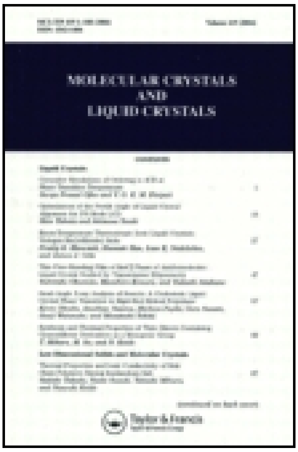

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Theory of Inhomogeneous Polymers Lattice Model for the Interface between Flexible Polymer and Small Molecular Liquid Crystal

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The Helfand's lattice theory of polymer interface has been extended to deal with the interface between thermotropic small molecular liquid crystals and flexible polymers. The main findings of the theoretical calculations are: (1) the interface of flexible polymer and the ordered nematic liquid crystal is very narrow due to the fact that the ordered nematic phase excludes strongly the flexible polymer segments; (2) the interfacial tension and the anisotropic factors of polymer bonds posses a first order transition, when the liquid crystal-rich phase undergoes the isotropic to nematic phase transition, which is characterized mainly by the fact that polymer bonds prefer to return back to the saturated polymer solution phase by reducing the probability of stretching into the liquid crystalline phase.

I. INTRODUCTION

In recent years, a new kind of material called nematic curvillinear aligned phase[1,2] (NCAP) or polymer dispersed liquid crystal (PDLC)[3,4] has been developed for overcoming various problems inherent with currently used display device. It is a composite material consisting of small nematic liquid crystal droplets confined in a polymer matrix, and can be fabricated into large or even flexible sheets. The diameter of the droplets is ordinarily in microns or submicrons. Various properties of these materials have been described in some detail.[4–6]

Concerning the forming process of PDLC composite, the phase equilibria in the mixtures of liquid crystals and flexible polymers are technically very important. Several theories have been developed to describe the phase equilibria between liquid crystals and polymers.[7,8] Some studies have also taken account of the influence of the semiflexibility of polymers.[9,10] Prediction of the occurrence of various biphasic areas is one of the main aims of these theoretical studies. However, in PDLC materials, liquid crystals at the interface are attached to the polymer surface with certain anchoring energy. Many physical properties of the liquid crystals droplets are influenced by the interfacial effects, such as the director configurations of the liquid crystal droplets and their transitions,[11–14] the switching speed of PDLC display device,[15] etc. Therefore, it is quite important both for academic and technical interests to know how the

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interface between liquid crystal and polymer is affected by temperature, the interaction between two components, etc.

The theory of inhomogeneous systems, particularly the interface, has received considerable attention over many years. Obviously, the importance to be attached to such an investigation is the common occurrence of inhomogeneity. Concerning the polymer system, the theory developed by Helfand and its variants have been applied to the interface between immiscible polymers,[16-18] bolck copolymer microdomain structures,[19-21] the interface of concentrated polymer solutions,[22,23] and the end-adsorbed polymer brushes[24] etc. To our knowledge, however, the interface between liquid crystals and flexible polymers has not been studied theoretically. One of the reasons might be due to the lack of corresponding experimental data.

The aim of this paper is to extend Helfand's lattice theory for interface to the case of interface between thermotropic small molecular liquid crystal and flexible polymer in order to obtain a more detailed microscopic picture such as interfacial free energy, the average arrangement of polymer molecules and the order parameters of liquid crystals at interface. The situations considered are those that the molecular weight of the flexible polymer is high enough as compared with the molecular weight of liquid crystal, so that the effect of the chain ends can be neglected. The interaction between the polymer segment and liquid crystal is assumed to be purely isotropic, what is equivalent to the assumption of completely flexible polymer chain. The previous studies[7-10] revealed that the flexible polymer coil is almost excluded completely from the ordered phase to form a pure liquid crystalline phase of nematogenic molecules. Therefore, the interface between small molecular liquid crystal in ordered state and flexible polymer can be considered as an interface between pure liquid crystalline phase of nematogenic molecules and the saturated solution of flexible polymer and liquid crystal.

There are two verisons of Helfand's theory, i.e., the Gaussian random walk model and the lattice model. In this work, we prefer the lattice model in order to match the lattice model for the small molecular liquid crystals introduced by Lebwohl and Lasher.[25,26] Another advantage of Helfand's lattice model is that it gives the anisotropic factors for the polymer bond direction near the interfacial region by which the more detailed microscopic pictures about the average chain conformation close to the interface are provided. Of course, the lattice model might be not so fine as the Gaussian random walk model for the case of narrow interface such as the interface considered in this paper. However, we believe that it should be very useful in obtaining the general trends and some qualitative predictions.

This paper is organized as follows: In section II, a brief description of the Lebwohl–Lasher nematogen model is given and then is combined with the Helfand's lattice theory of inhomogeneous polymeric system to describe the interface between flexible polymers and small molecular liquid crystals. The numerical results and the discussions are given in section III. Finally, the summary and the conclusions are given in Section IV.

