This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Elastic theory for Langmuir-Blodgett films

A. L. Alexe-ionescu[a][b]; G. Barbero[b][c]; A. Th. Ionescu[b][d]; A. K. Zvezdin[c][e]
[a] Department of Physics, Polytechnical Institute of Bucharest, Bucharest, Romania [b] Dipartimento di Fisica, Università della Calabria, Arcavacata di Rende, Italy [c] Dipartimento di Fisica, Politecnico di Torino, Torino, Italy [d] Department of Physics, University of Bucharest Magurele, Bucharest, Romania [e] Institute of General Physics, Russian Academy of Sciences, Moscow, Russia

To cite this Article Alexe-ionescu, A. L. , Barbero, G. , Ionescu, A. Th. and Zvezdin, A. K.(1996) 'Elastic theory for Langmuir-Blodgett films', Liquid Crystals, 20: 1, 9 — 16
To link to this Article: DOI: 10.1080/02678299608032020
URL: http://dx.doi.org/10.1080/02678299608032020

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1996, VOL. 20, NO. 1, 9–16

Elastic theory for Langmuir–Blodgett films†

by A. L. ALEXE-IONESCU*‡§, G. BARBERO§¶, A. Th. IONESCU§||,
A. K. ZVEZDIN¶††

‡Department of Physics, Polytechnical Institute of Bucharest, Splaiul
Independentei 313, R77216 Bucharest, Romania
§Dipartimento di Fisica, Università della Calabria, 87036 Arcavacata di Rende,
Italy
¶Dipartimento di Fisica, Politecnico di Torino, Corso Duca degli Abruzzi 24,
10129 Torino, Italy
||Department of Physics, University of Bucharest Magurele, P.O. Box Mg-11,
R-76900 Bucharest, Romania
††Institute of General Physics, Russian Academy of Sciences Vavilov Str. 38,
117942 Moscow, Russia

(Received 30 June 1995; accepted 10 July 1995)

An elastic theory for Langmuir–Blodgett films is presented. The expression for the free energy density of the film is obtained in terms of the deformation tensor by means of symmetry considerations and by making use of a quasi-microscopic model. The influence of a linear term in the deformation tensor in the elastic energy density is analysed. It is shown that when the elastic constant of the linear term is larger than a critical value, the ground state of the film is periodically distorted.

Downloaded At: 09:32 26 January 2011

1. Introduction

Nematic liquid crystals are constituted of elongated molecules that, in a first approximation, may be considered as rod-like [1]. The molecular interaction is such that the molecular major axes are tendentially parallel to a given direction **n**, called the director [1]. When **n** is position-independent, the nematic is undistorted. On the contrary, in the case $\mathbf{n} = \mathbf{n}(\mathbf{r})$, where **r** is the vector position with respect to the origin of a Cartesian reference frame, the nematic is distorted. When the $\mathbf{n}(\mathbf{r})$ variation takes place over a distance l that is very large with respect to a molecular dimension a, it is possible to describe the nematic director field by means of an elastic theory. This was proposed long ago by Oseen and Frank [2] and it is very similar to the usual elastic theory for solid materials. According to this theory, the nematic elastic properties are taken into account by introducing four (or five) elastic constants [2]. They may be connected with the intermolecular interaction energy [3]. A simple analysis shows that the elastic description near a limiting surface is different from that in the bulk, and new elastic constants appear in the elastic description [4, 5]. The aim of our paper is to build an elastic theory for a two-dimensional nematic with polar properties (broken up and down symmetry). This extension of the usual Frank elastic theory is important because Langmuir–Blodgett films behave in this manner [6]. In §2, the elastic energy density of a Langmuir–Blodgett film is obtained, and the number of elastic constants needed to describe the elastic properties deduced, taking into account the intrinsic biaxiality of the system. In particular, a contribution linear in the deformation tensor having the form of a Lifchitz invariant [7] is shown to exist in the expression for the elastic energy density of the film. It is also shown that the uniform part of the elastic energy is partially due to the anisotropic interaction between the film and the solid substrate and partially to the interaction among the molecules of the film itself. It represents the anisotropic part of the surface tension of the film–substrate interface. In §3, the actual orientation of the film is deduced by minimizing the total energy of the film. We show that a possible stable solution of the elastic equilibrium equations is connected to spatially modulated structures, if the elastic coefficient connected with the Lifchitz invariant is large enough. In §4, the elastic constant associated to the Lifchitz invariant is deduced by means of a simple pseudo-molecular model. The main results of our paper are discussed in §5, where we discuss the importance of the Lifchitz invariant on the stable orientation of the

---

*Author for correspondence.

†Invited paper presented at the European Conference on Liquid Crystals, Bovec, Slovenia, March 1995.

0267–8292/96 $12·00 © 1996 Taylor & Francis Ltd.

film and from what kind of molecular interactions the relevant elastic constant takes its origin.

