RESEARCH ARTICLE
doi: 10.2306/scienceasia1513-1874.2007.33.321

ScienceAsia 33 (2007): **321-327**

A New Approach to the Mean Field Theory for Nematic Liquid Crystals

Saman Mongkolsakulvong[a] and I Ming Tang[b*]

[a] Department of Mathematics, Faculty of Science, Mahidol University, Bangkok 10400, Thailand.
[b] Department of Physics, Faculty of Science, Mahidol University, Bangkok, 10400 Thailand.

* Corresponding author, E-mail: scimt@mahidol.ac.th

Received 28 Apr 2006
Accepted 26 Mar 2007

ABSTRACT: We have developed a new method to calculate the properties of the nematic liquid crystals (NLC). The new method involves the separation of the NLC molecules into two groups; those on a chain embedded in the liquid crystal and the rest. The interactions between the nearest neighbor molecules on the chain are treated exactly while the interaction between a molecule on the string and remaining molecules is treated via a mean field approach. We have calculated the partition function to the order 0(β^3) for the molecules on the chain using the cumulant expansion. Using the standard conditions for a nematic-isotropic (NI) transition to occur, we obtain the values of the interaction energies needed to fit the published data on the NI transitions in the homologous series of NLC's p,p′-di-n-alkoxyazobenzene. We find that the values of the strength of the microscopic interaction between the molecules (J) exhibit an even-odd dependence on the number of (CH_2) groups in the tails of the molecules in this series. The values of A (the strength of the mean field interaction) do not exhibit an even-odd effect.

KEYWORDS: Nematic liquid crystal/mean-field theory, order parameter, cumulant expansion, p,p′-di-n-alkoxyazobenzene.

INTRODUCTION

In the present age of powerful but inexpensive computers, there is a tendency to think that serious physics requires the use of intensive computational techniques such as first principle calculations[1] or Monte Carlo simulations[2]. Much however can be still gained by using simple mean field approaches. For instance, Zhang and his coworkers[3] have been able gain insights into the interactions existing in the rare earth-transition metal compounds through the use of the two sub-lattice molecular field model. One of the present authors (IMT) was able to modify the Weiss molecular field model to take into account the disorder that occurs in the substituted ferrites[4]. This modification was later used to account for the local field fluctuations seen in the substituted aluminum iron garnets[5]. In this paper, we are interested in the mean field model used to describe a different phenomena, the nematic-isotropic (NI) transition in the homologous series of NLC's, the p,p'-di-n-alkoxyazobenzenes.

In the NLC's, the molecules in the liquid develop spontaneous long range orientation ordering where the molecules tend to line up parallel to each other. Maier and Saupe[6] (MS) introduced a mean field theory to account for what was seen at the transition from the isotropic (disordered liquid) phase to a nematic liquid crystal (ordered) phase. MS assumed that the stability of the nematic phase arose from the dipole-dipole part of the anisotropic dispersion forces. Their theory predicts that the ratio $A/k_B T_{NI} V^2$ is equal to 4.541 and that the value of the order parameter s_c at the transition temperature T_{NI} was 0.4293, regardless of which liquid crystal (LC) was being considered. This is however inconsistent with the measured values of the order parameters (OP's) of the members of the homologous series, p, p'-di-n-alkoxyazobenzene. In that series, the values of the order parameters[7] changes from 0.43 to 0.50, then to 0.44, then to 0.55, then to 0. 48 and finally to 0.56 as the number of CH_2 groups in the end chains of this homologous series increases (See the structure shown in Fig. 1). A plot of

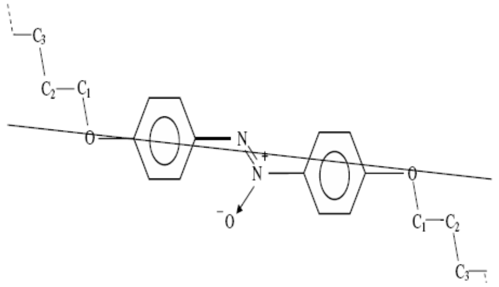

Fig 1. Molecular Structure of the p, p'-di-n-alkoxyazobenzene Nematic Liquid Crystal. Not shown in the structure is the terminating methoxy group CH_3, at the end of the CH_2 chain. As is clearly shown, the CH_2 groups form a zig-zag pattern as more CH_2 groups are inserted onto the chain.

