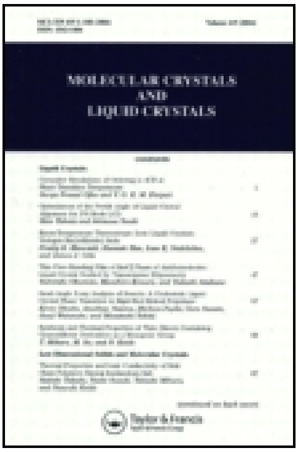

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STATISTICAL-MECHANICAL CALCULATIONS OF THE SURFACE FREE ENERGY AND ANCHORING TRANSITIONS

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Abstract

A statistical-mechanical theory which takes into account the correlations between translational-translational, orientational-orientational and mixed correlations, based upon the method of conditional distribution functions, is applied to calculations of the surface free energy and anchoring transitions of a system composed of interacting ellipsoidal molecules near an interacting wall.

1 Introduction

Among the surface properties of liquid crystals(LCs) which have been a subject of intense interest for many years, one, known as anchoring, plays a crucial role in the fabrication of LC displays. In this paper I shall restrict myself to the anchoring of nematic liquid crystals (NLCs), although other mesophases have been shown to exibit similar behaviour [1].

Recent theoretical studies have shed significant light on this phenomena [2 – 10]. However, the underlaying physical mechanisms are not yet fully understood.

Recently a kind of Bethe theory, which takes account of intercell pair correlations for describing NLC systems composed of interacting ellipsoidal molecules near an interacting wall has been proposed[11].

But in this approach, only one orientation of the director, parallel to the surface (homogeneous anchoring) has been investigated.

The aim of the present paper is to extend the above approach in order to describe not only homogeneous anchoring, but investigate the question of which orientation of the director $\gamma_{tilt} = \cos^{-1}(\mathbf{n}\cdot\mathbf{k})$, where $\mathbf{n}$ is the director and $\mathbf{k}$ is the normal vector to the surface, minimizes the Helmholtz free energy.

2. Model

I consider a one-component fluid consisting of molecules with coordinates $i \equiv (\mathbf{r}_i, \mathbf{e}_i)$, describing the molecular positions $\mathbf{r}_i$ and orientations $\mathbf{e}_i$ ($|\mathbf{e}_i| = 1$) of prolate ellipsoids of revolution, of major semiaxis $\sigma_{\|}$ and minor semiaxis $\sigma_{\perp}$, respectively, in contact with a solid planar wall.

One uses a statistical scheme in which the total volume V of the system of N molecules is divided into n molecular layers parallel to the solid wall. In layer L there are N_L cells, so that $N = \sum N_L$, and the volume of each cell is $v = V/N$. The model which is used here assumes that every cell is occupied by a molecule and thus the number of cells equals that of molecules, which seems reasonable for a condensed system. The potential energy associated with the N particles is a sum of potentials $U = \frac{1}{2}\sum_{i\neq j}\Phi(ij) + \sum_i \Phi(i)$, where $\Phi(ij)$ is the intermolecular pair potential which depend on the positions $\mathbf{q}_i$ and $\mathbf{q}_j$ and orientations $\mathbf{e}_i$ ($|\mathbf{e}_i| = 1$) and $\mathbf{e}_j$ of molecules with numbers i and j, and $\Phi(i)$ is the molecule-wall potential which depend on the position $\mathbf{q}_i$ and orientation $\mathbf{e}_i$ of the molecule with number i.

The theory is based on the method of conditional distribution functions. Details are given in Ref.[11]. The molecules are taken to interact pairwise *via* the Gay-Berne [12] intermolecular potential

$$\Phi(\mathbf{q}_{ij},\mathbf{e}_i,\mathbf{e}_j) = 4\epsilon_0\epsilon(\mathbf{e}_i,\mathbf{e}_j,\mathbf{e}_{ij})\{(\frac{\sigma_0}{\mathbf{r}_{ij}})^{12} - (\frac{\sigma_0}{\mathbf{r}_{ij}})^{6}\} , \qquad (1)$$