II. THE MODEL AND THEORY

1. Lebwohl–Lasher Model of Nematic Liquid Crystal

Many statistical theories of the nematic phase have been presented. Among the best known are those of Onsager,[27] Maier and Saupe[28,29] and Flory.[30] Those theories have contributed substantially to the understanding of the nematic phase. However, the thermotropic small molecular liquid crystal is better described by Lebwohl–Lasher model[25,26] which is easier to be extended to the case of inhomogeneous system.

In the Lebwohl–Lasher nematogen model, a system of uniaxial particles placed at the sites of a cubic lattice interacts through a nearest neighbor pair potential of the form

$$u_{ij} = -\varepsilon_{ij} P_2(\cos\theta_{ij}), \tag{1}$$

where ε_{ij} is a positive constant of the nearest neighbor particles i and j, $P_2(x)$ is a second Legendre polynomial and θ_{ij} is the angle between the axes of these two molecules. From a formal point of view, Equation (1) is a simplified version of the attractive anisotropic interaction put forward by Maier and Saupe.[28,29] Therefore, Lebwohl–Lasher model can be considered as the discretized version of Maier–Saupe model. The potential under the mean-field approximation is obtained by standard means[31] upon averaging the pair potential in Equation (1), we find

$$u = -\varepsilon_b P_2(\cos\theta)\langle P_2\rangle_0, \tag{2}$$

where θ is the angle between the long axes of molecular and the director, and $\langle P_2\rangle$ is defined by self-consistent equation,

$$\langle P_2\rangle = \langle \tfrac{1}{2}(3\cos^2\theta - 1)\rangle_0 = \int P_2(x) f(x)\, dx, \quad x = \cos\theta, \tag{3}$$

with the orientational distribution function,

$$f(x) = \frac{1}{Z_0}\exp\left\{\left(\frac{z\varepsilon_0}{kT}\right) P_2(x)\langle P_2\rangle_0\right\}, \tag{4}$$

where z is the coordination number ($z = 6$ for the cubic lattice), and the subscript “0” represents pure liquid crystal; Z_0 is the orientational partition function,

$$Z_0 = \int \exp\left\{\left(\frac{z\varepsilon_b}{kT}\right) P_2(x)\langle P_2\rangle_0\right\} dx, \tag{5}$$

from which the orientational entropy can be calculated through the Boltzmann relation,

$$S_{\text{orient}} = -k \int f \ln(4\pi f)\, dx. \tag{6}$$

In the mixture of the flexible lattice chain and Lebwohl–Lasher nematogen, the z neighboring sites are not all occupied by Lebwohl–Lasher nematogen. Therefore, the potential energy term in Equations (3)–(5) should be modified when the volume fraction of the Lebwohl–Lasher nematogen is φ_0 ($= 1 - \varphi_p$, φ_p is the volume fraction of polymer segment), then the corresponding partition function is written as

$$Z = \int \exp\left\{\left(\frac{z\varepsilon_b}{kT}\right)\varphi_0 P_2(x)\langle P_2\rangle\right\}dx, \tag{7}$$

To deal with the inhomogeneous system, $\langle P_2\rangle$ and S_{orient} etc., are all layer number dependent. In the following, we will cooperate the Lebwohl–Lasher model with Helfand's lattice theory for the interface.

2. Theory of Interface Between Flexible Polymer and Liquid Crystal

We use the same lattice model as that of Helfand's theory. In order to keep the integrity of this paper, we briefly review the model.

In a cubic lattice of n sites, there are n_p polymer units and n_0 liquid crystal molecules, and

$$n = n_0 + n_p \tag{8}$$

The lattice consists of layers labeled with the index l and each layer contains n_s cells. Each cell interacts with its z ($z = 6$ for cubic lattice) nearest neighbors, a fraction m of which is in the layer above, a fraction m in the layer below, and a fraction $(1 - 2m)$ in the same layer. We assume that the polymer chain is very long so that all units of the polymer can be regarded as middle segments and the chain end effect can be neglected. As in the previous publications,[8] we assumed that the interaction between polymer segment and liquid crystal is purely isotropic and characterized by a single energetic parameter ε_{0p}. Actually, this is corresponding to the assumption of completely flexible polymer chain. From Helfand,[18] we learn that the configurational entropy of the polymer can be written as:

$$\Delta S_{\text{conf}} = -kn_s\sum_l \{\varphi_{l,0}\ln\varphi_{l,0} + \varphi_{l,p}[mg_l^+\ln g_l^+ + (1-2m)g_l^0\ln g_l^0 + mg_l^-\ln g_l^-]\} \tag{9}$$

and the enthalpy of mixing is the following:

$$\Delta H_{\text{mix}} = \chi_{0p}kTn_s\sum_l \varphi_{l,p}[\varphi_{l,0} + m(\varphi_{l+1,0} - 2\varphi_{l,0} + \varphi_{l-1,0})] \tag{10}$$

