Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Zhang Zhidong & Huang Ximin (1997): Two Particle Cluster Theory for Nematic Liquid Crystals Confined by Parallel Planes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 300:1, 219-227

To link to this article: http://dx.doi.org/10.1080/10587259708042349

Mol. Cryst. Liq. Cryst., 1997, Vol. 300, pp. 219-227
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Two Particle Cluster Theory for Nematic Liquid Crystals Confined by Parallel Planes

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(Received 18 September 1996; In final form 15 January 1997)

We present a two-particle cluster variation theory to treat the inhomogeneous nematic system confined by two parallel planes which align the surface molecules perpendicular to them. Numerical calculations are made for a film composed of 20 molecular layers. The nematic-isotropic transition temperatures for typical values of the strength of the surface field are given and the layer dependences of the order parameter are shown. The Monte Carlo simulation data are needed to demonstrate our results.

Keywords: Nematic liquid crystal; inhomogeneous finite system; surface field; two particle cluster theory

1. INTRODUCTION

The importance of short range correlations between molecules in the homogeneous nematic phase of liquid crystals has been demonstrated by experimental data and computer simulations [1]. There have been a few forms of molecular theories published on the subject of the short range correlations, including the Bethe method [2], the constant coupling theory [3], two particle cluster theory [4] and our functional variation theory based on the cell model [5]. Compared with the simple mean field theory, all these theories lead to improved values for all quantities, characteristic for the nematic-isotropic phase transition within the Maier-Saupe model [6].

Recently, molecular theories taking account of short range correlations between molecules have been presented to investigate nematic liquid crystal films [7, 8] which are performed by the Lebwohl-Lasher lattice model [9] of finite width, having parallel free surfaces at the top and bottom. For nematic-isotropic transition temperature, averaged energy per particle, order parameter profile and adsorption, etc., the theoretical results are better agreement with the Monte Carlo simulation data than those of the mean field theory [10]. Thus, the short range correlations are as important in the inhomogeneous finite nematic system as in the homogeneous infinite one.

In this paper, we present a two-particle cluster variation theory to treat the inhomogeneous nematic system confined by two parallel planes which align the surface molecules perpendicular to them. Such a system is important because substrate alignment of nematic liquid crystals is widely used technique to produce uniform director configurations in liquid crystal display cells. It has been studied by using the mean field approximation of the appropriate lattice model [11] and by the Landau-de Gennes theory [12, 13].

2. THEORY

Let us consider a system of N liquid crystal molecules. The direction of the long axis of a molecule is described by the spherical coordinates θ, ϕ. Denote $\Omega \equiv (\theta, \phi)$. We define one body and two body distribution functions $g^{[i]}(\Omega_i)$ and $g^{[ij]}(\Omega_i, \Omega_j)$, where superscript $[i]$ refers to the definite molecule i and $[ij]$ to the definite molecules i and j. It is implied that molecules may have different distributions when the system is inhomogeneous. The distribution functions satisfy the normalization condition and the consistency condition

$$\int g^{[i]}(\Omega_i)\, d\Omega_i = 1, \tag{1}$$

$$\int g^{[ij]}(\Omega_i, \Omega_j)\, d\Omega_j = g^{[i]}(\Omega_i), \tag{2}$$

where $d\Omega = \sin\theta\, d\theta\, d\phi$ and the angular integration is taken over the whole solid angle.

Suppose the molecular pair potential is $V(\Omega_i, \Omega_j)$. Each molecule can experience a generalized external potential $E^{[i]}(\Omega_i)$, where superscript $[i]$ implys that the external potential may be different for individual molecules. Within the two particle cluster approximation, the free energy of the system is expressed as [5, 8]

$$\beta F = \frac{1}{2}\sum_{i}\sum_{j=1}^{z^{[i]}}\iint[\beta V(\Omega_i, \Omega_j) + \beta E^{[i]}(\Omega_i)/z^{[i]} + \beta E^{[j]}(\Omega_j)/z^{[j]}$$

$$+ \ln g^{[ij]}(\Omega_i, \Omega_j) - (1 - 1/z^{[i]})\ln g^{[i]}(\Omega_i)$$

$$-(1 - 1/z^{[j]})\ln g^{[j]}(\Omega_j)]g^{[ij]}(\Omega_i, \Omega_j)\,d\Omega_i\,d\Omega_j, \tag{3}$$

where $\beta \equiv 1/kT$; the first summation is taken over all molecules of the system and the second over $z^{[i]}$ neighbours of the molecule i. Compared with the expression which is used to treat the free nematic films [8], two terms contributed by the external field have been added to Eq. (3). The equilibrium distribution results from the minimization of the free energy with respect to the variations of the distribution functions. So we have

