic state is called a soliton lattice.

We have considered the cholestric-nematic phase transition from the viewpoints of softening and soliton-condensation. In the present case, an interaction between solitons is repulsive,[12] and the transition is the second order one. In case the interaction changes to attractive, the transition necessarily becomes the first order one as in the case of the chiral smectic C phase discussed in section 4.

3. ORDER OF PHASE TRANSITION

In this section we consider phase transitions from a topological point of view to discuss the possibility of continuous transition between the periodic phase and the uniform one.

Topological aspects of phase transitions are discussed pertinently as topological defects are on the order parameter space.[18] At the cholesteric-nematic phase transition the angle ϕ is considered as an order parameter, and the order parameter space is a circle as shown

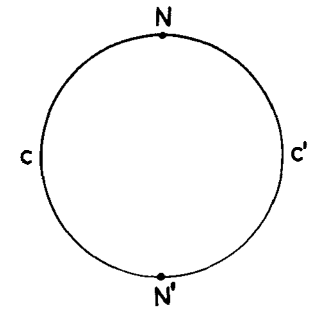

FIGURE 1 The order parameter space, circle, at cholesteric-nematic phase transition. The circle NcN′c′N denotes the cholesteric phase, points N and N′ the nematic one and the semicircles NcN′ and N′c′N the soliton or anti-soliton.

in Figure 1, where points N and N′ represent the nematic phase, the circle NcN′c′N the cholesteric one and the semicircle NcN′ connecting the two points N and N′ the soliton (or anti-soliton). It is clearly impossible to contract the circle to one point N, or N′, continuously. Accordingly, a continuous phase transition between the cholesteric and nematic phases never occurs except for the case where the wave number q vanishes. In reality, this exceptional case occurs at cholesterics as shown in the preceding section.

Next, we consider the chiral smectic C phase, where the order parameter with two components is expressed in terms of a polar, or tilt angle θ and an azimuthal one ϕ of the director[19] and the order parameter space is a projective space P^2. In Figure 2(a) the chiral

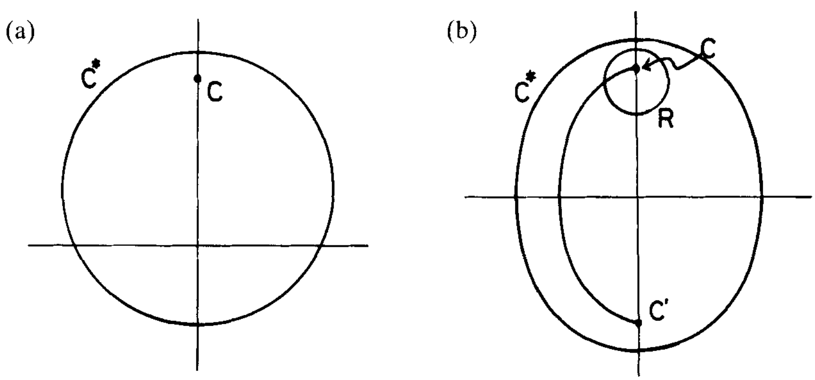

FIGURE 2 The order parameter space P^2 of ferroelectric smectics in the magnetic field (a) and in the electric field (b). The circles C* indicate the chiral smectic C phase, points C and C′ the smectic C phase, curve CC′ the soliton and circle R the rippled phase if it exists.

smectic C phase in the magnetic field is described by loop C* and the smectic C phase by points C and C′. The curve CC′ indicates the soliton. Though the magitude of the order parameter, θ in the present case, can be varied, the loop C* has two-fold symmetry, so that it is also impossible to contract the loop to one stationary point C (or C′). Consequently, the phase transition between the chiral smectic C and smectic C phases is necessarily a discontinuous one, as in the case of cholestrics, unless the wave number q vanishes. According to the thermo-statistical calculations, both the continuous phase transition accompanied by soliton condensation and the discontinuous one are shown to occur, and in the latter case a soliton lattice with finite spacing between solitons corresponding to the chiral smectic C phase changes directly to the uniform state, the smectic C phase.[10]

We have other systems similar to the above one with n-fold symmetry; $n = 1$ at the chiral smectic C phase in the electric field,[8,13] $n = 3$ at the charge density wave of two-dimensional metals[6] and $n = 4$ and 6 in ferroelectrics.[4] Though the order parameter space is a two-dimensional surface R^2 for the charge density wave and ferroelectrics, the present argument is irrespective of a difference between P^2 and R^2, and accordingly above prospects on the chiral smectic C phase in the magnetic field can be applied to systems with n $(2 \leq n < \infty)$. For $n = \infty$, the uniform states are located densely, making a circle, so that the concept soliton such as CC′ for $n = 2$ in Figure 2(a) becomes meaningless. As a result, the nature of continuous phase transition occurring in the limit of the vanishing wave number is altered. The commensurate-incommensurate phase transition occurring in a system with cylindrical symmetry ($n = \infty$) has been investigated by Michelson,[20] who has shown that the commensurate phase (uniform state) becomes unstable with respect to harmonic perturbation and bifurcates to incommensurate ones (periodic state) with the wave number $\pm q$. At the transition point q vanishes. Consequently, this phase transition with $n = \infty$ is considered as the instability type.

