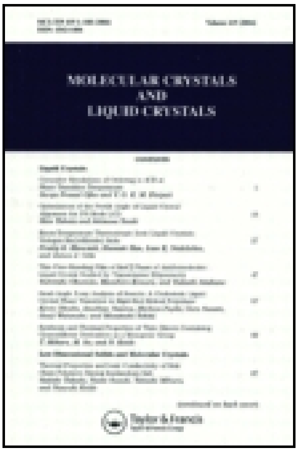

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The Kimura's Approach to the Short-Range Interactions Between a Liquid Crystal and a Polymer Alignment Layer. A Model

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THE KIMURA'S APPROACH TO THE SHORT-RANGE INTERACTIONS BETWEEN A LIQUID CRYSTAL AND A POLYMER ALIGNMENT LAYER. A MODEL.

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Abstract The Kimura's approach to the ordering of the liquid crystals at the free surface is extended on the presence of the polymer molecules at the interface. The polymer molecules are considered to form a fixed network of rod-like molecules (monomers) of given steric parameters and orientational distribution. The model considers the excluded volume approximation as well as the Van der Waals interactions in the simplest Mayer-Saupe form.

INTRODUCTION.

The aligning properties of the polymer layers are of immense importance in the field of liquid crystals applications. The rubbed polymer layers are extensively used in all kind of liquid crystal displays in order to induce a homogeneous alignment of the liquid crystal (LC). The interface interactions between the LC and polymer molecules are widely studied in experiments as well as from theoretical point of view. Among the latter two main approaches can be distinguished. Phenomenological approach, based on the continuum theory of liquid crystal and symmetry properties of the interface [1] and, the microscopic one, considering the molecular interactions in detail [2,3]. The microscopic approach is of particular interest due to the possibility of finding relations between the molecular and structural parameters of the both substances and features of the resulting alignment [3]. The main obstacle in the micromolecular approach is the complicity of the intermolecular potential and a big number of the interacting constants usually very difficult to approximate numerically [2,3]. In our, Kimura's based [2], approach we tried to use the simplest forms of those potentials in order to make the experimental verification possible. In the original work of Kimura and in our model the interface is assumed to be flat on the microscopic level, i.e., we do not take into account the effects coming from long-range, deformational type interactions. According to the existing experimental data those effects (so called microgrooves mechanism) are about two orders of magnitude smaller than the ones arising from the short range molecular interactions.

The model is based on expanding the Kimura's free surface by adding the polymer layer beneath the LC. The results recover the original result for no polymer existing and , on the other hand, the planar alignment in case of high-density, isotropic polymer (hard wall), to provide consistence with the Okano's [4] result. This two expectations form the base of the model verification.

In this paper we study numerically the changes in the surface potential, i.e., energy, responsible for coupling the polymer and liquid crystal at the interface, induced by various molecular factors like polymer density, polymer orientation, temperature, etc.

THEORY.

Lets assume that the potentials between two molecules is of the well known form [5]:

$$U_{ij} = U(\mathbf{a}_i, \mathbf{a}_j, \mathbf{r}_{ij}) = \begin{cases} \infty & \textit{if overlap} \\ -\dfrac{A}{\mathbf{r}_{ij}^6} P_2(\cos(\theta_{ij})) & \textit{otherwise} \end{cases} \tag{1}$$

where θ_{ij} is the angle between $\mathbf{a}_i$ and $\mathbf{a}_j$ versors and P_2 is the second Legandre polynomial. We limit ourselves to the simplest form of the potential but as it will appear later the use of the most general form of the interaction potential between the cigar like molecules can be easy incorporated. This potential has a universal form and can be applied as well to the LC-LC molecules as to Polymer-LC molecules interaction. The difference will be in the A constant and the "overlapping" volume (the excluded volume) which we consider more precisely later.

