Corresponding states of periodic structures in nematic liquid crystals

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The discovery of a universal behavior for the distortion of one-dimensional walls, formed in nematic liquid crystal samples under the action of a magnetic field, above the Fréedericksz threshold is reported. By means of a simple theoretical approach it is shown that the length of these walls, when properly scaled and considered as a function of the reduced magnetic field, stays in a common line of corresponding states. This behavior is confirmed by experimental data on lyotropic as well as in thermotropic nematic liquid crystals. [S1063-651X(97)10409-3]

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I. INTRODUCTION

One of the most amazing aspects of some thermodynamical systems is that, close to a critical point, the macroscopic behavior of very distinct microscopic systems can be put in a single line of corresponding states [1]. The classical example is the coexistence curve of many fluids that can be superimposed when the temperature and density are scaled by their corresponding critical values [2,3], giving a unique curve characterizing the universality of that critical point. This possibility gives us a powerful insight into the physical nature of these systems because by a single change of scale all the particular properties of a singular system can be put aside, and all that remains is a universal behavior presenting the essential features of some large thermodynamical class. In the nematic state we have the well-known Fréedericksz transition [4,5]. In this way we can suspect that just around the Fréedericksz transition the nematic state could have in some sense a universal behavior. If true, this result can constitute a well-established background for the measurement of the nematic parameters. The report of experimental evidence of this fact is the main aim of this paper where we relate the experimental discovery of a line of corresponding states for the nematic structure just above the Fréedericksz threshold. In order to verify it we choose to work with domains, separated by so-called walls, that frequently appears as a unidimensional periodic array just above this second-order phase transition [5].

Periodic distortions in nematic liquid crystals (NLC's) under the action of a magnetic or electric field have been widely investigated. The basic feature of these phenomena is that under the action of the magnetic field two symmetrical distorted textures can be created and separated by a wall [5]. In the last few years the nature and physical properties of these walls have been considered in several works [6–9]. Recently, their interaction has been explicitly taken into account for a lyotropic system in order to analyze new experimental data [10]. Moreover, the connection between the dimensionality and the periodic behavior in these systems has been established in analytical basis [11].

From the experimental data it is possible to connect the wavelength of the periodic distortion (λ) with the applied magnetic field [10,12]. To account for the observed dependence of the wavelength on the applied magnetic field, it has been necessary to consider an interaction between the walls, producing a saturated portion in the director bend profile [10], which is characterized by a constant that is independent of the nematic media (lyotropic or thermotropic) with positive diamagnetic anisotropy. We show that the measured points (the wavelength vs the reduced magnetic field), when properly scaled, lies along the same universal curve being, therefore, a line of walls' corresponding states. Our conclusions are corroborated by three distinct measurements performed on lyotropic samples and by some published data on thermotropics [7].

II. FUNDAMENTALS

In order to obtain the law for corresponding states, we briefly present the theoretical main lines of the approach that we are proposing to treat the problem. We consider a slab with dimensions a along the x axis, b along the y axis and d along the z axis, in such a way that $a \gg b \gg d$. The director is initially uniformly aligned along the x axis. An external controlled magnetic field H is applied along the y axis. This geometry produces twist-bend walls in the sample [5,10]. A typical periodic distortion is exhibited in Fig. 1 of Ref. [10]. To describe them we assume that the components of the director are $n_x = \cos\theta(x,y,z)$, $n_y = \sin\theta(x,y,z)$, $n_z = 0$, where $\theta(x,y,z)$ is the angle between the director $\vec{n}$ and the x-axis direction. Furthermore strong boundary conditions are assumed at the sample edges.

In order to work with a handleable expression for the free energy we will use the two-elastic-constant approximation ($K_{11} = K_{33}$). This will not change our fundamental result, whose only requisite is the existence of the critical point, the Fredericks threshold, which does not depends on how many elastic constants we use in the statement of the problem [5]. In this way the free energy becomes [5,13]