On the other hand, for $n = 1$, there exists only one uniform state labelled as C in Figure 2(b). The periodic state C* is obviously contracted to the point C continuously. Accordingly, the continuous phase transition between these two states can occur irrespectively of the wave number. This phase transition belongs to the instability type, because the magnitude of the order parameter increases gradually. The chiral smectic C phase in the electric field corresponds to this case and we will show in section 5 that this type of phase transition truly occurs between chiral smectic C and smectic C phases[8,13] in addition to the phase transitions of nucleation type. In some ferroelectric materials phase transitions of this instability type occur,[14] which is explained also in section 5.

In the above, the periodic phases have been restricted to ones with n-fold symmetry. We can consider another kind of periodic phase around one stationary state, labelled as R in Figure 2(a). This is called the rippled phase.[9,15] The relation of this phase to the uniform one is similar to that between chiral smectic C and smectic C phases in the electric field mentioned above, and consequently continuous phase transition may occur between them. A certain binary mixture showing smectic A phases[21] belongs to this category.[16,17]

A phase transition between two periodic phases C* and R of Figure 2(a) also occurs provided that the phase R appears. This transition is necessarily the first order one because of the difference of symmetries. In case the two-fold symmetry of C* is lost due to suitable external agents, the continuous phase transition may occur. In a certain model system, the critical point between these two periodic phases is found.[9]

We have discussed the possibility of continuous phase transitions from the topological point of view. It is necessary to examine by thermo-statistical arguments whether such transitions truly occur or not.

4. SOLITONS AND SOLITON LATTICES

The helical structure of the chiral smectic C phase is unwound by the electric field due to a coupling between an electric polarization and the electric field, or by a magnetic field due to an anisotropy of diamagnetic susceptibility. This unwinding mechanism looks very much like the one in cholestrics. However, in the present case, the order parameter has two components and the variation of the magnitude plays an important role in a rather high-temperature region, in contrast with the case of cholestrics where the order parameter is a phase variable. In the preceding section, the possibilities of various phase transitions are discussed. In this section, we examine the phase transitions occurring in ferroelectric smectics from the thermo-statistical point of view.

The free energy of ferroelectric smectics is expressed in terms of tilt angle θ and an azimuthal one ϕ of the director field as[19]

$$F = \int \left[a\theta^2 + b\theta^4 + \frac{1}{2}K\left(\frac{d\theta}{dz}\right)^2 + \frac{1}{2}K\theta^2\left(\frac{d\phi}{dz} - q_0\right)^2 - \chi\mu_p E\theta\sin\phi \right] dz, \tag{10}$$

where the z-coordinate is chosen in a direction of the normal to smectic layer, the electric field E is applied in the x-direction, $a = a'(T - T_c)$ with temperature T, a', T_c, b, K, q_0, χ and μ_p are positive constants. By transforming z into a nondimensional coordinate u ($= q_0 z$), F is rewritten as

$$F = F_0 \int \left[\frac{1}{2}A\rho^2 + \frac{1}{4}\rho^4 + \frac{1}{2}\left(\frac{d\rho}{du}\right)^2 + \frac{1}{2}\rho^2\left(\frac{d\rho}{du} - 1\right)^2 - \tilde{E}\rho\sin\phi \right] du, \tag{11}$$

where ρ and $\tilde{E}$ are proportional to θ and E, respectively, $A = A'(T - T_c)$, A' and F_0 are constants.

In the case of magnetic field H, the last term (11) should be replaced by $-\Gamma\rho^2\cos2\phi/2$ with $\Gamma(\propto H^2)$ and $A = A'(T - T_c) - \Gamma$.[10] By replacing the last term by $-n^{-1}\Gamma\rho^n \sin n\phi$ we can discuss various systems; $n = 3$ for the charge density wave and $n = 4$ and 6 for ferroelectrics.

The Euler-Lagrange equations for the case of magnetic field are derived from Eq. (11) with the replacement mentioned above as[10]

$$A\rho + \rho^3 - \frac{d^2\rho}{du^2} + \rho\left(\frac{d\phi}{du} - 1\right)^2 - \Gamma\rho\cos2\phi = 0, \tag{12}$$

$$\rho\frac{d^2\phi}{du^2} + 2\frac{d\rho}{du}\left(\frac{d\phi}{du} - 1\right) - \Gamma\rho\sin2\phi = 0. \tag{13}$$

In the case of constant ρ, Eq. (13) is nothing but the static sine-Gordon equation. The uniform solution of Eqs. (12) and (13) representing the smectic C phase (Sm C) is obtained as $\phi = m\pi$ with integer m and $\rho = \rho_0$ given by

$$\rho_0 = (\Gamma - A - 1)^{1/2}. \tag{14}$$

An integral of Eqs. (12) and (13) is obtained with integration constant C as

$$\frac{1}{2}\left(\frac{d\rho}{du}\right)^2 + \frac{1}{2}\rho^2\left(\frac{d\phi}{du}\right)^2 = \frac{1}{2}(A + 1)\rho^2 + \frac{1}{4}\rho^4 - \frac{1}{2}\Gamma\rho^2\cos 2\phi + C. \quad (15)$$

For SmC and the soliton solution, C is equal to C^* $(=\rho_0^4/4)$.