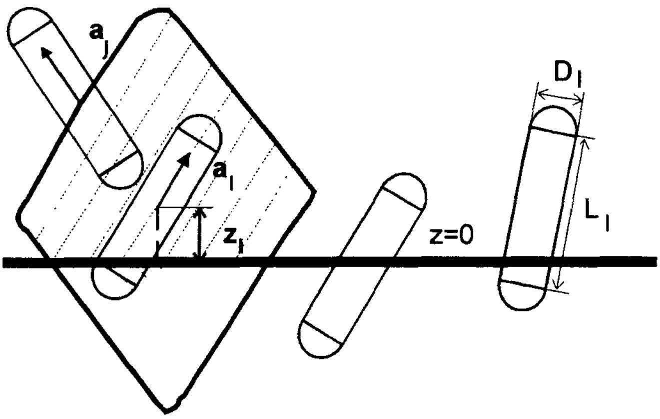

FIGURE 1 The LC molecules at the Kimura free surface [3]. z_i refers to the Z coordinate of the i-molecule, L, D describe the molecule size. The surface is described by the condition z ≥0. Above the surface, distribution of the LC molecules is uniform. Versors a , a point the molecular directions of i j molecules. The shaded area contributes to the excluded volume interactions [3].

Let us treat the plane z=0 as an impenetrable for the centers of mass of LC molecules. Above the surface (z>0) we assume a uniform density of the LC molecules like in Fig.1.

Below the surface, which in fact can be partially penetrated by LC molecules provided that its center of mass fulfills z≥0, let's place the uniformly distributed polymer molecules, all of them oriented parallel to **d** (Fig.2). Steric parameters of the molecules are L_l, D_l and L_p, D_p for LC and polymer respectively.

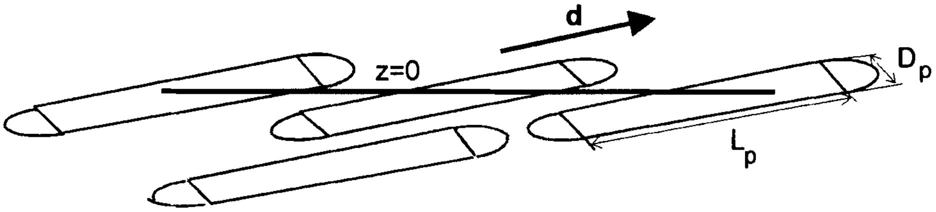

FIGURE 2 Model of polymer molecules placed at the surface (z=0).

The Van der Waals potential between the LC and polymer molecules is assumed to have the same shape as in Eq.1 but the interaction constant is different, A_{lp}.

Construction of a partition function, describing the LC, is led in a similar way as Kimura did, except for the additional terms of excluded volume or Van der Waals potential due to interactions with polymer. The details of the calculation method are published in [3,5], for a general idea of the method see Appendix.

Since the centers of masses of LC molecules can not cross the z=0 level only the upper parts of the excluded volume are to be considered (shaded area in Fig.1 and Fig.3). What is important, the polymer here is not treated as the free media but as a fixed, stiff network, so it will participate in the partition function only as additional, outer constrains. We assume that the direction **d** is known as well as the steric parameters L_p, D_p and A_{lp}. After applying the Kimura approach in order to obtain the free energy we have to calculate the partition function of the form [3]

$$Z(\eta) = \int \cdots \int \prod_{i=1}^{N} d\mathbf{r}_i d\Omega_i \exp\left[\eta \sum_{i=1}^{N} P_2(\mathbf{n}\cdot\mathbf{a}_i) - \sum_{i>j} U_{ij} / kT \right],$$
$$Z(\eta) \cong \{VI_o(\eta)\}^N \left[1 + \tfrac{N^2}{2} \tfrac{1}{\{VI_o(\eta)\}^2} \int \cdots \int d\Omega_i d\Omega_j d\mathbf{r}_i d\mathbf{r}_j f_{ij} \exp\big(\eta P_2(\mathbf{n}\cdot\mathbf{a}_i) + \eta P_2(\mathbf{n}\cdot\mathbf{a}_j) \big) \right] \tag{2}$$
$$I_o(\eta) = \int \exp(\eta P_2(\mathbf{n}\cdot\mathbf{a}_i)) d\Omega_i$$

η is a coefficient of the symmetry breaking potential, **n** the director of the LC [3,6]. The second line of Eq.2 is a second virial approximation and is obtained by the first order expansion in f_{ij}, where:

$$f_{ij} = \exp(-U_{ij} / kT) - 1 \begin{cases} = -1 & \text{if } i \text{ and } j \text{ intersect} \\ \approx -U(\mathbf{a}_i, \mathbf{u}_j, \mathbf{r}_{ij}) / kT,\ \mathbf{u}_j = \mathbf{d}, \mathbf{a}_j & \text{otherwise} \end{cases} \tag{3}$$

In order to calculate the free energy first we perform the spatial integrations:

$$\int\limits_{z_i<0} d\mathbf{r}_i \int\limits_{z_i<0} d\mathbf{r}_j f_{ij} = \int\limits_{z_i<0} d\mathbf{r}_i[-v_{ex}(\mathbf{a}_1,\mathbf{u},z_i)] - \tfrac{1}{kT}\int\limits_{z_i<0} d\mathbf{r}_i \int\limits_{z_i<0} d\mathbf{r}_j U(\mathbf{a}_1,\mathbf{u},r_{ij}),\ \mathbf{u}=\mathbf{d},\,\mathbf{a}_j \tag{4}$$

Excluded volume interactions.