where $\mathbf{r}_{ij} = |\mathbf{q}_{ij}| - \sigma(\mathbf{e}_i,\mathbf{e}_j,\mathbf{e}_{ij}) + \sigma_0$, and $\mathbf{e}_i$,$\mathbf{e}_j$ are , respectively, unit vectors along the molecular symmetry axes, $\mathbf{q}_{ij}$ the vector between the molecular centers, and $\mathbf{e}_{ij} = \mathbf{q}_{ij}/|\mathbf{q}_{ij}|$. The potential energy parameter $\epsilon(\mathbf{e}_i,\mathbf{e}_j,\mathbf{e}_{ij})$ and size parameter $\sigma(\mathbf{e}_i,\mathbf{e}_j,\mathbf{e}_{ij})$ are angle-dependent functions defined in Eqs.(3),(4) and (8)-(10), respectively, of Ref.[12] The former depends on the molecular elongation or length-to-breadth ratio γ (denoted $\sigma_{\|}/\sigma_{\perp}$ in Ref.[12]) while $\epsilon(\mathbf{e}_i, \mathbf{e}_j, \mathbf{e}_{ij})$ depends on both γ and another parameter which can be used to adjust the ratio between the end-to-end and side-by-side well depth, denoted ϵ_l/ϵ_s. In our calculations the parameters μ and ν of Ref.[12] have been fixed at the values 1 and 2, respectively.

The presence of the wall is suggest that the nematic molecules occupy the half-space $x \geq 0$ (the x-axis of the coordinate frame is chosen to be normal to the wall), and the space-fixed $z-$ axis is chosen so that the nematic director lies in the xz plane. The wall also interacts with the molecules at $x \geq 0$ through a long-range anchoring potential,

$$\Phi(\mathbf{e}_i, x_i) = \frac{2\pi}{3} \frac{\epsilon_w}{\sigma_w^2} \left[\frac{2}{15} \left(\frac{\sigma_0}{\sigma_w x_i}\right)^9 - \left(\frac{\sigma_0}{\sigma_w x_i}\right)^3 \right] . \tag{1}$$

The energy parameter ϵ_w and size parameter σ_w are also angle-dependent functions defined in Eqs.(20),(21) of Ref.[13], respectively, and $\epsilon_{ow} = \epsilon\epsilon_0$, and ϵ is a strength parameter, x_i denotes the distance from the wall to the molecule i , and $\mathbf{e}_i = (e_{i,x}, e_{i,y}, e_{i,z})$.

Henceforth, the strength ϵ_0 of the interaction in (1) is used as the unit of energy, while the minor diameter of the molecules, $\sigma_\perp$, is the unit of distance.In these units, the theory involves the number of independent microscopic parameters,namely, the reduced volume $v^* = v/\sigma_\perp^3$, the reduced temperature $\theta = kT/\epsilon_o$, the strength parameter ϵ and anisotropy parameter γ. The latter was chosen to be $\gamma = 3$.

The equilibrium surface free energy (SFE) profile at the solid-nematic fluid interface corresponding to the layers can be expressed by means of the functions $\psi_L(i) = \Pi_{j \neq i} \psi_{i,j}(i)$, for $i \in L$ (for details see Eq.(23) in Ref.[11]) as

$$f_s(L) = -\beta^{-1} \ln \frac{\int_L d(i)\ \psi_L(i)}{\int_b d(i)\ \psi_i^b(i)} , \quad f_s = \sum_L f_s(L) , \tag{2}$$

where $\psi_L(i)$ is the singlet full mean force potential(MFP) corresponding to the L^{th} layer, satisfying the Eq.(13) Ref.[11], and $\psi_i^b(i)$ is the full bulk MFP.

In the absence of external fields or boundaries, the free energy of a nematic is independent on the direction of the director $\mathbf{n}$. However, if the translational symmetry is broken, for example by a solid surface, the free energy of the system will depend in general on the direction of **n**, and the molecules will adopt the orientation that minimizes it.

I have obtained solutions of the theory outlined in the section 2 Ref.[11] over a wide range of values of the temperature θ and volume v^*, for each such state including a scan over values of the bulk tilt angle $\gamma_{tilt} = \cos^{-1}(\mathbf{n}\cdot\mathbf{k})$, i.e. the angle between the bulk director and the x axis. The associated surface free energy f_s was calculated for each state and value of γ_{tilt} from 0 to $\frac{\pi}{2}$ with the step of $\Delta\gamma_{tilt} = \frac{\pi}{10}$. The final value of the tilt angle had been chosen providing the minimum surface Helmholtz free energy.