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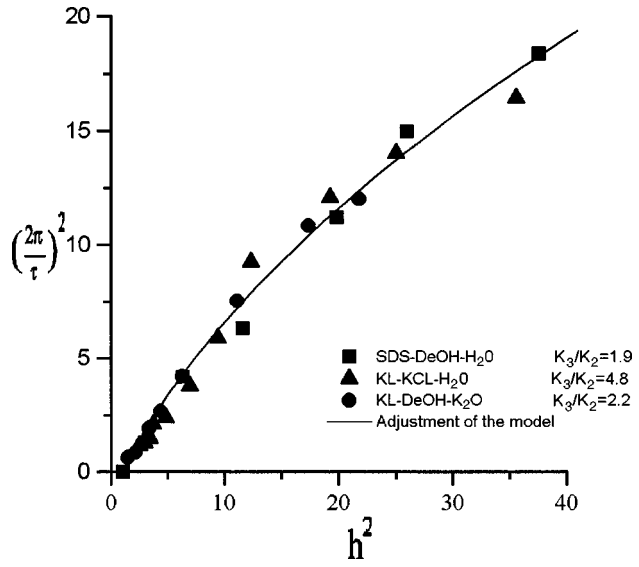

FIG. 1. The behavior of $(2d/\tau)^2$ as a function of h^2 for three different lyotropic substances. All the experimental data were scaled according to the presented model. The continuous line refers to our calculations. The predicted ratios between the elastic constants are also exhibited.

$$F=\int \{\tfrac{1}{2}K_{33}[(\partial_x\theta)^2+(\partial_y\theta)^2]+\tfrac{1}{2}K_{22}(\partial_z\theta)^2 - \tfrac{1}{2}\chi_a H^2\sin^2\theta\}dV, \tag{1}$$

where K_{11}, K_{22}, and K_{33} are, respectively, the elastic constants of splay, twist, and bend, $\chi_a>0$ is the diamagnetic anisotropy, and V is the volume of the sample. The general solution satisfying the boundary conditions is assumed to be of the form

$$\theta(x,y,z)=\eta(x)\sin\left(\frac{\pi y}{b}\right)\sin\left(\frac{\pi z}{d}\right), \tag{2}$$

for $0\leqslant x\leqslant a$, $0\leqslant y\leqslant b$, and $0\leqslant z\leqslant d$, where $\eta(x)$ is the configuration of the nematic structure along the x axis.

By introducing the quantities

$$\begin{aligned}\chi_a H_c^2&=K_{33}(\pi/b)^2+K_{22}(\pi/d)^2,\\ h&=H/H_c,\\ x&=\sqrt{K_{33}/(\chi_a H_c^2)}\,t,\\ \theta_0^2&=\tfrac{8}{3},\end{aligned} \tag{3}$$

and observing that the magnetic free-energy density of the configuration $\eta(x)$ along the $\vec{e_x}$ direction can be put in the form of a functional: $I[\eta(x)]=\int \sin^2\theta\, dy\, dz\simeq\frac{1}{4}\eta^2(x) -\frac{3}{64}\eta^4(x)+O(\eta^6(x))$, where its polynomial approximation gives a good fit until the neighborhoods of its second extremum. In this way the free energy, Eq. (1), can be written in the form

$$F=\tfrac{1}{4}bd\sqrt{K_{33}(\chi_a H_c^2)}N\int_0^\tau \mathcal{F}\,dt,$$

where

$$\mathcal{F}=\tfrac{1}{2}(\partial_t\eta)^2+\tfrac{1}{2}(1-h^2)\eta^2+\frac{1}{4\theta_0^2}h^2\eta^4, \tag{4}$$

and N is the number of walls along the x direction, and the period is given by $\lambda=\sqrt{K_{33}/(\chi_a H_c^2)}\,\tau$.

The new free energy density $\mathcal{F}$ does not have any particular parameter characterizing the actual system. The elastic constants, the critical field and the sample dimensions have been put aside. Therefore the resulting equation for $\eta(t)$ will be, save for the geometry, completely independent of the NLC sample, and the equation for the field $\eta(t)$ appears to describe a kind of equation of corresponding states [1] for the walls that assumes the form

$$\partial_t^2\eta-(1-h^2)\eta-\frac{1}{\theta_0^2}h^2\eta^3=0, \tag{5}$$

with the boundary conditions $\eta(0)=\eta(\tau)=0$.

In order to find the solution of this equation we remember that the spatial homogeneity of Eq. (4) warrants the conservation of

$$C=\tfrac{1}{2}(\partial_t\eta)^2-\tfrac{1}{2}(1-h^2)\eta^2-\frac{1}{4\theta_0^2}\,h^2\eta^4. \tag{6}$$

This equation can be used to find $\eta(t)$. By the usual procedure we find

$$t-t_0=\frac{\sqrt{2\theta_0^2}}{h}\int^\eta \frac{d\tilde{\eta}}{\sqrt{(\tilde{\eta}^2-\eta_0^2)(\tilde{\eta}^2-\eta_1^2)}}, \tag{7}$$

where

$$\eta_0^2=\frac{\theta_0^2(h^2-1)}{h^2}\left[1-\left(1-\frac{4h^2C}{\theta_0^2(h^2-1)^2}\right)^{1/2}\right],$$

$$\eta_1^2=\frac{\theta_0^2(h^2-1)}{h^2}\left[1+\left(1-\frac{4h^2C}{\theta_0^2(h^2-1)^2}\right)^{1/2}\right],$$

and $\pm\eta_0$ are the turning points of the oscillating function $\eta(t)$. In this way η_0 gives its amplitude.

