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Liquid Crystals

Publication details, including instructions for authors and subscription information:
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To cite this Article Grosberg, A. Yu. and Pachomov, D. V.(1991) 'The structure of the nematic-isotropic interface in polymer systems', Liquid Crystals, 10: 4, 539 — 553

To link to this Article: DOI: 10.1080/02678299108036441

URL: http://dx.doi.org/10.1080/02678299108036441

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LIQUID CRYSTALS, 1991, VOL. 10, NO. 4, 539–553

The structure of the nematic–isotropic interface in polymer systems

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(*Received 2 October 1990; accepted 19 April 1991*)

The structure of the nematic–isotropic interfacial layer is studied theoretically for systems formed by rod-like and persistent macromolecules. It is shown that the width of interfacial layer is normally of the order of the straight part of a molecule. This allows us to use the approach which describes intermolecular interactions phenomenologically (i.e. it allows us to consider all interactions), at the same time this approach describes molecular flexibility microscopically (i.e. it allows us to study the effects of flexibility correctly). It was found, that non-monotonic gradient profiles in the surface layer of the order parameter or of the concentration of molecules as a function of the coordinate perpendicular to the interface are possible. For example, a thin layer with abnormal ordering of molecules along the surface may exist near the interface for some systems.

1. Introduction

The problem of determining the interfacial structure for a system exhibiting a first order phase transition is one of the general questions in condensed matter physics. The application of this question to the nematic–isotropic interface has attracted a great deal of attention in recent years [1]. Such a problem was considered first by van der Waals [2] who dealt with the ordinary liquid–gas interface. In the framework of his theory the structure of the interface was described in terms of a spatial density or concentration, c, profile and the profile

$$c(x)=\frac{c_1+c_2}{2}+\frac{c_1-c_2}{2}\tanh(x/L), \tag{1}$$

was obtained where x is the coordinate normal to the interfacial surface, L is the characteristic length for the concentration gradient and c_1 and c_2 are concentrations in the coexisting phases. One of the important results of the classic van der Waals theory was the explanation of the fact that sometimes the interfacial structure may be analysed macroscopically. This proves to be possible when the characteristic length L is large enough. For the ordinary liquid–gas interface L is only large enough in the neighbourhood of the critical point. However in this situation the van der Waals theory, being a mean field theory, is inapplicable due to the great fluctuations in the critical region. As we shall explain in this paper, for polymer systems, especially for polymer liquid crystals, L becomes macroscopic, in a certain sense, even far from the critical point. This fact alone allows us to construct a theory for the nematic–isotropic interface for polymer systems. Generally speaking, the description of the surface layer for liquid crystals is a more complex problem than for ordinary liquids, because it

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requires us to take into account not only the concentration profile $c(x)$ but also the orientational order parameter profile $\alpha(x)$.

The sequential microscopic approach to the problem under consideration is quite complicated. If we try to work out a complete microscopic theory and to do this we choose from the very beginning the particular form of the molecular interaction potential, then it will be necessary to calculate not only the interfacial structure of interest, but also (and in fact first of all) the macroscopic equation of state, in other words to solve the general problem of a microscopic theory for simple liquids. As is well-known, such a calculation necessarily includes some assumptions (for example the second virial approximation). These assumptions are much more unclear for spatial non-uniform systems with long range orientational correlations. Although some theories of this type have been given [3, 4] the search for more constructive approaches remains of interest. The simplest phenomenological approach is based on the assumption that both $c(x)$ and $\alpha(x)$ obey equation (1) in the surface layer. This was used for the athermal solution of rod-like molecules [5]; however the same interface has been considered, using another *a priori* assumption of an abrupt change of the order parameter [6].

Our approach here concerns polymer molecules and is based on the explicit consideration of two strongly distinguished length scales. For the simplest polymeric mesogens, such as rod-like or worm-like molecules, these two characteristic lengths are d and l: d is the thickness of the chain or the characteristic radius of volume interactions between segments of a polymer, and l is the length of a rod or a Kuhn segment of the persistent worm-like chain. For real polymers the l/d ratio varies from about 7 for flexible chains (such as polystyrene) to about 50 for the DNA double helix [7] or more for other rigid chains. The inequality $l/d \gg 1$ means that the spatial scale of orientational correlations, which spread over distances of order l, is essentially larger than the scale of molecular interactions, which is of order d (see figure 1). Therefore, as it is easy to see in figure 1, two opposite ends of a macromolecular segment, having practically the same directions, take part in intermolecular collisions and interactions in different

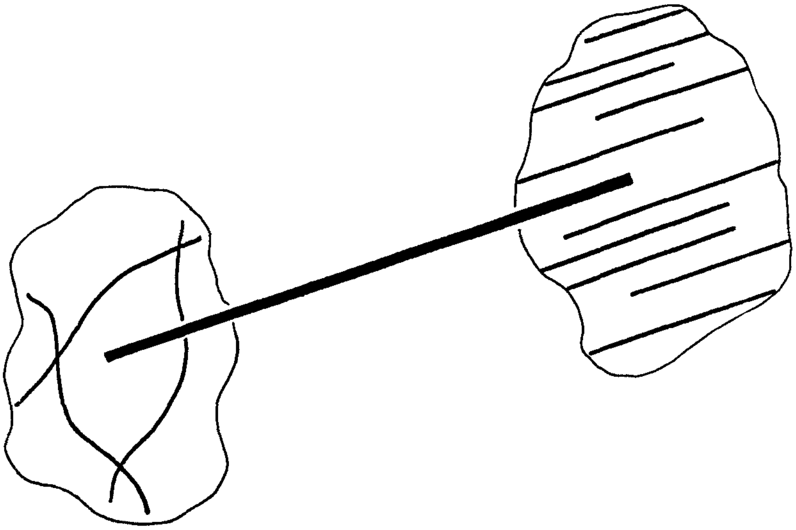

Figure 1. The straight segment of a molecule in spatially non-uniform surrounding is shown. Two opposite ends of such a segment are placed at distant space points with different orientational order parameters and densities.

regions of space with different order parameters and densities of the surrounding particles.