In the general case, of course, one should investigate the question which orientation of the director $\gamma_{tilt}(L)$ for each perturbed layer minimizes the Helmholtz free energy and describe the equilibrium $\gamma_{tilt}(L)$ profile at the solid-nematic fluid interface.

One can readly see from Fig.1, that for the case of a strong interaction between the solid wall and nematic phase ($\epsilon_{ow} = 5\epsilon_o$) the value of the tilt angle which provide the minimum of f_s is $\gamma_{tilt} = \frac{\pi}{2}$ (Fig.1, curve 1)(homogeneous anchoring). All oblique orientations of the director (Fig.1, curves 2,3) not provide the minimum of f_s, as well homeotropic (Fig.1, curve 4) one. The dependence of the scaled SFE f_s on the reduced temperature $\theta = kT/\epsilon_o$ is plotted in Fig.2 for the case of a weak interaction ($\epsilon_{ow} = 0.5\epsilon_o$), and for scaled volume $v/\sigma_\perp^3 = 4.0$. Such behavior of the f_s shows that the values of the tilt angle which provide the minimum of SFE are

$$\gamma_{tilt} = \begin{cases} \frac{2\pi}{5}, & \textit{oblique anchoring}, \quad \textit{for}\ 0.5 \le \theta \le 0.575 \\ \frac{\pi}{10}, & \textit{oblique anchoring}, \quad \textit{for}\ 0.575 \le \theta \le 0.75, \end{cases}$$

and characterized by a conical to conical anchoring transition approximately at the reduced temperature $\theta \approx 0.575$.

The fact that the homogeneous anchoring more preferable in the case of a strong interaction between the solid surface and nematic phase not strange, because the direct interaction between the solid wall and nematic molecules approximately in the five times more ($\epsilon_{ow} = 5.0\epsilon_o$) than the interaction between nematic molecules. In the case of