The excluded volume contribution we obtain by integrating the Eq.2b (Eq.4) over space coordinates, i.e.,$d\mathbf{r}_i d\mathbf{r}_j$. The result is equal to the original result of Kimura plus certain modification due to the polymer. After the first spatial integration the excluded volume looks as follows:

$$v_{ex} = \begin{cases} v_{ll}, \quad |z_i| > d(\mathbf{a}_1) + d(\mathbf{a}_j) \\ \frac{1}{2}v_{ll}\left(1 + \dfrac{|z_i|}{d(\mathbf{a}_1)+d(\mathbf{a}_j)}\right) +, \quad 0 < |z_i| < d(\mathbf{a}_1)+d(\mathbf{a}_j) \\ \text{plus additional term comming from interaction with polymer :} \\ +\frac{1}{2}v_{lp}\left(1 - \dfrac{|z_i|}{d(\mathbf{d})+d(\mathbf{a}_1)}\right), \quad 0 < |z_i| < d(\mathbf{a}_1)+d(\mathbf{d}) \end{cases} \tag{5}$$

$$v_{ll} = 2L_l^2 D_l |\mathbf{a}_1 \times \mathbf{a}_j| + v_m = \bar{v}_{ll}|\mathbf{a}_1 \times \mathbf{a}_j| + v_m, \quad v_m = \frac{\pi}{4}2L_l 4D_l^2\left(1 + \frac{2D_l}{3L_l}\right)$$

$$v_{lp} = L_l L_p (D_l + D_p)|\mathbf{a}_1 \times \mathbf{d}| + v_{mp} = \bar{v}_{lp}|\mathbf{a}_1 \times \mathbf{d}| + v_{mp},$$

$$v_{mp} = \frac{\pi}{4}(L_l + L_p)(D_l + D_p)^2\left(1 + \frac{2(D_l + D_p)}{3(L_l + L_p)}\right)$$

where v_{ij} refers to the usual form of the excluded volume between two cylindrical molecules. Other symbols are as in Fig.1 and Fig.3. The $d(\mathbf{u})$ refers to half of the projection of the molecule (LC or polymer) on the Z axis and is equal respectively:

$$d(\mathbf{a}_1) = L_l/2\,(\mathbf{z}\cdot\mathbf{a}_1) + D_l,\ d(\mathbf{d}) = L_p/2\,(\mathbf{z}\cdot\mathbf{d}) + D_p \tag{6}$$

It also corresponds to the maximum depth the chosen molecule can penetrate under the surface plane (z=0).

To evaluate Eq.5 we applied the linear approximation between the excluded volumes for the molecule in the bulk (out of range of polymer or surface, Fig.3) and the molecule which center of mass lies in the z=0 plane [3]. In these calculations we assumed that if a LC molecule penetrates the surface plane (z=d(**d**), Fig.3), the part which is under this plane interact with polymer. Besides, the part of the LC molecule above the surface (z=0) interacts with other LC molecules. This assumption is reasonable for the low density of LC molecules which is in agreement with general approximations used by Kimura (the virial expansion [3]).

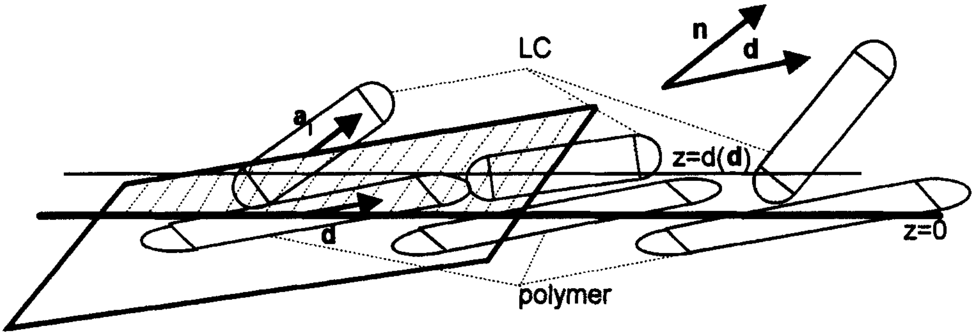

FIGURE 3 The additional contribution from polymer-LC interaction. Only the shaded area is taken into account. This interaction is different to 0 only if LC molecule penetrates the surface (z=d(**d**)), i.e. the range of polymer chains.