2. Elastic theory of a two-dimensional orientationally ordered medium (2-D nematic)

Let us consider a two-dimensional orientationally ordered medium, like a 2-D nematic, in contact with a flat isotropic substrate of surface Σ and border γ. The molecules forming the film are supposed to be rod-like. The molecular major axis will be indicated by $\mathbf{m}$ and it will be supposed to be of modulus one: $m_i m_i = 1$ (see figure 1). The distribution of the molecules over Σ is supposed to be liquid-like. In the case $\mathbf{m}(\Sigma) = \mathbf{m}_0$, i.e. when $\mathbf{m}$ is position-independent, the film is considered as undistorted. On the contrary, if $\mathbf{m}$ is position dependent, the film is considered to be distorted. Let m_i be the Cartesian components of $\mathbf{m}$ and $m_{i,j} = \partial m_i/\partial x_j$ the elements of the deformation tensor. In the elastic limit $|m_{i,j}| \ll 1/l_0$, l_0 being the distance between the neighbouring molecules, the elastic free energy per unit area f may be regarded as an analytical function of the deformation tensor, of elements $m_{i,j}$. This means that

$$f = f(m_i, m_{i,j}). \qquad (1)$$

In the elastic limit, $m_{i,j}$ are small quantities. Hence it is possible to expand equation (1) in a power series of $m_{i,j}$s. At the second order approximation, we obtain

$$f = f_o(m_i) + A_{ij} m_{i,j} + \tfrac{1}{2} B_{ijke} m_{i,j} m_{k,e}. \qquad (2)$$

where $f_o(m_i)$ is the energy density of the undistorted state. It can be expanded in a power series of $\mathbf{m}\cdot\mathbf{k}$, where $\mathbf{k}$ is the geometrical normal to Σ (see figure 1). By taking into account that $\mathbf{m}$ is not equivalent to $-\mathbf{m}$ (owing to the broken up/down symmetry supposed in the present analysis), at the second order in $\mathbf{m}\cdot\mathbf{k}$, f_o is given by

$$f_o(m_i) = -w_1(\mathbf{m}\cdot\mathbf{k}) - \tfrac{1}{2} w_2(\mathbf{m}\cdot\mathbf{k})^2. \qquad (3)$$

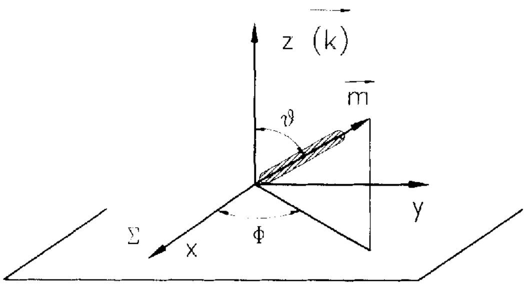

Figure 1. Rod-like molecule forming a Langmuir–Blodgett film. Σ is the flat isotropic surface over which the film is deposited. $\mathbf{m}$ coincides with the molecular long axis. $\mathbf{k}$ is the geometrical normal to the surface. ϑ and ϕ are the tilt and twist angles, respectively.

As stressed before, equation (3) is a consequence of the polar structure of the amphiphilic molecules forming the Langmuir–Blodgett film. In equation (3), w_1 and w_2 take their origin from the intermolecular interaction among the molecules forming the film and from the interaction of the molecules of the substrate with those of the film. f_o represents the anisotropic part of the uniform contribution to the surface energy density of the film. Hence it can be considered as the anisotropic component of the surface tension of the film–substrate interface. As is evident, f_o has an extrinsic part due to the film–substrate interaction and an intrinsic part which depends only on the physical properties of the film. The orientation of the film minimizing f_o may be considered as the 'easy direction' imposed by the presence of the film–substrate interface or the film itself. In the absence of the linear term in (2) ($A_{ij} = 0$), this orientation also minimizes $f(m_i, m_{i,j})$, because $(1/2)B_{ijke} m_{i,j} m_{k,e} \geqslant 0$. However, as will be shown in the following, the presence of the linear term in (2) can drastically change the orientation of the ground state. This means that the easy direction minimizing f_o, could no longer minimize the total energy of the film. Of course, this conclusion remains valid even in the case in which the easy direction is uniform on the surface.

In (2), A_{ij} and B_{ijke} play the role of 'elastic parameters'. They are defined by

$$A_{ij} = \left(\frac{\partial f}{\partial m_{i,j}}\right)_{m_{i,j}=0} \qquad (4)$$

and

$$B_{ijke} = \left(\frac{\partial^2 f}{\partial m_{i,j}\, \partial m_{k,e}}\right)_{m_{i,j}=0}. \qquad (5)$$

These parameters may be evaluated when the intermolecular interaction energy is known. This will be shown in §4 in relation to the tensor A of elements A_{ij}. As a consequence of (5), the elastic tensor of elements B_{ijke} is such that $B_{ijke} = B_{keij}$. The elastic tensors appearing in (2) have to be decomposed in terms of the elements of symmetry of the medium under consideration, of the identity tensor of elements δ_{ij} and of the Levi-Civita antisymmetric tensor of elements ε_{ijk}, according to well-known rules [8]. The elements of symmetry of the film are $\mathbf{m}$ and the geometrical normal of the flat and isotropic surface $\mathbf{k}$.