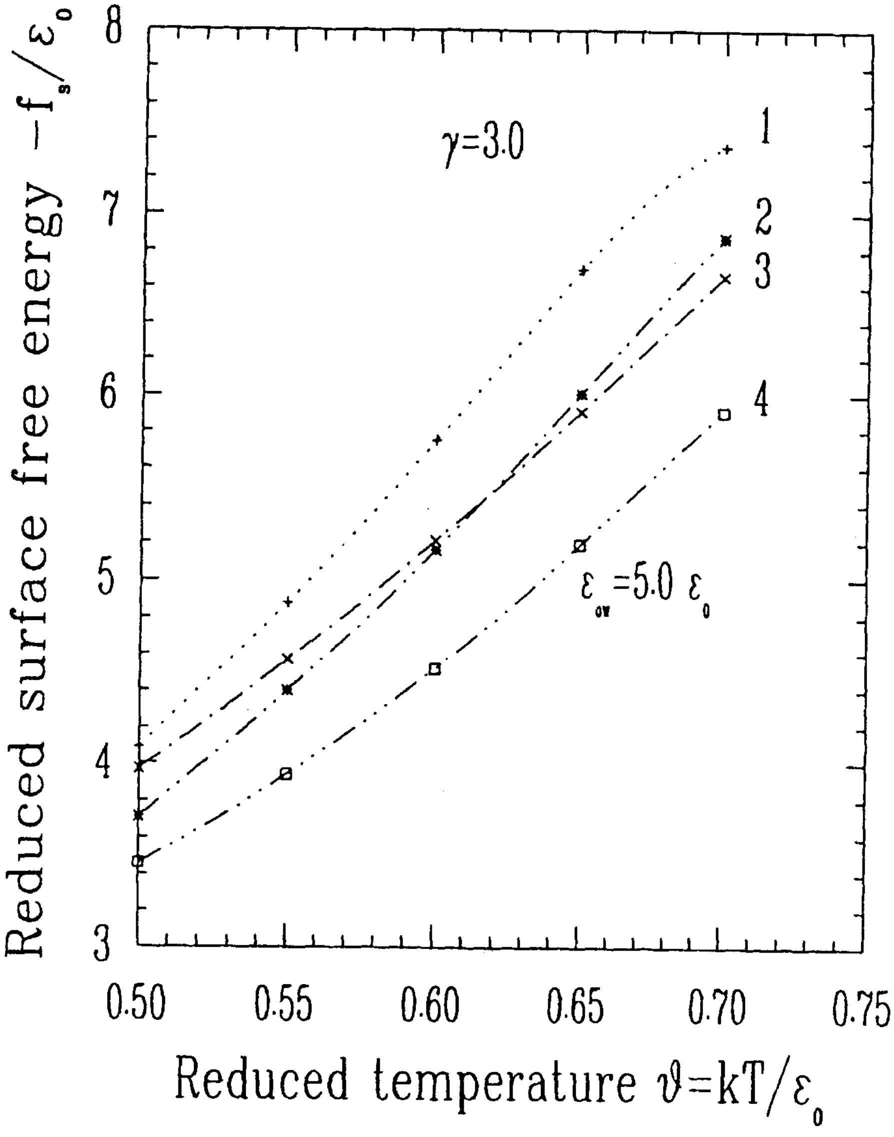

Fig.1. Temperature dependence $\theta = kT/\epsilon_0$ of the reduced surface free energy $-f_s/\epsilon_0$, for the case of a strong interaction ($\epsilon_{ow} = 5.0\epsilon_0$) between the solid wall and nematic phase for different values of the tilt angle: $\gamma_{tilt} = \frac{\pi}{2}$ (homogeneous anchoring)(curve 1); $\gamma_{tilt} = \frac{2\pi}{5}$ (oblique anchoring) (curve 3); $\gamma_{tilt} = \frac{\pi}{10}$ (oblique anchoring)(curve 2); $\gamma_{tilt} = 0$ (homeotropic anchoring)(curve 4), respectively.