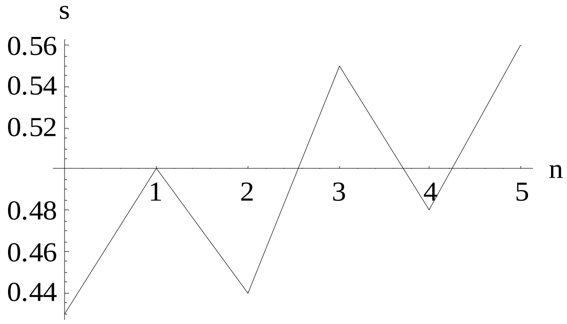

Fig 2. **Values of the Order Parameter 's' for the Different Members of the p, p'-di-n-alkoxyazobenzene Series.** The different members of the series are defined by the number of CH_2 groups in the chains. When n = 0, the NLC is PAA; n = 1, the NLC is PAP; n = 2, PDPAB; n = 3, PBAB; n = 4, PPAB and n = 5, PHAB.

the values of the OP's vs. the number of CH_2 groups in the end chain (Fig. 2) exhibits an even old effect, the values the OP's go up and then down as the number of (CH_2) groups increases.

This even-odd change in the values of the OP's of this series is inconsistent with the prediction of the MS mean field theory. In addition, a second shortcoming of the present formulation of the MS theory is that it neglects short rage correlations and nearest neighbor interactions. This means that the MS theory is correct only for high temperatures, i.e., for $T \to \infty$ or $\beta \to 0$. This is a critical limitation since it means that based on the MS theory, one can not estimate the strength of the nearest neighbor interaction from experimental data.

The aim of our study is to resolve the inconsistency between the theory and the experiments with regards to the critical order parameter s_c and to take into consideration the nearest neighbor interaction between the liquid crystal molecules. Particular goals of our study are to extract the nearest neighbor interaction parameters from the experimental data and to discuss the even-odd effect in the framework of a generalized mean field.

In Section IIa, we introduce the basic assumptions we have made about the nature of the interaction in the NLC's. The partition function for a collection of molecules located on a fictitious string embedded in the liquid crystal is calculated in Section IIb. By dividing the partition function by the mean field partition functions, we find that the evaluation is equivalent to performing a cumulant expansion. The treatment is exact to the order β^2 in the present study (though a treatment to any order of accuracy is possible). An expression for the Helmholtz free energy for the molecules located on the string, F_{string} is obtained in Section IIc. In Section III, we numerically plot the Helmholtz free energy as a function of the order parameter. The values of two parameters in the expression for the free energy are varied until the curve of the free energy is such that at the values of the observed OP's for each member of the homologous series, $F_{string}(s_c,T_{NI}) = 0$ and $\partial F_{string}/\partial s\big|_{s_c,T_{NI}} = 0$. In Section IV, we discuss the results.

PARTITION FUNCTION

Model.

The stability of the nematic phase is believed to arise from the dipole-dipole part of the anisotropic dispersion forces. The orientation energy originates from the factor cos ³ where ³ is the angle between the **directors** of the two molecules that are interacting with each other. In terms of the orientation angles of the individual molecules,

$$\cos\gamma = \sum_{n=0}^{\text{¥}} \sum_{m=-n}^{n} Y_{n,m}(\theta_i,\varphi_i)Y^{*}_{n,m}(\theta_j,\varphi_j)$$

where $Y_{n,m}((\theta_j,\varphi_j)$ are the spherical harmonics and with the subscripts i (j) on the angles θ and φ indicate that the angles are the orientation of the i-th molecule. Invoking symmetry arguments, we find that the leading term in the interaction energy between molecules 'i' and 'j' would be

$$u_{ij} = -\frac{J}{V^2}P_2(\cos\theta_i)P_2(\cos\theta_j)$$

where J is the strength of the inter molecular interaction and here is taken to be dependent on the nature of the NLC molecule, V is the volume occupied by the molecules and $P_2(\cos\theta)$ is the second Legendre polynomial given by

$$\frac{1}{2}(3\cos^2\theta - 1)$$

The mean field approximation is obtained when one of the Legendre polynomials is replaced by its thermal average, i.e.

$$u_{mean,i} = -\frac{A}{V^2}sP_2(\cos\theta_i)$$

where the order parameter 's' is the ensemble average of the second Legendre polynomial and A is the strength of the mean field interaction. This replacement of a two body interaction by a one body mean field interaction is standard in physics. The most common example of this is the replacement of the two body gravitation force by the mean field force F = mg where g is equal to 9.8 m/sec^2.

