Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Maier-Saupe Nematic Isotropic Phase Transition in the Presence of an External Field

Mamoru Yamashita [a]

[a] Department of Physics Engineering, Mie University, Kamihama 1515, Tsu, 514-8507, Japan

Version of record first published: 18 Oct 2010

To cite this article: Mamoru Yamashita (2003): Maier-Saupe Nematic Isotropic Phase Transition in the Presence of an External Field, Molecular Crystals and Liquid Crystals, 398:1, 75-85

To link to this article: http://dx.doi.org/10.1080/15421400390221204

Mol. Cryst. Liq. Cryst., Vol. 398, pp. 75–85, 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390122120

MAIER-SAUPE NEMATIC ISOTROPIC PHASE TRANSITION IN THE PRESENCE OF AN EXTERNAL FIELD

Mamoru Yamashita
Department of Physics Engineering, Mie University, Kamihama 1515, Tsu 514-8507, Japan

The nematic-isotropic phase transition in an external field is studied in the frame of Maier-Saupe model, where a global phase diagram including both cases of positive and negative susceptibility anisotropic is obtained. In the extreme case of infinitely large negative anisotropy, the system is reduced to the classical XY model because the rotational degree of freedom is restricted to lie in the plane perpendicular to the field, in which the second order phase transition occurs. The crossover of the directional degree of freedom between 3-dimension and 2-dimension is depicted. On the other hand, the critical point appears at a certain strength of the positive anisotropy, beyond which the transition disappears. The theory can be applied to the phase transition of very thin systems with homeotropic and planar anchorings.

Keywords: maier-saupe model; nematic-isotropic phase transition; phase diagram; 3d-2d crossover; susceptibility anisotropy; biaxialit

INTRODUCTION

The phase transition between the isotropic and the nematic phases is described by Maier-Saupe model [1,2]. However, to have a complete understanding of such transition, the behaviour of the model in an external field conjugate to the order parameter has to be clarified.

We study here the nematic-isotropic phase transition occurring in a liquid crystal according to the Maier-Saupe model subjected to an external field, where a global phase diagram including both positive [3–5] and negative [6] susceptibility anisotropy is considered. In the case of negative anisotropy the transition order is known to change from the first to the second one [6]. We clarify this behaviour by taking a limit of infinitely large

This study was partly supported by a Grant-in Aid from the Ministry of Education, Science, Sports and Culture (No. 14540355).

negative anisotropy, in which the directional degree of freedom is restricted to the in-plane rotation which is equivalent to the classical XY model. This model is known to exhibit a second order phase transition, that leads to the appearance of a tricritical point. As the magnitude of the field is reduced, the fluctuation of the degree of freedom out-of the plane is enhanced, destabilising the planar order; there is a crossover of directional degree of freedom from 2-dimension to 3-dimension. We will determine the position of tricritical point in the harmonic approximation for the fluctuation. In the case of positive anisotropy the behaviour of the system is simple, where a critical point arises at a certain field strength, over which the transition disappears [3–5]. The applicability of the results to phase transitions at very thin systems with homeotropic and planar anchoring walls will be mentioned [7,8]. The wall effect is replaced by an effective external field and the behaviour of the system will be summarised on the basis of the global phase diagram of field versus temperature for the bulk system.

MAIER-SAUPE MODEL IN THE EXTERNAL FIELD

In the mean field theory, the directional degree of freedom is decoupled with the positional one, and the Hamiltonian of Maier-Saupe model is written essentially as

$$H_0 = -V \sum_{(i,j)} P_2\big(\cos\theta_{ij}\big), \tag{1}$$

where the factor V is the effective energy intensity, θ_{ij} the angle between the long axes of i-th and j-th molecules, and $P_2(x)$ the second Legendre's polynomial, $\big(3x^2-1\big)/2$. The nematic order parameter s is given by the thermal average,

$$s = \frac{1}{N}\sum_{i=1}^{N}\langle P_2(\cos\theta_i)\rangle, \tag{2}$$

where θ_i is the polar angle of the i-th molecular long axis and N the total number of molecules. Generally, the coupling of the order parameter s to a conjugate field h is given by the form,

$$H_{\text{ext}} = -h\sum_{i} P_2(\cos\theta_i). \tag{3}$$

In contrast with the case of the polar order parameter such as for magnetism where both positive and negative values of the symmetry breaking field are valid, the symmetry breaking field h in Eq. (3) should be restricted to positive value because of the tensor character of s. In fact, for negative value of h, the nematic order should appear in the plane perpendicular

to the field, and accordingly the true symmetry breaking field has to be introduced in the direction of the nematic order in that plane. However, for an external magnetic field, the anisotropic energy is given by:

$$H_{\text{ext}} = -\frac{1}{2}\chi_a H^2 \sum_i \cos^2\theta_i. \tag{4}$$

This equation is valid for both sign of susceptibility anisotropy χ_a. Since the expressions (3) and (4) are similar, the form (3) can be generalised for all range of real values of h, both positive and negative. In this paper the system (1) in the generalised external field (3) is investigated.