Van der Waals interactions.

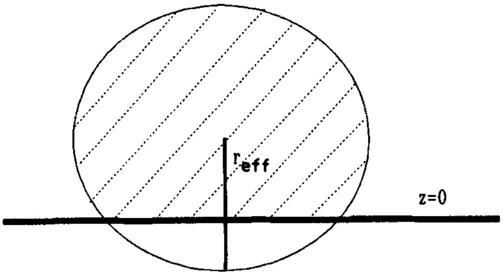

FIGURE 4 The effective range of the Van der Waals potential $(AP_2(\cos(\theta))\frac{1}{r^6})$,.[5]. The shaded area comes from LC-LC, the remaining part from Polymer-LC interactions.

The Van der Waals contribution raises from the spatial integration of the second term in Eq.2. We assume that the part under the surface (z=0) comes from polymer whereas above the surface the interactions are purely between LC molecules. r denotes the distance between centers of mass of the 2 interacting molecules.

Final results are calculated within the Mayer-Saupe approach [5], i.e., the Van der Waals interaction are effective only within certain small volume around the molecule (first neighbors approximation). The range of this interaction we approximate as the average of the molecular length and diameter. On this basis, the combined integral of A and r is given by the Mayer-Saupe constant (A^I_{lp} for polymer-LC and A^I for LC-LC, Eq.7) multiplied by the characteristic distance of the interaction between the LC and surroundings (either LC or the polymer). This simplifications allowed to relate the clearing point temperature to the interaction constants of LC [5].

$$\begin{aligned}
&\rho_p \int A_{lp}(r)dr \approx \rho_p \rho_l A_{lp}^I \\
&\rho_l \int A\ (r)dr \approx \rho_l^2 A^I \\
&\rho_p \int A_{lp}(r)rdr \approx \rho_p \rho_l \tfrac{1}{2}(L_l + D_l) A_{lp}^I = \rho_l^2 A_{lp1} \\
&\rho_l \int A\ (r)rdr \approx \rho_l^2 \tfrac{1}{2}(L_l + D_l) A^I = \rho_l^2 A_1
\end{aligned} \tag{7}$$

where ρ_p, ρ_l denote densities of polymer and liquid crystal respectively.

A Surface Tension.

Finally applying the Kimura's procedure we are able to calculate a surface density of a difference between the free energies of a pure bulk LC and a bulk with surface contribution ([3], see Appendix). This result is a surface tension (γ). The expression for γ looks as follows:

$$\begin{aligned}
\gamma = \tfrac{1}{8}\rho_l^2 kTL_l \Big\{ & \frac{A_1}{L_l kT} S^2 - \frac{A_{lp1}}{L_l kT} S\, P_2(\mathbf{n}\cdot\mathbf{d}) + \left[\tfrac{\pi}{4}(\bar{v}_{lp}/2 - \bar{v}_{ll})\right]\frac{J_0}{I_0} - \\
& \left[\tfrac{5\pi}{32}(\bar{v}_{lp} P_2(\mathbf{n}\cdot\mathbf{d})/2 - \bar{v}_{ll} S)\right]\frac{J_1}{I_0} + \\
& \tfrac{\pi}{4}\left[\bar{v}_{lp}\left(D_p + D_l\right)\left(1 - \tfrac{5}{8}P_2(\mathbf{n}\cdot\mathbf{d})S\right) - 2\bar{v}_{ll} D_l\left(1 - \tfrac{5}{8}S^2\right)\right]/(2L_l) + \\
& \tfrac{\pi}{8}\bar{v}_{lp}\tfrac{L_p}{L_l}\cos(\theta_p)\left(1 - \tfrac{5}{8}S\right) \Big\},
\end{aligned} \tag{8}$$

$$|\mathbf{a}\times\mathbf{b}| \approx \tfrac{\pi}{4} - \tfrac{5\pi}{32} P_2(\mathbf{a},\mathbf{b})$$

where the usual approximation for the vector product was applied, the constants are defined in Eq.7 and Fig.1 and Fig.3 and S is the order parameter of LC (Appendix).