To go beyond the mean field approximation, we consider a system containing N molecules on a string which is embedded in a system of the remaining molecules. The interaction between a molecule 'i' on the string with its nearest (two) neighbors on the string is treated exactly while the interaction of the molecule 'i' with the nearest neighbor molecules in the rest of the system is treated by the mean field approximation. The self consistency condition has been given by Ypma and Vertogen[9]. The OP of a molecule on the string is equal to the OP of the molecules in the rest of the system.

$$s_{string} = <P_2(\cos\theta_{string})> = s$$

The reason for this condition is that the designation of a molecule to be on the string or to be in the rest of the system is arbitrary.

Having said this, the interaction energy for the i-th molecule becomes

$$u_i = -\frac{J}{V^2}\{P_2(x_{i-1})P_2(x_i) + P_2(x_i)P_2(x_{i+1})\} - \frac{As}{V^2}P_2(x_i) \quad (1)$$

where $x_i = \cos\theta_i$. The partition function for the molecules on the string is

$$Z_{string} =$$

$$\int_{-1}^{1}\int_{-1}^{1}..\exp[\beta\frac{J}{V^2}\sum_{i=1}^{N}\{P_2(x_{i-1})+P_2(x_{i+1})\}P_2(x_i)]\exp[\beta\frac{As}{V^2}\sum_{i=1}^{N}P_2(x_i)\}]\, dx_1 dx_2 ..dx_N \quad (2)$$

We now introduce a fictitious system in which the molecules on the string experience only a mean field interaction, i.e., $u_{\text{fictitous system}}(i) = -\frac{A}{V^2}sP_2(\cos\theta_i)$. The partition function for this systemis

$$Z_0 = \int_{-1}^{1}\int_{-1}^{1}...e^{\beta\frac{A}{V^2}s\sum_{i=1}^{N}P_2(x_i)}dx_1dx_2...dx_N \quad (3)$$

Dividing eqn. (2) by eqn. (3), the ratio Z_{string}/Z_0 becomes

$$\frac{Z_{string}}{Z_0} =$$

$$\frac{\int_{-1}^{1}\int_{-1}^{1}..\exp[\beta\frac{J}{V^2}\sum_{i=1}^{N}\{P_2(x_{i-1})+P_2(x_{i+1})\}P_2(x_i)]\{\prod_{i}^{N}(\exp[\beta\frac{As}{V^2}P_2(x_i))\}dx_1dx_2...dx_N}{\int_{-1}^{1}\int_{-1}^{1}\{\prod_{i}^{N}(\exp[\beta\frac{As}{V^2}P_2(x_i))\}dx_1dx_2...dx_N}$$

The right-hand side of eqn. (4) looks to be an expression for the average of

$$\exp[\beta\frac{J}{V^2}\{P_2(x_{i-1})+P_2(x_{i+1})\}P_2(x_i)] \quad (4')$$

taken over the distribution function, $f(x_i) = \exp[\beta\frac{A}{V^2}sP_2(x_i)]$.

The evaluation of eqn. (4) is carried out by first integrating every other variable. Once this is done, these variables no longer appear. We then integrate over every other variable of the remaining variables. This decimation of the variables is carried out until there are no variables remaining. If we are only interested in an accuracy of order β^n, the number of decimations required will be small.

Evaluation of the Partition Function

When we decimate eqn. (4) for the first time, we encounter the following type of terms in the multiple integral

$$\frac{\int_{-1}^{1}\exp[C_{i-1,i+1}P_2(x_i)]f(x_i)dx_i}{\int_{-1}^{1}f(x_i)dx_i} \qquad i = 1, 3, 5, \ldots.. \quad (5)$$

where $C_{i-1,i+1} = 2\beta\frac{J}{V^2}(P_2(x_{i-1})+P_2(x_{i+1}))$ As we have mentioned, we are averaging the exponential function, $\exp\{C_{i-1,i+1}P_2(x)\}$, over the distribution, $\exp\{\frac{A}{V^2}sP_2(x)\}$.

We note that the average of an exponential can be expressed as an exponential of a cumulant expansion, i.e.,

$$<\exp X> = \exp\{K_1(X) + K_2(X) + \ldots\} \quad (6)$$

where K_1 and K_2 are the first and second cumulant functions, respectively. The two cumulants are defined as $K_1(X) = <X>_i$ and $K_2(X) = \frac{1}{2}\{<X^2>_i - <X>_i^2\}$ where the subscript means that the averaging is over the distribution function $f(x_i)$. Letting $X = C_{i-1,i+1}P_2(x_i)$, we get

$$K_1(X) = <X_i>_{x_i} = <C_{i-1,i+1}P_2(x_i)>_{x_i} = C_{i-1,i+1}<P_2(x_i)>_{x_i} = C_{i-1,i+1}s \quad (7)$$

where $s = <P_2(x_i)>_i$. The ensemble average of X^2 is also easily done to get

$$<X^2>_i = C^2_{i-1,i+1}<P_2^2(x_i)>_i = C^2_{i-1,i+1}\alpha \quad (8)$$

where $\alpha = <P_2^2(x_i)>_i$.