Our approach can be characterized as phenomenological within the length scale of order d and as microscopic at scales of order l or more. Our main idea is to write the free energy of the system as

$$F=\int \varepsilon d^3\mathbf{r}+F_{\text{orient}}+F_{\text{gradient}}. \tag{2}$$

Here the first term corresponds to the contribution of volume interactions, the density ε is formed within the d scale (see figure 1). Its calculation is a problem of the statistical theory of liquids, but we shall suppose it to be a known local function of density and order parameter. This is the phenomenological part of our approach. At the same time F_{orient} and F_{gradient} are caused by the orientational correlations and are formed on the length scales of order l. We shall calculate them subsequently using the Lifshitz method known in polymer theory [8]. This is the microscopic part of our approach. In fact, the free energy representation in the form of equation (2) is one of several possible versions of a mean field formulation and it is known in polymer theory that this approximation is valid for rigid chains with $l/d\gg 1$ (see, for example [9]). Here we shall consider two different systems: one formed by rod-like molecules and another by hard chain persistent (worm-like) molecules. It is important to consider these different types of molecular flexibility separately because liquid crystals formed by different molecules differ essentially from each other, for example by their elasticity constants [10, 11].

The paper is organized as follows. In § 2.1 we introduce the distribution function to describe polymer systems. In § 2.2 we obtain the free energy of spatial non-uniform states of macromolecular systems as a function of the distribution function, the self-consistent potential being given. In §§ 2.3 and 2.4 we find the self-consistent field potential supposing the free energy of the homogeneous state to be known. In § 2.5 we consider the combined minimization equations for weak orientational anisotropy. The qualitative discussion of the minimization equations is given in § 3.1. The results obtained for systems formed by molecules with different kinds of flexibility are compared in § 3.2. In § 3.3 the graphical method of solving the equations is described. Some possible structures of the interfacial layer are presented in § 3.4.

2. Main equations

2.1. *Generalized distribution function of the system*

Let us start with the definition of the distribution function, most convenient for the description of spatial non-uniform states of our system. It is the function $f(\mathbf{r},\mathbf{n})$, the distribution function, which is proportional to the number of molecular parts spaced at the point $\mathbf{r}$ with the direction of the unit tangential vector $\mathbf{n}$. Of course, in the case of interest here, i.e. near the flat interface all $\mathbf{r}$ dependencies are in fact one-dimensional and can be reduced to an x dependency. The function $f(\mathbf{r},\mathbf{n})$ contains information on the spatial distribution of polymer concentration $c(\mathbf{r})$ as well as on the local orientational distribution $f_{\mathbf{r}}(\mathbf{n})$. Really,

$$c(\mathbf{r})=\int f(\mathbf{r},\mathbf{n})\,d\Omega_{\mathbf{n}},$$

is the total density of polymer links with all possible orientations placed near the point $\mathbf{r}$; and

$$f_{\mathbf{r}}(\mathbf{n}) = f(\mathbf{r}, \mathbf{n})/c(\mathbf{r}); \quad \int f_{\mathbf{r}}(\mathbf{n})\, d\Omega_{\mathbf{n}} = 1,$$

is the orientational distribution of these segments. Therefore,

$$\alpha(\mathbf{r}) = \int f_{\mathbf{r}}(\mathbf{n}) P_2(\mathbf{n})\, d\Omega_{\mathbf{n}},$$

for uniaxial symmetry or

$$\alpha_{lm}(\mathbf{r}) = \int f_{\mathbf{r}}(\mathbf{n}) Y_{lm}(\mathbf{n})\, d\Omega_{\mathbf{n}},$$

for the general case of a local orientational ordering tensor (P_2 and Y_{lm} are Legendre polynomial and spherical harmonic functions, respectively).

Using the $f(\mathbf{r}, \mathbf{n})$ function as a Landau order parameter and equation (2) for the free energy, we can obtain the local dependence of the energy term $\int \varepsilon d^3\mathbf{r}$ on this generalized order parameter, i.e. $\varepsilon = \varepsilon(\mathbf{r}) = \varepsilon(c(\mathbf{r}), \{f_{\mathbf{r}}(\mathbf{n})\})$, or, in the simple case, $\varepsilon = \varepsilon(c(\mathbf{r}), \alpha(\mathbf{r}))$; later we shall assume the dependence $\varepsilon = \varepsilon(c, \alpha)$ to be known. We note that in the theory of liquid crystals the other distribution function is usually used, but it is less convenient for us. For example, a system of rod-like molecules is usually characterized by the distribution of directions $\mathbf{n}$ of the initial parts of rods (but not arbitrary ones as we have chosen) placed near the point $\mathbf{r}$ (see, for example, [5]). In this case the entropy is a local functional, but the interaction energy turns out to be a complex non-local one, without the standard methods of calculations.

The other terms F_{orient} and F_{gradient} can be interpreted in a standard way, as the so-called conformational entropy. In fact, this part is determined by the number of replacements of unbroken chains with given flexibility mechanism in the surface layer with the fixed distribution $f(\mathbf{r}, \mathbf{n})$, i.e. with fixed concentration and order parameter profiles $c(\mathbf{r})$ and $\alpha(\mathbf{r})$ (or $c(x)$ and $\alpha(x)$ for a flat interface). For this entropy calculation there exists in polymer theory the standard Lifshitz method [8].

2.2. *Free energy of a polymer molecule placed in spatial non-uniform surroundings*

To use the mean field approximation (which is applicable due to the inequality $l/d \gg 1$, see [9]), it is necessary to calculate the free energy from equation (2) for an arbitrary distribution $f(\mathbf{r}, \mathbf{n})$ and then to minimize F with respect to f, i.e. to solve the Euler equation of the type $\delta F/\delta f = 0$. As to the energy term, we can write:

$$\delta\left(\int \varepsilon d^3\mathbf{r}\right)\Big/\delta f = U(\{f(\mathbf{r}, \mathbf{n})\}), \tag{3}$$

where U is the self-consistent field which describes the effective interactions between chain links and which does not depend on the molecular flexibility mechanism. The main problem is the evaluation of the conformational entropy for an arbitrary distribution $f(\mathbf{r}, \mathbf{n})$.