We notice here a useful identity which is employed in the further treatment:

$$\begin{aligned} P_2\big(\cos\theta_{ij}\big) &= P_2(\cos\theta_i)P_2\big(\cos\theta_j\big) \\ &\quad + 2\sum_{l=1}^{2}\frac{(2-l)!}{(2+l)!}P_2^l(\cos\theta_i)P_2^l\big(\cos\theta_j\big)\cos l\big(\varphi_i-\varphi_j\big), \end{aligned} \tag{5}$$

in which $P_2^l(x)$ is the associated Legendre's polynomial and φ_i the azimuthal angle for the i-th molecule.

POSITIVE ANISOTROPY

First, we review the case of positive field h, which corresponds to the positive magnetic anisotropy. The system is uniaxial and the second term in the right hand side of Eq. (5) can be neglected in the mean field theory. Thus, the Hamiltonian of Maier-Saupe model writes

$$H_0 = -V\sum_{(i,j)} P_2(\cos\theta_i)P_2\big(\cos\theta_j\big). \tag{6}$$

The self consistency equation for s is given by

$$s = f(\beta(h + Vzs)), \tag{7}$$

where β is the inverse temperature $1/k_BT$ rescaled by Boltzmann constant k_B, z an averaged coordination number and $f(x) = f_1(x)/f_0(x)$ with $f_n(x)$ defined by

$$f_n(x) = \int_0^1 P_2^n(y)\exp\{xP_2(y)\}\mathrm{d}y. \tag{8}$$

The free energy $F(s)$is given by

$$F(s) = F(0) + \int_0^s h(s)\mathrm{d}s - h_{\text{ext}}s, \tag{9}$$

where the reduced field $h(s)$ is derived from Eq. (7) as a function of s, and h_{ext} is the actual field intensity. By neglecting the last term, $-h_{\text{ext}}s$, Eq. (9) turns out to be the ordinary Maier-Saupe free energy. The free energy (9) can be expanded as

$$F(s) = F(0) + k_{\text{B}}\text{T}\{\frac{1}{2}(5 - \frac{Vz}{k_{\text{B}}T})s^2 - \frac{25}{21}s^3 + \frac{425}{196}s^4 + O(s^5)\} - h_{\text{ext}}s. \quad (10)$$

On the basis of expression (10), the phase transition of the system can be discussed analytically. Here, and hereafter, the energy variables, T and h, are scaled in the Unit Vz, and the unit $k_{\text{B}} = 1$ is utilised. In case $h_{\text{ext}} = 0$, the transition temperature, T_{c} is obtained as 153/715 ($=0.214$) while numerical calculation based on Eq. (9) is 0.220. It has to be noticed that the result of first order phase transition is unaffected by the present approximation because of the invariant of cubic term in the free energy.

In the finite field, the disordered phase is uniaxial as the nematic phase as well. Accordingly, there is the possibility to get a critical point like in the case of liquid-gas phase transition. In the limit of infinite field each molecular long axis aligns in the direction of the field with saturated order parameter, $s = 1$, and no phase transition occurs at finite temperature. From these consideration, the existence of the critical point is proved.

On the basis of the free energy (10), the critical point, $T = T_{\text{cp}}$ and $h_{\text{ext}} = h_{\text{cp}}$, is obtained as $T_{\text{cp}} = 51/230 (= 0.222)$ and $h_{\text{cp}} = 35/7038$ ($= 0.00497$). Numerical estimates from Eq. (9) are those; $T_{\text{cp}} = 0.232$, $h_{\text{cp}} = 0.0065$. Experimentally, the existence of the critical point has not yet been confirmed, though the tendency to approach the critical point has been observed [5].

