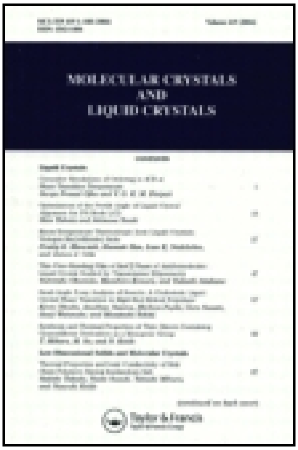


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Theory of Homologous Liquid Crystals. I. Phase Diagrams and the Even-Odd Effect

Shu Changqing [a] & Lin Lei [b c]
[a] Institute of Physics, Chinese Academy of Sciences, Beijing, China
[b] Department of Physics, Chinese University of Hong Kong, Hong Kong, and Institute of Physics, Chinese Academy of Sciences, Beijing, China
[c] Physics Department, City College, CUNY, New York, N.Y., 10031, U.S.A.

To cite this article: Shu Changqing & Lin Lei (1984): Theory of Homologous Liquid Crystals. I. Phase Diagrams and the Even-Odd Effect, Molecular Crystals and Liquid Crystals, 112:3-4, 213-231

To link to this article: http://dx.doi.org/10.1080/00268948408071836

Mol. Cryst. Liq. Cryst., 1984, Vol. 112, pp. 213–231
0026-8941/84/1124-0213/$20.00/0

Theory of Homologous Liquid Crystals. I. Phase Diagrams and the Even-Odd Effect†

SHU CHANGQING
Institute of Physics, Chinese Academy of Sciences, Beijing, China

and

LIN LEI‡
Department of Physics, Chinese University of Hong Kong, Hong Kong, and Institute of Physics, Chinese Academy of Sciences, Beijing, China

(*Received December 14, 1983*)

Effect of the molecular length d in a homologous series of liquid crystal is considered. The McMillan hamiltonian is generalized to be $H = F(d)\sum_{i>j}V(i, j)$. The mean-field form of the hamiltonian is derived explicitly and systematically for the first time. For $F(d) = d^{\lambda}$, results of McMillan and Lee et al. are recovered with correction when $\lambda = 1$ and $\lambda = 0$, respectively. Different types of the isotropic-nematic-smectic A phase diagrams are explained and new ones are predicted. The even-odd effect may be understood when the width of the molecule is also included in our formalism. As illustrations, even-odd variations of transition temperatures, order parameters and supercooling temperatures are calculated showing good agreement with experiments.

I. INTRODUCTION

The early molecular theory describing liquid crystals of rod-like molecules is that of Maier–Saupe (MS).[1] It describes only the nematic (N)-isotropic(I) transition and gives a transition temperature T_{NI} independent of the molecular length d. Subsequently, Kobayashi[2] and McMillan[3,4] independently generalized the MS theory to include the

---

† Work presented at the Ninth International Liquid Crystal Conference, Bangalore, India, December 6–10, 1982, under the title, "Pressures, Mixtures and Reentrant Phenomena."

‡ Correspondence address: Physics Department, City College, CUNY, New York, N.Y. 10031, U.S.A.

molecular separations into the hamiltonian and are able to describe the I-N-A (A represents smectic A) phase transitions. In the mean-field approximation this model gives the same T_{NI} as that of MS (which is also independent of d). On this basis, Lee et al.[5] modified slightly the McMillan hamiltonian and obtained a T_{NI} which decreases with d increasing.

There exists some confusion in the literature concerning these results. At one point, the McMillan result[3] was deemed[5] incorrect. Although the relationship between the models of McMillan[3] and Lee et al.[5] was later clarified by Tan[6] and found to differ from each other by only a d-dependent factor in their respective hamiltonians, however, the d-dependent factor of McMillan was thought to be "unphysical".[6]

On the other hand, there definitely exists more types of I-N-A phase diagrams[7] (characterized by the trend of T_{NI} as a function of n, the number of carbon atoms in the end-chain) than the two types mentioned above.

One of the purposes of this paper is to investigate the effect of d in a more systematic way and to try to clarify these issues. In the next Section, the McMillan hamiltonian[3] is generalized and the resulting mean-field hamiltonian is *derived* in some detail (Appendix A), a crucial step which surprisingly has not been reported anywhere in the literature [e.g. Refs. (2)–(6)], to the best of our knowledge. This is also a necessary step when the more complicated statistical mechanical properties (e.g. correlation functions, apparent exponents,[8] etc.) of the homologous series are studied.[9] Phase diagrams are discussed in Section III.

When the systematic variation of the molecular width D is taken into account (Section IV) a new explanation of the even-odd effect (other than the one of Marcelja[10]) becomes possible (Section V).

While our attention here is confined to the relatively simple McMillan hamiltonian of rod-like molecules our formalism is clearly also applicable to the other molecular theories of both rod-like[11,12] and disc-like[13] molecules.

A brief summary of this and the following paper[9] can be found in Ref. (14).

II. THE HAMILTONIAN

The interaction between two rod-like molecules i and j (with cylindrical symmetry) is given, to second order, by

$$W(i, j) = W_0(r_{ij}) + W_2(r_{ij})P_2(\cos\theta_{ij}) \qquad (2.1)$$

where r_{ij} and θ_{ij} are the separation between the centers of mass and the angle between the orientations of the two molecules, respectively. From physical arguments,[14] in general, both W_0 and W_2 depend on d, the molecular length. If

$$W_{2l} = F_{2l}(d)V_{2l}(r_{ij}), \qquad l = 0, 1 \tag{2.2}$$

then (i) $F_0(0) = 1$, $F_2(0) = 0$, and (ii) $F_{2l}(d)$ is a non-decreasing function of d.[14] For simplicity, we assume

$$F_0(d) = F_2(d) = F(d) \tag{2.3}$$

which obviously does not satisfy (i) and hence is invalid for $d \simeq 0$. However, as we shall show below, all the liquid crystal materials have d away from zero and Eq. (2.3) is thus applicable in real cases.