2.2.1. *A system of rod-like molecules*

For a system of rod-like polymers we have obtained (see the Appendix) the expressions:

$$F_{\text{orient}} = \int f(\mathbf{r}, \mathbf{n}) \ln (f(\mathbf{r}, \mathbf{n}))\, d^3\mathbf{r}\, d\Omega_{\mathbf{n}},$$

$$F_{\text{gradient}} = \frac{l^2}{24} \int \frac{(\mathbf{n} \cdot \nabla f)}{f(\mathbf{r}, \mathbf{n})} d^3\mathbf{r}\, d\Omega_{\mathbf{n}}.$$

Here $\mathbf{n} \cdot \nabla$ is the derivative operator with respect to the coordinates of the direction $\mathbf{n}$. In the case of interest here, near the flat interface, the distribution $f(\mathbf{r}, \mathbf{n})$ depends only on the x coordinate (normal to the interface), $f(\mathbf{r}, \mathbf{n}) = f(x, \mathbf{n})$ and

$$\mathbf{n} \cdot \nabla = \cos(\theta^*)\, d/dx,$$

where θ^* is the angle between the molecular direction $\mathbf{n}$ and the x axis. The result for the free energy minimization given by equation (2) in this one-dimensional case can be written as

$$\left.\begin{aligned} \frac{l^2}{24}\cos^2\theta^*\left(\frac{2f''}{f} - \frac{f'^2}{f^2}\right) &= U\{f(x, \mathbf{n})\} + \partial F_{\text{orient}}/\partial f - \mu, \\ \partial F_{\text{orient}}/\partial f &= \ln(f) + 1, \end{aligned}\right\} \tag{4}$$

where $(\ldots)' = d(\ldots)/dx$, μ is a lagrangian multiplier defined by the normalization condition

$$c(x) = \int f(x, \mathbf{n})\, d\Omega_{\mathbf{n}}.$$

2.2.2. *A system of persistent molecules*

The conformational entropy for a system of infinite worm-like persistent chains with given distribution $f(\mathbf{r}, \mathbf{n})$ can be calculated using the Lifshitz method [11]

$$F_{\text{orient}} = \int \psi(\mathbf{r}, -\mathbf{n}) \Delta_{\mathbf{n}}(\psi(\mathbf{r}, \mathbf{n}))\, d^3\mathbf{r}\, d\Omega_{\mathbf{n}},$$

$$F_{\text{gradient}} = l \int \psi(\mathbf{r}, -\mathbf{n})\mathbf{n} \cdot \nabla(\psi(\mathbf{r}, \mathbf{n}))\, d^3\mathbf{r}\, d\Omega_{\mathbf{n}},$$

where $\psi(\mathbf{r}, \mathbf{n})$ is the auxiliary function, associated with $f(\mathbf{r}, \mathbf{n})$ via

$$f(\mathbf{r}, \mathbf{n}) = \psi(\mathbf{r}, -\mathbf{n}) \cdot \psi(\mathbf{r}, \mathbf{n}), \tag{5}$$

$\Delta_{\mathbf{n}}$ is the angular part of the Laplace operator.

The condition for a minimum free energy F given by equation (2) leads to

$$-l\mathbf{n} \cdot \nabla(\psi(\mathbf{r}, \mathbf{n})) = \Delta_{\mathbf{n}}(\psi(\mathbf{r}, \mathbf{n})) + (U\{f(\mathbf{r}, \mathbf{n})\} - \mu) \cdot \psi(\mathbf{r}, \mathbf{n}), \tag{6}$$

which for persistent chains plays the same role as equation (4) for rod-like particles where, as it will be important later,

$$\Delta_{\mathbf{n}}(\psi(\mathbf{r}, \mathbf{n}))/\psi(\mathbf{r}, \mathbf{n}) = \delta F_{\text{orient}}/\delta f.$$

For the sake of clarity we discuss the qualitative explanation of the physical meaning of equation (6). This is well-known in polymer theory; it can be called the Lifshitz equation. The polymer chain can be imagined as the trajectory of a brownian particle in $(\mathbf{r}, \mathbf{n})$ space, i.e. in the space of coordinates and orientations. In this terminology $\psi(\mathbf{r}, \mathbf{n})$ is the distribution function of chain end or of the generalized coordinates of a walking particle. This function is analogous to the quantum mechanical ψ function, and so it should obey some diffusion-like equation; equation (6) is just of this type. The term with $\Delta_\mathbf{n}$ describes simple diffusion in orientational space. The term with $l\,\mathbf{n}\cdot\nabla$ describes the drift of a particle along the $\mathbf{n}$ direction to distances of order l in $\mathbf{r}$ space, i.e. it reflects the persistent flexibility mechanism of a chain with persistent length l. The term with $U\psi$ describes sources and drains in the brownian motion problem and characterizes the difference between probabilities for the chain to be placed at different spatial points with different values for the potential U. Finally, the term $\mu\psi$ arises from a time derivative of the non-steady state diffusion equation, because the solution we are interested in depends upon time as $\exp(\mu t)$.

In the one dimensional case near the flat interface, as in equation (4), $\psi(\mathbf{r}, \mathbf{n}) = \psi(x, \mathbf{n})$ and

$$\mathbf{n}\cdot\nabla = \cos(\theta^*)\,d/dx.$$

To solve our problem, we should

(i) determine the self-consistent potential $U\{f\}$ from physical reasons, and
(ii) elaborate the method for the solution of equations (4) or (6) with the boundary conditions $f(x, \mathbf{n})|_{x\to-\infty} = f_{\text{iso}}(\mathbf{n}), f(x, \mathbf{n})|_{x\to+\infty} = f_{\text{aniso}}(\mathbf{n})$, where $f_{\text{iso}}(\mathbf{n}) = 1/4\pi$ and $f_{\text{aniso}}(\mathbf{n})$ are equilibrium molecular orientational distributions in coexisting phases.

2.3. *The self-consistent potential*

The self-consistent field U is defined by the character of volume interactions of the macromolecular segments. When a phenomenological description of the volume interactions is used, then it is natural to characterize them macroscopically, with equation of states for a spatial uniform system, instead of intermolecular potential modelling. We shall use the equation of states in the form of the dependence of the free energy on concentration c and orientational order parameter $\hat{\alpha}: F = F_0(c, \hat{\alpha})$ (here $\hat{\alpha}$ symbol denotes the three components of the tensorial order parameter α_{lm}). It is noteworthy, that we shall suppose the $F_0(c, \hat{\alpha})$ dependence to be known not for equilibrium values of c and $\hat{\alpha}$ only, but rather for arbitrary ones. The free energy $F_0(c, \hat{\alpha})$ for our system would have two minima, which correspond to the isotropic ($c = c_\text{i}$, $\hat{\alpha} = \hat{\alpha}_\text{i} = 0$) and to the liquid-crystalline ($c = c_\text{a} > c_\text{i}$, $\hat{\alpha} = \hat{\alpha}_\text{a} \neq 0$) phases.