Since Eq. (7) is an elliptic integral of the first kind, it can be written in terms of elliptic functions [17], giving

$$\eta()=\eta_0\mathrm{sn}\left[\eta_1\left(\frac{h^2}{2\theta_0^2}\right)^{1/2}t,k\right], \tag{8}$$

where $\mathrm{sn}(u,k)$ is the elliptic sine function of argument k and we have chosen $t_0$in such a way that $\mathrm{sn}(0,k)=0$. For Eq. (8) we have $k^2=\eta_0^2/\eta_1^2$. Therefore the argument is limited to the interval $0\leqslant k^2\leqslant 1$.

From Eq. (7) it is also possible to obtain the period τ. Writing it in a form convenient for future use, we obtain

$$\left(\frac{2\pi}{\tau}\right)^2=\left(\frac{\pi}{2}\right)^2(h^2-1)\left(\frac{1}{(1+k^2)}\,\frac{1}{(K(k))^2}\right). \tag{9}$$

where $K(k)$ is the complete elliptic integral of the first kind [14].

Using the definition of k^2 given above it is possible to express C, η_1 and η_0 in terms of k^2. We obtain

$$C=\theta_0^2\,\frac{k^2}{(1+k^2)^2}\,\frac{(h^2-1)^2}{h^2},$$

$$\eta_0=\theta_0^2\,\frac{2k^2}{(1+k^2)}\,\frac{(h^2-1)}{h^2},$$

$$\eta_1=\frac{\eta_0}{k^2}.$$

Therefore, since k^2 is a function of C, we conclude that it is just a constant of integration controlling the shape of the elliptic sine function [14], i.e., as $k\to 0$ we have $\mathrm{sn}(u,k)\to\sin u$, and as $k\to 1$ we have $\mathrm{sn}(u,k)\to\tanh u$. Moreover the solution $\eta(t)$ can be separated into two terms: the amplitude of the oscillation, given by η_0, and the shape of the wall given by the elliptic sine function [10]. Hence, to solve Eq. (5) exactly, it is enough to determine k^2.

From Eq. (9), we see that in the case in which k^2 is not a function of h, a plot of $1/\lambda^2$ vs h^2 should be a straight line. But, as there is a bending in the curve, this is not observed in the experiment. Thus k^2 must change with the magnetic field. In order to find this dependence it would be necessary to consider the physics of the system in the instant in which the walls were created, which would involve the study of a nonlinear process, which is not our aim here. We want just describe the existence of the corresponding states. In this way we will just give an *ad hoc* argument to find the relation between k^2 and h. So, observe that the parameter k^2 grows with the magnetic field (above the Fréedericksz threshold) having an asymptotic value given by $k^2=1$ (the maximum deformation). This can be put in the simple differential relation

$$\frac{dk^2}{d(h-1)}=\alpha(1-k^2), \tag{10}$$

which can be easily integrated, giving

$$k^2=1-e^{-\alpha(h-1)}, \tag{11}$$

where we have used the fact that at the Fréedericksz threshold the walls should disappear, that is, as $h\to 1$, $k^2\to 0$. In this way Eq. (10) is the simplest relation between k^2 and h affording the k^2 limits, and α now plays the rule of a new constant of integration being, therefore, unique, and meaning that the shape of the walls is given in a universal way by the reduced magnetic field.

At this point we can use the experimental points to test our model. Since Eq. (9) does not depend on a particular system we hope that, if scaled according to the rules leading to Eqs. (4), the measured points will be located along the same universal line, and give us the ratio (K_{22}/K_{33}) and the parameter α that appears in Eq. (11). Of course, in order to achieve such a requirement, each particular system could give a particular value to these parameters. We have found not only that all the experimental points can indeed be put along the same universal line, giving us the ratio between the elastics constants, but that α is indeed a universal parameter.