The underlined parts correspond to new terms and include the coupling potential between the director, **n**, and the polymer orientation, **d**, other symbols are defined like in 3.

$$
\begin{aligned}
J_o &= J_o(\eta, \cos(\theta)) = \int \exp(\eta P_2(\mathbf{n}\cdot\mathbf{a}_i))\left|\mathbf{z}\cdot\mathbf{a}_j\right| d\Omega_i \\
J_1 &= J_1(\eta, \cos(\theta)) = \frac{dJ_o}{d\eta} \\
\cos(\theta_p) &= \left|\mathbf{z}\cdot\mathbf{d}\right|
\end{aligned}
\tag{9}
$$

The director orientation is also implicite included in J_0 and J_1 terms and S value.

For order parameter, S, we used values obtained for bulk LC, i.e., without surface and polymer influence, calculated as in [5,3]. Since Eq.8 is calculated by integrating over the whole medium (a cell), therefore the application of the bulk order parameter, S, for further calculations is not connected with a big error. The changes in order parameter occur only close to the surface [1], so they very weakly influence the average value.

Distribution of polymer orientations.

The formula for the surface tension can be easily generalized for different orientations of polymer chains. We approximate the polymer chain as a number of joined rods. Since polymer is treated as outer constrains, the average value of surface tension, as a function of director orientation (**n**), densities, etc. can be obtained by averaging Eq.8 with the polymer orientational distribution function, g(**d**). If we assume coordination system as in Fig.1-3,5 we can write:

$$g(\mathbf{d}) = g(\theta_p, \phi_p), \tag{10}$$

where θ_p, ϕ_p denote polar and azimuthal angles of a chosen polymer direction.

Averaging:

$$\left\langle \gamma(\mathbf{n}) \right\rangle_p = \int_0^{\pi/2} \int_{-\pi}^{\pi} \gamma(\mathbf{n}, \theta_p, \phi_p) g(\theta_p, \phi_p) d\phi \sin(\theta) d\theta \tag{11}$$

Eq.11 allows us to calculate the surface tension of LC dependent on the polymer distribution which can be related to the surface pre-treatment (rubbing) [7]. From the tension profile we can find direction of **n** (easy axis) at minimum of γ(**n**) and anchoring energy values from the tension shape near minimum in **n** .

To obtain the g(**d**) function some experimental results can be applied [7,8]. The most effective are the SHG measurements of the LC monolayer on a rubbed polymer [7]. From these measurements, treating the polymer as stiff, joined rods, a general shape of the polymer orientational distribution function can be extrapolated as:

$$g(\theta_p, \phi_p) = N \exp\left[\frac{-(\theta_p - \theta_o)^2}{2\sigma^2}\right]\left(1 + a\cos(\phi) + b\cos(2\phi)\right) \tag{12}$$

The distribution is described by 4 parameters: $\theta_o, \sigma, a, b,$ Finding the relation between the parameters and the polymer treatment conditions (rubbing) should allow to predict of the resulting LC alignment [7,9,10].

RESULTS.

The orders of model parameters we took from [3,5,8,12]. The parameters chosen for polymer were also established basing on average properties of the polymer applied, values for LC are as for GR41 mixture [8]. The A_{lp} constant was approximated as similar with respect to the molecule length, as for LC-LC interactions. Precise values for polymer can be established from a detailed molecular structure.

$$A = 10^{-75}[J/m^6], \quad A_{lp} = 2*10^{-75}[J/m^6], \quad T \approx 305\,[K],$$

$$D_p = D_L = 5*10^{-10}[m], \quad L_l = 1.5*10^{-9}[m], \quad L_p \cong 2*10^{-9}[m],$$

$$S = 0.4 - 0.6, \quad \rho_l = 2.68*10^{27}[1/m^3], \quad \rho_p \cong 4.7*10^{27}[1/m^3], \quad \mathbf{d} = (\theta_p = \frac{\pi}{2}, \phi_p = \mathbf{0})$$

The general frame of reference used in calculations:

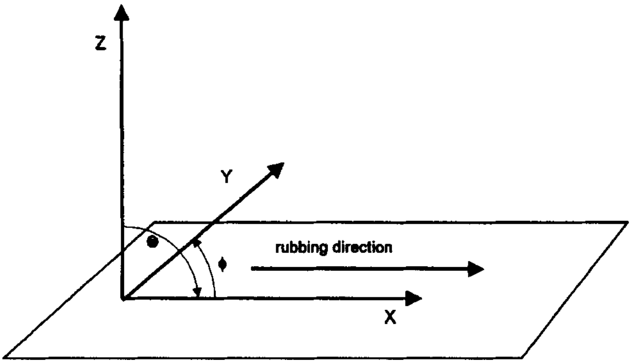

FIGURE 5. Reference frame for the model. The substrate is situated in X-Y plane with X being the rubbing direction.

As a first approximation we assumed that all polymer molecules (monomers) are parallel to **X** axis of the reference frame (very strong rubbing condition).

Some main properties of the surface tension profiles can be easy deduced from the Eq.8, as for instance proportionality to densities. Temperature dependence is not that clear due to the implicit reliance $S = S(T)$. Orders of calculated values are generally in agreement with experimental results [8,9,10,11]. Numerical examples are presented in Fig.6. and Fig.7.

The anchoring force of the LC (polar and azimuthal) can be understood (Fig.6) as a gradient of the surface tension profile with respect to the director orientations (θ,ϕ). The anchoring energy can be evaluated as a difference between the minimum value of γ and the value corresponding to the relevant director orientation. This change in the LC energy is required to allow for the chosen deformation. The minimum of γ in (θ,ϕ) describes the easy axis direction. The corresponding value of θ shows the preferred pretilt angle. Due to the model symmetry (Fig.5) the minimum value of ϕ is equal 0. Eq.8, with γ understood as the anchoring potential, recovers also the popular Rapini-

Papoular potential form in the limit of second order expansion in (θ,ϕ) around the minimum [12] (Fig.5, Fig.6):

$$\gamma - \gamma_{\min} \cong \frac{A_\phi}{2}\sin^2(\phi) + \frac{A_\theta}{2}\sin^2(\theta - \theta_p) \qquad (13).$$