Since the function $F_0(c, \hat{\alpha})$ is the free energy of a spatial uniform (and, consequently, phase uniform) system, than $F_{\text{gradient}} = 0$ and

$$F_0(c, \hat{\alpha}) = \int \varepsilon d^3\mathbf{r} + F_{\text{orient}}.$$

Therefore, the self-consistent field U, in accord with equation (3), can be written as

$$U = \delta\left(\int \varepsilon d^3\mathbf{r}\right)\Big/\delta f = \delta(F_0(c, \hat{\alpha}) - F_{\text{orient}})/\delta f. \tag{7}$$

However, just the combination of the type $U+\partial F_{\mathrm{orient}}/\partial f$ is involved in equations (4) and (6), as it ought to be physically. So, equations (4) and (6) can be formulated using just the field

$$U_0=\delta(F_0(c,\vec{\alpha}))/\delta f. \tag{8}$$

It leads to simplified equations of the form

$$\frac{l^2}{24}\cos^2\theta^*\left(\frac{2f''}{f}-\frac{f'^2}{f^2}\right)=U_0\{f(x,\mathbf{n})\}-\mu, \tag{9}$$

for rod-like particles (instead of equation (4)) and

$$-l\cos\theta^*(\psi(x,\mathbf{n}))'=(U_0\{f(x,\mathbf{n})\}-\mu)\cdot\psi(x,\mathbf{n}), \tag{10}$$

for worm-like persistent chains (instead of equation (6)).

2.4. *The symmetry of the distribution function $f(\mathbf{r},\mathbf{n})$ and of the self-consistent potential U_0*

Most of the polymer bulk nematics have uniaxial orientational symmetry and only we consider this case here. It means, that in the standard expansion of the type

$$f(\mathbf{r},\mathbf{n})=c(\mathbf{r})\cdot(1+\alpha(\mathbf{r})P_2(\cos\theta)+\alpha_1(\mathbf{r})Y_{21}(\theta,\varphi)+\alpha_2(\mathbf{r})Y_{22}(\theta,\varphi)), \tag{11}$$

the α_1 and α_2 components of $\vec{\alpha}$ should be zero in the equilibrium bulk material only, of course, if a suitable coordinate system is used. For our problem this can be constructed as follows: let θ be the angle between $\mathbf{n}$ and the director of the bulk volume of liquid crystal, and let φ be the angle between $\mathbf{n}$ and the line perpendicular to the director and lying in the plane of the director and the normal to the interface. In this coordinate system the $f(\mathbf{r},\mathbf{n})=f(x,\mathbf{n})$ function does not depend on φ in the bulk liquid crystal, i.e. $\alpha_1=\alpha_2=0$ in the liquid-crystalline phase. In the isotropic phase $\alpha=\alpha_1=\alpha_2=0$ by definition. Therefore, the structure of the flat interface can be characterized with concentration profiles $c(\mathbf{r})=c(x)$, which change from c_i to c_a, of order parameter $\alpha(\mathbf{r})=\alpha(x)$, which change from zero to α_a, and of $\alpha_1(x)$ and $\alpha_2(x)$, which can be non-zero only in the interface.

If $f(\mathbf{r},\mathbf{n})$ has the symmetry form from equation (11), then the self-consistent field U_0, accordingly to equation (8), has the same symmetry. As can be easily proven using equation (8), the expression

$$U_0(\mathbf{r},\mathbf{n})=u_{00}(\mathbf{r})+u_{20}(\mathbf{r})P_2(\cos\theta)+u_{21}(\mathbf{r})Y_{21}(\theta,\varphi)+u_{22}(\mathbf{r})Y_{22}(\theta,\varphi) \tag{12}$$

is valid for U_0 where

$$\left.\begin{aligned} u_{00}&=(1/4\pi)(\partial F_0/\partial c-(1/c)(\alpha\partial F_0/\partial\alpha+\alpha_1\partial F_0/\partial\alpha_1+\alpha_2\partial F_0/\partial\alpha_2)),\\ u_{2i}&=5/4\pi(2-i)!/(2+i)!(1/c)(\partial F_0/\partial\alpha_i).\end{aligned}\right\} \tag{13}$$

2.5. *Equation analysis for the case of weak anisotropy*

Equations (9) and (10), describing the interfacial structure, are too complicated for an analytical solution and even for a numerical one. For their qualitative analysis we suppose that the anisotropy of the distribution function $f(\mathbf{r},\mathbf{n})$ is small at any spatial point. We wish to emphasize, that this assumption will allow us to obtain some results, whose physical meaning gives an expectation that they are also qualitatively applicable in the general case.

2.5.1. *A system of rod-like molecules*

According to our assumption $|\alpha|$, $|\alpha_1|$, $|\alpha_2| \ll 1$. Using these inequalities and expressions (11) for $f(\mathbf{r}, \mathbf{n})$ and (12) for $U_0(\mathbf{r}, \mathbf{n})$, it is easy to convert equation (9) into the combined equations

$$l^2 \frac{(c^{1/2})''}{c^{1/2}} = 18\kappa, \tag{14a}$$

$$5\chi = 2\kappa P_2(\theta_0), \tag{14b}$$

$$\alpha_1 = \kappa P_{21}(\theta_0), \quad \alpha_2 = \kappa P_{22}(\theta_0), \tag{14c}$$

where $\chi = (1/c)\,\partial F_0/\partial\alpha$ and $\kappa = \partial F_0/\partial c - \mu$ are known functions of c and α, θ_0 is the angle between the director of the liquid-crystalline bulk phase and the normal to the interface. P_{ij} are the associated Legendre polynomials. The solution of equation (14) with the given boundary conditions allows us to obtain the interfacial structure for rod-like molecules.