It is difficult to solve Eqs. (12) and (13) analytically, and so we solve them numerically.[10] In Figure 3 solitons with boundary conditions $\phi = 0$, $\rho = \rho_0$ at $u = -\infty$ and $\phi = \pi$ and $\rho = \rho_0$ at $u = \infty$, are shown. The phase boundary between the chiral smectic C phase (Sm C*) and Sm C is determined from the condition that the excitation energy of soliton vanishes, provided that the interaction between solitons is repulsive.

On the other hand, it has been shown[6,22,23] that owing to variable amplitude the interaction changes to attractive in case the soliton tail decays oscillatorily, like b in Figure 3. Due to this interaction, the phase transition becomes the first order one and the coexisting curve between Sm C* and Sm C is determined from the condition that the free energy of soliton lattice coincides with the one of uniform solution. At the transition curve, the soliton lattice minimizing the free energy is obtained for the vanishing value of ΔC $(= C - C^*)$.[23,24]

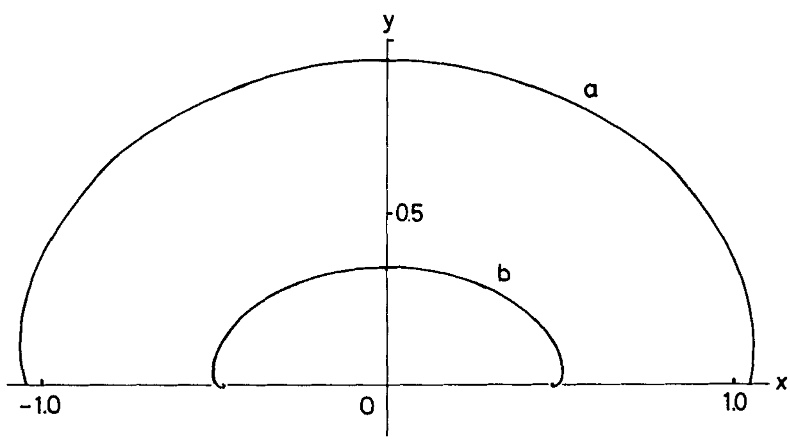

FIGURE 3 Profiles of solitons with values $A = -6.5$, $\Gamma = 1.287$ $\Delta C = 0$ (a) and $A = -1.0$, $\Gamma = 1.4$, $\Delta C = 0$ (b).

We show the phase diagram in Figure 4, where the full curves indicate the continuous transition, the broken curve the discontinuous one and LP the Lifshitz point. The phase transitions between Sm C* and the smectic A phase (Sm A) and between Sm C and Sm A studied by Michelson[25] are of instability type.

Thus, the phase transition of nucleation type changes to the first order one in a rather high temperature region, where ρ_0 is small and accordingly the variation of ρ becomes important. Owing to the variation of ρ, we can obtain various solitons and multi-soliton solutions[26] of the Euler-Lagrange equations, from which the nature of the attractive interaction is studied.[23] As to the profiles of soliton lattices see the original manuscripts.[6,10,23,27]

The results of Sm C* (incommensurate phase) and Sm C (commensurate phase) mentioned above are applied to every value of n.[6,8,24,27] However, for $n = 1$, the chiral smectic C phase in the electric field, one more type of phase transition also occurs[8,13] in addition to the above ones. The phase diagram on the electric field versus temperature plane is shown in Figure 5, where the tricritical point TC appears and at temperatures above TC the phase transition of instability type occurs.

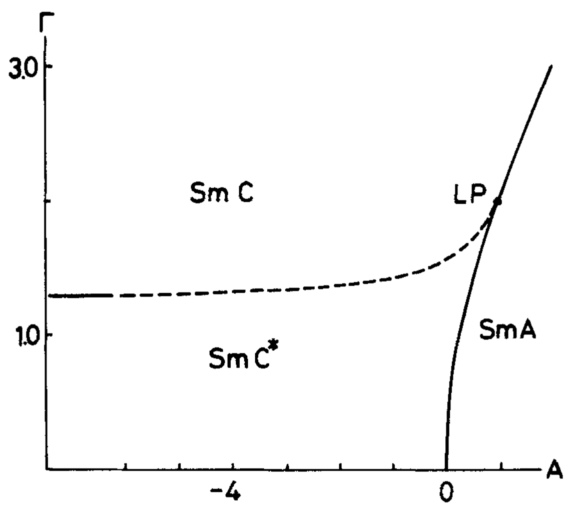

FIGURE 4 Phase diagram of ferroelectric smectics on the $\Gamma(\propto H^2)$ versus A plane. Full curves show the second order transition, broken curve the first order one and LP the Lifshitz point.