where $\varphi_{l,0}$ and $\varphi_{l,p}(= 1 - \varphi_{l,0})$ are the volume fractions of liquid crystal and polymer segment in l-th layer respectively; g_l^+, g_l^0 and g_l^- are the anisotropic factors of polymer bond directions for returning back to the saturated polymer solution, laying in the same layer and stretching into the liquid crystal phase respectively; where χ_{0p} is defined as

$$\chi_{0p} = \frac{z\varepsilon_{0p}}{kT} \tag{11}$$

As the solvent is thermotropic liquid crystal, the orientational entropy and the enthalpy of ordering of the liquid crystal

$$\Delta S_{\text{orient}} = -\varphi_{l,0} n_s k \sum_l \left\langle \ln \left\{ \frac{\exp[\chi_0(m\varphi_{l-1}\langle P_2\rangle_{l-1} + (1-2m)\varphi_l\langle P_2\rangle_l + m\varphi_{l+1}\langle P_2\rangle_{l+1})P_2(x)]}{\int_0^1 \exp[\chi_0(m\varphi_{l-1}\langle P_2\rangle_{l-1} + (1-2m)\varphi_l\langle P_2\rangle_l + m\varphi_{l+1}\langle P_2\rangle_{l+1})P_2(x)]dx} \right\} \right\rangle \tag{12}$$

$$\Delta H_{\text{orient}} = -\tfrac{1}{2}\chi_0 kTn_s \sum_l \varphi_{l,0}[m\varphi_{l-1,0}\langle P_2\rangle_{l-1} + (1-2m)\varphi_{l,0}\langle P_2\rangle_l + m\varphi_{l+1,0}\langle P_2\rangle_{l+1}]\langle P_2\rangle_l \tag{13}$$

should be included into the total free energy. In Equations (12) and (13), $\langle P_2\rangle_l$ is the order parameter of liquid crystal in l-th layer. Due to the fact that n_s sites in the l-th layer are not all occupied by liquid crystals, instead of Equation (3), $\langle P_2\rangle_l$ should be obtained by modified self-consistency relation,

$$\langle P_2\rangle_l = \frac{\int_0^1 P_2(x)\exp[\chi_0(m\varphi_{l-1,0}\cdot\langle P_2\rangle_{l-1} + (1-2m)\varphi_{l,0}\cdot\langle P_2\rangle_l + m\varphi_{l+1,0}\cdot\langle P_2\rangle_{l+1})\cdot P_2(x)]dx}{\int_0^1 \exp[\chi_0(m\varphi_{l-1,0}\langle P_2\rangle_{l-1} + (1-2m)\varphi_{l,0}\langle P_2\rangle_l + m\varphi_{l+1,0}\langle P_2\rangle_{l+1})\cdot P_2(x)]dx} \tag{14}$$

From Equations (9)–(14), we finally get the free energy of the inhomogeneous system of polymers and liquid crystals,

$$\begin{aligned}
\frac{\Delta G}{n_s kT} = \sum_l \Big[& \chi_{0p}\varphi_{l,p}(m\varphi_{l-1,0} + (1-2m)\varphi_{l,0} + m\varphi_{l+1,0}) + \varphi_{l,0}\ln\varphi_{l,0} \\
& + \varphi_{l,p}(mg_l^+\ln g_l^+ + (1-2m)g_l^0\ln g_l^0 + mg_l^-\ln g_l^-) \\
& + \frac{\chi_0}{2}\varphi_{l,0}(m\varphi_{l-1,0}\langle P_2\rangle_{l-1} + (1-2m)\varphi_{l,0}\langle P_2\rangle_l + m\varphi_{l+1,0}\langle P_2\rangle_{l+1})\langle P_2\rangle_l \\
& - \varphi_{l,0}\ln\left\{\int_0^1 \exp[\chi_0(m\varphi_{l-1}\langle P_2\rangle_{l-1} + (1-2m)\varphi_{l,0}\langle P_2\rangle_l \right. \\
& \left. + m\varphi_{l+1}\langle P_2\rangle_{l+1})P_2(x)]\right\}\Big]
\end{aligned} \tag{15}$$

Obviously, ΔG should be subjected to a number of constrains as follows.[18]

1. The fixed numbers of polymer units and liquid crystalline solvent molecules are related to the volume fraction by

$$n_p = n_s \sum_l \varphi_{l,p}, \tag{16}$$

$$n_0 = n_s \sum_l \varphi_{l,0}, \tag{17}$$

2. Complete occupancy requires that

$$\varphi_{l,p} + \varphi_{l,0} = 1. \tag{18}$$

3. The normalization of bond anisotropy factors is represented by

$$mg_l^+ + (1-2m)g_l^0 + mg_l^- = 1. \tag{19}$$

4. The relation between φ's and g's, which is called the flux constant, is determined by

$$\varphi_{l,p} g_l^+ = \varphi_{l+1,p} g_{l+1}^- . \tag{20}$$

The constraints are introduced with Lagrange multipliers: $\Delta\mu_p$ for Eqution (16), $\Delta\mu_0$ for Equation (17), $kTn_s\omega_l^\gamma$ for Equation (18), $kTn_s\varphi_{l,p}(\xi_l - 1)$ for Equation (19) and $m\lambda_l$ for Equation (20). Where $\Delta\mu_p$ and $\Delta\mu_0$ are the chemical potentials of polymer and liquid crystal, which can be written as