2.5.2. *A system of persistent molecules*

Equation (10) deals with auxiliary function $\psi(\mathbf{r}, \mathbf{n})$ instead of $f(\mathbf{r}, \mathbf{n})$. Nevertheless, for this function an expansion of the type

$$\psi(x, \mathbf{n}) = \sum_{l=0}^{2} \sum_{m=0}^{l} \psi_{lm}(x) Y_{lm}(\theta, \varphi),$$

is valid for the case of small α due to the relation of equation (5) between functions f and ψ (but it contains the $l = 1$ terms because $\psi(\mathbf{r}, -\mathbf{n}) \neq \psi(\mathbf{r}, \mathbf{n})$, unlike $f(\mathbf{r}, -\mathbf{n}) = f(\mathbf{r}, \mathbf{n})$). It is useful to mention that the functions $\psi_{lm}(x)$ under the constraint of $\alpha \ll 1$ are proportional to the following powers of the order parameter: $\psi_{00} \sim \alpha^0$; $\psi_{1m} \sim \alpha^{1/2}$; $\psi_{2m} \sim \alpha^1$. Equation (5) leads to the following relations between the components $\psi_{lm}(x)$ and $c(x)$, $\alpha(x)$

$$c(x) = \psi_{00}^2(x) - (\psi_{10}^2(x) + \psi_{11}^2(x))/3\psi_{00}^2(x),$$

$$\alpha(x) = 2\psi_{20}(x)/\psi_{00}(x) - (2\psi_{10}^2(x) - \psi_{11}^2(x))/3\psi_{00}^2(x),$$

$$\alpha_1(x) = 2\psi_{21}(x)/\psi_{00}(x) - (2\psi_{10}(x) \cdot \psi_{11}(x))/3\psi_{00}^2(x),$$

$$\alpha_2(x) = 2\psi_{22}(x)/\psi_{00}(x) - \psi_{11}^2(x)/6\psi_{00}^2(x).$$

Using this expansion and equations (5), (10), (11) and (12), we can obtain the following combined equations for the system of persistent chains

$$l^2 \frac{(c^{1/2})''}{c^{1/2}} = 6\kappa, \tag{15a}$$

$$5\chi = 2(\kappa - (c^{1/2})'^2/4c)P_2(\theta_0), \tag{15b}$$

$$\alpha_1 = (\kappa - (c^{1/2})'^2/4c)P_{21}(\theta_0), \quad \alpha_2 = (\kappa - (c^{1/2})'^2/4c)P_{22}(\theta_0), \tag{15c}$$

where χ and κ are the same functions as in equations (14) and θ_0 is, as before, the angle between the director of the liquid-crystalline bulk phase and the normal to the interface.

We can see that the systems of equations (14) and (15) have the same structure. First of all, equations (14 *b*) and (15 *b*) give us the local relations between the functions $c(x)$ and $\alpha(x)$ in the surface layer. These local relations play the key role in our theory. They mean physically, that the local concentration and local order parameter balance each other through the local d scale volume interactions and under the influence of self-consistent space gradient of the l scale. If these relations are known, then the concentration profiles can be found from equations (14 *a*) and (15 *a*); finally, the functions $\alpha_1(x)$ and $\alpha_2(x)$ can be found from equations (14 *c*) and (15 *c*).

3. The results

3.1. *Qualitative discussion: turn effect*

We discuss now the solutions of the equations obtained. From equations (9) and (10) it can be seen that orientational ordering in the interface layer is produced not only by specific forms and interactions of mesogenic molecules, but also by the concentration gradient. Thus even if we have the interface between two coexisting isotropic phases of different concentrations, the concentration gradient will produce in the surface layer some orientational ordering in accord with equations (9) or (10) depending on the mechanism of molecular flexibility. Such an effect was discussed previously [3]: it was shown that the order parameter differ from zero in the layer separating isotropic and gaseous phases in a system of rod-like molecules.

The effect of orientational ordering induction due to a spatial concentration gradient has a simple physical meaning and can be called the turn effect. The origin of this name is especially clear for the case of extremely long worm-like chains. To form the concentration gradient in some layer it is necessary for each chain having one end on the region of higher density to have a high probability to turn out in this layer and put its other end back. Moreover, this turn effect can produce a non-trivial type of orientational ordering in the interfacial layer with negative values of α, i.e. with a preferable arrangement of the molecular parts along the surface plane. This possibility was demonstrated earlier [12], where it was shown that spontaneous orientational ordering with $\alpha<0$ exists at the boundary of an isolated globule formed by a long persistent chain.

To understand the nature of the turn effect it is useful to consider the simplest artificial non-realistic case when the self-consistent field U (but not U_0) has uniaxial symmetry, i.e. U is proportional simply to $P_2(\cos\theta)$ not only in the bulk material, but even in the interfacial layer. It was found that in this case the distribution function can be written as

$$f(x,\mathbf{n})=c(x)(1+\alpha_0(x)P_2(\cos\theta)+\alpha^*(x)P_2(\cos\theta^*)).$$

We note that θ is the angle between the molecular vector $\mathbf{n}$ and the director of the bulk liquid crystal, while θ^* is the angle between the $\mathbf{n}$ vector and the interfacial normal. This expression means that the anisotropic part of the distribution function in this artificial case consists of two contributions: (i) the turning effect with an anisotropy of the P_2 type with respect to the surface normal with the order parameter $\alpha^*(x)$, and (ii) the anisotropy caused by the self-consistent field of the P_2 type also but with respect to the director of the bulk volume of the liquid crystal. Thus it is possible to say that the self-consistent field orders molecules along the director and the concentration gradient orders them with respect to the interfacial normal.

In a more realistic case the intermolecular interactions change the symmetry of U in the surface layer, then the ordering influence of the self-consistent field becomes more complicated. However the turning effect keeps its symmetry, essentially P_2 with respect to the interfacial normal, unchanged.

3.2. *Comparison of the results for rod-like and persistent molecules*

We have solved numerically the systems of equations (14) and (15). We have examined several examples of the expressions for $F_0(c, \hat{\alpha})$ in such a form that permits the coexistence of the two phases, isotropic and liquid-crystalline. The order parameter of the liquid crystal phase was assumed to be small, i.e. $\alpha_a \ll 1$. The following conditions were accomplished: equality of chemical potentials and pressures in the two coexisting phases and the condition $\partial F_0/\partial\alpha|_{\mathrm{iso,aniso}} = 0$, which means that both uniform states of the system correspond to local minima of the free energy. It was found that solutions of the systems (14) and (15) are practically equivalent to each other if coexisting phases are dense enough. This means that equivalent structures of the nematic–isotropic interface will appear in the systems of rod-like and persistent molecules with the same equations of state, i.e with the same expressions for a spatial uniform sample free energy.

This result is in obvious qualitative agreement with the fact that the most dependent on the flexibility mechanism among the Frank elasticity modulus is the one of cross splay (the coefficient of $(\operatorname{div} \mathbf{n})^2$ in the Frank energy expression) [11], while the situation in the surface layer is more similar to a longitudinal deformation.

