

## PHASE TRANSITIONS IN A SEMI-INFINITE SYSTEM OF LYOTROPIC LIQUID CRYSTAL

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*Received September 16, 2005*

In the frame of the Landau – de Gennes phenomenological theory applied to lyotropic liquid crystals, and introducing the concentration dependence of the surface free energy, the influence of the surface on the phase transition is discussed. The model is applied to a well-known lyotropic liquid crystal (CsPFO/water) and predicts a surface order parameter different from zero in a temperature range above the critical temperature characterizing the bulk phase transition. The application of the model to the evaluation of the surface tension leads to anomalous behavior of this one.

*Key words:* liquid crystals, lyotropics, phenomenological theory.

The Landau-de Gennes theory well describes the behavior of phase transitions in nematic liquid crystals [1-3]. Attempts to extend it to lyotropic nematics, as well as to determine the coefficients that appear in the expansion of the free energy density were made [4-6] and they well describe the temperature and concentration dependence of the order parameter. The theory was initially built by assuming an infinite thermodynamical system and characterizing it with position independent parameters. The presence of a limiting surface introduces a non-uniformity of some physical parameters, especially of the order parameter. The Landau theory was extended by writing the spatial non-uniformity of the system near the critical temperature,  $T_c$ , as a square gradient of the order parameter and by introducing the physical properties of the limiting surface of the system [7-10].

In this paper we will apply the results of the Landau-Ginzburg-de Gennes theory to a lyotropic liquid crystal taking into account the concentration dependence for the phenomenological coefficients obtained in [6]. The surface order parameter, as well as the anisotropic contribution to the surface tension of the system will be calculated and the results will be applied to a well-known lyotropic system. An anomalous behavior of surface tension with temperature is predicted.

Let us consider a semi-infinite system limited by a surface. The co-ordinate perpendicular to the surface is denoted by  $z$ , with  $z=0$  coinciding with the surface.

The presence of a surface breaks the translational invariance and consequently, the order parameter  $y$  depends on  $z$  i.e.  $y=y(z)$ . The free energy *per* unit area of the system is:

$$F = \int_0^{\infty} \left[ \frac{1}{2} K \dot{y}^2 + f_v(y) \right] dz + f_s(y_0) \quad (1)$$

where  $\dot{y} = dy/dz$ ,  $f_v(y)$  is the bulk free energy density,  $K$  is an “elastic constant” and  $f_s(y_0)$  is the surface free energy density with  $y_0 = y(0)$ . For a system with first order bulk phase transition,  $f_v(y)$  is written as the power series:

$$f_v(y) = \frac{1}{2} A(x, T) y^2 - \frac{1}{3} B y^3 + \frac{1}{4} C y^4 \quad (2)$$

$T$  is the temperature and  $x$  is the concentration of the surfactant in the lyotropic system.  $A(x, T)$ ,  $B > 0$  and  $C > 0$  are phenomenological coefficients. We suppose as previously [6] that the transition from nematic to isotropic is controlled both by temperature and concentration by means of the phenomenological coefficient  $A(x, T)$  which has the expression:

$$A = \alpha(T - T_c^*) + a(x_c^* - x) \quad (3)$$

Equation (3) shows that at least one pair of critical parameters exists, namely a critical temperature,  $T_c^*$ , and a critical concentration,  $x_c^*$ , so that the ordered phase is stable for  $T < T_c^*$  and  $x > x_c^*$ . The temperature  $T_c^*$ , the lowest temperature of existence of the isotropic phase, is slightly different of the nematic to isotropic transition temperature  $T_c$  and they are related by the equation [6]:

$$T_c = T_c^* + \frac{2B^2}{9aC} - \frac{\alpha}{a}(x_c^* - x).$$

Parameters  $B$  and  $C$  which are temperature independent, can be concentration dependent.