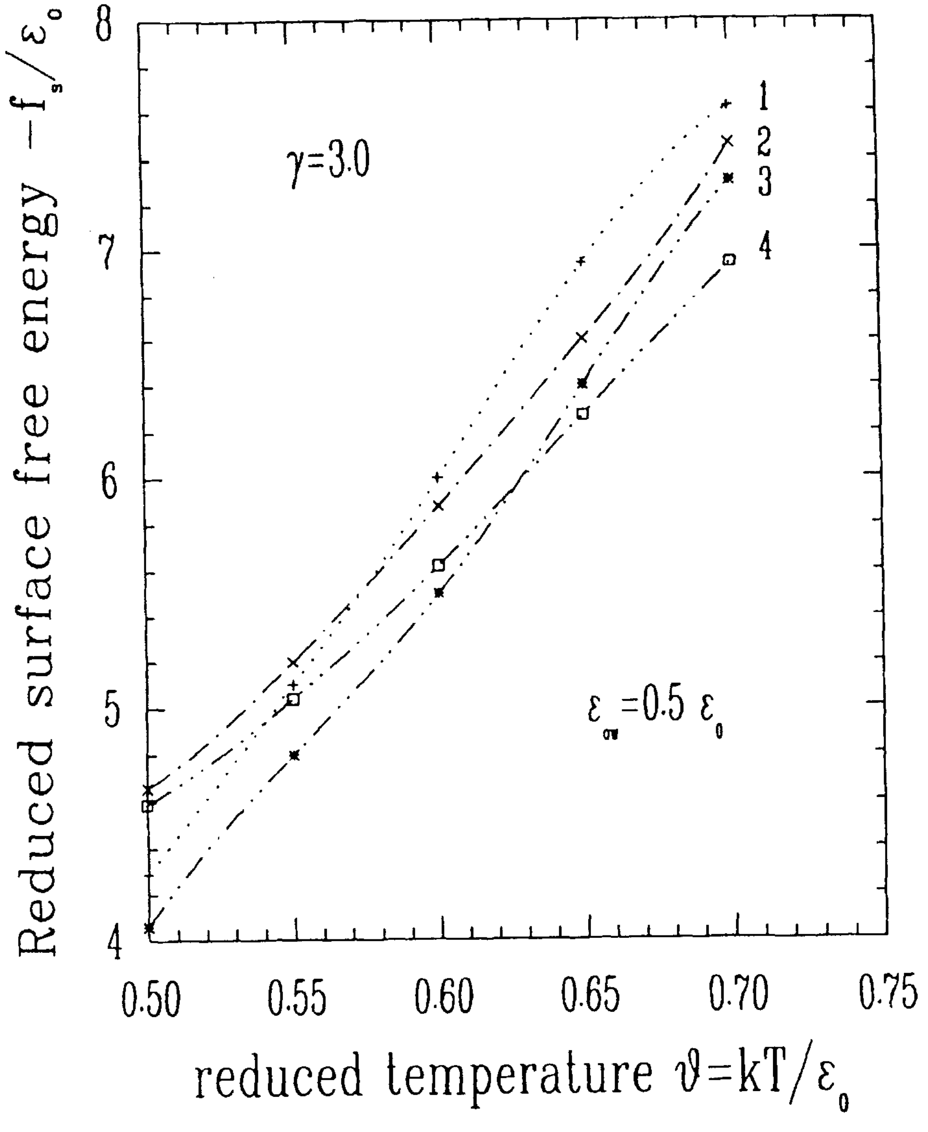

Fig.2. Temperature dependence $\theta = kT/\epsilon_0$ of the reduced surface free energy $-f_s/\epsilon_0$, for the case of a weak interaction ($\epsilon_{ow} = 0.5\epsilon_0$) between the solid wall and nematic phase for different values of the tilt angle: $\gamma_{tilt} = 0$ (homeotropic anchoring) (curve 3); $\gamma_{tilt} = \frac{\pi}{2}$ (homogeneous anchoring) (curve 4); $\gamma_{tilt} = \frac{2\pi}{5}$ (oblique anchoring)(curve 2); $\gamma_{tilt} = \frac{\pi}{10}$ (oblique anchoring)(curve 1), respectively.

a weak interaction between the solid surface and nematic phase due to the character of cell correlations and the strong interaction among molecules which compose of the nematic phase, the director prefer oblique anchoring. The fact that with increasing of the temperature take place anchoring transition from one type of oblique orientation of the director to other, which characterized by decreasing of the tilt angle, shows that the influence of the surface on the nematic phase decrease.

3 Conclusion

In this paper has been developed a statistical-mechanical theory which takes into account of intercell pair correlations for describing the equilibrium surface free energy and different type of anchoring transitions at the solid-nematic fluid interface. The calculations have been carried out for a cubic close packed system composed of molecules interacting by means of the Gay-Berne potential and with a (9-3) like orientation dependent molecule-wall interaction and shows that for the case of a strong interaction ($\epsilon_{ow} = 5.0\epsilon_o$) the value of the tilt angle which provide the minimum of SFE is $\gamma_{tilt} = \frac{\pi}{2}$ (homogeneous anchoring),whereas for the case of a weak interaction ($\epsilon_{ow} = 0.5\epsilon_o$) take place oblique to oblique anchoring transition, which characterized by decreasing of the tilt angle.

The key results are that,for strong strength of the substrate potential, there is only one orientation of the director, perpendicular to the surface (homogeneous anchoring), which minimizes the free energy. When the substrate strength is decreased the easy axis makes an angle with the normal to the surface with is neither zero nor $\frac{\pi}{2}$ (oblique anchoring). The fact that with increasing of the temperature take place anchoring transition from one type of oblique orientation of the director to other, which characterized by decreasing of the tilt angle,seems encouraging. These transitions akin to those observed experimentally by Ryschenkow and Kleman[12] and Di Lisi *et al* [13].

The calculation also show that the number of distinct layers which must be taken into account depend mainly on the character of cell correlations. The anisotrotic solid potential is strong influence on the alignment of the nematic molecules in the first layer. However, after the first layer the character of cell correlations become relatively more important and the order parameter $\eta(L) = \langle P_2^{(L)}(\cos\theta_i)\rangle$, where $P_2(\cos\theta_i)$ is the Legendre polynomial of order 2, reach the bulk value after three layers. The same character of the behavior of the nematic molecules at the solid wall has been observed in the framework of the mean-field theory for the Helmholtz free energy of an inhomogeneous molecular fluid [3].

Acknowledgments

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