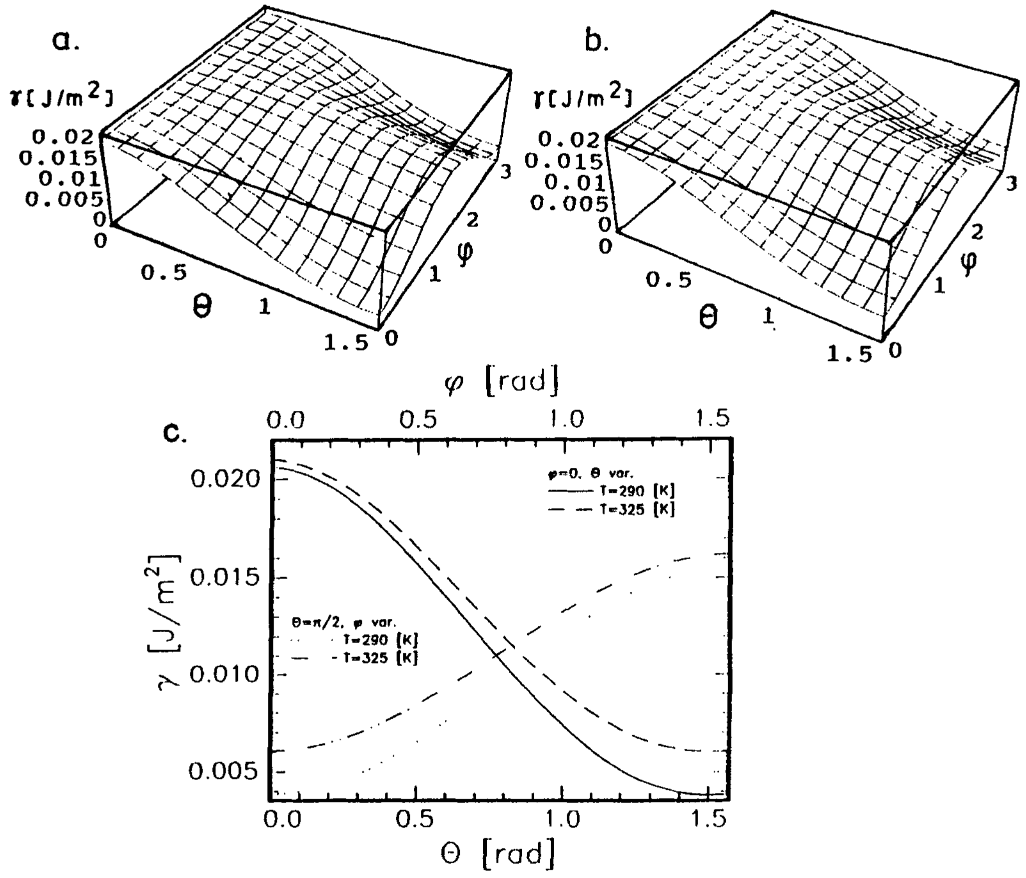

FIGURE 6. The surface tension, γ, as a function of the director, **n**(θ,ϕ), orientation and temperature, T=280 [K] (a), 325 [K] (b). Corresponding values of S(T) are: 0.57 (a), and 0.45 (b). Angles denoted as in Fig.5. In (c) cross sections near the minimum of γ a numerical fit of Eq.13 covers idealy with caculated curves near minimum (Eq.8)[12]

Numerically fitted values of A_ϕ and A_θ are (Eq.13,Fig.6):

TABLE I. Calculated anchoring energies for small distortions.

T [K]	A_ϕ [J/m^2]	A_θ [J/m^2]
280	0.023	0.025
325	0.020	0.022

The shape of the surface tension profile as a function of the director orientation changes with temperature increase (Fig.6.). The corresponding values of the anchoring energies decrease and similarly the pretilt angle (Fig.6(c), Tab.I). The values obtained in Tab.I are a little high but this is the case of ideal polymer orientation which is difficult to reach in real process [8,9]. Incorporation of polymer disribution (Eq.10) should lead to correct values [13].

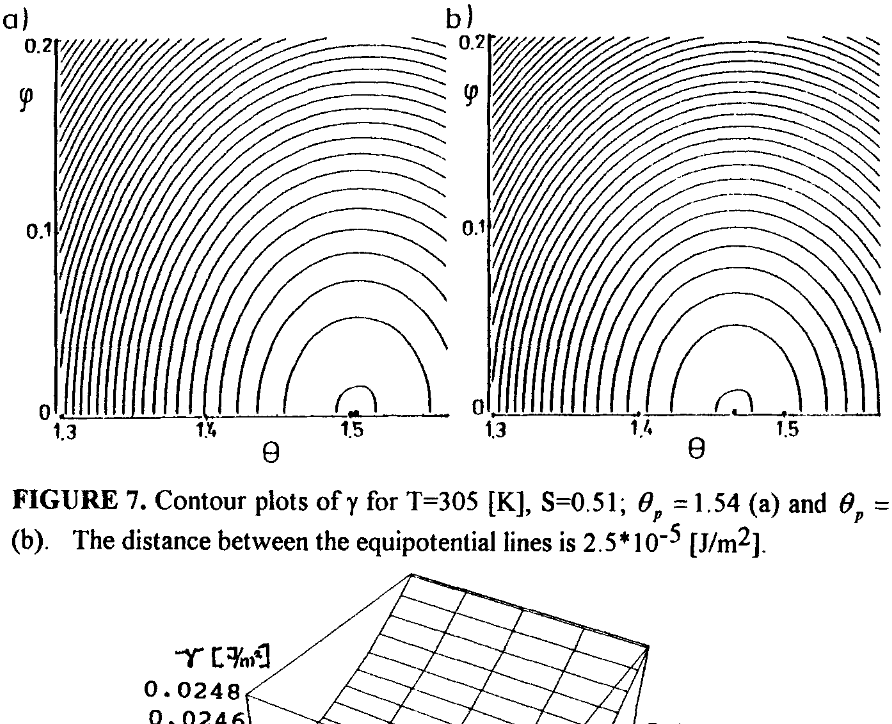

FIGURE 7. Contour plots of γ for T=305 [K], S=0.51; $\theta_p = 1.54$ (a) and $\theta_p = 1.5$ (b). The distance between the equipotential lines is 2.5*10^{-5} [J/m^2].