Using the minimum condition for the free energy density we obtain that the bulk order parameter  $y_b$ , far from the surface ( $z \rightarrow \infty$ ) is:

$$y_b^{(1)} = 0, \text{ for } A(x, T) > \frac{2B^2}{9C} \text{ (isotropic state)} \quad (4)$$

$$y_b^{(2)} = \left( \frac{B}{2C} \right) + \sqrt{\left( \frac{B}{2C} \right)^2 - \frac{A}{C}}, \text{ for } A(x, T) < \frac{2B^2}{9C} \text{ (nematic state).} \quad (5)$$

In equation (1),  $f_s(y_0)$  takes into account the microscopic changes of the bulk interaction parameters near the surface. According to [9,10] we propose for the surface free energy  $f_s(y_0)$  an expression resulting from expanding the surface free energy in power series of  $y_0$ . By neglecting the first order term in this power series, we will take into account only the incomplete interaction of the molecules near the substrate. Retaining only the second term in the power series:

$$f_s(y_0) = \frac{1}{2} A_s y_0^2 \quad (6)$$

Equation (6) shows that if the phenomenological coefficient  $A_s > 0$ ,  $f_s$  is minimum for  $y_0 = 0$ , and if  $A_s < 0$ ,  $y_0 = 0$  corresponds to a maximum of  $f_s$ . It follows that, if  $A_s > 0$ , the surface tends to decrease the order and vice versa.

For a lyotropic liquid crystal, we will suppose for  $A_s$  the expression:

$$A_s = a_s (x_s - x) \quad (7)$$

with  $a_s > 0$ . In eq.(7) a characteristic concentration,  $x_s$  that separate the disordered from the ordered surface phase, was introduced. For  $x < x_s$  we observe that  $A_s > 0$  and the surface phase is disordered as  $f_s$  is minimum for  $y_0 = 0$ . For  $x > x_s$  an ordered surface phase is obtained. The critical micellar concentration ( $x_{CMC}$ ) can play the role of  $x_s$ . For amphiphilic surfactants solution in polar solvents (the usual lyotropic solutions), it separates the states of molecular and micellar solution. The surface layer of such lyotropic systems seems, in view of amphiphilic nature of the surfactant, to be of lamellar type [11]. For  $x > x_{CMC}$ , it becomes complete and consequently, ordered at some degree.

The actual profile of the order parameter,  $y(z)$  is deduced by minimizing equation (1) and taking into account the equations (2) and (6). The resulting Euler-Lagrange equation is:

$$K\ddot{y} - Ay + By^2 - Cy^3 = 0 \text{ for } 0 \leq z < \infty, \quad (8)$$

with the boundary condition

$$-K\dot{y}_0 + A_s y_0 = 0 \text{ for } z=0. \quad (9)$$

Integrating equation (8) once and determining the constant of integration by taking into account that at  $z \rightarrow \infty$ ,  $y \rightarrow y_b$  and  $\dot{y} = 0$ , we obtain:

$$\frac{dy}{dz} = \pm \sqrt{\frac{2}{K} \sqrt{|f_v(y) - f_v(y_b)|}}. \quad (10)$$

The plus or minus sign corresponds, respectively, either to the case  $y_0 < y_b$  (increasing function) or  $y_0 > y_b$  (decreasing function).

The equilibrium surface order parameter  $y_0$  is obtained by solving the following equation resulted from eq.(9) using the value of  $\dot{y}_0$  given by eq. (10):

$$y_0^4 - \frac{4}{3} \frac{B}{C} y_0^3 + \frac{2}{C} \left( A - \frac{A_s^2}{K} \right) y_0^2 + \left( -y_b^4 + \frac{4}{3} \frac{B}{C} y_b^3 - \frac{2A}{C} y_b^2 \right) = 0 \quad (11)$$