The direct graphical method of solution of the more simple system given by equation (14) will imply that the results are suitable to both cases under consideration: to rod-like and to persistent molecules.

3.3. *Graphical interpretation of the solution of the equations obtained*

In equations (14) (as well as in equations (15)) the first equation (14 *a*) determines the value of the concentration gradient in the surface layer, i.e. determines the width of the interfacial layer. Equation (14 *b*) gives the relationship between functions of concentration $c(x)$ and order parameter $\alpha(x)$ (the order parameter α is determined in the coordinate system discussed previously, see equation (11)). Equations (14 *c*) give us the functions $\alpha_1(x)$ and $\alpha_2(x)$ if we know the concentration gradient profile. Thus we can see that the key to the system of combined equations (14) is equation (14 *b*), because it gives the dependence of $\kappa(c)$ with which to solve the differential equation (14 *a*) and algebraic equations (14 *c*) and (14 *d*).

We have found an explicit and simple way to solve equation (14 *b*). It is based on the use of the new function F_1 instead of the function F_0. This new function F_1 can be defined as

$$F_1 = F_0 - \mu c + p,$$

where μ and p are respectively the chemical potential and osmotic pressure in coexisting phases. The F_1 function, as well as F_0, depends on four arguments, c, α, α_1 and α_2. Therefore, as a thermodynamical potential, the F_1 function is considered here with an unusual set of arguments. However, it is easy to see that the function $F_1(c, \alpha, \alpha_1, \alpha_2)$ in contrast to F_0 has two minima of the same depth at the points, which correspond to equilibrium coexisting phases. In these points the values of F_1 are equal to zero.

As to the dependence of the F_1 function on α_1 and α_2, it is natural to assume the simple minimum character, for example, of the quadratic type, α_m^2, because these two parameters describe the non-uniaxiality of the distribution function and in both bulk phases they should be equal to zero: $\alpha_1|_{\mathrm{aniso}}^{\mathrm{iso}} = \alpha_2|_{\mathrm{aniso}}^{\mathrm{iso}} = 0$. Since the anisotropy is assumed to be small, then, in accord with a simple estimate, we can neglect the dependence of F_1 on α_1 and α_2 to determine the relationship between c and α. Therefore, when equation (14 *b*) is considered, it is possible to take F_1 to be a function of two variables only, namely concentration c and order parameter α.

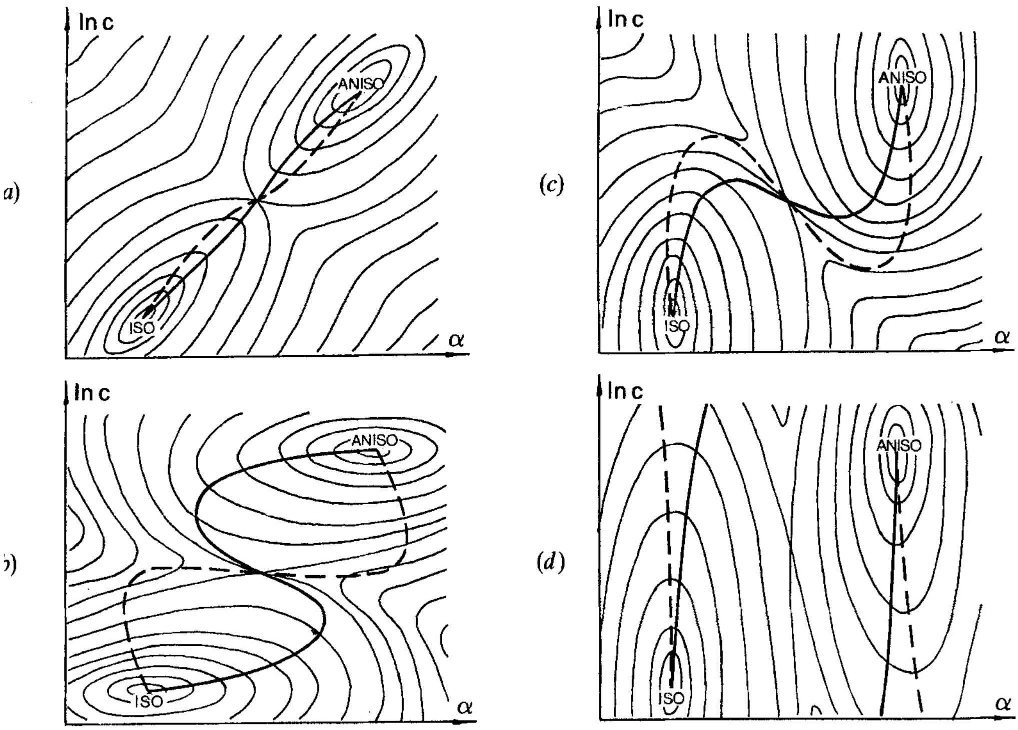

Figure 2. The different pictures of the F_1 function isolines are shown. The minimum of the F_1 function corresponds to one of the coexisting phases, either isotropic or liquid crystal. Different cases (*a*)–(*d*) correspond to different thermodynamics of the molecular systems. The relationship between the concentration c and the order parameter α in the surface layer is shown with solid lines (if the liquid crystal director is perpendicular to the interface) and with dotted lines (if the director is parallel to the interface).

The function $F_1(c, \alpha)$ can be represented using a system of lines of equal values of F_1 (isolines) in the (c, α) plane, or, as will be more convenient, in the $(\ln(c), \alpha)$ plane. The topology of these lines is determined by the fact that F_1 should have two minima at the points corresponding to both coexisting phases (see figure 2). There can be other minima of F_1 corresponding to metastable states. In terms of the function $F_1(c, \alpha)$ equation (14 b), after simple transformation, becomes

$$\partial F_1/\partial\alpha = ((2/5)P_2(\theta_0))\partial F_1/\partial(\ln(c)). \tag{16}$$

This equation determines the line, or the way, on the plane $(\ln(c), \alpha)$. The geometric sense of equation (16) is as follows: this way intersects isolines of the F_1 function at points where these lines have a fixed slope with $\tan\gamma = (-2/5)\,P_2\,(\cos\theta_0)$, where γ is the angle between the direction of the isoline at the given point and the direction of the α axis. It is important to note that the sought way passes through the points of both coexisting phases minima and through the saddle point between them, independent of the value of the angle γ. This angle depends on the orientation of the director in the volume of liquid-crystal, i.e. on the angle θ_0 between the bulk nematic director and the interfacial normal. The value of $\tan\gamma$ is changed from $(-2/5)$ when the director is perpendicular to the surface $(\theta_0 = 0)$ to $(1/5)$ when the director lies in the surface plane $(\theta_0 = 90°)$.