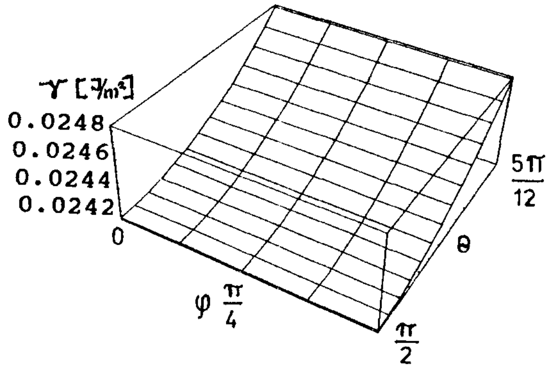

FIGURE 8. γ for isotropic (L_p=0, A_{lp}=0) polymer. T=305[K], S=0.51. Polymer density ρ_p=2.23*10^{28} (the same volume concentration as for previous calculations).

From Fig.7 we notice that the director orientation follows the polymer molecules direction. But some small difference between the easy axis direction (θ) and the relevant polymer inclination (θ_p) exist. Originally, this difference is caused by Kimura's "free surface" terms preferring the homeotropic alignment. This effect can be compensated by high density of polymer (which is a real case) and also by other terms of the intermolecular potential (Eq.1, [3]). However, in the experimental measurements these kind of pretilt shift was also observed [8].

Finally we calculated the anchoring profile for isotropic polymer layer (L_p=0). This result (Fig.8) confirmed the Okano prediction of the excluded volume interaction near a hard wall, what also support the model validity [4]. The resulting alignment, in agreement with expectations, is homogenous without any orientational preferences in XY plane.

CONCLUSIONS:

The model developed seems to be working quite well in the wide range of the parameters. Using the model we are able to predict the anchoring energy profile for nematic director provided that we know the microscopic parameters of the system, including the alignment layer. The values of the azimuthal and polar anchoring energies can be evaluated as well as the direction of preferred pretilt angle. The numerical values obtained are reasonable in order of magnitude. As it is seen from Eq.8 the parameters of essential importance are the molecular properties of polymer molecules and they, first of all, should be approximated very precisely.

The influence of polymer orientational distribution can be easily incorporated, and what follows, the influence of rubbing process can be simulated and with relation to its influence on the anchoring and pretilt conditions, what we would like to study in the future [13]

APPENDIX.

General scheme of the Kimura's calculation method is based on the symmetry breaking potential or canonical transformation of the partition function, Z' [6]. Let the free energy be:

$$F(S)=-kT\ln[Z'(S)] \tag{A1}$$

where $S=\left\langle \frac{1}{N_l}\sum_{i=1}^{N} P_2(\mathbf{n}\cdot\mathbf{a}_i)\right\rangle$ and N_l is a number of molecules. The canonical partition function can be expressed [3,5]:

$$Z(\eta)=\int_{\Gamma}\exp(\eta S)Z'(S)d\Gamma \tag{A2}$$

where Γ denotes the thermodynamic space. Having performed both, the space and the angular integrations on Eq.2 we obtain the free energy as in Eq.A2, $Z(\eta)$. The canonical average of S is equal:

$$S=N_l^{-1}\partial\ln[Z(\eta)]/\partial\eta \tag{A3}$$

from Eq.A3 we can find η(S) and the free energy of the system is written [3,5]:

$$F(S) = F(0) + N_t kT \int_0^S \eta(S) dS \qquad \text{(A4)}$$

The minimum condition for F(S) is expressed as [6]:

$$\eta(S) = 0 \qquad \text{(A5)}$$

S can be evaluated from Eq.A2,A3 and Eq.2:

$$S = S(I_0, I_1, J_0, J_1; A, L, D, \mathbf{d}) \qquad \text{(A6)}$$

where $I_1 = dI_0 / d\eta$, I_0, J_0, J_1 are defined in Eq.9,2. Other parameters refer to the interaction constants and molecular sizes. Eq.A6. can be solved in the first order approximation with respect to the molecular interaction constants and gives the formula for [3,5]

$$\eta(S) = \eta(S; I_0, I_1, J_0, J_1; A, L, D, \mathbf{d}) \qquad \text{(A7)}$$

The free energy of the system can be now found from Eq.A4, and this result was used in Eq.8. In case of the surface interactions finding solution for S from Eq.A5 with use of Eq.A7 is very complex so we found the solution of Eq.A5,A7 for pure, bulky liquid crystal as in [5]. This value of S was used in further calculations.

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