$$\sum_{j=1}^{z[i]}[\beta V(\Omega_i, \Omega_j) + \beta E^{[i]}(\Omega_i)/z^{[i]} + \beta E^{[j]}(\Omega_j)/z^{[j]} + \ln g^{[ij]}(\Omega_i, \Omega_j)$$

$$-(1 - 1/z^{[i]})\ln g^{[i]}(\Omega_i) - (1 - 1/z^{[j]})\ln g^{[j]}(\Omega_j)] - \lambda^{[i]} = 0, \tag{4}$$

where $\lambda^{[i]}$ is a variational constant.

Adopting the Lebwohl-Lasher model [9], the molecular centers of mass are located at the sites of a simple cubic lattice. The substrate planes are assumed to be normal to the Z axis and they remove the homogeneity of the system in the Z direction but not in the XY plane. We label the layers parallel to the substrates with the letter m, with $m = 1$ and $m = n$ denote the two surface layers. We suppose that the external field supplied by the substrates acts only on the molecules in the surface layers. When the molecule i is in the surface layers, $E^{[i]}(\Omega_i) = E(\Omega_i)$; when the molecule i is not in the surface layer, $E^{[i]}(\Omega_i) = 0$. The one body distribution function is localized according to the layer in which the molecule is located; i.e., we have $g^{[i]}(\Omega_i) = g^{(m)}(\Omega_i)$, if the molecule i is in the mth layer. From Eqs. (1), (2) and (4), we obtain a set of equations for the one body distribution functions,

$$g^{(m)}(\Omega_1) = A^{(m)}\{\int[g^{(m)}(\Omega_2)]^{1-1/z^{(m)}}\exp[-\beta V(\Omega_1, \Omega_2)$$

$$-\beta(E(\Omega_1) + E(\Omega_2))(\delta_{m1} + \delta_{mn})/z^{(m)}]\,d\Omega_2\}^4$$

$$\times \{\int[g^{(m-1)}(\Omega_2)]^{1-1/z^{(m-1)}}\exp[-\beta V(\Omega_1,\Omega_2)$$

$$-\beta E(\Omega_1)\,\delta_{mn}/z^{(m)}-\beta E(\Omega_2)\,\delta_{m2}/z^{(m-1)}]d\Omega_2\}^{1-\delta_{m1}}$$

$$\times \{\int[g^{(m+1)}(\Omega_2)]^{1-1/z^{(m+1)}}\exp[-\beta V(\Omega_1,\Omega_2)$$

$$-\beta E(\Omega_1)\,\delta_{m1}/Z^{(m)}-\beta E(\Omega_2)\,\delta_{m,n-1}/Z^{(m+1)}]d\Omega_2\}^{1-\delta_{mn}},$$

$$(m=1,2,\ldots,n) \tag{5}$$

where $Z^{(m)}$ is equal to 5 for $m=1,n$, otherwise it is equal to 6; $A^{(m)}$'s are the constants determined by Eq. (1).

The molecular pair potential and the surface action potential are taken, respectively, as

$$V(\Omega_1,\Omega_2)=-JP_2(\cos\theta_{12}), \tag{6}$$

$$E(\Omega_1)=-J_sP_2(\cos\theta_1). \tag{7}$$

Here θ_{12} is the angle between the long axes of the neighbouring molecules 1 and 2; θ_1 is the angle of the molecule 1 in the surface layers with respect to the Z axis; P_2 is the second order Legendre polynomial; $J(>0)$ is the coupling constant and J_s is the strength of the surface field. In this paper, J_s is taken to be positive, which means that the system is uniaxial; i.e., the one body distribution function $g^{(m)}(\Omega)$ depends only on the polar angle θ.

In order to solve the set of equations (5), we choose a representation for $g^{(m)}(\Omega)$; i.e., we expand $\ln g^{(m)}(\Omega)$ in Legendre polynomials [5, 8]. For the simple potentials (6) and (7), we retain only the leading term of the expansion and write [8, 14]

$$g^{(m)}(\Omega)=\exp[\beta J\sigma^{(m)}P_2(\cos\theta)]/Z_1^{(m)}, \tag{8}$$

$$Z_1^{(m)}=\int\exp[\beta J\sigma^{(m)}P_2(\cos\theta)]d\Omega, \tag{9}$$

where $\sigma^{(m)}$'s are functions of temperature and are determined by requiring that this set of equations will give the orientational order parameters