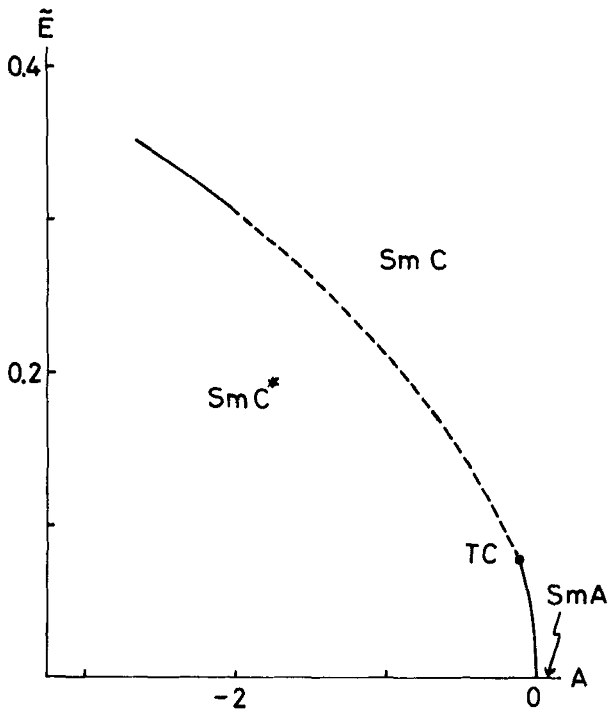

FIGURE 5 Phase diagram of ferroelectric smectics in the electric field versus temperature plane. The tricritical point is shown by TC.

5. BIFURCATION TO PERIODIC PHASES AND CRITICAL POINT

In order to investigate the phase trasnsition of instability type between Sm C* and Sm C in the electric field, we express the order parameters ρ and ϕ in an expanded form with small parameter ξ as[8,13]

$$\rho_1 = \rho_0 + \xi\sigma_1\cos qu + \xi^2(\overline{\sigma}_1\cos 2qu + \alpha) + O(\xi^3), \tag{16}$$

$$\rho_2 = -\xi\sigma_2\sin qu + \xi^2\overline{\sigma}_2\sin 2qu + O(\xi^3), \tag{17}$$

where $\rho_1 + i\rho_2 = \rho e^{i(\phi-\pi/2)}$ and q, σ_1, σ_2, $\overline{\sigma}_1$, $\overline{\sigma}_2$ and α are variational parameters with the condition

$$\sigma_1^2 + \sigma_2^2 = 1. \tag{18}$$

By substituting (16) and (17) for (11) and integrating those with respect to u, we obtain the average free energy density f as

$$f = f_0 + \frac{1}{2}c_2\xi^2 + \frac{1}{4}c_4\xi^4 + O(\xi^6), \tag{19}$$

in which f_0 is the value of f at Sm C and c_2 and c_4 are given by

$$c_2 = \frac{1}{2}\left(A + 2\rho_0^2 - \frac{1}{4}\rho_0^4\right) + \frac{1}{2}(q^2 - 2\sigma_1\sigma_2)^2 + 2\left\{\sigma_1^2 - \frac{1}{2}\left(1 - \frac{1}{2}\rho_0^2\right)\right\}^2, \tag{20}$$

$$\begin{aligned} c_4 = {} & 2(A + 1 + 3\rho_0^2)\alpha^2 + 2\rho_0(2\sigma_1^2 + 1)\alpha \\ & + (A + 1 + 3\rho_0^2 + 4q^2)\bar{\sigma}_1^2 - 8q\bar{\sigma}_1\bar{\sigma}_2 \\ & + (A + 1 + \rho_0^2 + 4q^2)\bar{\sigma}_2^2 \\ & + \rho_0(3\sigma_1^2 - \sigma_2^2)\bar{\sigma}_1 + 2\rho_0\sigma_1\sigma_2\bar{\sigma}_2 \\ & + \frac{1}{4} + \frac{1}{8}(\sigma_1^2 - \sigma_2^2)^2. \end{aligned} \tag{21}$$

