

Reentrant isotropic-nematic phase transitionM. Simões,^{1,*} M. Pazetti,¹ S. M. Domiciano,¹ D. A. Oliveira,^{2,3} and A. J. Palangana²¹*Departamento de Física, Universidade Estadual de Londrina, Campus Universitário, 86051-990-Londrina, Paraná, Brazil*²*Departamento de Física, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-900-Maringá, Paraná, Brazil*³*Universidade Tecnológica Federal do Paraná, Campus Campo Mourão, 87301-006-Campo Mourão, Paraná, Brazil*

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This work aims at a geometrical semimicroscopic model to study the reentrant isotropic-nematic phase transition. It will be assumed that the micellar change of shape in lyotropics can be understood as the deformation of an ellipsoid which is assumed to have the idealized form of a micelle. It will be shown that such deformation is characterized by two kinds of quantities. The first one, which is a scalar determined by the ellipsoidal eccentricity, gives the intensity of the ellipsoidal deformation. The second one, which has a tensorial nature, describes the spatial distribution of such deformation and is proportional to the tensorial nematic order parameter. We construct the invariants of such deformation and couple it with the orientational order parameter to study the reentrant isotropic–nematic phase transition. We determine the thermodynamical characteristics of this phase transition and shown that it is a second-order phase transition. By comparing the theory so constructed with the experimental data, the parameters of the model will be determined.

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I. INTRODUCTION

The diversity of phases and structures found in liquid crystal materials makes them ideal substances to study phase transitions [1]. Continuous and noncontinuous phase transitions have been found on them and, sometimes, unexpected phase transitions are observed on their sequence of phases, in particular on the so-called reentrant phases. In this way, configurations apparently more symmetric occur as the temperature is reduced, insinuating the violation of one of the basic laws of nature where a decrease of the temperature would be followed by a decrease of the entropy, not by an increase [2]. Such (apparently) contradictory outcomes are found in lyotropic liquid crystal (LLC) materials [3,4]. In this LLC system, the classical isotropic (I) phase is observed at high temperatures as well as a reentrant isotropic (I_{RE}) phase at lower temperatures. Between these two limiting isotropic phases an important sequence of phase transitions can be found, including the discotic nematic (N_D), the biaxial nematic (N_B), and the calamitic nematic (N_C). All of them have been subject to experimental and theoretical studies by several authors [5–16], with special attention to the biaxial nematic and reentrant phases. Using experimental data, of order parameter and density, a comparison between the nature of the two nematic-isotropic phase transitions present in the above sequence of phases has been made [12,17]. The nonusual aspect of these transitions follows from the fact that, under normal conditions, the N_C – I phase transition would be expected to be a consequence of the random thermal fluctuations that, due to the temperature increase, becomes large enough to overcome the molecular orientation, annulling their global coherent alignment [1]. However, as such a mechanism cannot be responsible for the N_C – I_{RE} phase transition, which occurs with the reduction of the temperature, this reentrant phase transition must result from another

mechanism [7,18]. Nowadays, it is accepted that the lyotropic micellar change of form is the cause of the N_C – I_{RE} transition; with the temperature reduction, the micellar anisotropic form of the lyotropic system is reduced to a point in which it is not enough to sustain an ordered nematic phase. Our aim here is to provide a mean-field theory which explains how this micellar shape transformation alters the stability of the nematic phase, and propose how such a mechanism is coupled with the micellar orientation.

Some time ago, the high temperature of the N_C – I phase transition was found to be essentially different from the lower temperature of the N_C – I_{RE} phase transition. While the N_C – I transition has the usual behavior of the nematic-isotropic phase transition, a first-order phase transition with a very small latent heat gap [1], the N_C – I_{RE} transition, seems to be a second-order phase transition and, furthermore, presents a critical exponent which is different from the higher temperature one [9,12,17]. We will construct here a pseudomicroscopic theory which provides a fundament to these facts. Such theory will follow from a previous study of the micellar deformation [19] and it will provide a description of how the anisotropic form of the micelles is coupled with its orientation. It will be shown that the lyotropic micellar deformation is in fact a tensor, whose intensity is measured by the ellipsoidal eccentricity and the directional components are given by the nematic order parameter tensor. As a consequence of this approach we will demonstrate that the N_C – I_{RE} phase transition is in fact a second-order phase transition. We will construct a Landau [1,20] mean-field theory which, as usual, cannot be used to determine the exact values of the critical exponents but, nonetheless, it will provide solid evidence that they may not be equal.