It was found that for different F_1 functions the interfacial layer structure may vary significantly, i.e. this structure depends on temperature, quality and quantity of low molecular solvent, etc. Some typical examples are discussed in the next section.

3.4. *Possible structures of the interfacial layer*

The system of the function $F_1(c, \alpha)$ isolines characterizes the thermodynamic properties of the homogeneous system, and in a certain sense describes the intermolecular interactions. Due to that there is an almost unlimited number of different pictures of the isolines. The existing opportunities we classify as follows.

First order phase transitions between nematic and isotropic phases may be conventionally located between the following two limiting cases. In the first case the transitional energy depends mostly on density changes (concentration changes). The change of order parameter in this case influences the molecular energy slightly, and the orientational ordering may be considered as a kind of indicator of the more dense phase. In the opposite limiting case the phase transition energy is determined mainly by the orientational ordering, and the density change does not play a significant role. Real systems obviously are located between these two limiting situations. Pictures of the $F_1(c, \alpha)$ isolines for the limiting cases described are shown in figures 2(*b*) and (*c*). In figure 2(*a*) the simplest intermediate case is shown.

In figure 2 the c–α relationships are shown with dotted lines for planar orientation of the bulk nematic director ($\theta_0 = 90°$) and with solid lines when the director is normal to the surface ($\theta_0 = 0$). In the first case the F_1 isolines are intersected at points where their tangent is $\tan\gamma = (-2/5)$; in the second case $\tan\gamma = (1/5)$; when the director has an intermediate orientation ($0 < \theta_0 < 90°$) the sought way intersects the isolines at points where the tangent has an intermediare value: $(-2/5) < \tan\gamma < (1/5)$.

The concentration profiles $c(x)$ and order parameter profiles $\alpha(x)$ are presented in figures 3(*a*)–(*c*) for two limiting director orientations: $\theta_0 = 0$-planar orientation (dotted lines) and $\theta_0 = 90°$-normal orientation (solid lines). Let us discuss the situation corresponding to the cases (*a*)–(*d*) in figures 2 and 3.

Figure 2(*a*): Closed loop type isolines surrounding points for the isotropic and the liquid-crystalline states are stretched one to another. This situation occurs if orientational order and concentration gradients bring comparable contributions to the phase transition energy. With such a picture of isoenergetic lines the interface layer has a thickness of order l; the concentration and order parameter behave monotonically in the surface layer. The relationships between the functions $c(x)$ and $\alpha(x)$ are shown in figure 2(*a*). The corresponding gradient profiles are shown in figure 3(*a*).

Figure 2(*b*): Closed isolines surrounding points of homogeneous states are stretched along the α axis. In this case the essential part in the transition energy belongs to the concentration gradient. The relationship between c and α in the surface layer is shown in figure 2(*b*). The interface thickness is of order l, and the order parameter may change non-monotonically. The associated profiles $\alpha(x)$ and $c(x)$ are shown in figure 3(*b*).

Figure 2(*c*): Closed isoenergetic lines surrounding points of homogeneous states are stretched along the c axis. This situation occurs if the transition energy is determined mainly by the orientational ordering. The relationship between c and α in the surface layer for this case is shown in figure 2(*c*). As well as in the previous cases the interface width is about of order l. The order parameter changes monotonically in the surface layer, but the concentration can change non-monotonically. Profiles of the gradient of c and α are plotted in figure 3(*c*).

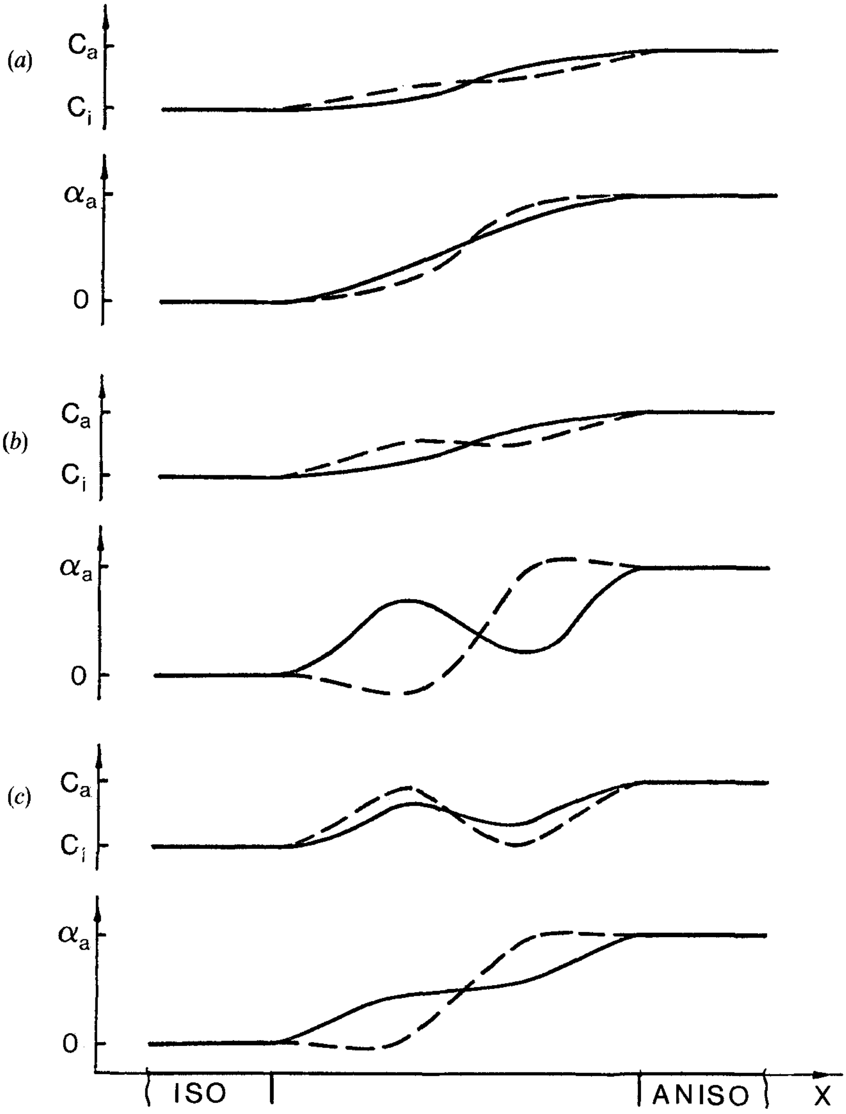

Figure 3. Possible profiles of the order parameter α and concentration c in the interface layer between isotropic and liquid-crystalline phases are shown as a function of the x coordinate normal to the interface. The solid lines show the profiles for perpendicular director orientation and the dotted lines planar orientation.