Following Refs. (3)–(5), V_0 and V_2 are assumed to be Gaussian functions and the hamiltonian is then

$$H = -\sum_{i,j}{}'(4\pi^{1/2})^{-1}JF(d/r_0)\exp(-r_{ij}^2/r_0^2)[\delta + P_2(\cos\theta_{ij})] \tag{2.4}$$

where J and δ are constants, r_0 the effective range of interaction between two molecules. The prime in the summation sign indicates the exclusion of $i = j$ terms.

Taking the normal of the layers of the A phase as the z-axis, $r_i \equiv (x_i, y_i, z_i)$, $x_{ij} \equiv x_i - y_j$, etc., we have

$$\exp(-r_{ij}^2/r_0^2) = \exp(-\rho_{ij}^2/r_0^2)\exp(-z_{ij}^2/r_0^2) \tag{2.5}$$

where

$$\rho_{ij}^2 \equiv x_{ij}^2 + y_{ij}^2 \tag{2.6}$$

When $\exp(-z_{ij}^2/r_0^2)$ is Fourier transformed and only the two lowest-order terms are kept, under the mean-field approximation, H becomes (see Appendix A)

$$H_{\mathrm{MF}} = \sum_i V(z_i, \theta_i) \tag{2.7}$$

$$V(z_i, \theta_i) = -\bar{J}\left\{\bar{\alpha}\delta\tau\cos(2\pi z_i/d) + I\eta + \bar{\alpha}\sigma\cos(2\pi z_i/d)]S_i\right\} \tag{2.8}$$

where $s_i \equiv P_2(\cos\theta_i)$, θ_i the angle between the orientation of the ith molecule with the z-axis, τ, η, σ are respectively the position, orientation and mixed order parameters defined by

$$\tau \equiv \langle \cos(2\pi z_i/d) \rangle \tag{2.9}$$

$$\eta \equiv \langle P_2(\cos\theta_i) \rangle \tag{2.10}$$

$$\sigma \equiv \langle \cos(2\pi z_i/d) P_2(\cos\theta_i) \rangle \tag{2.11}$$

Also,

$$\bar{\alpha} = \bar{\alpha}(t) \equiv 2\exp\left[-(\pi/t)^2\right] w(t) \tag{2.12}$$

$$w(t) \equiv 1 + \pi^{-1/2}\exp(-1/4t^2)R^{-1}(t/2) \times \int_0^{2\pi/t} \exp(-y^2/4)\sin(yt/2)\,dy \tag{2.13}$$

$$R(x) \equiv 2\pi^{-1/2}\int_0^x \exp(-y^2)\,dy \tag{2.14}$$

with $t \equiv d/r_0$ and $\bar{J} = \bar{J}(t)$ given by (for molecules of zero width)

$$\bar{J} = (2t)^{-1} J F(t) R(t/2) \sum_{j(\neq i)} \langle \exp(-\rho_{ij}^2/r_0^2) \rangle \tag{2.15}$$

Under the mean-field approximation of Eq. (2.7), in Eqs. (2.9)–(2.11) the thermal averages are defined by ($\beta \equiv 1/k_B T$)

$$\langle f(z,\theta) \rangle \equiv \frac{\int_0^d dz \int_0^\pi d\theta\, f(z,\theta)\exp(-\beta V)\sin\theta}{\int_0^d dz \int_0^\pi d\theta \exp(-\beta V)\sin\theta} \tag{2.16}$$

$R(x)$ is a monotonic increasing function of x with $R(0) = 0$ and $R(\infty) = 1$. For $x > 1.6$, $R(x) \simeq 1$ [see Figure 1 of Ref. (14)]. $w(x)$ is as shown in Figure 1. For $x < 4$, $w(x) \simeq 1$.

If the approximations $w(t) = 1$ and $R(t) = 1$ are assumed in Eqs. (2.12), (2.13) and (2.15), then, for $F(t) = t$, Eq. (2.8) reduces to the hamiltonian of McMillan[4] [the one in Ref. (3) corresponds to the further approximation $\delta = 0$]; for $F(t) = 1$, Eq. (2.6) reduces to the case of Lee et al.[5] However, as will be shown in Section III, within the relevant domain of t in the phase diagrams, $R(t) = 1$ is not a very good approximation.

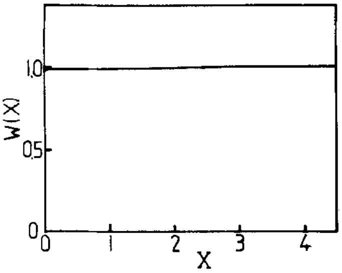


FIGURE 1 The curve $w(x)$ [see Eq. (2.13) for definition].

III. PHASE DIAGRAMS

Generally speaking, $\bar{J}$ of Eq. (2.15) is temperature dependent. In mean-field approximation, it is assumed to be independent of temperature (see Section IV). The transition temperatures T_{NI}, T_{NA} and T_{IA} are obtained when the solutions of the three self-consistent Eqs. (2.9)–(2.11) are solved using Eqs. (2.8), (2.15) and (2.16) and then substituted into the free energy expressions.[3,5] This type of calculation has been carried out before in Ref. (3) (for $\delta = 0$) and Ref. (5) (for $\delta = 0.65$). Since our mean-field hamiltonian of Eq. (2.8) differ from that of Ref. (5) in only the specific form of $\bar{J}$ it is possible to show, for molecules of zero with ($D = 0$), that [see Appendix B of Ref. (15)]

$$v_0 = 2\pi^{-1/2} J F(t) R(t/2) \tag{3.1}$$

where v_0 is the interaction strength given in Eq. (6) or (8) of Ref. (5). Using further the (pretty accurate) approximation of $w(x) \simeq 1$ it is then possible to obtain phase diagrams corresponding to different forms of $F(t)$ from that of Ref. (5) by a simple rescaling of the temperature.