$$\frac{\Delta\dot{\mu}_p}{kT} = \frac{\Delta\mu_p'}{x_p kT} = \chi_{0p}\varphi_0^{*2} + \tfrac{1}{2}\chi_0\langle P_2\rangle^2 \varphi_0^{*2} - \varphi_0^* \tag{21}$$

$$\frac{\Delta\mu_0}{kT} = \chi_{0p}\varphi_p^{*2} + \ln\varphi_0^* + \varphi_p^* - \ln\int_0^1 \exp[\chi_0\varphi_0^*\langle P_2\rangle P_2(x)]\,dx \tag{22}$$

where φ_0^* and $\varphi_p^* = 1 - \varphi_0^*$ are the volume fractions of liquid crystals and polymers in the saturated solution phase.

The function to be minimized is

$$\begin{aligned}
\frac{\Delta G}{n_s kT} = \sum_l [&\chi_{0,p}\varphi_{l,p}(m\varphi_{l-1,0} + (1-2m)\varphi_{l,0} + m\varphi_{l+1,0}) + \varphi_{l,0}\ln\varphi_{l,0} \\
&+ \varphi_{l,p}(mg_l^+(\ln g_l^+ + \xi_l - 1 + \lambda_l) + (1-2m)g_l^0(\ln g_l^0 + \xi_l - 1) \\
&+ mg_l^-(\ln g_l^- + \xi_l - 1 - \lambda_{l-1}) - \xi_l + 1) + \omega_l^\gamma(\varphi_{l,p} + \varphi_{l,0} - 1) \\
&- (\chi_{0p}\varphi_0^{*2} - \varphi_0^*)\varphi_{l,p} - (\chi_{0p}\varphi_p^{*2} + \ln\varphi_0^* + \varphi_p^*)\varphi_{l,0} \\
&+ \frac{\chi_0}{2}\varphi_{l,0}(m\varphi_{l-1,0}\langle P_2\rangle_{l-1} + (1-2m)\varphi_{l,0}\langle P_2\rangle_l + m\varphi_{l+1,0}\langle P_2\rangle_{l+1})\langle P_2\rangle_l
\end{aligned}$$

$$-\varphi_{l,0}\ln\int_0^1 \exp[\chi_0(m\varphi_{l-1,0}\langle P_2\rangle_{l-1}+(1-2m)\varphi_{l,0}\langle P_2\rangle_l$$

$$+m\varphi_{l+1,0}\langle P_2\rangle_{l+1})P_2(x)]dx+\frac{\Delta\mu_p n_p+\Delta\mu_0 n_0}{n_s kT} \tag{23}$$

Following the same procedure as that of ref. (18), a set of nonlinear equations are obtained,

$$-\xi_l+2\chi_{0p}(\varphi_{l,0}-\varphi_0^*)+2m\chi_{0p}(\varphi_{l-1,0}+\varphi_{l+1,0}-2\varphi_{l,0})-\ln\frac{\varphi_{l,0}}{\varphi_0^*}$$

$$+\ln\int_0^1 \exp[\chi_0(m\varphi_{l-1,0}\langle P_2\rangle_{l+1}+(1-2m)\varphi_{l,0}\langle P_2\rangle_l+m\varphi_{l,0}\langle P_2\rangle_{l+1})P_2(x)]\,dx=0 \tag{24}$$

$$\left(2-\frac{1}{m}\right)\exp(-\xi_l)-\left(\frac{1-\varphi_{l-1,0}}{1-\varphi_{l,0}}\right)^{1/2}\exp\left(-\frac{\xi_l+\xi_{l-1}}{2}\right)$$

$$-\left(\frac{1-\varphi_{l+1,0}}{1-\varphi_{l,0}}\right)^{1/2}\exp\left(-\frac{\xi_l+\xi_{l+1}}{2}\right)+\frac{1}{m}=0. \tag{25}$$

Equation (24) and Equation (25) can be solved numerically by following the method of ref. (23) and with $\langle P_2\rangle_l$ determined by Equation (14). By solving Equation (24) and Equation (25), we obtain a set of variables $\{\varphi_{l,0}\}$, $\{\xi_l\}$ and $\{\langle P_2\rangle_l\}$. It is clear that Equations (24) and (25) can be reduced to the case of isotropic solvent discussed by Helfand[22,23] when $\langle P_2\rangle_l=0$. The anisotropic factors can be calculated by following relations,[18]

$$g_l^+=\exp(-\xi_l-\lambda_l) \tag{26}$$

$$g_l^0=\exp(-\xi_l) \tag{27}$$

$$g_l^-=\exp(-\xi_l-\lambda_{l-1}) \tag{28}$$

where λ_l is determined by

$$\exp(-2\lambda_l)=\frac{\varphi_{l+1,p}}{\varphi_{l,p}}\exp(\xi_l-\xi_{l+1}). \tag{29}$$