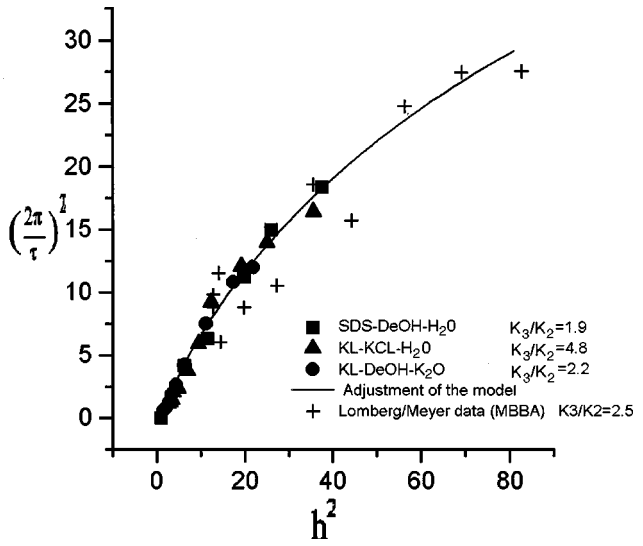

FIG. 2. The behavior of $(2d/\tau)^2$ as a function of h^2 for the same three lyotropic substances exhibited in Fig. 1 with the data of a thermotropic substance (MBBA) obtained from Ref. [7]. For the MBBA we have used for K_{33}/K_{22} the value reported in Ref. [7].

We tested our results for α in different liquid crystalline systems. For this purpose three lyotropic samples were prepared according to the usual procedure. The first sample (mixture 1) is a lyotropic mixture of potassium laurate (KL, 29.4), decanol (DeOH, 6.6), and water (64.0) [15]. The second sample (mixture II) is a lyotropic mixture of sodium decylsulfate (NadS, 41.6), decanol (DeOH, 6.6), and water (51.8) [16]. The third sample (mixture III) is a lyotropic mixture of potassium laurate (KL, 34.5), potassium chloride (KCl, 3.0), and water (62.5) [17]. The concentrations are indicated in weight percent. All the systems are in the nematic calamitic phase (N_c) at room temperature, for which the measurements were performed.

The method of generating the periodic distortion of the director consists in orienting a N_c sample in a planar geometry, with a high magnetic field (10 kG along the x axis). After a well-oriented sample is achieved, the field is switched off, and a controlled magnetic field is applied along the y axis. The resulting competition between the magnetic susceptibility (which tends to align the director along the field) and the elastic energies (which favors a director orientation consistent with the orientation at the surface) is responsible for the distortion of the director at values of the magnetic field above the Fréedericksz threshold. The reason is that, inside the sample, the director is subjected to a torque which tries to rotate it. At the same time, the director experiences an elastic restoring torque to the anchored surface layers.

In Fig. 1 the best fits of experimental data obtained from Eq. (9) are depicted. The ratio (K_{22}/K_{33}) in each case was obtained by using the least-square procedure and a universal value ($\alpha\approx 0.13$) for the parameter α. This figure refers to different lyotropic systems. In Fig. 2, besides the data on lyotropic systems, we also report the experimental data of a thermotropic nematic sample [7] with the corresponding ratio for the elastic constants, and by assuming the same value for the parameter α.

Observe that the significant differences in the ratio between the elastic constants in the lyotropic systems are not surprising because the compositions of these complex systems are very different. Also, the sequence of phase transitions in these compounds is distinct. For instance, in heating the mixture III the system passes to the hexagonal phase ($\approx$40 °C) [17], whereas the mixtures I and II, respectively near 50 and 40 °C, change to the isotropic phase.

III. CONCLUSION

In this work we have used the static exact solution of the Eq. (5) to describe a universal behavior of the periodic walls appearing above the Fréedericksz threshold. In a previous work [10] we used an approximated solution of this equation to describe these same walls and, with then, found a profile of the wavelength of this periodic structures as a function of the magnetic field. Of course, as they describe the same solution of Eq. (5), they give approximately the same behavior for the wavelength. Now, with the exact one, we have shown that the family of periodic walls appearing above the Fréedericksz threshold, for lyotropic and thermotropic compounds, can be reduced to a single physical picture through a law of corresponding states through a scaling of the elastic constants and the Fréedericksz critical field. We have also discovered a universal constant characterizing the correlation between the geometric form of the wall and the reduced magnetic field. This constant must be determined by the physics of the system in the moment in which the walls were produced, despite the fact we are dealing with a metastable system. A practical consequence of the entire approach we are proposing is that it can be used as a method to measure the elastic constants of a broad class of nematic liquid crystals, with positive diamagnetic anisotropy.

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