$$S^{(m)}=\int P_2(\cos\theta)]g^{(m)}(\Omega)d\Omega, \tag{10}$$

consistently. When two sets of solutions appear, the one with lower free energy is more stable. The free energy can be written as

$$\beta F(n)=\sum_{m=1}^{n}\beta F^{(m)}=\frac{1}{2}L\sum_{m=1}^{n}[4(1-1/z^{(m)})\ln Z_1^{(m)}+(1-\delta_{m1})$$
$$(1-1/z^{(m-1)})\ln Z_1^{(m-1)}+(1-\delta_{mn})$$
$$(1-1/z^{(m+1)})\ln Z_1^{(m+1)}-\ln Z_2^{(m)}], \tag{11}$$

where $L=N/n$ is the number of molecules in each layer and

$$Z_2^{(m)}=\int\{\int\exp[\beta J(1-1/z^{(m)})\sigma^{(m)}P_2(\cos\theta_1)+\beta JP_2(\cos\theta_{12})$$
$$+\beta J_s(P_2(\cos\theta_1)+P_2(\cos\theta_2))(\delta_{m1}+\delta_{mn})/z^{(m)}]d\Omega_2\}^4$$
$$\times\{\int\exp[\beta J(1-1/z^{(m-1)})\sigma^{(m-1)}P_2(\cos\theta_1)+\beta JP_2(\cos\theta_{12})$$
$$+\beta J_sP_2(\cos\theta_1)\delta_{mn}/z^{(m)}+\beta J_sP_2(\cos\theta_2)\delta_{m2}/Z^{(m-1)}]d\Omega_2\}^{1-\delta_{m1}}$$
$$\times\{\int\exp[\beta J(1-1/z^{(m+1)})\sigma^{(m+1)}P_2(\cos\theta_1)+\beta JP_2(\cos\theta_{12})$$
$$+\beta J_sP_2(\cos\theta_1)\delta_{m1}/z^{(m)}+\beta J_sP_2(\cos\theta_2)$$
$$\delta_{m,n-1}/Z^{(m+1)}]d\Omega_2\}^{1-\delta_{mn}}d\Omega_1. \tag{12}$$

3. NUMERICAL RESULTS AND DISCUSSION

We have made numerical calculations for the film composed of 20 molecular layers. Two sets of $\sigma^{(m)}$'s are found to be the solutions of the set of equations (5), which give the order parameters consistently. In one set of the solutions, $\sigma^{(m)}\neq 0$ for all molecular layers and the order parameters in the middle molecular layers are very close to those of the bulk system (The differences are the effects of finite system size [8, 10]). This set of solutions appears in a range of low temperature and represents the nematic phase. In the other set of the solutions, $\sigma^{(m)}\neq 0$ only for the molecular layers approaching the substrates and $\sigma^{(m)}=0$ for the middle molecular layers (in the case of $J_s=0$, $\sigma^{(m)}=0$ for all molecular layers). This set of the solutions represents the isotropic phase. The stable set of solutions is determined by the free energy given by equation (11). In the low temperatures, the former has lower free energy, i.e. the system is in the nematic phase. At a certain temperature which depends on the strength of the surface potential J_s, two sets of solutions have the same free energy, and the nematic to isotropic phase transition occurs. Our theory predicts the first order nematic-isotropic phase transition on the calculated range of relative strength $\delta = J_s/J$. The transition temperatures are listed in Table I for typical values of δ, where the scaled temperature $t = kT/J$ has been introduced. For comparison the numerical results of the mean field theory are also listed.

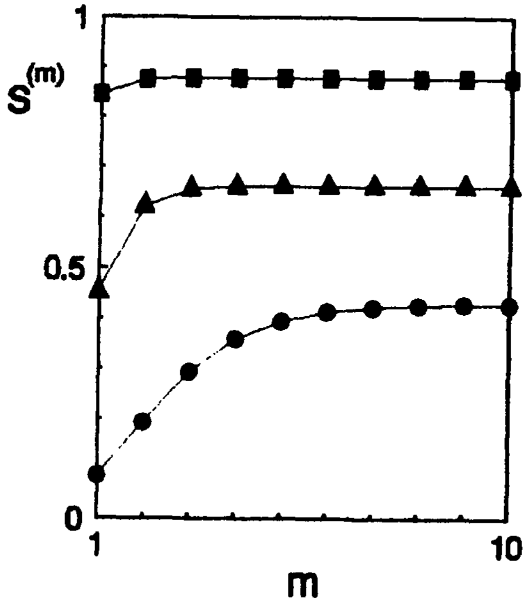
From Table I, we can see that the short range correlations between molecules reduce the nematic-isotropic transition temperature in comparison with the mean field theory. In the case of freely suspended film which corresponds to $\delta = 0$, our numerical result is identical to that of Telo da Gama *et al.* (in Fig. 2 of Ref. 7) and is better agreement with the Monte Carlo simulation data than that of the mean field theory [8, 10]. The Monte Carlo simulation data are needed to demonstrate our results for $\delta \neq 0$.