In the rest of this Section, $w(x) = 1$, $\delta = 0.65$ are used. In Figure 2, we assume

$$F(t) = t^{\lambda} \tag{3.2}$$

and the calculated T_{NI} curves a, b, c and d correspond, respectively, to $\lambda = 0, \frac{1}{2}$, 1 and 2. At $t \simeq 2.62$, T_{NI} meets the curve T_{NA} [see Figure 4(a)–(d)]. For $\lambda = 0$, T_{NI} decreases monotonically as t increases. In contrast, for $\lambda = 1$, T_{NI} is a monotonic increasing function of t; T_{NI} is not really horizontal for $2.33 < t < 2.58$. The case of $\lambda = 2$ is similar to that of $\lambda = 1$ except that T_{NI} increases faster. The curve corre-

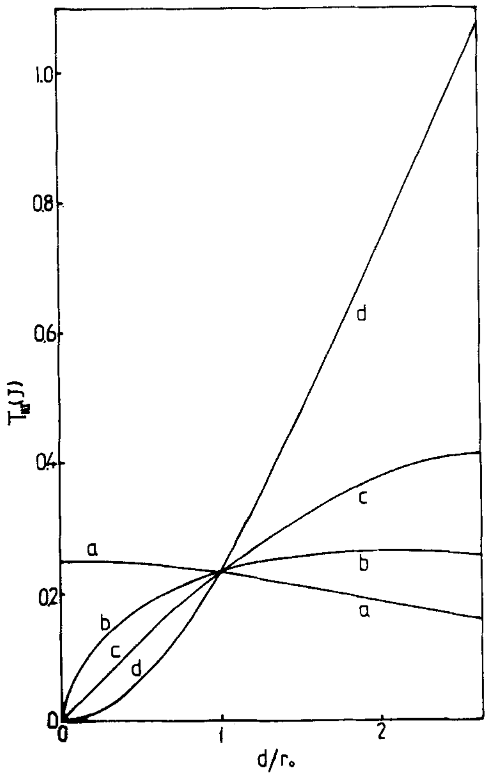


FIGURE 2 Calculated transition temperature T_{NI} vs. t ($\equiv d/r_0$). $F(t) = t^{\lambda}$. Curve a: $\lambda = 0$; b: $\lambda = \frac{1}{2}$; c: $\lambda = 1$; d: $\lambda = 2$.

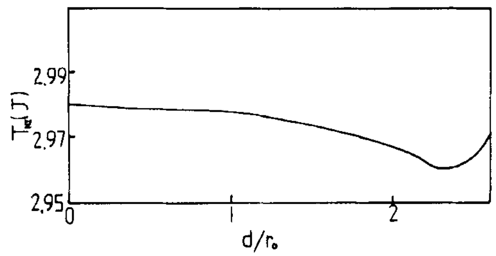


FIGURE 3 Calculated transition temperature T_{NI} vs. t. $F(t) = 12 + t^2$.

sponding to $\lambda = \frac{1}{2}$ differs from all the other three; there is a maximum at $t \simeq 2$.

On the other hand, when

$$F(t) = At^{\lambda_1} + Bt^{\lambda_2} \tag{3.3}$$

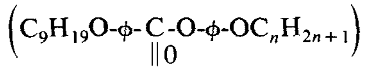
it is possible to obtain completely different cases. For example, in Figure 3, with $\lambda_1 = 0$, $\lambda_2 = 2$, $A = 12$ and $B = 1$ T_{NI} has a minimum at $t \simeq 2.3$. If $\lambda_1 = 0$, $\lambda_2 = 1$ or $\lambda_1 = \frac{1}{2}$, $\lambda_2 = 0$ (or 1) results similar to curve b of Figure 2 (i.e. T_{NI} has a maximum) are obtained. For $\lambda_1 = 1$, $\lambda_2 = 2$ or $\lambda_1 = \frac{1}{2}$, $\lambda_2 = 2$, T_{NI} increases monotonically, similar to curve d of Figure 2.

Comparison with experiments

1. In Figure 4(a)–(d), some calculated I-N-A phase diagrams are plotted. They correspond to various existing real systems [see Ref. (16) for details].

2. In some homologous series, e.g. 4-*n*-alkyloxy-4′-cyanobiphenyl (*n*OCB),[17] the T_{NI} vs. *n* curves of both the even and the odd series have the same shape. The two series may therefore correspond to the same $F(t)$ function. However, in other homologues, e.g. 4-*n*-alkyloxybenzylidene-4′-*n*-butylaniline ($C_nH_{2n+1}O$-ϕ-$CH = N$-ϕ-C_4H_9) as shown in Figure 5, the even series has a minimum corresponding to Figure 3 [or Figure 4(d)] and hence $F(t)$ of Eq. (3.3); the odd series corresponds to curve c of Figure 2 [or Figure 4(c)] and hence the $F(t)$ of Eq. (3.2). In other words, Figure 5 may be considered as a superposition of Figures 4(c) and 4(d).

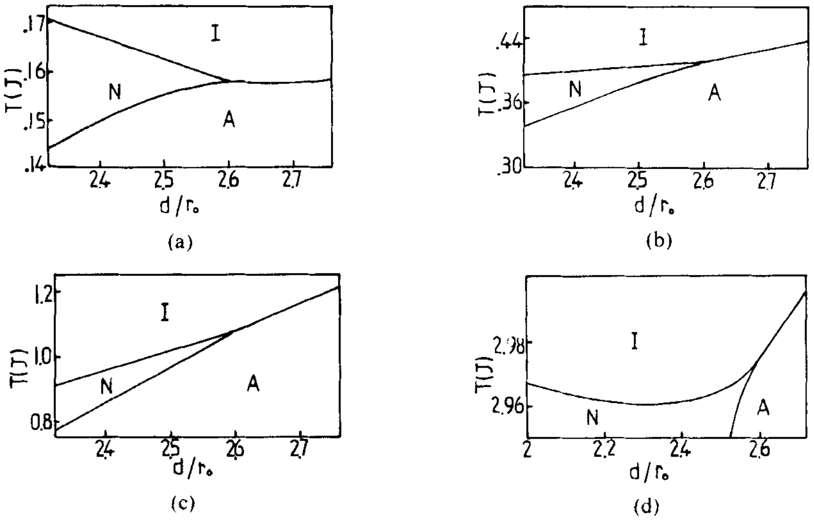
In Figure 6, where the phase diagram of 4-*n*-alkyloxyphenyl-4′-*n*-nonylbenzoate