NEGATIVE ANISOTROPY

In the case of negative anisotropy, the long range order appears in the plane perpendicular to the field and apparently the system is not uniaxial [6]. So, the term with $l = 2$ in Eq. (5) should be taken into account while the one with $l = 1$ can be neglected because of the factor $\sin 2\theta_i \sin 2\theta_j$. The Hamiltonian (1) is rewritten as

$$H_0 = -V \sum_{(i,j)} \left[P_2(\cos\theta_i) P_2(\cos\theta_j) + \frac{3}{4} \sin^2\theta_i \sin^2\theta_j \cos 2(\varphi_i - \varphi_j) \right]. \quad (11)$$

The disordered phase is uniaxial irrespective of the sign of field. At low temperature the ordered phase appears in which the planar symmetry is

broken, and the phase becomes biaxial. Thus, the phase transition line which separates the ordered from the disordered phase is proved not to end into any critical point.

Planar Limit

We consider here the extreme case of the limit of negative infinity of h, where θ_i is frozen to the value $\pi/2$. Then, the Hamiltonian is reduced to the form,

$$H_2 = -V_2 \sum_{(i,j)} \cos(\psi_i - \psi_j), \tag{12}$$

that is really the classical XY model where $\psi_i = 2\varphi_i$ and $V_2 + 3V/4$. The transition of this system is known to be of the second order, and in the mean field approximation the transition temperature is given by $T_2(= V_2 z/2 = 3/8\,\mathrm{Vz})$. As the transition of Maier-Saupe model is first order, we have proved that the transition changes from the second to first order at a certain value of the field strength h_t. This change comes from the degree of freedom of θ_i fluctuating around $\pi/2$.

It is interesting to rewrite the Hamiltonian (12), neglecting the vanishing terms in the mean field theory, as

$$H_2 = -V_2 \sum_{(i,j)} (2\cos^2\varphi_i - 1)(2\cos^2\varphi_j - 1). \tag{13}$$

By comparing Hamiltonian (13) with (6), it's easy to see that $(3\cos^2\theta_i - 1)/2$ in (6) is replaced by $(2\cos^2\varphi_i - 1)$ in (13). This means that in the limit of negative infinity of h, $(2\cos^2\varphi_i - 1)$ vanishes at the disordered phase, resulting $s = 1/4$. Of course, both $(3\cos^2\theta_i - 1)/2$ and $(2\cos^2\varphi_i - 1)$ are equal to 1 at absolute zero temperature. From these constraints together with the continuity consideration of the change of temperature dependence of s for the increase of $|h|$, we obtain s-T relation for various values of $|h|$ as shown in Figure 1, where (a) $h = 0$, (b) $|h| < |h_\mathrm{t}|$, (c) $|h| = |h_\mathrm{t}|$ (tricritical value), (d) $|h_\mathrm{t}| < |h| < \infty$, (e) $|h| \to \infty$. The curves show the crossover from 3-dimensional rotational degree of freedom to 2-dimensional.

General Case

Here, the effect of the fluctuation of θ_i around $\pi/2$ on the nematic ordering is investigated and the tricritical point is evaluated. The Gaussian variable $\omega_i = \theta_i - \pi/2$ is introduced, and the Hamiltonian (11) is rewritten up to the order ω_i^2 as

$$H_\mathrm{eff} = -V_2 \sum_{(i,j)} \left[(1-\omega_i^2)(1-\omega_j^2)\cos\psi_i \cos\psi_j + \frac{1}{3}(1-3\omega_i^2)(1-3\omega_j^2) \right]. \tag{14}$$

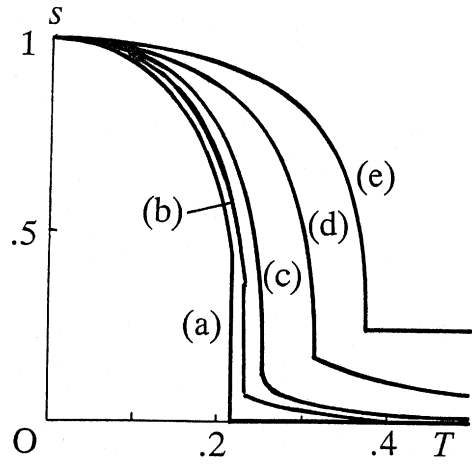

FIGURE 1 Temperature dependence of s for various values of field, where (a) $h=0$, (b) $0<|h|<|h_t|$, (c) $|h|=|h_t|$, (d) $|h_t|<|h|<\infty$ *and* (*e*) $|h|\to\infty$.