The layer dependences of the order parameter are shown in Figure 1 for the typical values of δ at typical temperatures. We see that the order parameter near the substrate are sensitive to the strength of the surface field. We also see that the order parameters can be induced in the isotropic phase near the substrate. For typical values of δ, the order parameters in the first layer vary with temperature are given in Figure 2, they are discontinuous at the nematic-isotropic transition points and they are not equal to zero in the isotropic phase for $\delta \neq 0$. For lack of the Monte Carlo simulation data, the comparison between these numerical results and those of the mean field theory is not given.

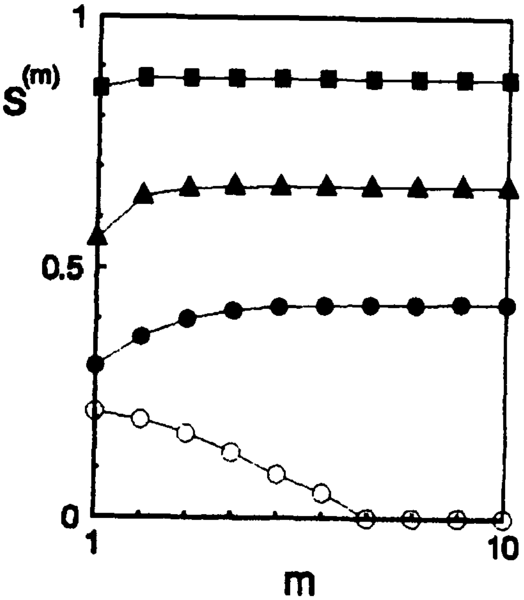
We have constructed the two-particle cluster theory to study nematic liquid crystals confined by parallel planes. The theory in this paper is an important generalization of the previous theory [8] used to treat the freely suspended films. Our theory is better than the mean field theory in the case of $\delta = 0$, demonstrated by the Monte Carlo simulation method [7, 8, 10].

TABLE I The nematic-isotropic transition temperatures t_c ($t = kT/J$) for typical values of relative strength δ

δ	*0*	*0.2*	*0.5*	*1.0*
Two-Particle cluster Theory	1.1533	1.1627	1.1696	1.1722
Mean Field Theory	1.3128	1.3205	1.3296	1.3320

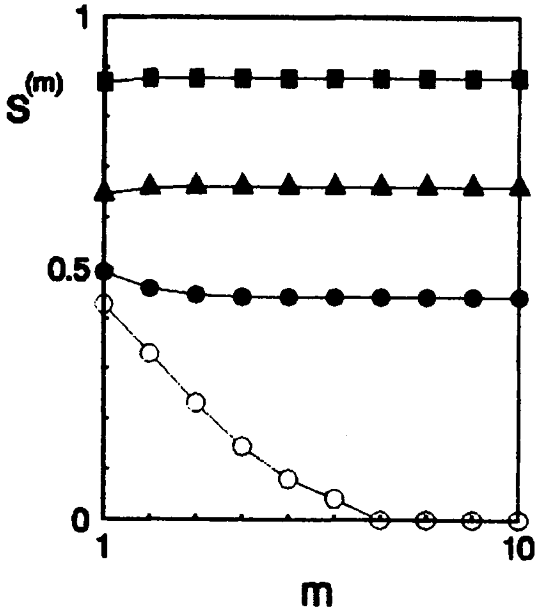


(a)



(b)

FIGURE 1 The layer dependences of the order parameter for the typical values of δ at typical temperatures. (a) $\delta = 0$; (b) $\delta = 0.2$; (c) $\delta = 0.5$; (d) $\delta = 1.0$. ■ for $t = 0.5$; ▲ for $t = 1.0$; ● for $t = 1.15$; ○ for $t = 1.2$.