$$\left(C_9H_{19}O\text{-}\phi\text{-}\underset{\|O}{C}\text{-}O\text{-}\phi\text{-}OC_nH_{2n+1}\right)$$

is plotted, the even series belongs to the type shown in Figure 4(d) provided the point $n = 12$ is excluded. Figure 6 may then be considered as the superposition of Figures 4(b) (or curve c of Figure 2) and 4(d). However, there exists a maximum between $n = 8$ and 12 in the even series which really does not belong to the types shown in Figures 2, 3 or 4. We note that for $F(t) = At^{\lambda_1} + Bt^{\lambda_2} + Ct^{\lambda_3}$ it is possible to obtain a T_{NI} curve with both a maximum and a minimum when proper parameters are chosen.

Note that when the width of the molecule (in addition to the length) is taken into account the above discussion of the even-odd



(a) (b) (c) (d)

FIGURE 4 Calculated phase diagrams. (a) $F(t) = 1$, (b) $F(t) = t$, (c) $F(t) = t^2$, (d) $F(t) = 12 + t^2$.

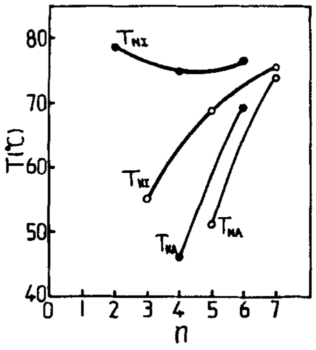


FIGURE 5 Experimental phase diagram of 4-*n*-alkyloxybenzylidene-4′-*n*-butylaniline.

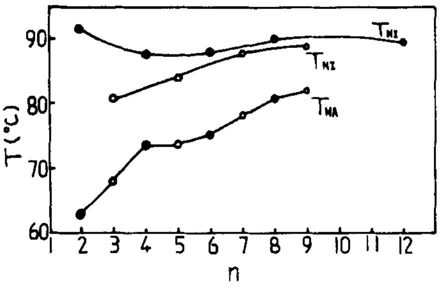


FIGURE 6 Experimental phase diagram of 4-*n*-alkyloxyphenyl-4′-*n*-nonylbenzoate.

effect of transition temperatures becomes more complicated (see Section V).

3. In the odd series of Figure 6, the rate of decrease of T_{NI} as n decreases is higher when n is small. This is exactly the case predicted by curve b of Figure 2.

4. In curve b of Figure 2 a maximum in T_{NI} is predicted with $F(t) = t^{1/2}$. From the above systematic analysis, its existence seems logical and is quite expected. To our knowledge, no experimental phase diagram of this type has been reported yet. An experimental search will be most desired.

5. Under the assumption of Eq. (3.2), the case of $\lambda > 2$ is basically the same as that of $\lambda = 2$. By point (ii) of Section II, we have $\lambda \geqslant 0$. Therefore, corresponding to Eq. (3.2) there are only three types of phases diagrams, viz., the $T_{\mathrm{NI}} \sim t$ curve increasing monotonically, decreasing monotonically and having a maximum. In contrast, the phase diagram shown in Figure 3 represents only one of the several possibilities when Eq. (3.3) is assumed.

6. In our theory, there does not exist any T_{NI} which is really independent of t, in contrary to the result of McMillan.[3] This is due to the fact that in Ref. (3) the approximation of $R(t) = 1$ is implicitly used. In Figure 4(b), $2.33 < t < 2.7$ leading to $1.17 < t/2 < 1.35$ in the $R(t/2)$ function in Eq. (3.1) [or Eq. (2.15)]. Since R is nowhere near unity within this range [see Figure 1 of Ref. (14)] the McMillan's result[3] is thus not completely accurate [the same goes for Ref. (5)]. In fact, experimentally there does not exist any homologous series with T_{NI} straightly independent of t. Our Figure 4(b) agrees better with experiments.

It should be emphasized that, in our opinion, the assumption of $F(t) = t$ used implicitly by McMillan[3] is not "unphysical", as reported by Tan.[6] It just corresponds to homologues that are different from that considered by Lee et al.[5]

IV. EFFECT OF THE MOLECULAR WIDTH

In Section III, the molecules are assumed to be of zero width ($D = 0$). When the steric effects in the free energy expression can be safely ignored ($D/r_0 \ll 1$) the results of Section II remains valid for finite D and the only place that D shows up is in $\bar{J}$ of Eq. (2.15) resulting in a modified Eq. (3.1). In this case, under proper approximations (see Appendix B)

$$\bar{J} = 2JR(t/2)F(t)t^{-1}\exp(-u^2) \qquad (4.1)$$

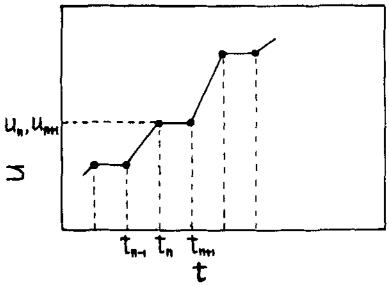


FIGURE 7 The assumed $u(t)$ curve for a typical homologous series.

where $u \equiv D/r_0$. Similar to Section III, we may obtain phase diagrams from the calculated results of Lee et al.[5] by using the following relation [see Ref. (15)]:

$$v_0 = 2\pi^{-1/2} J F(t) R(t/2) \exp(-u^2) \tag{4.2}$$

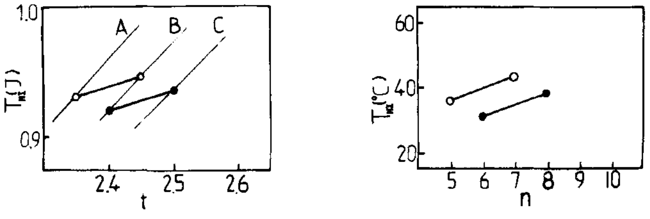
which obviously reduces to Eq. (3.1) when $D = 0$.