On the basis of these expressions (19) ~ (21), the phase transition is discussed. At a point $c_2 = 0$, the continuous phase transition occurs provided that c_4 is positive and the tricritical point TC appears at a point, $c_2 = 0$, $c_4 = 0$. From Eqs. (18) and (20) we obtain at the transition point

$$q = 2\sigma_1\sigma_2, \tag{22}$$

$$\sigma_1^2 = \frac{1}{2}\left(1 - \frac{1}{2}\rho_0^2\right), \tag{23}$$

$$\sigma_2^2 = \frac{1}{2}\left(1 + \frac{1}{2}\rho_0^2\right), \tag{24}$$

where ρ_0 is determined in the electric field not by Eq. (14) but from the following relation

$$(A + 1)\rho_0 + \rho_0^3 - \tilde{E} = 0 \tag{25}$$

The critical line is determined with the aid of Eq. (25) by

$$A + 2\rho_0^2 - 1/4\rho_0^4 = 0, \tag{26}$$

and the tricritical values of A and $\tilde{E}$, A_{TC} and $\tilde{E}_{TC}$, respectively, from (21) as $A_{TC} = -0.232$ and $\tilde{E}_{TC} = 0.076$, in which parameters α, $\bar{\sigma}_1$ and $\bar{\sigma}_2$ are obtained by the minimum condition of c_4 like q, σ_1 and σ_2 in c_2. From these results, the phase diagram in Figure 5 is drawn. For $A > A_{TC}$, the phase transition is of instability type, because the amplitude ξ increases continuously as discussed in Figure 2(b) and takes the value $\xi_0(= (|c_2|/c_4)^{1/2})$ or $-\xi_0$ at the chiral smectic C phase.

For $A < A_{TC}$ the transition is the first order one. The amplitude ξ at the coexisting state increases rapidly as A decreases from A_{TC}. Like the case of the usual first order phase transition, another branch of solution with a larger value of free energy is obtained near the tricritical point.[8] We show soliton lattices of both branches in Figure 6, where a dependence of free energy density f on ΔC is drawn. It

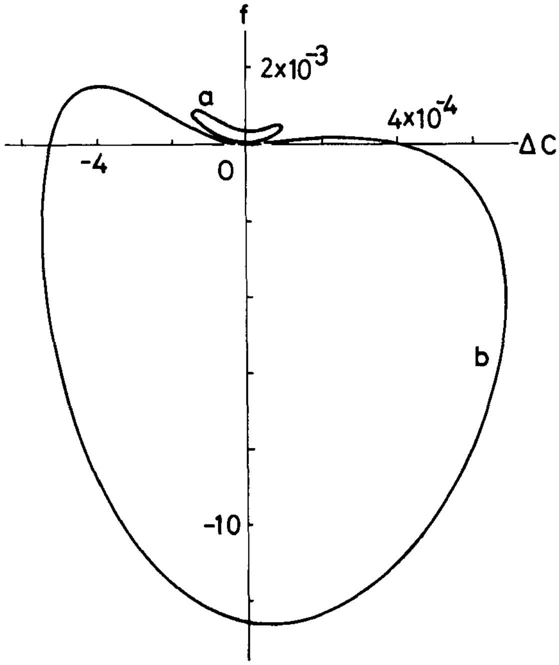

FIGURE 6 The free energy versus ΔC relation of soliton lattices. The free energy densities f of the two branches are connected smoothly at critical values of $|\Delta C|$. The values of the parameters are the following; $A = -0.3$, $\tilde{E} = 0.0842$ (a), 0.08 (b).

is noticed that the soliton lattice of this branch becomes unstable at $\Delta C = 0$ as observed in b[8]. Another type of instability of the soliton lattice occurs at a large value of $|\Delta C|$ as shown in Figure 6, where solitons of both branches coincide with each other and for $|\Delta C|$ exceeding the critical value no soliton lattice solution exists.[8,23]

Anyway, the phase transition of this instability type is characterized by a bifurcation of the uniform state to periodic ones. In some ferroelectrics and certain mixtures of liquid crystals, such bifurcation phenomena occur. Next, we study these systems.

The commensurate-incommensurate phase transition occurring at thiourea[14,28] is studied by the following type of free energy as[4]

$$F = \int \left[\frac{\alpha}{2} P^2 + \frac{\beta}{4} P^4 + \frac{\kappa}{2} \left(\frac{dP}{dz} \right)^2 + \frac{\lambda}{2} \left(\frac{d^2P}{dz^2} \right)^2 - EP \right] dz, \quad (27)$$

where the order parameter P denotes an electric polarization, α depends on temperature, κ is a negative constant, β and λ the positive ones. In expression (27) there is no so-called Lifshitz invariant, consisting of a term proportional to the first derivative of the order parameter. The periodic phase appears due to the negativeness of κ. For the case of $NaNO_2$ the coefficient β is considered to be negative[29,30] and accordingly, the sixth-order term of P should also be taken into account.