II. FUNDAMENTALS

Recently, a geometrical model has been introduced to compute the elastic constants of a nematic liquid crystal [19]. One important aspect of this model is that it can be used to

*simoes@uel.br

provide a pseudomicroscopic interpretation to the micellar deformation in lyotropic liquid crystals. Namely, by considering a three-dimensional quadratic form, $A_{ij}x_i x_j = cte$, where the matrix A_{ij} characterizes an ellipsoid if it has a set of real and positive eigenvalues. Its eigenvectors correspond to the ellipsoid semiaxis directions and the eigenvalues to its lengths. It has been found [19] that when the de Gennes [1] prescription to construct microscopic order parameters is applied to A_{ij} , the resulting order parameter $D_{ij} = A_{ij} - \delta_{ij} \text{Tr}(A_{ij})/3$ can be interpreted as a micellar deformation; it measures how an ellipsoid differs from a sphere. For the uniaxial case, the corresponding micellar deformation is given by

$$D_{ij} = \frac{e}{1-e} \left(\frac{1}{3} \delta_{ij} - n_i n_j \right), \quad (1)$$

which reveals that the deformation of the micelles, conduced by the change of micellar eccentricity (e), is coupled with a tensor, which is formally identical with the orientation order parameter $Q_{ij} = \delta_{ij}/3 - n_i n_j$ of the uniaxial nematic phase, where \vec{n} is the direction of the main direction axis of a uniaxial ellipsoid. Of course, in the context of a geometrical interpretation of the micellar geometry, Q_{ij} is a spatial measure of the micellar deformation. Nevertheless, taking the proper statistical averages to define a macroscopic order parameter and to describe the deformation of the micelles, the proper macroscopic order parameter has been shown to be given by $D_{ij} = DSQ_{ij}$, where $D = e/(1-e)$, S is the scalar order parameter, and Q_{ij} is the macroscopic order parameter where now \vec{n} is the director.

In order to construct the free energy determined by this order parameter we need to calculate the invariants determined by D_{ij} . By adopting the usual prescription which assures that it is enough to consider the trace of the order parameter, we arrive at

$$\begin{aligned} t_1 &= \text{Tr}(D_{ij}) = 0, \\ t_2 &= \text{Tr}(D_{ik}D_{kj}) = \frac{2}{3}D^2S^2, \\ t_3 &= \text{Tr}(D_{ik}D_{kl}D_{lj}) = -\frac{2}{9}D^3S^3, \\ t_4 &= \text{Tr}(D_{ik}D_{kl}D_{lm}D_{mj}) = \frac{2}{9}D^4S^4. \end{aligned} \quad (2)$$

Consequently, to study the deformation of the micelles, the free energy F_d can be expressed by

$$F_d = a_1 t_1 + a_2 t_2 + a_3 t_3 + a_4 t_4 = -a_2 D^2 S^2 - a_3 D^3 S^3 + a_4 D^4 S^4, \quad (3)$$

where a_2 , a_3 , and a_4 are the Landau phenomenological coefficients [20]. This free energy describes the deformation of the micelles; if we want to describe the orientational order of the nematic material we must use the usual free energy F_o [1],

$$F_o = -b_2 S^2 + b_3 S^3 + b_4 S^4. \quad (4)$$

In this context, if we want to study the coupling between the micellar deformation and its orientation, we must consider the total free energy, $F = F_d + F_o$,

$$F = -c_2 S^2 - c_3 S^3 + c_4 S^4, \quad (5)$$

where $c_2 = a_2 D^2 + b_2$, $c_3 = a_3 D^3 - b_3$, and $c_4 = a_4 D^4 + b_4$.

This result shows how the Landau coefficients of the expansion of the free energy in terms of the order parameter S are the functions of the micellar eccentricity through the parameter D . Consequently, to study the coupling between the deformation of the micelles and its orientational order, the free energy to be studied is the one given by Eq. (3).

III. RESULTS AND DISCUSSION

With the free energy stated, Eq. (5), the N_C - I_{RE} phase transition can be carefully considered. Along the nematic phase and for temperatures below the N_C - I phase transition point, Eq. (5) gives the following expression for the order parameter:

$$S = \frac{3c_3 + \sqrt{9c_3^2 + 32c_2c_4}}{8c_4}, \quad (6)$$

where, according to Landau, c_2 would be proportional to the temperature (T) in the range of the N_C phase. Making $c_2 = -[\alpha 9c_3^2/(32c_4)]\theta$, where $\theta = \Delta T + T_c$ and T_c is the calamitic nematic-isotropic (or reentrant isotropic) transition temperature, we arrive at

$$S = \frac{3c_3}{8c_4} (1 + \sqrt{1 - \alpha\theta}). \quad (7)$$

By substituting the values found in Eq. (5) in this equation we arrive at

$$S = \frac{3a_3}{8(a_4 D^4 + b_4)} \left(D^3 - \frac{b_3}{a_3} \right) (1 + \sqrt{1 - \alpha\theta}). \quad (8)$$