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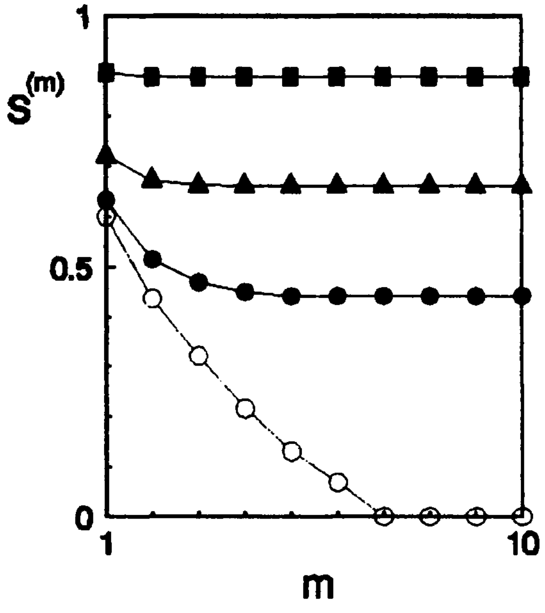

(d)

FIGURE 1 (Continued).

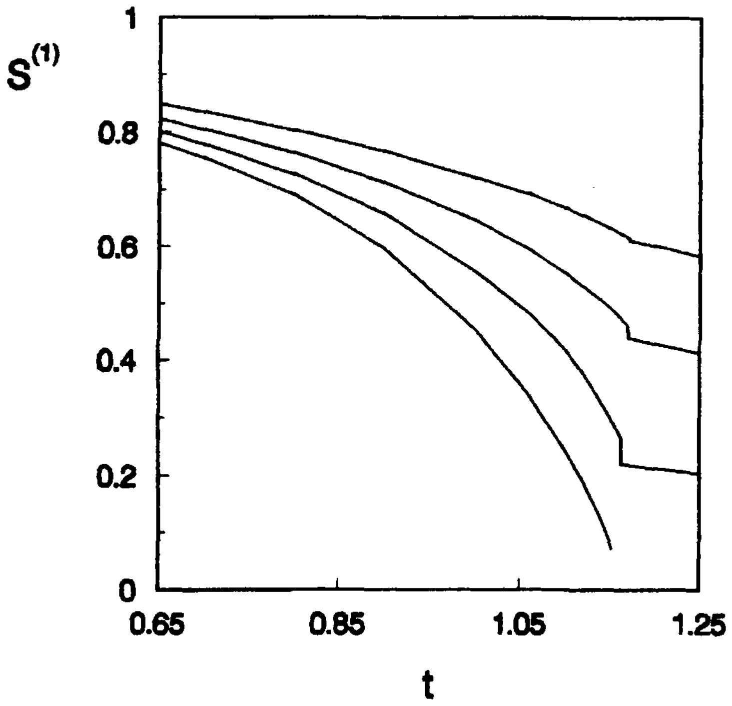

FIGURE 2 The order parameters in the first layer vary with temperature. From the top to bottom, they are for $\delta = 1.0$, $\delta = 0.5$, $\delta = 0.2$, $\delta = 0$, respectively.

We hope that the results described above can interest someone who works on the Monte Carlo simulation of nematic liquid crystals.

References

[1] C. Zannoni, in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press, 1979), Chap. 9.
[2] N. V. Madhusudana and S. Chandrasekhar, *Sol. State Commun.*, **13**, 377 (1973).
[3] P. Sheng and P. J. Wojtowicz, *Phys. Rev.* **A14**, 1883 (1976).
[4] J. G. J. Ypma, G. Vertogen and H. T. Koster, *Mol. Cryst. Liq. Cryst.*, **37**, 57 (1976).
[5] G. C. Yang and Z. D. Zhang, *Acta Phys. Sin.*, **37**, 638 (1988).
[6] W. Maier and A. Saupe, *Z. Naturforsch.*, **14a**, 882 (1959).
[7] M. M. Telo da Gama *et al.*, *Molec. Phys.*, **71**, 801 (1990).
[8] Z. D. Zhang and G. C. Yang, *Chin. Phys. Lett.*, **12**, 175 (1995).
[9] P. A. Lebwohl and G. Lasher, *Phys. Rev.*, **A6**, 426 (1972).
[10] G. R. Luckhurst, T. J. Sluckin and H. B. Zewdie, *Molec. Phys.*, **59**, 657 (1986).
[11] M. M. Telo da Gama and P. Tarazona, *Phys. Rev.*, **A41**, 1149 (1990).
[12] P. Sheng, *Phys. Rev.*, **A26**, 1610 (1982).
[13] A. Poniewierski and T. J. Sluckin, *Liq. Cryst.*, **2**, 281 (1987).
[14] R. Van der Haegen *et al.*, *J. Chem. Phys.*, **73**, 2469 (1980).