By adding a term proportional to $(dP/dz)^4$, Jacobs *et al.*[15] have studied the stability of the uniform state (commensurate phase) at the vanishing value of E and found that the rippled phase appears between the commensurate phase and the periodic one (incommensurate phase). Here, we discuss this system in the electric field.[9]

By suitable scale transformations, the free energy (27) with the additional term $(dP/dz)^4$ is reduced to

$$F = F_0 \int \left[\frac{1}{2} A\rho^2 + \frac{1}{4}\rho^4 - \left(\frac{d\rho}{du} \right)^2 + \left(\frac{d^2\rho}{du^2} \right)^2 + H \left(\frac{d\rho}{du} \right)^4 - \tilde{E}\rho \right] du. \quad (28)$$

The Euler-Lagrange equation is derived from (28) as

$$A\rho + \rho^3 + 2\frac{d^2\rho}{du^2} + 2\frac{d^4\rho}{du^4} - 12H \left(\frac{d\rho}{du} \right)^2 \frac{d^2\rho}{du^2} - \tilde{E} = 0. \quad (29)$$

Uniform states, the commensurate phase (C) and the normal one (N), are given by $\rho = \rho_0$ which is determined from

$$A\rho_0 + \rho_0^3 - \tilde{E} = 0. \tag{30}$$

In the vicinity of the uniform states, ρ is expressed in the expanded form of small parameter ξ as

$$\rho = \rho_0 + \xi\cos qu + \xi^2(\sigma_0 + \sigma_2\cos 2qu) + \xi^3\sigma_3\cos 3qu + O(\xi^4), \tag{31}$$

where q, σ_0, σ_2 and σ_3 are variational parameters. The functional forms of orders ξ^2 and ξ^3 are determined with the aid of Eq. (29). By substituting (31) for (28) and carrying out the integration, the free energy density f is obtained as

$$f = f_0 + \frac{1}{2}c_2\xi^2 + \frac{1}{4}c_4\xi^4 + \frac{1}{6}c_6\xi^6 + O(\xi^8), \tag{32}$$

where c_2 and c_4 are given by

$$c_2 = \frac{1}{2}\left(A + 3\rho_0^2 - \frac{1}{2}\right) + \left(q^2 - \frac{1}{2}\right)^2, \tag{33}$$

$$c_4 = 2(A + 3\rho_0^2)\sigma_0^2 + 6\rho_0\sigma_0 + (A + 3\rho_0^2 - 8q^2 + 32q^4)\sigma_2^2 + 3\rho_0\sigma_2 + \frac{3}{2}q^4H + \frac{3}{8}. \tag{34}$$

The explicit expression for c_6 is omitted for simplicity.[9]

Similar to the case of the ferroelectric smectics in the electric field, the phase transition is discussed. For H smaller than a certain value H_{te}, the tricritical point is stable and the phase diagram on the $\tilde{E}$–A plane is obtained as shown in Figure 7(a). These features are quite like those of ferroelectric smectics in the electric field. In the present system, $d\rho/du$ versus ρ plane, that is, the phase space, is considered as the order parameter space, and the incommensurate phase (IC) corresponds to the circle C* in Figure 2(b) and phases C and N to point C.

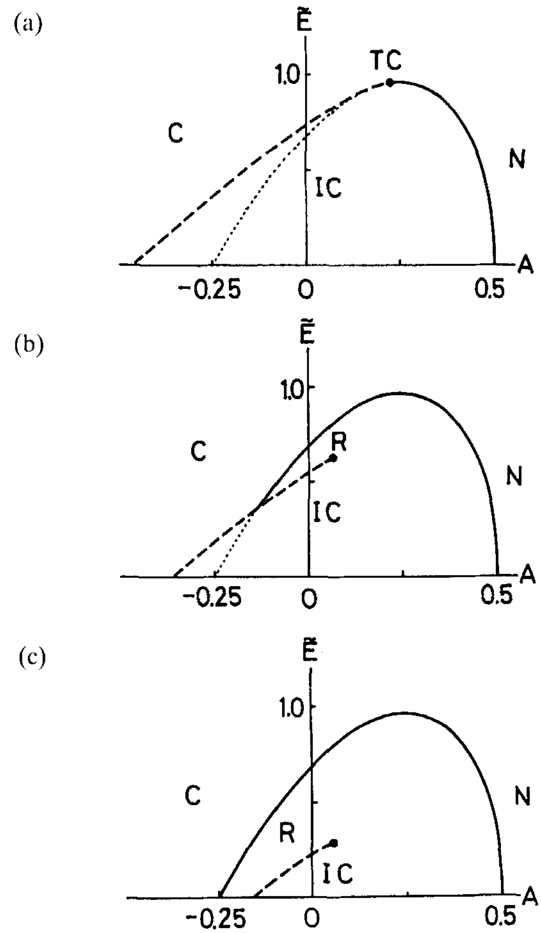

FIGURE 7 Phase diagram of a system showing commensurate-incommensurate phase transition. The full curves show the second order transition and the broken curves the first order ones, C, IC, N and R indicate the commensurate, incommensurate, normal and rippled phases, respectively and TC the tricritical point. The condition for H is as follows; (a) $H < H_{te}$, (b) $H_{te} < H < H_c$, (c) $H_c < H$.