The interfacial tension is defined by subtracting from the total free energy and the free energy of the molecules in the uniform phases,

$$\gamma n_s a=\Delta G-n_0\Delta\mu_0-n_p\Delta\mu_p, \tag{30}$$

and a is the cross-sectional area of a cell. With $\{\xi_l\}$, $\{\varphi_{l,0}\}$, $\{\langle P_2\rangle_l\}$ and using Equations (26)–(28) in Equations (23) and (30), the interfacial tension can readily be calculated according to the following equation:

$$\begin{aligned}\frac{\gamma}{kT}=\sum_{l}\Big\{&-(1-\varphi_{l,0})\xi_l-\chi_{0,p}(\varphi_{l,0}-\varphi_0^*)+\chi_{0p}m(1-\varphi_{l,0})(\varphi_{l+1,0}-2\varphi_{l,0}+\varphi_{l-1,0})\\&+\varphi_{l,0}\ln\left(\frac{\varphi_{l,0}}{\varphi_0^*}\right)-(\varphi_{l,0}-\varphi_0^*)+\frac{\chi_0}{2}\varphi_{l,0}(m\varphi_{l-1,0}\langle P_2\rangle_{l-1}+(1-2m)\varphi_{l,0}\langle P_2\rangle\\&+m\varphi_{l+1,0}\langle P_2\rangle_{l+1})\langle P_2\rangle_l-\varphi_{l,0}\ln\int_0^1\exp[\chi_0(m\varphi_{l-1,0}\langle P_2\rangle_{l-1}\\&+(1-2m)\varphi_{l,0}\langle P_2\rangle_l+m\varphi_{l+1,0}\langle P_2\rangle_{l+1})P_2(x)]\,dx\Big\}\end{aligned}$$

In the following numerical calculations, square lattice has been assumed, i.e., $m = 1/4$. We must note that the main conclusions will be the same for the cubic lattice ($m = 1/6$).

III. NUMERICAL RESULTS AND DISCUSSION

In the inhomogeneous system of polymer and liquid crystal, the solvent molecules are mesogenic so that the phase separation is not only driven by isotropic interaction between polymer segment and liquid crystal which is characterized by Flory–Huggins interaction parameter χ_{0p}. The orientational potential of liquid crystal excludes the flexible polymer strongly whereby the phase separation is promoted. Therefore, even when the Flory–Huggins' interaction parameter χ_{0p} is smaller than the critical value $\chi_{0p}^c = 0.5$ (or even negative), the phase separation still occurs if the liquid crystal is in the nematic phase, i.e., $\chi_0\varphi_{l,0} > 4.541$.[8] Figure 1 shows the concentration profiles of the liquid crystal for $\chi_0 = 6.0$ and two χ_{0p} values. It is shown by Figure 1b that the phase separation does happen for $\chi_0 = 6.0$ despite of negative value of χ_{0p}. On the other hand, it is not surprising that the interface will be narrower and the liquid crystal concentration in the saturated polymer solution is decreased with increasing χ_{0p} value, Figure 1a and Figure 1b.

Not only the concentration profile, the numerical solution also provides a detailed microscopic picture of polymer conformation and the order parameters of liquid crystal at the interface. As an example, the concentration profile, the layer number dependencies of the chain segment anisotropic factors and the order parameters of liquid crystal for the case of $\chi_0 = 6.0$ and $\chi_{0p} = 1$ are shown in Figures 2–4. For the square lattice, $m = 1/4$, $g_l^+/4$, $g_l^0/2$ and $g_l^-/4$ represent the probability of polymer segment returning back to the bulk polymer solution; the probability of polymer segment laying in the same layer and the probability of polymer segment stretching into liquid crystal phase, respectively. As can be seen from the figures, the relatively large g^+ value indicated that most of polymer segments return back to the saturated polymer solution phase near the interface. From Figure 3, we can see that in the middle of the interface ($l = 0$), the polymer segments have relatively high probability of laying in the