A straightforward substitution of this equation on the free energy given by Eq. (3) gives

$$F = -\frac{27a_3^4 \left(D^3 - \frac{b_3}{a_3} \right)^4}{4096(a_4 D^4 + b_4)^4} [8 - 3\alpha\theta(4 - \alpha\theta) + 8(1 - \alpha\theta)^{3/2}], \quad (9)$$

which shows that this free energy presents a change in the ground-state configuration (from $S=0$ to $S \neq 0$), when two conditions are fulfilled,

$$\theta < \frac{8}{9\alpha} \quad \text{and} \quad D > \sqrt[3]{\frac{b_3}{a_3}}, \quad (10)$$

which reveals the existence of two phase transition points. The first one is attained when $\theta < 8/9\alpha$ and describes the usual N_C - I first-order phase transition, which occurs with a discontinuity in S , given by

$$\Delta S = \frac{3a_3}{8(a_4 D^4 + b_4)} \left(D^3 - \frac{b_3}{a_3} \right) (1 + \sqrt{2}). \quad (11)$$

The other phase transition is a continuous phase transition, occurring when $D \rightarrow \sqrt[3]{b_3/a_3}$ and, according to Eq. (8), it happens without a gap in the value of S . As D is entirely

determined by the micellar eccentricity, this last transition would be the N - I_{RE} second-order reentrant phase transition [21,22]. Furthermore, the free energy equation (2), determining the thermal behavior of e , reveals that it would have a thermal dependence given by a usual Landau theory, which would have the canonical form

$$D = d\sqrt{\theta - T_c}. \quad (12)$$

As a consequence of this study, the temperature dependence of the order parameter would be given by

$$S = \frac{3a_3}{8[a_4^4 d^4 (\theta - T_c)^2 + b_4]} \left(d\sqrt{\theta - T_c}^3 - \frac{b_3}{a_3} \right) (1 + \sqrt{1 + \alpha\theta}). \quad (13)$$

In order to compare this curve with the experimental result, we have used the optical birefringence (Δn) as a function of temperature, obtained as described in Refs. [9,12,13] near the N_C - I_{RE} and N_C - I phase transitions. This phase sequence, N_C - I_{RE} (11.0 °C) and N_C - I (47.0 °C), was determined by optical microscopy, optical refractometry, and optical conoscopy in a lyotropic mixture (concentration in weight percent) of potassium laurate (KL: 29.4), decanol (DeOH: 6.6), and water (64.0). The macroscopic order parameter (Δn) of the N_C phase can be related to the order parameter (S) by $\Delta n = \eta S$, where η is a normalization constant. The constant η is chosen in such a manner that the maximum of Δn corresponds to $\Delta n = 1$ and in this way, Eq. (13) can be rewritten as

$$S = A \frac{[(\sqrt{T + \epsilon + c})^3 - c^{3/2}]}{[d + (T + \epsilon + c)^2]} (b + \sqrt{1 - T}), \quad (14)$$

where $A = 3\sqrt{aa_3}/(8da_4)$, $b = 1/\sqrt{1-t_o}$, $c^{3/2} = \alpha^{3/2}b_3/[d_3(1-t_o)^{3/2}a_3]$, $d = -\alpha^2 b_4/[d_4(1-t_o)^2 a_4]$, $\epsilon = (t_o - \alpha T_c)/(1-t_o) - c$. We have linearly rescaled the temperature scale, $\theta = [(1-t_o)T + t_o]/\alpha$, by choosing t_o in such a way that $T=1$ corresponds to the last experimental data measured below the N_C - I , and $T=0$ corresponds to the first measured experimental data above the N_C - I_{RE} phase transition. Furthermore, the parameter ϵ has been introduced to measure the distance from the first measured experimental data to the point of the N_C phase. The profile of the curve that we have obtained is shown in Fig. 1 along the N_C phase and near the N_C - I_{RE} and N_C - I phase transitions.

To sum up, we have proposed a geometric model to study the lyotropic micellar deformation and its coupling with the nematic orientation. With the invariants of this theory we have constructed a Landau model to study the corresponding thermal behavior and show that such a model predicts that the calamitic nematic-reentrant isotropic phase transition is a