In Section III, when $F(t)$ is given, using Eq. (3.1), phase diagrams are obtained from that of Ref. (5), in which there is only one $T_{\mathrm{NI}}(t)$ curve. When Eq. (4.2) is used instead of Eq. (3.1), this single curve is replaced by a family of curves $T_{\mathrm{NI}}(t, u)$ [see curves A, B and C in Figure 8(a) and 9(a)]. The original curve of $T_{\mathrm{NI}}(t)$ in Section III actually corresponds to $T_{\mathrm{NI}}(t, 0)$. When t is fixed, $T_{\mathrm{NI}}(t, u)$ moves towards smaller values of T_{NI} as u increases.

In a homologous series (described by the same δ and r_0, see Section VI), as n increases t also changes, i.e., $t = t(n) = t_n$. At the same time, D also changes [see Figure 6 of Ref. (10)], i.e., $u = u(n) = u_n$. Combining these two equations, one has $u = u(t)$. With Figure 6 of Ref. (10) in mind, we may assume $u = u(t)$ as shown in Figure 7. Here, $t_n = t_{n-1} + \Delta t$, $\Delta t =$ constant, $u_{n+1} = u_n$, $u_{n-1} < u_n$, but $u_n - u_{n-1}$ not necessarily equal to $u_{n+2} - u_{n+1}$. Note that the specific form of $u(t)$ really depends on the homologue under consideration (see Section VI). Figure 7 is just one of the possibilities (though pretty general). In the next Section, some numerical results are presented.

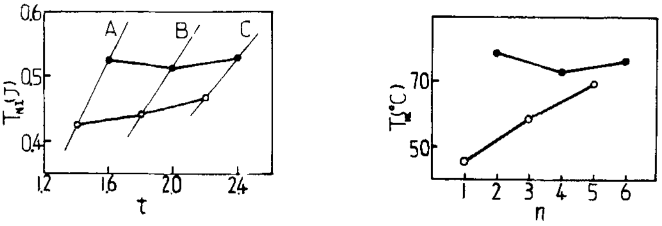
V. THE EVEN-ODD EFFECT

For simplicity, we will assume here that both the even and the odd series of a homologue corresponds to the same $F(t)$.



(a) (b)

FIGURE 8 The even-odd effect of T_{NI} for *n*CB. (a) Theory. The curves A, B and C are $T_{\mathrm{NI}}(t, u)$ with $u = 0$, 0.206, 0.285, respectively. (b) Experiment.[18]



(a) (b)

FIGURE 9 The even-odd effect of T_{NI} for *n*0.4. (a) Theory. The curves A, B and C are $T_{\mathrm{NI}}(t, u)$ with $u = 0$, 0.626, 0.783, respectively. (b) Experiment.[19]

A. Transition temperature

Taking *n*CB (4′-*n*-alkyl-4-cyanobiphenyl) as an example, assume $F(t) = t^2$ and n in Figure 7 as an even number, $u_5 \simeq 0$, $u_6 = u_7 = 0.206$, $u_8 = 0.285$, $t_5 = 2.35$, $t_{n+1} = t_n + 0.05$, $n = 5, 6, 7$. Our calculated T_{NI} are plotted in Figure 8(a) which compared well with the experimental results in Figure 8(b). Note that $u_5 \simeq 0$ is taken for convenience; similar results are obtained if $u_5 \neq 0$.

If in Figure 7, n is assumed to be odd, $u_1 = u_2 \simeq 0$, $u_3 = u_4 = 0.626$, $u_5 = u_6 = 0.783$, $t_1 = 1.4$, $t_{n+1} = t_n + 0.1$, $n = 1, \ldots, 5$, we obtain the T_{NI} curve as shown in Figure 9(a). Here $F(t) = t^2$ as before. The diagram corresponds roughly to the experimental one[19] of *n*0.4(*p*-alkoxybenzylidenebutylaniline).

Similar results for T_{NA} and T_{IA} can be obtained along the same line of reasoning.

B. Order parameter at T_{NI}

In many cases, the order-parameter curve $S(T)$ calculated from Eq. (2.1) agrees only roughly with experiments and it is necessary to include the $P_4(\cos\theta_{ij})$ term in the hamiltonian.[20] Eq. (2.4) then becomes

$$H = \sum_{i,j}{}' \left[W_0(r_{ij}) + W_2(r_{ij})P_2(\cos\theta_{ij}) + W_4(r_{ij})P_4(\cos\theta_{ij}) \right] \quad (5.1)$$

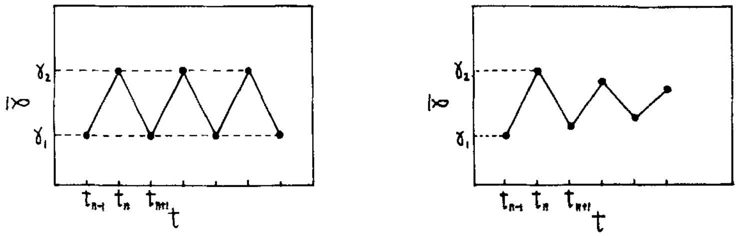
In parallel to the considerations of Section II, W_4 should contain a factor $f(t,u)$ which needs not be equal to $F(t)\exp(-u^2)$. Also, to treat this problem properly one would expand $W_4(r_{ij})$ and $P_4(\cos\theta_{ij})$ with respect to z_{ij} and $P_4(\cos\theta)$, respectively and obtain the effective hamiltonian H_{eff} under the mean-field approximation. The order parameter at T_{NI}, S_c, is then calculated using the H_{eff}. In the following, for simplicity, instead of using Eq. (2.8) we assume that

$$V = v_2\left(P_2\bar{P}_2 + \gamma P_4\bar{P}_4\right) \quad (5.2)$$

which is the Eq. (3.1) of Ref. (12). The meanings of v_2 and γ are given in Ref. (12). When $\gamma = 0$, Eq. (5.2) reduces to Eq. (2.8) in the N and I phases ($\tau = \sigma = 0$); v_2 corresponds to $\bar{J}$ and hence $v_2 = v_2(t,u)$. In general, $\gamma = \gamma(t,u)$. For a homologous series, according to Figure 7, we have $u = u(t)$ which when substituted into $\gamma = \gamma(t,u)$ gives $\gamma = \bar{\gamma}(t)$, say.