In these three cases the profiles of α_1 and α_2 do not depend qualitatively on the intermolecular interactions. The typical profile is shown in figure 4.

Figure 2(*d*): Some isolines of the F_1 function do not form a closed loop. This situation may occur if the energy barrier between the two coexisting phases is high, states with intermediate values of concentration or order parameter cannot appear. In this case the continuous line connecting points of isotropic and nematic phases in the $(\ln(c), \alpha)$ plane does not exist. A sharp interface with a width $\sim d \ll l$ between two phases will appear if the intermolecular potential corresponds to the isoenergetic lines as shown in figure 2(*d*). The existence of such an interface is due to the fact that

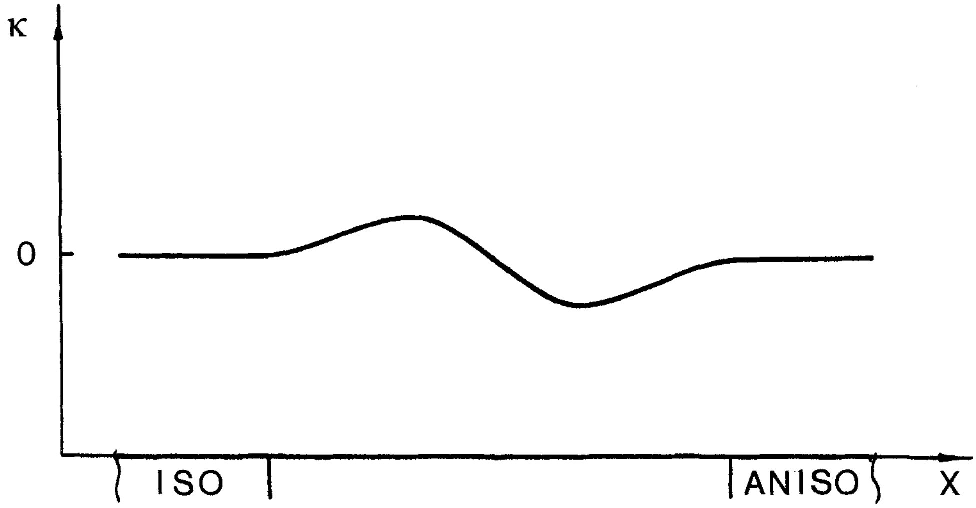

Figure 4. The profile of κ value gradient in the surface layer. Components of the order parameter α_1 and α_2 are connected with κ through $\alpha_1 \sim \kappa P_{21}(\theta_0)$ and $\alpha_2 \sim \kappa P_{22}(\theta_0)$, respectively.

macromolecular systems in contrast to those of low molecular weight have two characteristic lengths: the length of the molecule and the molecular diameter. Therefore besides the natural situation where spatial changes are characterized by the largest of these two scales a different situation is also possible. In this case the width of the interface is characterized by the molecular diameter.

To conclude our consideration it is possible to say that different structures at the nematic–isotropic interface may exist in systems of asymmetric molecules and their particular structure depends on the intermolecular interactions. However the interface structure is almost independent of the mechanism of molecular flexibility if both phases are sufficiently dense.

Appendix

The generalization of the Onsager's entropy expression [13] for the spatially non-uniform state of a system of rod-like molecules can be written as

$$-S = k \int f_0(\mathbf{r}, \mathbf{n}) \ln (f_0(\mathbf{r}, \mathbf{n}))\, d^3\mathbf{r}\, d\Omega_{\mathbf{n}}, \qquad \text{(A 1)}$$

where $f_0(\mathbf{r}, \mathbf{n})$ is the probability of the rod to start at $\mathbf{r}$ and to have the direction $\mathbf{n}$. We should rewrite expression (A 1) in terms of the function $f(\mathbf{r}, \mathbf{n})$. For this we divide one rod into N segments each of length λ ($\lambda/d \gg 1$, where d is the molecular diameter) in such a way that on the λ scale the surrounding of the segment may be considered as homogeneous. The situation corresponds to a weak spatial non-uniformity. Then

$$f(\mathbf{r}, \mathbf{n}) = (1/N) \int f_t(\mathbf{r}, \mathbf{n})\, dt,$$

where $f_t(\mathbf{r}, \mathbf{n})$ is the probability that the tth segment has a direction $\mathbf{n}$ at point $\mathbf{r}$. Taking into account the weak non-uniformity of the system we can write

$$f_t(\mathbf{r}, \mathbf{n}) = f_0(-t\lambda\mathbf{n}, \mathbf{n}),$$
$$= f_0(\mathbf{r}, \mathbf{n}) - t\lambda\mathbf{n} \cdot \nabla(f_0(\mathbf{r}, \mathbf{n})) + (1/2)(t\lambda)^2(\mathbf{n} \cdot \nabla)^2(f_0(\mathbf{r}, \mathbf{n})),$$

and we obtain after integration and some transformations

$$f_0(\mathbf{r},\mathbf{n})=f(\mathbf{r},\mathbf{n})+(l/2)\mathbf{n}\cdot\nabla(f(\mathbf{r},\mathbf{n}))+(l^2/12)(\mathbf{n}\cdot\nabla)^2(f(\mathbf{r},\mathbf{n})). \qquad \text{(A 2)}$$

Here we assume that $\lambda N=l$.

After substitution of equation (A 2) into equation (A 1) we have obtained the entropy of the solution of rod-like molecules as a functional of the f function

$$-S=k\int f(\mathbf{r},\mathbf{n})\ln(f(\mathbf{r},\mathbf{n}))\,d^3\mathbf{r}\,d\Omega_{\mathbf{n}}+\frac{l^2}{24}k\int\frac{(\mathbf{n}\cdot\nabla f)}{f(\mathbf{r},\mathbf{n}}\,d^3\mathbf{r}\,d\Omega_{\mathbf{n}}.$$

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