Putting everything together, we get

$$<\exp[C_{i-1,i+1}P_2(x_i)]>_i =$$

$$\exp\{G(P_2(x_{i-1})+P_2(x_{i+1}))+F[(P_2(x_{i-1})+P_2(x_{i+1}))^2]\} \quad (9)$$

where $G = 2\beta\frac{J}{V^2}s = Ds$ and $F = -2\beta^2\frac{J^2}{V^4}(\alpha - s^2)$. It should be noted that the squaring of $(P_2(x_{i-1})+P_2(x_{i+1}))$ leads to a product involving the variables x_{i-1} and x_{i+1}. The subsequent integrations over dx_{i-1} and dx_{i+1} cannot be done independently of each other since the resulting integrant contains terms which couples x_{i-1} and dx_{i+1} together. For instance, the integration over dx_3 will lead to a product of the functions $P_2(x_2)$ and $P_2(x_4)$ while the integration over dx_5 will lead a product of the functions $P_2(x_4)$ and $P_2(x_6)$. When the integrant does not contain any cross terms, it can be factorized in products of identical functions of each of the integration variables. We then have

$$\int_{-1}^{1}\ldots\int_{-1}^{1}(\prod_{i}^{N}F(x_i))(\prod_{i}^{N}f(x_i))dx_1\ldots dx_N=\{\int_{-1}^{1}F(x_i)f(x_i)dx_i\}^N$$

To see this more clearly, we explicitly carry out the integrations over dx_3 and dx_5 and get

$$\exp\{G(P_2(x_2)+P_2(x_4))+F(P_2^2(x_2)+2P_2(x_2)P_2(x_4)+P_2^2(x_4)) \tag{10a}$$

and

$$\exp\{G(P_2(x_4)+P_2(x_6))+F(P_2^2(x_4)+2P_2(x_4)P_2(x_6)+P_2^2(x_6)) \tag{10b}$$

Multiplying these two terms together and then collect the terms which depend on the variable x_4, we get

$$\exp\{2GP_2(x_4)+2FP_2^2(x_4)+2FP_2(x_4)[(P_2(x_2)+P_2(x_6)]\} \tag{11}$$

where F and G have previously been defined (the sentence following eqn. (9)). The integration over dx_4, i.e.

$$\frac{\int_{-1}^{1}dx_4(\exp\{2GP_2(x_4)+2FP_2^2(x_4)+2FP_2(x_4)[(P_2(x_2)+P_2(x_6)]\})f(x_4)}{\int_{-1}^{1}dx_4 f(x_4)} \tag{12}$$

can again be done by carrying out a cumulant expansion where the argument of the cumulant function, X, is now $2GP_2(x_4)+2FP_2^2(x_4)+2FP_2(x_4)[(P_2(x_2)+P_2(x_6)]$. The last bracket in the integrand of eqn. (12) couples the variable x_4 to x_2 and x_6. Performing the integration in eqn. (12), we get

$$\begin{aligned}&\exp\{K_1(2GP_2(x_4)+2FP_2^2(x_4)+2FP_2(x_4)[(P_2(x_2)+P_2(x_6)]) + \\ &K_2(2GP_2(x_4)+2FP_2^2(x_4)+2FP_2(x_4)[(P_2(x_2)+P_2(x_6)])+.\quad\}\end{aligned} \tag{13}$$

where $K_1(X)$ and $K_2(X)$ are the cumulate functions. It should now be remember that G is of order β and F is of order β^2. The coupling of the variables x_2 and x_6 is due to the appearance of the cross product term $P_2(x_2)P_2(x_6)$ in the 2nd cumulant function. This term is of order β^4. Since we are only interested in determining the free energy to order β^2, these terms would be dropped. This does not mean that all the terms in the 2nd cumulant should be dropped. The leading term in the averaging the square of $GP_2(x_4)+FP_2^2(x_4)+FP_2(x_4)[(P_2(x_2)+P_2(x_6)]$ is of order β^2 and should therefore be kept. At this point, the decoupling of the remaining variables occurs and the rest of the integrations can be carried in a straightforward manner.