For illustrative purpose, $\bar{\gamma}(t)$ is assumed to have the form shown in Figure 10(a) or (b). The dependence of S on T and γ have been given in Figure 3 of Ref. (12). Combining $\gamma = \bar{\gamma}(t)$ and $S = S(\gamma)$ we can obtain S_c.

When Figure 10(a) with $\gamma_1 = -0.544$ and $\gamma_2 = -0.425$ is assumed we obtain a S_c vs. n curve which is in good agreement with experiments of n0.4 [see Figure 4 of Ref. (14)]. For liquid crystal $AAB(p, p'$-di-n-alkoxyazoxybenenes) $\bar{\gamma}(t)$ of Figure 10(b) with $\gamma_2 = 0.07$, $\gamma_4 = 0.01$, $\gamma_6 = -0.05$, $\gamma_1 = -0.33$, $\gamma_3 = -0.27$, $\gamma_5 = -0.21$, $\gamma_7 = -0.15$, . . . , is used. The calculated $S_c(n)$ are represented by open circles in



(a) (b)

FIGURE 10 The two assumed forms of $\bar{\gamma}(t)$.

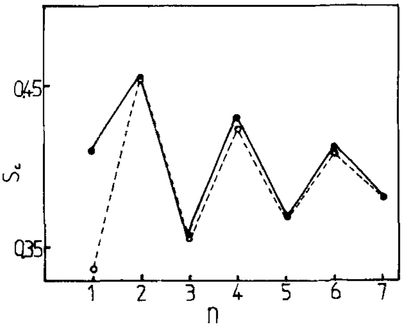


FIGURE 11 The curve $S_c(n)$ of AAB. ○: theory; ●: experiment.

Figure 11. The dots are the experimental points [see, e.g., Ref. (21)]. Better agreement between theory and experiment can be easily achieved by readjusting the assumed values of the γ's.

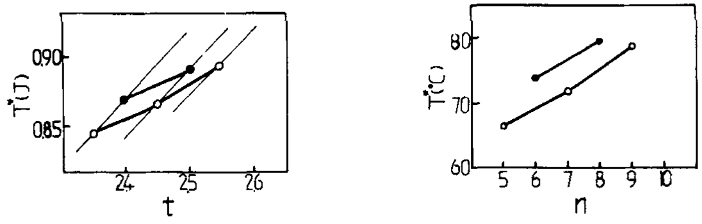
C. Supercooling temperature

By Eq. (4.27) of Ref. (9), the supercooling temperature, defined as the temperature at which the correlation function of the order parameter diverges, is given by ($k_B = 1$)

$$T^* = 0.2\bar{J} \tag{5.3}$$

When Eq. (5.3) is combined with Eq. (4.1) it is easy to see that the even-odd effect of T^* comes from the stepwise variation of u as t increases.

Taking nOCB as an example, by assuming $F(t) = t^2$, $u_5 = u_6 \simeq 0$, $u_7 = u_8 = 0.182$, $u_9 = 0.233$, $t_5 = 2.35$, $t_{n+1} = t_n + 0.05$ ($n = 5, \ldots, 8$), and using Eqs. (4.1) and (5.3) we obtain $T^*(t)$ as shown in Figure 12(a), in good agreement with the experimental results[18] of Figure 12(b). To our knowledge, this is the first time that any even-odd



(a)

(b)

FIGURE 12 Supercooling temperature T^* of nOCB. (a) Theory, (b) experiments.[18]

effects of the supercooling temperature has been calculated theoretically.

VI. DISCUSSION

Obviously, the functional form of $F(t)$ assumed in Section II or III is not unique. However, through a measurement of T^* for each member of the homologue and the use of Eqs. (4.1) and (5.3), $\bar{J}(t,u)$ or $JF(t)$ (assuming $u = 0$) may be determined.

In Section III, we pointed out that the odd and the even series may correspond to different $F(t)$; but in Section V, the two series is assumed to have the same $F(t)$ but different $D(t)$. These assumptions are taken for the sake of simplicity. The specific forms of $D(t)$ for a particular (even or odd) series have to come from a careful analysis of the conformational changes of the molecules. The analysis sketched in Section V is mean to be a guide to what can be expected from our formalism. A more systematic and detailed investigation is desired. Note that the even-odd effects of other physical quantities (e.g. entropy change) may be calculated similarly.

In the above calculations, since we have put all the d-dependence in W_0 into the factor $F_0(d)$ it then becomes clear that the part $V_0(r_{ij})$ should be the same for all members in the homologous series. In other words, δ is the same in a single series.

In this paper, the fluctuation of orientation of the smectic layers (the z-axis) have not been taken into account which, if included, will modify the above results quantitatively.

The approach to generalize the McMillan theory presented here obviously can be carried over to the case involving other smectic phases. Finally, we remark that the mechanism (based on the alternative variation of the width and length of the molecules in a homologue) proposed here for the even-odd effect is not meant to exclude the one due to Marcelja.[10] The extent to which the two mechanisms may compete, complement or reinforce each other in a given homologue is a problem still open for investigation.

Acknowledgement

One of us (L.L.) thanks Professor Y. W. Chan for his hospitality during the author's stay at the Chinese University of Hong Kong.