Then, the partition function Z versus the symmetry breaking field in the plane, η, and the field -ζ which is conjugate to ω_i can be written as,

$$Z(\eta,\zeta)=\prod_i\int_0^{2\pi}\mathrm{d}\psi_i\int_{-\infty}^{\infty}\mathrm{d}\omega_i\exp\left(\eta\sum_j\cos\psi_j-\zeta\sum_j\omega_j-\beta H_{eff}\right), \quad (15)$$

It is noticed that the line element, $\sin\theta_i\mathrm{d}\theta_i$, is replaced by $\exp(-\omega_i^2/2)\mathrm{d}\omega_i$ in Eq. (15), and by taking into account Eq. (3) ζ turns out to be related to h by the equation,

$$\zeta=\frac{1-3\beta h}{2}. \quad (16)$$

The partition function for one particle is introduced

$$z(\eta,\zeta)=2\int_0^{\pi}\mathrm{d}\psi\int_{-\infty}^{\infty}\mathrm{d}\omega\exp(\eta\cos\psi-\zeta\omega^2) \quad (17)$$

$$=2\sqrt{\frac{\pi}{\zeta}}\int_0^{\pi}\mathrm{d}\psi\exp(\eta\cos\psi), \quad (18)$$

in which variables η and ζ are decoupled. By defining $I(\eta)$ and $J(\zeta)$ as

$$I(\eta)=\frac{\partial\ln z(\eta,\zeta)}{\partial\eta}, \quad (19)$$

$$(\zeta)=-\frac{\partial\ln z(\eta,\zeta)}{\partial\zeta}, \quad (20)$$

we obtain the following expression in the mean field theory,

$$Z(\eta,\zeta)=\exp N\left[\ln z(\eta,\zeta)+\frac{\beta Vz}{2}\left\{(1-J)^2I^2+\frac{1}{3}(1-3J)^2\right\}\right]. \tag{21}$$

The self consistency equation for the average of $\cos\psi_i$, s_2, is given by,

$$\begin{aligned} s_2 &= \frac{1}{N}\frac{\partial}{\partial\eta}\ln Z(\eta,\zeta) \\ &= I(\eta+\beta V_2 z(1-\Omega)^2 s_2), \end{aligned} \tag{22}$$

where Ω, the average of ω_i^2, is determined from

$$\begin{aligned} \Omega &= -\frac{1}{N}\frac{\partial}{\partial\zeta}\ln Z(\eta,\zeta) \\ &= \frac{1}{2\{\zeta+\beta V_2 z(1-\Omega)s_2^2+1-3\Omega\}}. \end{aligned} \tag{23}$$

So long the critical line and the tricritical point are concerned, the expansion form,

$$\Omega=\Omega_0+\Omega_2 s_2^2+\cdots, \tag{24}$$

is useful. From Eq. (23) Ω_0 and Ω_2 are derived as

$$6\Omega_0^2-2\left(\frac{\zeta}{\beta V_2 z}+1\right)\Omega_0+\frac{1}{\beta V_2 z}=0, \tag{25}$$

$$\Omega_2=-\frac{\Omega_0(1-\Omega_0)}{\zeta/\beta V_2 z+1-6\Omega_0}, \tag{26}$$

respectively. On the other hand, η is derived from Eq. (22) as a function of s_2 as

$$\eta+\beta V_2 z(1-\Omega)^2 s_2=2s_2+s_2^3+\cdots, \tag{27}$$

and by substituting Eq. (24) into (27) we obtain

$$\eta=\{2-\beta V_2 z(1-\Omega_0)^2\}s_2+\{1+2\beta V_2 z(1-\Omega_0)\Omega_2\}s_2^3+\cdots, \tag{28}$$

and the free energy in the Landau expansion form writes

$$\begin{aligned} F(s_2) = F(0) &+ \left\{k_{\mathrm{B}}T-\frac{V_2 z}{2}(1-\Omega_0)^2\right\}s_2^2 \\ &+\frac{1}{4}\{k_{\mathrm{B}}T+2V_2 z(1-\Omega_0)\Omega_2\}s_2^4+\cdots. \end{aligned} \tag{29}$$

The ordered phase is biaxial while the disordered one is uniaxial, due to the negative field. The critical temperature T_{c} is determined from

expression (29) by

$$T_c = \frac{V_2 z}{2k_B}(1-\Omega_0)^2, \tag{30}$$

under the condition of positiveness of the quartic term in Eq. (29),

$$k_B T_c + 2V_2 z(1-\Omega_0)\Omega_2 > 0. \tag{31}$$

It is noticed that the factor Ω_0 in Eq. (30) contains T_c as we can see in Eq. (25). The critical line ends at the tricritical point where the left hand side of (31) vanishes.