Keeping the above in mind, we find that

$$\frac{Z_{string}}{Z_0}=\exp\{\frac{N}{4}[4Gs+4Fs^2+4F\alpha-4G^2(\alpha-s^2)]\}\ , \tag{14a}$$

where N is the number of molecules on the string. Eqn. (14a) can be rewritten as

$$Z_{string}=z_{0i}^N\ \exp\{N[Gs+Fs^2+F\alpha-G^2(\alpha-s^2)]\} \tag{14b}$$

where $z_{0i}=\int_0^1\exp[\beta\frac{A}{V^2}sP_2(x_i)]dx_i$.

In terms of the partition function, the Helmholtz Free energy for the molecules on the string is given by

$$F_{string}=\frac{1}{2}\frac{\partial}{\partial\beta}\ln Z_{string}-k_BT\ln Z_{string} \tag{15}$$

Helmholtz Free Energy

We start with

$$\ln Z_{string}=N\ln z_{0i}+N[Gs+Fs^2+F\alpha-G^2(\alpha-s^2)]\} \tag{16}$$

Taking the derivative with respect to β, we get

$$\frac{\partial}{\partial\beta}\ln Z_{string}=$$

$$N\frac{\partial}{\partial\beta}\ln z_{0i}+N[s\frac{\partial}{\partial\beta}G+s^2\frac{\partial}{\partial\beta}F+\alpha\frac{\partial}{\partial\beta}F-(\alpha-s^2)\frac{\partial}{\partial\beta}G^2) \tag{17}$$

Performing the partial derivatives with respect to β, the right-hand side of eqn. (17) becomes

$$\frac{1}{2}N\frac{\partial}{\partial\beta}\ln z_{0i}+N[\frac{J}{V^2}s^2-2\beta\frac{J^2}{V^4}(\alpha-s^2)(3s^2+\alpha)] \tag{18}$$

We also have

$$k_BT\ln Z_{string}=Nk_BT\ln z_{0i}+2N[\frac{J}{V^2}s^2-\beta\frac{J^2}{V^4}(\alpha-s^2)(3s^2+\alpha)] \tag{19}$$

The Helmholtz free energy of the fictitious system is

$$F_0=\frac{1}{2}N\frac{\partial}{\partial\beta}\ln z_{0i}-Nk_BT\ln z_{0i}$$

The first term is given by

$$\frac{1}{2}N\frac{\partial}{\partial\beta}\ln z_{0i}=\frac{1}{2}N\frac{A}{V^2}s\frac{\int_0^1P_2(x_i)\exp[\frac{\beta As}{V^2}P_2(x_i)]dx_i}{\int_0^1\exp[\frac{\beta As}{V^2}P_2(x_i)]dx_i}$$

$$=\frac{1}{2}N\frac{A}{V^2}s<P_2(x_i)>_{x_i}$$

$$=\frac{1}{2}N\frac{A}{V^2}s^2$$

while the second term is given by

$$Nk_BT\ln z_{0i}=Nk_BT\ln[\int_0^1\exp[\frac{\beta As}{V^2}P_2(x_i)dx_i]$$

$$=Nk_BT\ln[\int_0^1\exp[BsP_2(x_i)dx_i]$$

$$=Nk_BT\ln[\int_0^1\exp[\frac{1}{2}Bs(3x_i^2-1)]dx_i]$$

Putting the two terms together and evaluating the integrals, we get[10]

$$F_0 = Nk_BT\{\frac{1}{2}Bs(s+1) - \ln{}_1F_1[\frac{1}{2},\frac{3}{2};\frac{3}{2}Bs]\} \tag{20}$$

where ${}_1F_1[a,b;x]$ is the Congruent Hypergeometric function. This function has an expansion given by

$${}_1F_1[a,b;x] = 1 + \frac{a}{b}x + \frac{1}{2!}\frac{a(a+1)}{b(b+1)}x^2 + \ldots$$

From eqn. (15), we get

$$F_{string} = Nk_BT\{\frac{1}{2}\frac{A}{k_BTV^2}s(s+1) - \frac{J}{k_BTV^2}s^2 - \ln{}_1F_1[\frac{1}{2},\frac{3}{2};\frac{3}{2}\frac{A}{k_BTV^2}s]\} \tag{21}$$

By setting

$$B = \frac{A}{k_BTV^2} \text{ and } \frac{D}{2} = \frac{J}{k_BTV^2}\ , \tag{22}$$

eqn. (21) can be rewritten as

$$F_{string} = Nk_BT\{\frac{1}{2}Bs(s+1) - \frac{1}{2}Ds^2 - \ln{}_1F_1[\frac{1}{2},\frac{3}{2};\frac{3}{2}Bs]\} \tag{23}$$

The details of the derivation of the Helmhotz free energy is given in the Appendex.