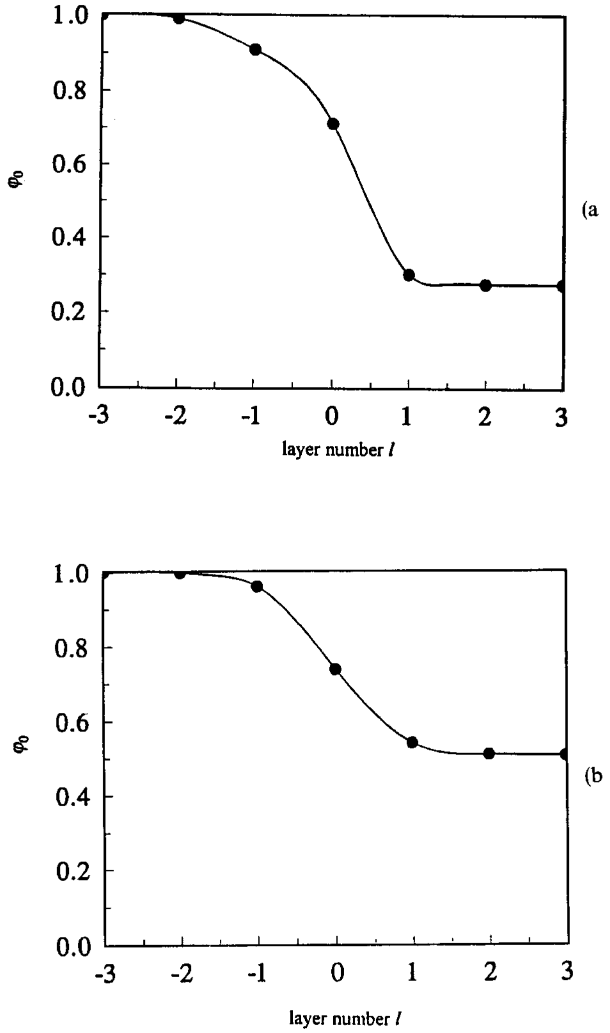

FIGURE 1 The concentration profile of the interface between flexible polymer and liquid crystal, where φ_0 is the concentration of liquid crystal. The calculation parameters are: (a) $\chi_0 = 6.0$, $\chi_{0_p} = 0.5$; (b) $\chi_0 = 6.0, \chi_{0_p} = -0.5$.

same layer. As is going further into the liquid crystal phase, the polymer segments have higher probability of returning back into the saturated polymer solution phase. Due to the same reason, the order parameter $\langle P_2 \rangle_l$ is also decreasing as going into the saturated polymer solution phase due to the fast decreasing of the liquid crystal concentration, Figure 4.

Figure 5 shows that χ_0 dependence of the interfacial tension calculated according to Equation (31). To obtain Figure 5, values of χ_{0_p} have been assigned to be 1.0, 1.5 and 2.0 respectively and χ_0 varies from 4.0–6.0. Obviously, the interfacial tension is not affected in the region of $\chi_0 < 4.541$, which is the critical value of isotropic to nematic transition

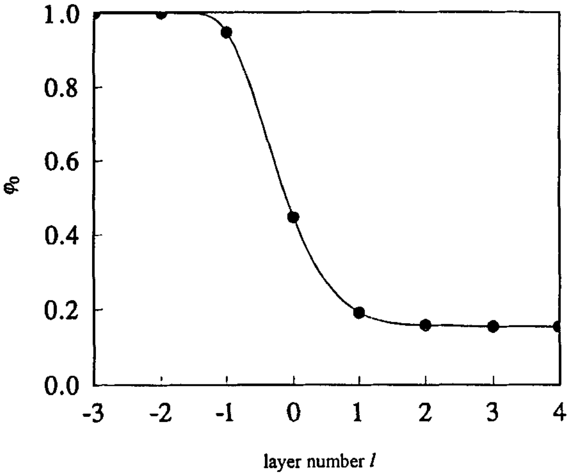

FIGURE 2 The concentration profile of the interface between flexible polymer and liquid crystal, where φ_0 is the concentration of liquid crystal. The calculation parameters are: $\chi_0 = 6.0$, $\chi_{0_p} = 1.0$.

for bulk liquid crystal phase. It is not surprising that the solvent is isotropic for $\chi_0 < 4.541$ so that the interfacial tension is only determined by χ_{0p} according to the present model. For $\chi_0 = 4.541$, there is a sudden jump due to the isotropic to nematic transition of the liquid crystal which resulted from strong exclusion of polymer segments from the liquid crystal phase. As χ_0 increasing further, such kind of exclusion becomes stronger and the interfacial tension further increased due to the narrowing of the interface. For large χ_0 the bulk liquid crystal phase behaves as a hard wall.

The χ_0 dependences of the anisotropic factors for the polymer bonds at interface ($l = +1, 0, -1$) are shown in Figure 6. As can be seen from Figure 6, the chain conformation at the interface undergoes a first order transition when χ_0 reaches the critical value. This kind of transition is mainly characterized by a sudden increase of the probability of polymer bond returning back to the bulk liquid crystal phase.

IV. CONCLUSIONS

The present theory is developed based on the Helfand's lattice theory for inhomogeneous system and Lebwohl–Lasher nematogen model. The interfacial tension and concentration profile of a polymer solution of anisotropic solvent have been calculated theoretically. Especially, the detailed information about the chain conformation near the interface is also provided. The main findings of this work can be summarized as follows: (1) the interface of our system is very narrow due to the fact that the ordered liquid crystal phase strongly excludes the flexible polymer segments; (2) the interfacial tension has a first order transition resulted from the isotropic to nematic phase transition of liquid crystal; (3) the liquid crystalline phase behaves as a hard wall when it is in the highly ordered state which causes the polymer bonds near the interface