TRICRITICAL POINT AND PHASE DIAGRAM

The conditions (30) and (31) are solved numerically. The tricritical values are obtained as follows; $T_t = 0.2301 (= 0.3068 V_2 z), \zeta_t = 1.1668$, $h_t = -0.1023$ and $\Omega_t = 0.2167$. The phase diagram of h versus T is shown in Figure 2, where the solid curves are the coexisting lines, the broken one is the critical line, the thin line at $T = 0.375$ is an asymptote, and CP and TCP represent the critical point and the tricritical point, respectively. As the field $|h|$ decreases, the deviation of the direction from the plane is enhanced

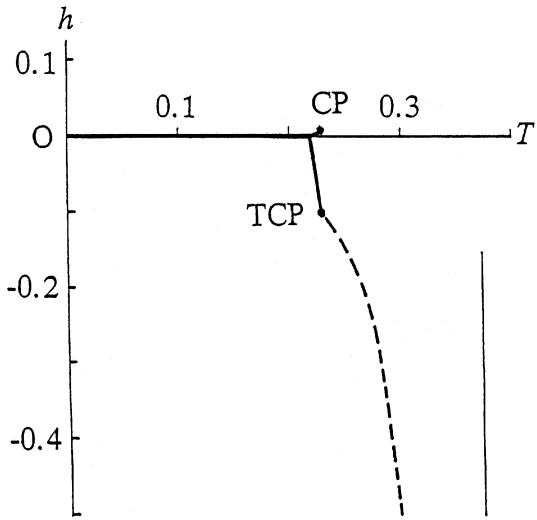

FIGURE 2 The phase diagram on h-T plane, in which the continuous lines represent the coexisting lines, the broken one is the critical line, the thin line at $T = .0375$ is an asymptote, and CP and TCP denote the critical point and the tricritical point, respectively.

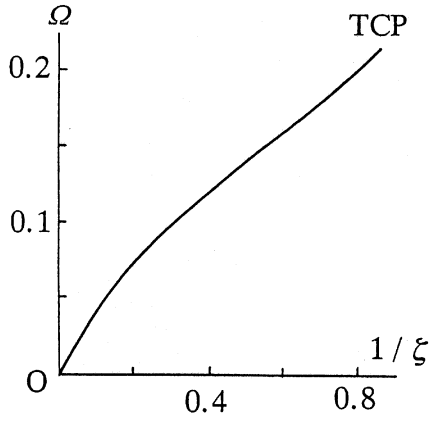

FIGURE 3 The field dependence of the average of ω_i^2, Ω, along the critical line, where TCP shows the tricritical point.

and T_2 decreases, and eventually the transition changes from the second to the first order. This course is nothing but the crossover of the directional degree of freedom from 2-dimension to 3-dimension. The dependence of Ω on the field ζ along the critical line is shown in Figure 3 in which ζ^{-1} is chosen as abscissa. The average of the deviation of θ_i from /2 is evaluated by the standard deviation of ω_i, which takes the value at the tricritical point, $\sqrt{\Omega_t}/(\pi/2) = 0.296$. From this estimate the harmonic approximation for ω_i is considered to be qualitatively justified.

The magnitude of tricritical field is very large in comparison with the critical value which is not yet achieved. However, the negative field part of phase diagram in Figure 2 is not artificial but useful in the quite thin system limited by planar wall, as shown in the next section.

THIN SYSTEMS

Effects of the boundary upon the liquid crystal ordering at very thin systems are important [7,8]. A homeotropic anchoring wall acts for smectic layer ordering as the symmetry breaking field, and in case the smectic order is decoupled from nematic order, the phase diagram is of type of XY model: hence the smectic order persists up to high temperature without phase transition [9]. Here, we see similar mechanism at the nematic-isotropic phase transition, which is observed on the phase diagram shown in Figure 2.