This type of phase diagram is applied to theouria.[14,28] In $NaNO_2$ a coexisting curve and critical point appear between C and N.[14]

At $H = H_{te}$, the coefficient of the sixth order ξ^6 vanishes and accordingly the tricritical point becomes unstable. To discuss this tetracritical phenomenon, a deviation of q^2 from 1/2 derived from (33) should be taken into account.[9] We write q^2 as

$$q^2 = 1/2 + \zeta. \tag{35}$$

Then, Eq. (32) is rewritten as

$$
\begin{aligned}
f &= f_0 + \frac{1}{2}(c_2 + \zeta^2)\xi^2 + (\frac{1}{4}c_4 + d\zeta)\xi^4 + \frac{1}{6}c_6\xi^6 \\
&= f_0 + \frac{1}{2}c_2\xi^2 + \frac{1}{4}c_4\xi^4 + \frac{1}{6}(c_6 - 3d^2)\xi^6 + \frac{1}{2}(\zeta + d\xi^2)^2\xi^2,
\end{aligned}
\tag{36}
$$

where d is given along the critical line as

$$
d = \frac{2}{3}\rho_0^2 + \frac{3}{8}H. \tag{37}
$$

Thus, the tetracritical point is determined by $c_2 = 0$, $c_4 = 0$ and $c_6 - 3d^2 = 0$, from which we obtain $H_{te} = 2.550.\ldots$ Phase diagrams for $H_{te} < H < H_c$ ($= 28.3$)[9,15] and $H_c < H$ are shown in Figures 7(b) and (c), respectively. At $H = H_{te}$, the phase IC at PC begins to bifurcate to two periodic phases, IC and the rippled one (R) and for $H > H_{te}$ the coexisting curve and critical point between them appear. For $H > H_c$, the rippled phase is observed even at the vanishing value of $\tilde{E}$.[15]

The relation between C and R resembles that between C and R in Figure 2(a) and continuous transition occurs as observed in Figures 7(b) and (c). In case $\tilde{E} = 0$ the phase IC corresponding to circle C* of Figure 2(a) has two-fold symmetry, while R does not. Accordingly, the phase transition between IC and R is necessarily the first order transition. On the other hand, for $\tilde{E} > 0$, continuous transition is possible, because the two-fold symmetry of IC is broken. In practice, we find the critical point between IC and R in Figures 7(b) and (c).

The above study about the rippled phase has been applied[16,17] to phase transitions between several smectic A phases of a binary mixture of cyanobenzoyloxybenzoate of pentylphenyl with 4 cyanobenzoyloxy 4′pentyl stilbene.[31] Benguigui[16] has introduced a model to discuss phase transitions occurring in the mixture as

$$
\begin{aligned}
\mathrm{F} = \iint \Bigg[&\frac{a}{4}p^2 + \frac{b}{36}P^4 + \frac{K_1}{4}\left(\frac{\partial P}{\partial z}\right)^2 + \frac{\lambda_1}{4}\left(\frac{\partial^2 P}{\partial z^2}\right)^2 \\
&+ \frac{K_2}{4}\left(\frac{\partial P}{\partial x}\right)^2 + \frac{\lambda_2}{4}\left(\frac{\partial^2 P}{\partial x^2}\right) + \frac{H}{36}\left(\frac{\partial P}{\partial x}\right)^4 \Bigg] dxdz,
\end{aligned}
\tag{38}
$$

where P denotes an electric polarization in the z-direction, a depends on temperature and K_1 and K_2 are negative constants. Various phases are identified by the order parameter $P = (P_1 + P_2\cos qx)\cos kz$ as

monolayered smectic A phase (A_1); $P_1 = 0$, $P_2 = 0$,
bilayered smectic A phase (A_2); $P_1 \neq 0$, $P_2 = 0$,
smectic A phase with centered rectangular symmetry ($\tilde{A}$)
; $P_1 = 0$, $P_2 \neq 0$ with $q \neq 0$
smectic A phase with simple rectangular symmetry (A_R),
; $P_1 \neq 0$, $P_2 \neq 0$ with $q \neq 0$.

In the electric field E, the system (38) is studied[17] similarly to those of (11) and (28). A typical phase diagram on the E–a plane is shown in Figure 8. Continuous phase transitions shown by full curves are of the instability type. By reason of symmetry, phase transitions between $\tilde{A}$ and A_R and between $\tilde{A}$ and A_2 are the first order ones, provided that P_1 does not vanish.

6. SUMMARY

Cholesteric-nematic phase transition is interpreted as a condensation process, and as a generalization of this phenomenon phase transitions accompanied by periodic phases are studied. We have classified them into two types on the basis of analyses about symmetrical and topological features of periodic phases on the order parameter space, and discussed also the possibility and nature of continuous phase transitions. One type is a directed generalization of cholesterics with soliton excitation and the other is characterized by the bifurcation of the referred phase to periodic ones.

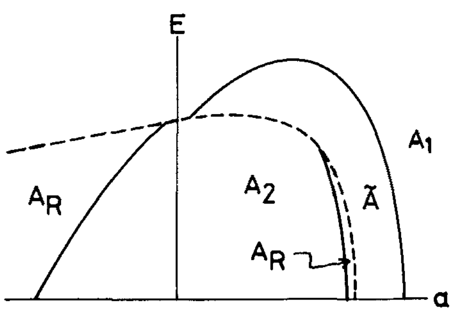

FIGURE 8 Phase diagram of binary mixture showing four smectic A phases in the electric field versus the temperature (a) plane.