RESULTS

The values of the nematic-isotropc transition temperatures and of the order parameters at T_{NI} of the six members of this series can be found in ref. 7. The T_{NI}'s are 408.3 K, 441 K, 396 K, 409 K and 396 K in order of the increasing number of CH_2 groups in the homologous series, p,p′-di-n-alkoxyazoxybenzene. The values of the order parameters are 0.43, 0.50, 0.44, 0.55, 0.48 and 0.56. A plot of the s_c's versus the number of CH_2 groups in the end chains of these NLC's yields Fig. 2, which illustrates the odd-even effect first pointed out by Marcelja[7]. If the 'n' in the structure is 0, we have the liquid crystal, p-azoxyanisole (PAA): for n = 1, we have p-azoxyphenetole (PAP); for n = 2, we have 4, 4′-di-n-propyloxy-azoxybenzene (PDPAB); for n = 3, we have 4, 4′-di-n butyloxyazoxybenzene (PBAB); for n = 4, we have 4, 4′- di-n-pentyloxy-azoxybenzene (PPAB) and finally, for n = 5, we have 4, 4′-di-n-hexyloxyazoxybenzene (PHAB).

Using the values of s_c's given in Fig. 2 and noting that at the critical point ($T = T_{NI}$, $s = s_c$), $F_{string}(s_c,T_{NI}) = 0$ and $\partial F_{string}/\partial s\big|_{s_c,T_{NI}} = 0$, where F_{string} is given by eqn (23), we have solved for B and D for each member of the homologous series. The results are given in Table 1. Using the values of the B's and D's given in Table 1, we have plotted F_{string}/Nk_BT_{NI} as a function of 's' in Fig. 3. We see that the curve for the Helmholtz free energy for each member of series is zero and has a minimum at the critical value s_c. These are the conditions for the nematic-isotropic transition to take place.

Table 1. The values of B and D for each member of the homologous series.

Type	S_{exp}	B	D
PAA	0.43	4.5312	0.0102318
PAP	0.50	3.8968	0.5531240
PDPAB	0.44	4.4282	0.1104130
PBAB	0.55	3.5426	0.7791800
PPAB	0.48	4.0592	0.4310450
PHAB	0.56	3.4793	0.8137300

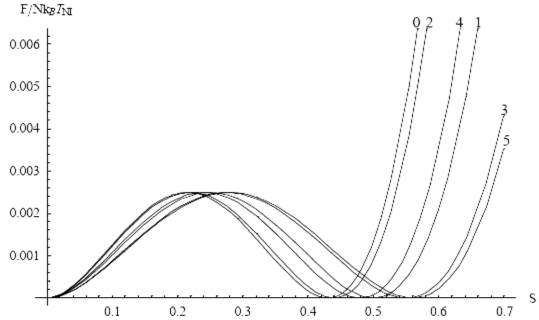

Fig 3. Helmholtz Free Energies of the Different Members of the p, p′-di-n-alkoxyazobenzene Series. The curves for the different members are obtained by using the values of B and D for each member in eqn (20) in the text. As noted the value of the order parameter is the value at which the conditions for a transition ($F_{string}(s_c,T_{NI}) = 0$ and $\partial F_{string}/\partial s\big|_{s_c,T_{NI}} = 0$) are met.

Using the definitions of B and D, eqn. (19), we have determined the values of A and J, the mean field interaction energy and the strength of the interaction between the liquid crystal molecules on the string. The values needed for both the Helmholtz free energy and its derivative to be zero at the critical value of the order parameter of each member of the homologous series are listed in Table 2. We have plotted the strength of

Table 2. The values of A and J for each type of nematic, n is the number of CH_2 molecules between O and CH_3.

Types	n	V (ml/mole)	T_{NI} (K)	$Ax10^{-27}$ Joule x m^6	$Jx10^{-30}$ Joule x m^6
PAA	0	225.0	408	1.29157	1.450
PAP	1	267.3	441	1.69445	120.256
PDPAB	2	299.0	396	2.16344	26.972
PBAB	3	338.5	409	2.29108	251.958
PPAB	4	368.9	396	3.01878	160.282
PHAB	5	406.0	402	3.18164	372.056

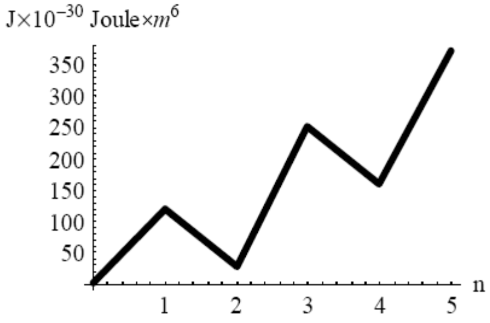

Fig 4. Strength of the Intermolecular Force as More CH_2 Groups Are Added. As is seen, the strengths exhibit an 'even-odd' effect. This 'even-odd' effect is most likely responsible for the 'even-odd' effect observed in the values of the order parameters of the p, p'-di-n-alkoxyazobenzene series of NLC's.