The above results will be applied to the lyotropic system caesium per-fluorooctanoate (CsPFO)/water which was well studied [4,5, 11-14]. The molecules of the CsPFO surfactant have hydrophobic and hydrophilic ends and aggregate at concentrations higher than the critical micelar concentration ( $x_{CMC}$ ) to form disklike micelles. At concentration higher than 20 wt%, the discotic micelles develop orientational and one-dimensional order and form nematic and lamellar phases. This system presents a nematic phase in a wide concentration domain. For this micelar system, one of authors [6], after introducing the concentration dependence of the phenomenological coefficient  $A$  given by equation (3), calculated the phenomenological parameters to fit the experimental data.  $B$  and  $C$  parameters are given in Table 1. From the same paper,  $a = 2.2 \times 10^4 \text{ Jm}^{-3}\text{K}^{-1}$ ,  $\alpha/a = 0.05 \text{ K}$  and  $x_c = 0.2$ . We will suppose  $a_s = 1 \times 10^4 \text{ Jm}^{-3}\text{K}^{-1}$  and  $x_s = x_{CMC}$ . For the CsPFO/water system, the Kraft point co-ordinates are  $T_K = 274 \text{ K}$  and  $x_{CMC} = 1.3 \text{ wt}\%$  [15]. As  $x_{CMC}$  slowly varies with temperature [16], we will consider at temperatures near  $T_c$  that  $x_{CMC} \cong 1.5 \text{ wt}\%$ .

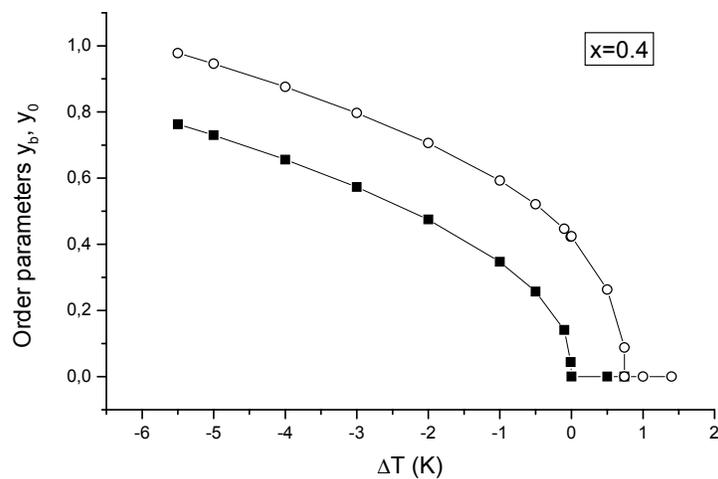
The surface order parameter corresponding to the stable state for a given set of phenomenological parameters was determined by comparing the total free energy of the system for the two real solutions of eq. (11).

Table 1

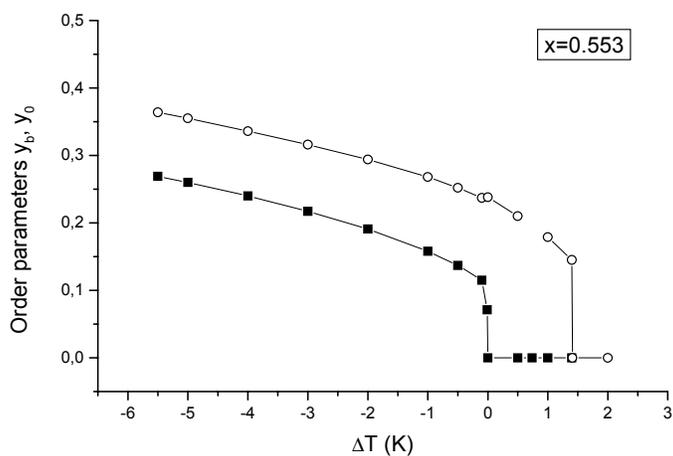
Phenomenological coefficients  $B$  and  $C$  as function of surfactant concentration,  $x$ .