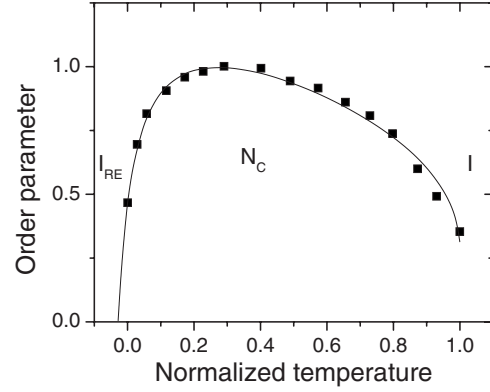


FIG. 1. Order parameter (rescaled birefringence) versus normalized temperature. The continuous curve gives the best fit of Eq. (14) obtained for the optical birefringence [9,12,13]. The values of the adjusted parameters are $A = 3.9 \pm 1.3$, $b = 0.33 \pm 0.05$, $c = 8.9 \pm 0.9$, $d = -784 \pm 34$, and $\epsilon = 0.03 \pm 0.02$. The errors on these parameters arise from adjusting parameters, are not experimental ones. I_{RE} , N_C , and I are the isotropic reentrant, calamitic nematic, and isotropic phases, respectively.

continuous phase transition, which is in accord with previous experimental observations, and the calamitic nematic-isotropic phase transition is a discontinuous transition, also in accord with the experimental observations. Furthermore, our model also predicted that the order parameter critical exponents of these two phase transitions would not be the same. Nevertheless, as the theory that we have elaborated is a mean-field theory, it is not necessary to compare the results of the present model with the experimental one, since we knew from the beginning that they would be different. It is very instructive to notice that even in a mean-field theory, these two critical exponents are distinct. The reason for this difference is straightforward. When we measure the orientational order parameter, we see from the theory that we have developed above that its dependence on the temperature would be the one expected by a usual Landau theory. Nevertheless, the free parameters present in S [a_3 in Eq. (8) of the present model] are functions of the micellar deformation D and, as long as this dependence is not linear, the corresponding critical exponent will be modified. We believe that the same will occur in the renormalization group approach to this problem.

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- [1] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon Press, Oxford, 1993).
 [2] P. E. Cladis, Phys. Rev. Lett. **35**, 48 (1975).
 [3] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).

- [4] A. M. Figueiredo Neto, L. Liébert, and Y. Galerne, J. Phys. Chem. **89**, 3737 (1985).
 [5] Y. Galerne and J. P. Marcerou, Phys. Rev. Lett. **51**, 2109 (1983).

- [6] Y. Galerne, A. M. Figueiredo Neto, and L. Liébert, *Phys. Rev. A* **31**, 4047 (1985).
- [7] M. J. de Oliveira and A. M. Figueiredo Neto, *Phys. Rev. A* **34**, 3481 (1986).
- [8] J. R. D. Pereira, A. J. Palangana, A. M. Mansanares, E. C. da Silva, A. C. Bento, and M. L. Baesso, *Phys. Rev. E* **61**, 5410 (2000).
- [9] P. A. Santoro, J. R. D. Pereira, and A. J. Palangana, *Phys. Rev. E* **65**, 057602 (2002).
- [10] A. R. Sampaio, A. J. Palangana, and R. C. Viscovini, *Mol. Cryst. Liq. Cryst.* **408**, 45 (2004).
- [11] N. M. Kimura, P. A. Santoro, P. R. G. Fernandes, and A. J. Palangana, *Liq. Cryst.* **31**, 347 (2004).
- [12] M. Simões, A. de Campos, P. A. Santoro, and A. J. Palangana, *Phys. Lett. A* **333**, 120 (2004).
- [13] M. Simões, A. J. Palangana, L. R. Evangelista, W. S. Braga, and F. S. Alves, *Phys. Rev. E* **72**, 031707 (2005).
- [14] M. Simões, F. S. Alves, K. E. Yamaguti, P. A. Santoro, N. M. Kimura, and A. J. Palangana, *Liq. Cryst.* **33**, 99 (2006).
- [15] P. A. Santoro, A. R. Sampaio, H. L. F. da Luz, and A. J. Palangana, *Phys. Lett. A* **353**, 512 (2006).
- [16] W. S. Braga, N. M. Kimura, D. D. Luders, A. R. Sampaio, P. A. Santoro, and A. J. Palangana, *Eur. Phys. J. E* **24**, 247 (2007).
- [17] P. A. Santoro, H. L. F. da Luz, and A. J. Palangana, *Mol. Cryst. Liq. Cryst.* **434**, 619 (2005).
- [18] C. Rosenblatt, *Phys. Rev. A* **34**, 3551 (1986).
- [19] M. Simões, A. de Campos, and D. Barbato, *Phys. Rev. E* **75**, 061710 (2007).
- [20] L. D. Landau, in *Collected Papers*, edited by D. Ter Haar (Gordon and Breach, New York, 1965).
- [21] J. P. McClymer, C. A. Oxborrow, and P. H. Keyes, *Phys. Rev. A* **42**, 3449 (1990).
- [22] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, Oxford, 1971).