Because of the existence of the wall, the system is inhomogeneous. Let x-axis be normal to the wall. Then, the order parameter s depends on x, $s(x)$. The molecular field Vzs in Eq.(7) is replaced by $h_m(x)$, which is given by

$$h_{\mathrm{m}}(x) = V\{(z-2)s(x) + s(x+a) + s(x-a)\}, \tag{32}$$

$$= Vzs(x) + h(x), \tag{33}$$

where the first term in Eq. (33) is the usual type in the case of the homogeneous system and the field $h(x)$ due to the inhomogeneity is given in the continuum limit with a stiffness of order parameter, K ($= Va^2$, where a is a length at atomic scale), as

$$h(x) = K\frac{\mathrm{d}^2 s}{\mathrm{d}x^2}. \tag{34}$$

In the case of the homeotropic anchoring wall, the nematic order parameter changes from the boundary value to the bulk equilibrium with concave shape. So, the filed h is positive, and the phase transition occurring of depends on the field strength at the centre of the system, h^*, referring to the positive field area of phase diagram in Figure 2. If h^* is larger than h_{cp} at critical temperature T_{cp}, no phase transition is observed, while if h^* is smaller than h_{cp}, $h(x)$ crosses the transition curve in Figure 1 and a discontinuity occurs. Whether h^* is larger than h_{cp} or not depends on wall thickness. By this interpretation of the field $h(x)$, numerical analyses of the Maier-Saupe model with homeotropic wall can be performed [10].

On the other hand, in the case of planar anchoring wall, the behaviour of the order parameter is considered to be convex and the field strength due to wall is negative. Then, the negative field part of the phase diagram of Figure 2 is relevant, where the phase transition line never ends. Accordingly, the phase transition occurs irrespectively of the thickness of the planar wall system. If the system is thin enough and $|h^*|$ exceeds $|h_{\mathrm{t}}|$, the transition is predicted to be of the second order.

SUMMARY AND DISCUSSIONS

The nematic-isotropic phase transition in an external field which couples to the nematic order parameter is studied in the frame of Maier-Saupe theory. In the limit of negative infinite field strength, the system is shown to be reduced to the classical XY model, which exhibits a second order phase transition, whereas the transition is of first order in the absence of the field. As a consequence, the change of order of phase transition is proved. The fluctuation of the molecular director out-of the plane of XY model leads to first order transition. The tricritical point has been evaluated in the harmonic approximation for the fluctuation. The appearance of critical point at the positive region of the field is also derived by the symmetry consideration in the particular case of infinite field strength, where no phase transition occurs at finite temperature. The global phase diagram of the field versus temperature is obtained.

The applicability of present results to the thin systems is mentioned. The phase transition at the homeotropic wall is ruled by the strength of the effective field at critical temperature T_{cp} (see the phase diagram of Figure 2). On the other hand the system with planar anchoring wall corresponds to the negative field case and whether the transition is continuous or not, it depends on the effective field strength due to the wall at the centre of the system.

The ordered phase in the negative field is biaxial. This biaxiality appearing in a system composed of cylindrical molecules differs from the one with the ordering of short axis of non-cylindrical molecule in which biaxiality appears due to the order of molecular short axis. At the absolute zero temperature, the former disappears while the latter is complete.

The theory of tricritical point due to Fan and Stephen [6] is based on the expansion form of free energy for both nematic and biaxial order parameters, which corresponds to the weak field theory, whereas the present approach implies a strong field.

REFERENCES

[1] Maier, W. & Saupe, A. (1985). *Z. Naturforsch.*, *13a*, 564.
[2] Maier, W. & Saupe, A. (1959). *Z. Naturforsch.*, *14a*, 882.
[3] Hanus, J. (1969). *Phys. Rev.*, *178*, 420.
[4] Wojtowicz, P. J. & Sheng, P. (1974). *Phys. Lett.*, *A48*, 235.
[5] Nicastro, A. J. & Keyes, P. H. (1984). *Phys. Rev.*, *A30*, 3156.
[6] Fan, C. & Stephen, M. J. (1970). *Phys. Rev. Lett.*, *25*, 500.
[7] Miyazaki, T., Shigematsu, K., & Yamashita, M. (1998). *J. Phys. Soc. Jpn.*, *67*, 3477.
[8] Miyazaki, T., Hayashi, H., & Yamashita, M. (1999). *Mol. Cryst. Liq. Cryst.*, *330*, 367.
[9] Yamashita, M. & Miyazaki, T. (2001). *J. Phys. Soc. Jpn.*, *70*, 1611.
[10] Yamashita, M. & Miyazaki, T. unpublished work presented at the annual meeting of Physical Society of Japan on Sept., 2001 at Tokushima.