As typical examples, ferroelectric smectics, binary mixtures showing several smectic A phases and some other systems, are introduced and discussed from thermo-statistical arguments together with such general considerations, where we have shown that various types of phase transitions do truly occur. Among such systems, ferroelectric smectics in the electric field are notable, because both types of phase transitions occur between chiral smectic C and smectic C phases, making a one-phase boundary separated by the first order transition.

Some of the above considerations are general ones and accordingly applied not only to liquid crystals but also to other systems, such as ferroelectrics and charge density waves of two-dimensional materials. Yet, liquid crystals are attractive, because we can find various types of phenomena therein.

References

1. M. Yamashita, *Phase Transitions in Liquid Crystals and Solitons*, Butsurigaku Saizensen **15** (Kyoritsu Syuppan, Tokyo, 1986), [in Japanese].
2. W. Cochran, *Phys. Rev. Lett.*, **3**, 412 (1959). R. Blinc and B. Zeks, Soft Modes in Ferroelectrics and Antiferroelectrics (North-Holland, Amsterdam, 1974).
3. R. G. de Gennes, *Fluctuations, Instability and Phase Transitions*, edited by T. Riste (Plenum Press, New York and London, 1975), p. 1.
4. Y. Ishibashi, Ferroelectrics **24**, 119 (1980).
5. W. L. McMillan, *Phys. Rev.*, **B14**, 1496 (1976). P. Bak and V. J. Emery, *Phys. Rev. Lett.* **36**, 978 (1976).
6. A. E. Jacobs and M. B. Walker, *Phys. Rev.*, **B21**, 4132 (1980).
7. M. Yamashita, *Solitons in Liquid Crystals*, edited by Lui Lam and J. Prost (Springer-Verlag, New York, 1988), Chap. 10.
8. M. Yamashita, *J. Phys. Soc. Jpn.*, **56**, 1414 (1987).
9. M. Yamashita, *Prog. Theor. Phys.*, **78**, 780 (1987).
10. M. Yamashita, *J. Phys. Soc. Jpn.*, **57**, No. 6 (1988).
11. P. G. de Gennes, *Solid State Commun.*, **6**, 163 (1968). R. B. Meyer, *Appl. Phys. Lett.*, **12**, 281 (1968).
12. M. Yamashita, H. Kimura and H. Nakano, *Mol. Cryst. Liq. Cryst.*, **68**, 79 (1981).
13. B. Schaub and D. Mukamel, *J. Phys.*, **C16**, L225 (1983).
14. P. Lederer and C. M. Chaves, *J. Phys. Lett. (France)*, **42**, L127 (1981). Y. Ishibashi, *J. Phys. Soc. Jpn.*, **56**, 195 (1987). M. Yamashita, *J. Phys. Soc. Jpn.*, **56**, 3333 (1987).
15. A. E. Jacobs, C. Grein and F. Marsiglio, *Phys. Rev.*, **B29**, 4179 (1984).
16. L. Benguigui, *Phys. Rev.*, **A32**, 1429 (1986).
17. M. Yamashita, *J. Phys. Soc. Jpn.*, **57**, 582 (1988).
18. N. D. Mermin, *Rev. Mod. Phys.*, **51**, 591 (1979).
19. S. A. Pikin and V. L. Indenbom, *Sov. Phys. -Uspekhi*, **21**, 487 (1978).
20. A. Michelson, *Phys. Rev.*, **B16**, 585 (1977).
21. A. M. Levelut, *J. Phys. Lett. (France)*, **45**, L603 (1984).
22. P. Prelovsek, *J. Phys.*, **C15**, L269 (1982).
23. M. Yamashita, *Prog. Theor. Phys.*, **74**, 622 (1985).
24. K. T. Mashiyama and H. Mashiyama, *J. Phys.*, **C19**, 6727 (1986).
25. A. Michelson, *Phys. Rev. Lett.*, **39**, 464 (1977).
26. M. Yamashita and O. Tamada, *J. Phys. Soc. Jpn.*, **54**, 2963 (1985).

27. M. Yamashita, *Jpn. J. Appl. Phys.*, **24**, Suppl. 24-2, 884 (1985).
28. J. P. Jamet, *J. Phys. Lett. (France)*, **42**, L123 (1981). M. N. Barreto, P. Lederer and J. P. Jamet, *Phys. Rev.*, **B28**, 3994 (1983).
29. Y. Ishibashi, W. Buchheit and J. Petersson, *Solid State Commun.*, **38**, 1277 (1981).
30. D. Durand, F. Denoyer, D. Lefur, R. Currant and L. Bernard, *J. Phys. Lett. (France)*, **44**, L207 (1983).
31. A. M. Levelut, *J. Phys. Lett. (France)*, **45**, L603 (1984).