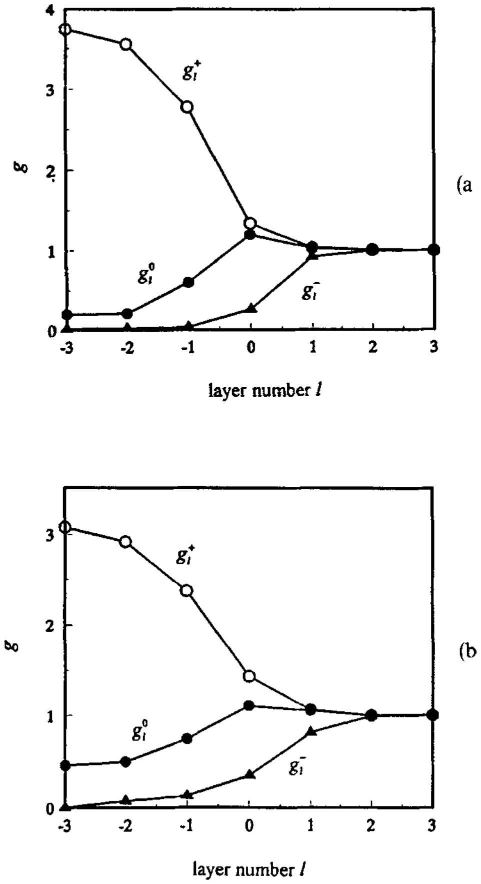

FIGURE 3 The layer dependence of polymer bond anisotropic factors. The calculation parameters are: (a) $\chi_0 = 6.0$, $\chi_{0_p} = 1.0$; (b) $\chi_0 = 6.0$, $\chi_{0_p} = -0.5$.

have higher anisotropy; (4) when the bulk liquid crystal undergoes the isotropic to nematic phase transition, the chain conformation near the interface has a first order transition which is mainly characterized by the fact that polymer bonds prefer to return to the saturated polymer solution phase by reducing the probability of stretching into the liquid crystalline phase.

No comparison with experiment is presented here because of lack of experimental data and uncertainty regarding *m*. etc. A number of extensions of the theory are required to make the predictions more precise for real systems. Furthermore one may include the anisotropic interaction between polymer segments and liquid crystalline molecules as revealed by experimental observations,[32] etc.

The most important advance would be to incorporate the nonlocal contributions to the free energy and removal of the restriction of infinite chain length.

Finally, one would hope for a theory which has taken the polymer flexibility into consideration. A formal step in this direction can be made by introducing the conformational energy.[33]

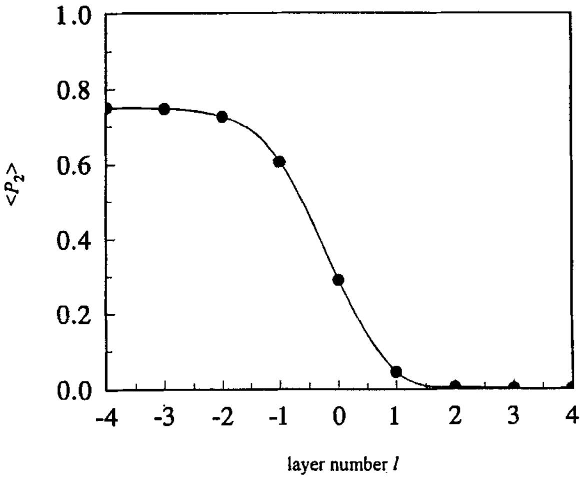

FIGURE 4 The layer dependence of the liquid crystalline order parameter. The calculation parameters are: $\chi_0 = 6.0$, $\chi_{0_p} = 1.0$.

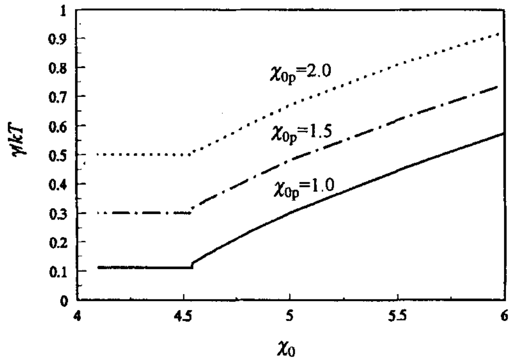

FIGURE 5 The χ_0 dependence of interfacial tension. The values of χ_{0_p} are shown in figure.

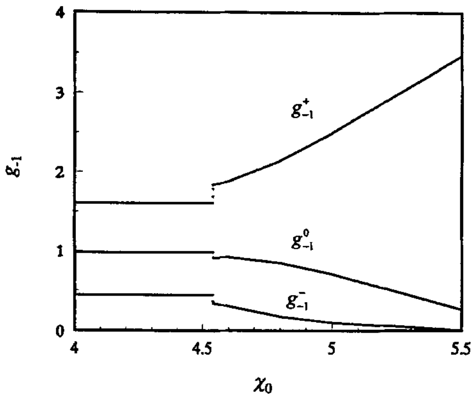

FIGURE 6a The χ_0 dependence of bond anisotropic factors at layer number $l = -1$, $\chi_{0_p} = 1.0$.