$x$	$B \cdot 10^{-4} \text{ (Jm}^{-1}\text{)}$ Ref.[6]	$C \cdot 10^{-4} \text{ (Jm}^{-1}\text{)}$ Ref.[6]
0.393	1.297	20.34
0.436	2.593	35.37
0.483	7.472	84.37
0.49	9.004	100.5
0.507	12.95	139.2
0.522	16.99	179.0
0.553	29.79	278.0

In the Figs. 1 and 2 the results for the bulk and surface order parameters are presented as function of the relative temperature ( $\Delta T = T - T_c$ ) and of concentration, respectively. As it can be seen, a more ordered surface than the bulk was obtained.



a



b

Fig. 1. Temperature dependence of bulk (■) and surface (○) order parameters at two surfactant concentrations. a)  $x=0.4$ ; b)  $x=0.553$ .

Relative temperature  $\Delta T = T - T_c$ . The continuous curves are drawn as a guide to the eye.

The bulk order parameter becomes zero at the transition temperature ( $\Delta T = 0$ ) and has a jump equal to  $2B/(3C)$  [6]. In the cases presented in Fig.1, the values for the bulk order parameter jumps are  $\Delta y_b = 0.0441$  and  $\Delta y_b = 0.0714$  for  $x=0.4$  and  $x=0.553$ , respectively. In contrast with it, the surface order parameter remains different from zero at temperatures above the bulk transition temperature. At the temperature corresponding to  $A = A_s^2 / K$ , the surface order parameter, in its turn, becomes zero.

For  $x=0.4$ , the surface order parameter becomes zero at  $\Delta T = 0.74$  K and has a jump of 0.088. For  $x=0.553$  the surface order parameter becomes zero at  $\Delta T = 1.41$  K and has a jump of 0.148. The surface order parameter has similar temperature dependence below and above the critical temperature.

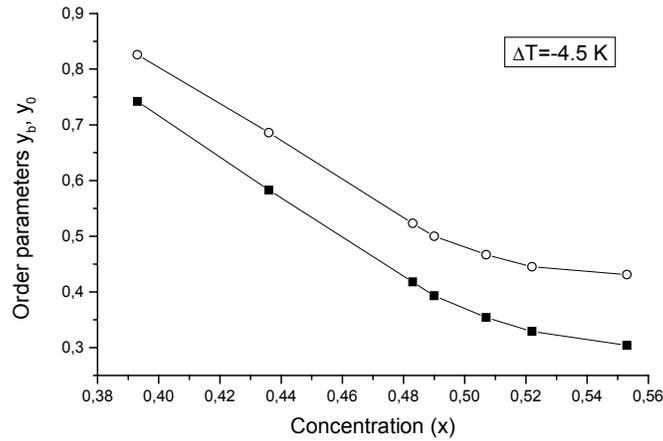


Fig. 2. Bulk (■) and surface (o) order parameter concentration dependence.  $x$  is the weight concentration of the surfactant in the lyotropic solution.

The relative temperature is  $\Delta T = -4.5$  K. The continuous curves are drawn as a guide to the eye.

The curves in Fig. 2 describe the concentration dependence of bulk and surface order parameter. The bulk order parameter concentration dependence, taken from [6], shows that  $y_b$  decreases with concentration, in good accordance with experience [14]. We observe that  $y_0$  also decreases with concentration, following the behavior of bulk order parameter, as the surface and bulk ordering state are linked. However, the surface is more ordered than the bulk, its structure being probably lamellar [11].