Table 3. Odd-even effect and model parameters.

	Phenomenological properties		Structural properties			
	T_{NI}	s_c	A	B	D	J
Odd-even effect	Yes	Yes	No	Yes	Yes	Yes

interaction J for the different NLC's in Fig. 4. Table 3 summarizes which parameters are affected by the odd-even effect. We see that there is a non-trivial relation between the parameter B and A on the one hand and the parameters D and J on the other. The odd-even effect in B does not carry over to A. In contrast, the odd-even effect in D does persist in J.

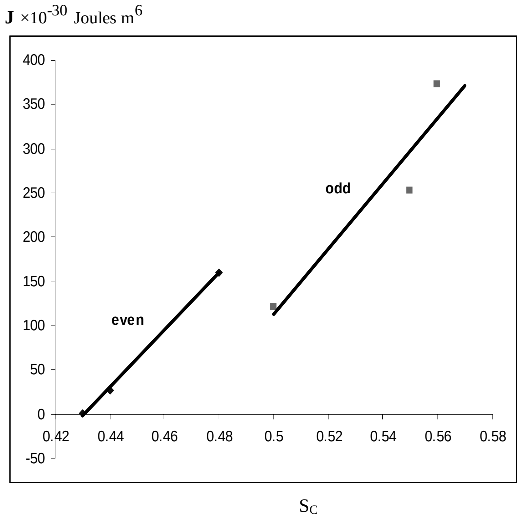

Fig 5. Correlation of the Intermolecular Potential J with the Order Parameter at T_{NI}. Plots of the strengths of the intermolecular interaction vs the values of s_c for the odd series and the even series points to a linear dependence of J on the order parameter at the transition temperature.

We now look at the odd-even effect in the nearest-neighbor interaction in a more quantitative fashion. Plotting J against s_c, we obtain Fig. 5. From Fig. 5, we see that within the odd and even liquid crystal series, the parameter J increases monotonically with s_c. The two sets of data points can be fitted by the linear equation $J = a_o + a_1 s_c$ where a least square best fit are achieved with $a_o = -1.387 \times 10^{-27}$ Jm^6 and $a_1 = 3.22 \times 10^{-27}$ Jm^6 for the even series and with $a_o = -1.73 \times 10^{-26}$ Jm^6 and $a_1 = 3.69 \times 10^{-26}$ Jm^6 for the odd series.

DISCUSSION

We have shown that it is possible to account for the even-odd effects seen in the observed values of the nematic-isotropic transition temperatures and of the order parameter at T_{NI} in the homologous series p,p'-di-n-alkoxyazobenzene within the Maier and Saupe mean field theory. This is done by introducing a chain of LC molecules in which the molecules on the chain interact via a two particle interaction ($u_{ij} = -\frac{J}{V^2} P_2(\cos\theta_i) P_2(\cos\theta_j)$) with their nearest neighbor molecular on the chain and with the rest of the molecules in the system via a Maier-Saupe-like mean field interaction ($u_{mean,i} = -\frac{A}{V^2} s P_2(\cos\theta_i)$), and keeping terms of order β^2 in the Helmholtz free energy. We find that the odd-even effect is reflected in a non-trivial manner in the parameters A, B, D and J of our generalized mean model. While the parameter A is not affected by the odd-even effect, the other three parameters are affected. Finally, we wish to point out that our approach yields a quantitative estimate of the nearest neighbor interaction J. Moreover, we found that J increases with s_c, i.e. $\Delta J = a_1 \Delta s_c$ where $a_1 = 3.22 \times 10^{-27}$ Jm^6 for the even series and 3.69×10^{-26} Jm^6 for the odd series.

Finally we wish to point out that unlike the standard mean field approach which does not take into account the effects of short range ordering or allow for the deter-mination of the nearest neighbor interaction from the experimental data, our approach does. Our generalized mean field approach produces an expression for the Helmholtz free energy of each member of the series which is zero at the different values of the s_c of each member and whose derivative is also zero at that value (Fig. 3). The Maier-Saupe theory gives a Helmholtz free energy which can only meet the required boundary conditions at a single critical value, $s_c = 0.4293$.