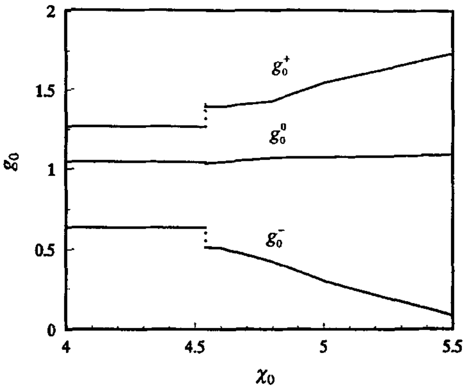

FIGURE 6b The χ_0 dependence of bond anisotropic factors at layer number $l = 0$ (the middle layer). $\chi_{0_p} = 1.0$.

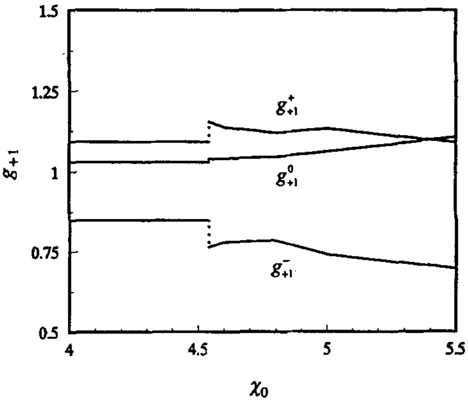

FIGURE 6c The χ_0 dependence of bond anisotropic factors at layer number $l = +1$. $\chi_{0_p} = 1.0$.

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References

1. J. L. Fergason, *US Patents*, **4**, 616, 903 (1986).
2. J. L. Fergason, *SID. Dig. Tech. Pap.*, **16**, 68 (1985).
3. J. W. Doane, N. A. Vaz, B. G. Wu and S. Zumer, *Appl. Phys. Lett.*, **48**, 269 (1986).
4. J. W. Doane, A. Gelemme, J. L. West, J. B. Whitehead, Jr., and B. G. Wu, *Mol. Cryst. Liq. Cryst.*, **165**, 511 (1988).
5. N. A. Vaz, *SPIE Proc.*, **1080**, 2 (1989).
6. P. S. Drzaic, *SPIE Proc.*, **1080**, 11 (1989).
7. M. Ballauff, *Mol. Cryst. Liq. Cryst.*, **136**, 175 (1986).

8. Y. Yang, J. Lu, H. Zhong and T. Yu, *Polymer J.*, **26**(8), 880 (1994).
9. A. ten Bosch, P. Maissa and P. Sixou, *J. Chem. Phys.*, **79**, 3462 (1983).
10. P. Maissa and P. Sixou, *Liq. Cryst.*, **5**, 1861 (1989).
11. A. Golemme, S. Zumer, D. W. Allender and J. W. Doane, *Phys. Rev. Lett.*, **61**, 2937 (1988).
12. G. Crawford, R. Stannarius and J. W. Doane, *Phys. Rev.*, **A44**, 4 (1991).
13. J. Ding and Y. Yang, *Jpn J. Appl. Phys.*, **3**, 2837 (1992).
14. J. Ding and Y. Yang, *Mol. Cryst. Liq. Cryst.*, **238**, 47 (1994).
15. B. G. Wu, J. H. Erdmann and J. W. Doane, *Liq. Cryst.*, **5**, 1453 (1989).
16. E. Helfand and Y. Tagami, *J. Polym. Sci.*, **B9**, 741 (1971).
17. E. Helfand and Y. Tagami, *J. Polym. Sci.*, **56**, 3592 (1971).
18. E. Helfand, *J. Chem. Phys.*, **63**, 2192 (1975).
19. E. Helfand and Z. R. Wasserman, *Macromolecules*, **11**, 960 (1978).
20. E. Helfand, *Macromolecules*, **8**, 552 (1975).
21. K. R. Shull, *Macromolecules*, **25**, 2122 (1992).
22. E. Helfand, *Macromolecules*, **9**, 307 (1976).
23. T. A. Webber and E. Helfand, *Macromolecules*, **9**, 311 (1976).
24. K. R. Shull, *J. Chem. Phys.*, **94**, 5723 (1991).
25. G. Lasher, *Phys. Rev. A*, **5**, 1350 (1972).
26. P. A. Lebwohl and G. Lasher, *Phys. Rev. A*, **6**, 426 (1972).
27. L. Onsager, *Ann., N.Y. Acad. Sci.*, **51**, 627 (1949).
28. W. Maier and A. Saupe, *Z. Naturforshg.*, **14a**, 882 (1959).
29. W. Maier and A. Saupe, *Z. Naturforshg.*, **15a**, 287 (1960).
30. P. J. Flory, *Proc. Royal. Soc., London. Ser. A*, **234**, 73 (1956).
31. G. R. Luckhurst and G. W. Gray (ed.), *The Molecular Physics of Liquid Crystals*, Academic Press, London, 1979.
32. A. Dubault, A. Ober, M. Veyssie and B. Cabane, *J. Physique*, **46**, 1227 (1985).
33. J. Naghizadeh and K. A. Dill, *Macromolecules*, **24**, 1768 (1991)