The evaluation of surface order parameter,  $y_0$ , allows to calculate the contribution to the surface tension due to the presence of bulk and surface ordered phases  $\Delta\gamma$ , given by the excess free energy per unit area [17]:

$$\Delta\gamma = \int_0^{\infty} [f(y, \dot{y}) - f_v(y_b)] dz + f_s(y_0) \quad (12)$$

Using eq. (10) for  $\dot{y}$  and observing that the first term in  $\Delta\gamma$  is always positive, we obtain:

$$\Delta\gamma = \sqrt{2K} \left| \int_{y_0}^{y_{\infty}} \sqrt{|f(y, \dot{y}) - f_v(y_b)|} dy \right| + f_s(y_0) \quad (13)$$

The surface tension of the liquid crystal is the sum of the isotropic contribution ( $\gamma_{is}$ ) which linearly decrease with temperature and the anisotropic contribution  $\Delta\gamma$ :

$$\gamma(T) = \gamma_{is}(T) + \Delta\gamma(T). \quad (14)$$

The results for the temperature dependence of the anisotropic part of the surface tension,  $\Delta\gamma$  for two different concentration of CsPFO/water nematic liquid crystal are given in Fig. 3.

From these results for  $\Delta\gamma(T)$ , an anomalous behavior of surface tension with temperature for the CsPFO system is predicted as, in eq. (14),  $\gamma_{is}(T)$  decreases and  $\Delta\gamma(T)$  increases with temperature.

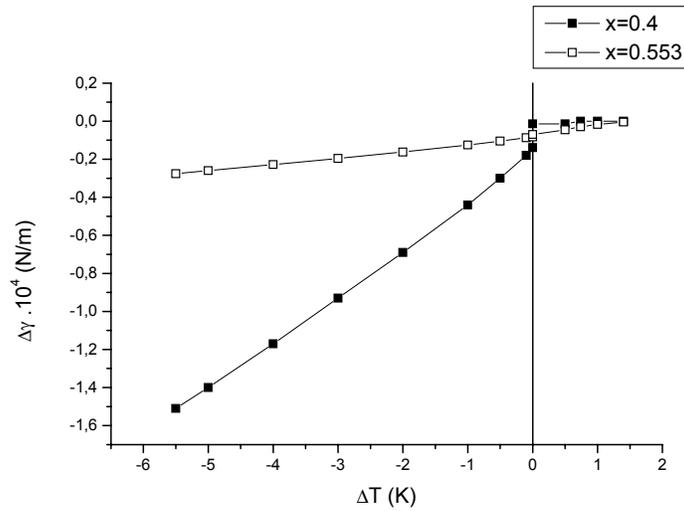


Fig. 3. Temperature dependence of the anisotropic part of surface tension,  $\Delta\gamma$ , for  $x = 0.4$  and  $0.553$ . The continuous curves are drawn as a guide to the eye.

Near the transition temperature, a more abrupt variation of  $\Delta\gamma(T)$  for  $x=0.4$  is observed, even if at the nematic to isotropic transition the jump  $\delta(\Delta\gamma) = 3 \cdot 10^{-7} \text{ N/m}$  is very small. For  $x=0.553$ , this jump is a little more important,  $\delta(\Delta\gamma) = 13 \cdot 10^{-7} \text{ N/m}$ . For  $\Delta T > 0$ , in comparison with  $\Delta T < 0$ ,  $\Delta\gamma(T)$  varies very little with temperature before it becomes zero together with  $y_0$ .

In conclusion, introducing a concentration dependence of the surface free energy, we obtained for the lyotropic system CsPFO/water in the nematic domain, a more ordered surface phase than the bulk phase, for different surfactant concentration. For a given temperature, the increasing of surfactant concentration produce more disordered surface phase. The jump of the surface order parameter at the nematic to isotropic transition increases with concentration, but remains very small. The temperature at which the surface order parameter becomes zero is greater than  $T_c$  and increases with concentration, even if a less ordered surface is obtained for more concentrated systems.

An anomalous behavior of surface tension of lyotropic system CsPFO/water can be predicted, as its anisotropic and isotropic parts vary with temperature with slopes of opposite sign. A more abrupt temperature variation and a (small) positive jump of  $\Delta\gamma(T)$  at the transition were obtained, again indicating an anomalous behavior of surface tension. The temperature dependence of the surface tension for temperature higher than  $T_c$  remains anomalous, as  $\Delta\gamma(T)$  has positive slope.

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