REFERENCES

1. Uebele P, Hummler K, Fahnle M, (1996) Full-potential linear-muffin-tin-orbital calculations of the magnetic properties of

rare-earth-transition-metal intermetallics. III $Gd_2Fe_{17}Z_3$ (Z = C, N, O, F). *Phys. Rev.* B **53**, 3296.

2. McBride C, Vega C, MacDowell LG, (2001) Isotropic-nematic phase transition: Influence of intramolecular flexibility using a fused hard sphere model. *Phys. Rev.* E **64**, 011703.
3. X.M. Zhang, R.W. Huang, Z.W. Zhang, (2002) Molecular field theory analysis of $R_3Co_{11}B_4$. *J. Magn. Magn. Mater.* **241**,131; Zhang ZM, Zhang XM, Wen SW, Han LP, Ni ZC, Liu ZY, (2003) Molecular field theory analysis of $R_3Co_{11}B_4$ (R = Pr, Nd, Gd,Tb, Dy, Ho, Er). *J. Magn. Magn. Mater.* **248**,158.
4. Tang IM, Varamit S, (1995) An improved mean field theory for mixed spinel ferrites. *J. Magn. Magn. Mater.* **150**, 93.
5. Thongmee S, Winotai P, Tang IM, (1999) Local field fluctuation in the sub-stituted aluminum iron garnets $Y_3Fe_{5-x}Al_xO_{12}$. *Sol. State Commun.* **109**, 471.
6. Maier W, Saupe A, (1058) Eine einfache molekulare Theorie des nematisshen kristallinflussigen Zustandes, *Z. Naturforsch.* **13a**, 564.
7. Chandrasekhar S, (1977) *Liquid Crystals*, Cambridge U. Press (Cambridge).
8. Marcelja S, (1964) Chain ordering in liquid crystals. I. Even-odd effect. *J. Chem. Phys.* **60**, 3599.
9. Ypma JGJ, Vertogen G, (1979) Short range order in nematic liquid crystals. *Sol, State Commun.* **18**, 475.
10. Phaovibul O, Tang IM, (1980) Nematic Isotropic Transition Temperature of Binary Liquid Crystal Mixtures. *J. Sci. Soc. Thailand* **6**, 112.

APPENDIX

Details of the calculation of the Helmholtz free energy

The Helmholtz free energy for a system of N molecules is defined as

$$F = U - TS \qquad (A1)$$

where U is the total internal energy, T is the temperature and S is the total entropy. To calculate U and S, we first need to calculate the partition function Z. To do this, we first need to write down the two particle interaction term

$$U=\frac{1}{2}\sum_{i,j} u_{ij}=-\frac{1}{2}\sum_{i,j}\frac{J_{ij}}{V^2}P_2(\cos\theta_i)P_2(\cos\theta_j) \qquad (A2)$$

where the ½ appears to take care of the problem of double counting. In the mean field approximation, the total internal energy becomes

$$U_{\text{mean field}} = \frac{1}{2}\sum_{i}^{N}\frac{A}{V^2}\, s\,(\frac{3x_i^2 - 1}{2}) \qquad (A3)$$

where $x_i = \cos\theta_i$. Introducing the one particle energy $u_i = -\frac{A}{V^2} s\,(\frac{3x_i^2 - 1}{2})$, we have for the partition function of a single molecule

$$z_i = \int_0^1 \exp[-\beta u_i]dx_i \qquad (A4)$$

The average of potential energy $\overline{u}$ is given by

$$\overline{u} = \frac{\int_0^1 u_i \exp[-\beta u_i]dx_i}{\int_0^1 \exp[-\beta u_i]dx_i} \qquad (A4)$$

The same result can be obtained by differentiating the ln of partition function (A3) and so we have

$$U = \frac{1}{2}\frac{\partial}{\partial\beta}\ln Z \qquad (A5)$$

Since the total entropy is equal to the natural log of the entropy of the system, i.e., $S = k_B \ln Z$, we have

$$F = \frac{1}{2}\frac{\partial}{\partial\beta}\ln Z - k_B T \ln Z \qquad (A6)$$

Finding the Helmholtz free energy for any system reduces to calculating the partition function for the system. Using the partition function for model of the liquid crystal, we get

$$F=(-\frac{1}{2}N_A kTBs^2)$$
$$-T(-\frac{1}{2}N_A k_B Bs(1+2s)+N_A k_B \ln(\int_0^1 \exp[\frac{3}{2}Bsx_i^2]dx_i)) \qquad (A7)$$

or

$$F = N_A k_B T\{\frac{1}{2}Bs(1+ s) - \ln(\int_0^1 \exp[\frac{3}{2}Bsx_i^2]dx_i)\} \qquad (A8)$$