APPENDIX A. DERIVATION OF THE MEAN-FIELD HAMILTONIAN

By Eqs. (2.4)–(2.6),

$$H = -\sum_{i,j}{}' (4\pi^{1/2})^{-1} J F(t) \exp(-\rho_{ij}^2/r_0^2) \times \left[\exp(-z_{ij}^2/r_0^2)(\delta + P_2(\cos\theta_{ij}))\right] \qquad \text{(A1)}$$

where $t \equiv d/r_0$. For any two operators A and B, the mean-field approximation (MFA) gives

$$AB \simeq A\langle B\rangle - \langle A\rangle B - \langle A\rangle\langle B\rangle \qquad \text{(A2)}$$

In Eq. (A1), taking the ρ_{ij} part as A and the square bracket part as B, we have

$$H = -\sum_{i,j}{}' (4\pi^{1/2})^{-1} J F(t) \langle \exp(-\rho_{i,j}^2/r_0^2)\rangle \times \exp(-z_{ij}^2/r_0^2)\left[\delta + P_2(\cos\theta_{ij})\right] + H'(\rho_{ij}) \qquad \text{(A3)}$$

where $H'(\rho_{ij})$ is independent of z_{ij} and θ_{ij}. Note that $\exp(-z_{ij}^2/r_0^2)$ is an even function of z_{ij}. When Fourier expanded and the two lowest-order terms are kept,

$$\exp(-z_{ij}^2/r_0^2) = a_0 + a_1\cos(2\pi z_{ij}/d) + \cdots \qquad \text{(A4)}$$

where

$$a_0 \equiv \pi^{1/2} t^{-1} R(t/2) \qquad \text{(A5)}$$

$$a_1 \equiv a_0 \bar{\alpha}(t) \qquad \text{(A6)}$$

R and $\bar{\alpha}$ are defined respectively by Eqs. (2.14) and (2.12). Putting Eq. (A4) into Eq. (A3), we have

$$H = -(4\pi^{1/2})^{-1} J F(t) \langle \exp(-\rho_{ij}^2/r_0^2)\rangle a_0(\bar{\alpha}\delta A + B + \bar{\alpha} C) + H''(\rho_{ij}) \qquad \text{(A7)}$$

where

$$A \equiv \sum_{i,j}{}' \cos(2\pi z_{ij}/d) \tag{A8}$$

$$B \equiv \sum_{i,j}{}' P_2(\cos\theta_{ij}) \tag{A9}$$

$$C \equiv \sum_{i,j}{}' \cos(2\pi z_{ij}/d) P_2(\cos\theta_{ij}) \tag{A10}$$

Using

$$\cos(2\pi z_{ij}/d) = \cos(2\pi z_i/d)\cos(2\pi z_j/d) - \sin(2\pi z_i/d)\sin(2\pi z_j/d) \tag{A11}$$

and by symmetry,

$$\langle \sin(2\pi z_i/d) \rangle = 0 \tag{A12}$$

Eq. (A8) becomes in MFA:

$$A = 2(N-1)\tau \sum_i \cos(2\pi z_i/d) + \text{const.} \tag{A13}$$

where N is the total number of molecules and τ is defined by Eq. (2.9). Since [see, e.g., Ref. (22)]

$$P_2(\cos\theta_{ij}) = \sum_{\mu=1}^{5} Q_{i\mu} Q_{j\mu} \tag{A14}$$

$$\begin{aligned}
Q_{i1} &\equiv \tfrac{1}{2}(3a_{iz}^2 - 1) = P_2(\cos\theta_i) \\
Q_{i2} &\equiv (3^{1/2}/2)(a_{ix}^2 - a_{iy}^2) \\
Q_{i3} &\equiv 3^{1/2} a_{ix} a_{iy} \\
Q_{i4} &\equiv 3^{1/2} a_{ix} a_{iz} \\
Q_{i5} &\equiv 3^{1/2} a_{iy} a_{iz}
\end{aligned} \tag{A15}$$

where the unit vector $\mathbf{a}_i$ is the orientation of the ith molecule. Because of cylindrical symmetry, $\langle Q_{i\mu} \rangle = 0$, $\mu = 2, \ldots, 5$.[22] Therefore, Eq. (A9) in the MFA becomes

$$B = 2(N-1)\eta \sum_i Q_{i1} + \text{const.} \tag{A16}$$

where η is defined by Eq. (2.10). Putting Eq. (A14) into Eq. (A10) and taking $\cos(2\pi z_i/d)Q_i$ as one of the operators in Eq. (A2), Eq. (A10) in the MFA becomes

$$C = 2(N-1)\sigma \sum_i \cos(2\pi z_i/d) Q_{i1} + \text{const.} \tag{A17}$$

where the symmetry results $\langle \sin(2\pi z_i/d) Q_{i\mu} \rangle = 0$, $\mu = 1, \ldots, 5$ and $\langle \cos(2\pi z_i/d) Q_{i\mu} \rangle = 0$, $\mu = 2, \ldots, 5$ are used, and σ is defined by Eq. (2.11). Substituting Eqs. (A13), (A16) and (A17) into Eq. (A7) we obtain the mean-field hamiltonian

$$H_{\mathrm{MF}} = -\bar{J} \sum_i \left[\bar{\alpha}\delta\tau \cos(2\pi z_i/d) + \eta S_i \right.$$
$$\left. + \bar{\alpha}\sigma \cos(2\pi z_i/d) S_i \right] + H'''(\rho_{ij}) \tag{A18}$$

where $S_i \equiv Q_{i1}$ and

$$\bar{J} \equiv (2t)^{-1} J F(t) R(t/2) \langle \exp(-\rho_{ij}^2/r_0^2) \rangle (N-1) \tag{A19}$$

or, equivalently, Eq. (2.15). Since $H'''(\rho_{ij})$ is independent of z_i and θ_i and is therefore ineffective in the thermal average of Eq. (2.16) there is no need to include it in Eqs. (2.7) and (2.8).

Note that as $z_{ij} \to \infty$ the thermal average of the left-hand side of Eq. (A4) is finite while the right-hand side in which only two terms (of periodic functions) are kept is not. To be consistent, the N in Eqs. (A13), (A16), (A17) and (A19) should be understood as

$$N' \equiv N^{2/3} \tag{A20}$$

and correspondingly, $\sum_j$ in Eq (2.15) is a summation of the molecules in a layer only.

APPENDIX B. DERIVATION OF EQ. (4.1)

To calculate $\langle \exp(-\rho_{ij}^2/r_0^2)\rangle$ in Eq. (2.15), we adopt Eqs. (2.22) and (2.26) of Ref. (23),

$$\langle f(i,j)\rangle = \frac{2}{N(N-1)} \sum_{i>j} \langle f(i,j)\rangle \tag{B1}$$

or

$$\langle f(i,j)\rangle = \frac{1}{V}\int d\mathbf{r}\, f(\mathbf{r})h(\mathbf{r}) \tag{B2}$$

where $h(\mathbf{r})$ is pair correlation function [see Eq. (2.12) of Ref. (23)], V the sample volume and

$$\frac{1}{V}\int d\mathbf{r}\, h(\mathbf{r}) = 1 \tag{B3}$$

The determination of the thermal average for a layer of molecules corresponds to a two-dimensional version of the above problem, i.e.,

$$\langle \exp(-\rho_{ij}^2/r_0^2)\rangle = \frac{1}{L_xL_y}\int_0^{L_x} dx_{ij}\int_0^{L_y} dy_{ij}\, h(\rho_{ij})\exp(-\rho_{ij}^2/r_0^2) \tag{B4}$$

where L_x and L_y are the dimensions of the sample in the x and y directions, respectively. The most simple approximation is

$$h(\rho_{ij}) = \begin{cases} 0, & \rho_{ij} < D \\ 1, & \rho_{ij} \geqslant D \end{cases} \tag{B5}$$

resulting in

$$\langle \exp(-\rho_{ij}^2/r_0^2)\rangle = (\pi r_0^2/L_xL_y)\exp(-u^2) \tag{B6}$$

where $u \equiv D/r_0$. Note that in Section III, $D = 0$ or $h(\rho_{ij}) = 1$ is assumed. By definitions of D and r_0, $u < 1$.

From geometric considerations, roughly speaking,

$$N'\pi(r_0/2)^2 \simeq L_xL_y \tag{B7}$$

Combining Eqs. (2.15), (A20), (B6) and (B7) we obtain Eq. (4.1).

References

1. W. Maier and A. Saupe, *Z. Naturf.* **A13**, 564 (1958); **A14**, 882 (1959); **A15**, 287 (1960).
2. K. Kobayachi, *Phy. Lett.* **31A**, 125 (1970); *J. Phys. Soc. Jpn.* **29**, 101 (1970).
3. W. L. McMillan, *Phys. Rev.* **A4**, 1238 (1971).
4. W. L. McMillan, *Phys. Rev.* **A6**, 936 (1972).
5. F. T. Lee, H. T. Tan, Y. M. Shih and C.-W. Woo, *Phys. Rev. Lett.* **31**, 1117 (1973).
6. H. Y. Tan, *Phys. Rev.* **A16**, 1715 (1977).
7. D. Demus et al., *Flussige Kristalle in Tabellen, 1 and 2 Aufl.* (Deutscher Verlag Grundstoffind, Leipzig, 1974 and 1976).
8. Lin Lei, *J. Physique* **43**, 251 (1982).
9. Shu Changqing and Lin Lei, the following paper [(II) in the series].
10. S. Marcelja, *J. Chem. Phys.* **60**, 3599 (1974).
11. L. Feijoo, V. T. Rajan and C.-W. Woo, *Phys. Rev.* **A19**, 1263 (1979); J. L. Shen, L. Lin, L. Yu and C.-W. Woo, *Mol. Cryst. Liq. Cryst.* **70**, 301 (1981); M. Nakagawa and T. Akahane, *Mol. Cryst. Liq. Cryst.* **90**, 53 (1982); G. Vertogen and B. W. Van der Meer, *Physica* **A99**, 237 (1979); W. Wagner, *Mol. Cryst. Liq. Cryst.* **98**, 247 (1983).
12. G. R. Luckhurst and G. W. Gray (eds.), *The Molecular Physics of Liquid Crystals* (Academic, London, 1979).
13. S. Chandrasekhar, K. L. Savithramma and N. V. Madhusudana, American Chemical Society Meeting, Las Vegas, March 1982; G. E. Feldkamp, M. A. Handschy and N. A. Clark, *Phys. Lett.* **85A**, 359 (1981); Lin Lei, *Phil. Trans. R. Soc. Lond.* **A309**, 103 (1983).
14. Shu Changqing and Lin Lei, *Acta Physica Sinica* **31**, 915 (1982).
15. Shu Changqing, M. Sc. Thesis, Institute of Physics, Chinese Academy of Sciences, Beijing, China (1981).
16. Shu Changqing, Lin Lei and Wang Liangyu, *Commun. Theor. Phys. (Beijing)* **1**, 107 (1982).
17. G. W. Gray and A. Mosely, *J. Chem. Soc. Perkin II*, 97 (1976).
18. K. Muta, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.* **18**, 2073 (1979).
19. R. Chang, F. Jones and J. Ratto, *Mol. Cryst. Liq. Cryst.* **33**, 13 (1976).
20. R. Humphries, P. James and G. Luckhurst, *J. Chem. Soc.*, Faraday Trans. II **68**, 1031 (1972).
21. S. Chandrasekhar, *Liquid Crystals* (Cambridge U. P., Cambridge, 1977).
22. Zhang Zhaoqing, Feng Kean and Lin Lei, *Acta Physica Sinica* **29**, 807 (1980) [Chinese Phys. (U.S.A.) **1**, 110 (1981)].
23. I. Z. Fisher, *Statistical Theory of Liquids* (University of Chicago Press, Chicago, 1964).