Let us consider first the tensor of elements A_{ij}. From the above discussion it may be decomposed in the

Downloaded At: 09:32 26 January 2011

following manner

$$A_{ij} = A_1 \delta_{ij} + A_2 k_i k_j + A_3 m_j k_i + A_4 m_i m_j + A_5 m_i k_j, \tag{6}$$

if the molecules forming the film are supposed to be non-chiral.

The energy term linear in $m_{i,j}$ is then

$$A_{ij} m_{i,j} = A_1 (\nabla \cdot \mathbf{m}) + A_2 (\mathbf{k} \cdot \nabla)(\mathbf{k} \cdot \mathbf{m}) + A_3 \mathbf{k} \cdot [\mathbf{m} \times (\nabla \times \mathbf{m})], \tag{7}$$

because from $m_i m_i = 1$, it follows that $m_i m_{i,j} = 0$ for every j. Note that for our 2-D nematic, $\mathbf{m} = \mathbf{m}(x, y)$, where (x, y) are the Cartesian coordinates of the considered point on Σ. This means that $\mathbf{m}$ is defined only over Σ and it is z-independent. In the case of a flat surface (as is supposed in our analysis), the geometrical normal is parallel to the z axis. Consequently $\mathbf{k} \cdot \nabla \equiv 0$ and the constant A_2 does not enter into the elastic description. It follows therefore that for a flat isotropic surface and a monomolecular film made of non-chiral molecules, the energy term linear in the deformation tensor of elements $m_{i,j}$ reduces to

$$A_{ij} m_{i,j} = A_1 (\nabla \cdot \mathbf{m}) + A_3 \mathbf{k} \cdot [\mathbf{m} \times (\nabla \times \mathbf{m})]. \tag{8}$$

The scalar parameters A_1 and A_3 depend on $\mathbf{m}_o \cdot \mathbf{k}$, where $\mathbf{m}_o$ is the molecular orientation of the undeformed film introduced before. They are position independent. Since $A_1(\nabla \cdot \mathbf{m})$ reduces to a line contribution for the Gauss theorem, it can be neglected in (2). In relation to the latter term in (8), a simple analysis shows that it may be rewritten as

$$\begin{aligned} \mathbf{k} \cdot [\mathbf{m} \times (\nabla \times \mathbf{m})] &= k_i m_j m_{j,i} - m_j m_{i,j} k_i = -m_j m_{i,j} k_i \\ &= -(\mathbf{m} \cdot \nabla)(\mathbf{m} \cdot \mathbf{k}), \end{aligned} \tag{9}$$

because $k_i m_j m_{j,i} = \mathbf{m} \cdot [(\mathbf{k} \cdot \nabla) \mathbf{m}] \equiv 0$. In conclusion, the term (7) is equivalent to

$$A_{ij} m_{i,j} = -\lambda (\mathbf{m} \cdot \nabla)(\mathbf{m} \cdot \mathbf{k}), \tag{10}$$

where $\lambda \equiv A_3$. It is known as the 'Lifchitz invariant' [9]. The quadratic term in (2) may be decomposed in the usual manner. In our case, in a first approximation, it may be written in the form $(1/2) K m_{i,j} m_{i,j}$, where $K > 0$ is the usual nematic-like elastic constant [10]. This expression for the quadratic term appearing in the free energy density of the film corresponds to the well-known Oseen–Frank energy density for a nematic liquid crystal in the one constant approximation (see for instance [10]). When

$$\mathbf{m} = \mathbf{i} \cos\phi \sin\vartheta + \mathbf{j} \sin\phi \sin\vartheta + \mathbf{k} \cos\vartheta, \tag{11}$$

where ϕ and ϑ are defined in figure 1, simple calculations give

$$\left.\begin{aligned} f_o &= -w_1 \cos\vartheta - \tfrac{1}{2} w_2 \cos^2\vartheta \\ A_{ij} m_{i,j} &= \lambda \sin^2\vartheta \left(\cos\phi \frac{\partial\vartheta}{\partial x} + \sin\phi \frac{\partial\vartheta}{\partial y} \right) \\ \frac{1}{2} B_{ijke} m_{i,j} m_{k,e} &= \frac{1}{2} K \left\{ \left[\left(\frac{\partial\vartheta}{\partial x} \right)^2 + \left(\frac{\partial\partial}{\partial y} \right)^2 \right] \right. \\ &\quad \left. + \sin^2\vartheta \left[\left(\frac{\partial\phi}{\partial x} \right)^2 + \left(\frac{\partial\phi}{\partial y} \right)^2 \right] \right\} \end{aligned}\right\} \tag{12}$$

for the different contributions to the elastic energy density of the distorted monomolecular film appearing in equation (2). The actual function $\mathbf{m}(x, y)$ is obtained by minimizing the total elastic energy.

3. Total elastic energy and molecular orientation of the film

The total elastic energy F of the monomolecular film deposited over a flat and isotropic substrate is obtained by integrating (2) over the surface of the film Σ. By taking into account (12) we have

$$\begin{aligned} F = \iint_\Sigma \Bigg(& \frac{1}{2} K \left\{ \left[\left(\frac{\partial\vartheta}{\partial x} \right)^2 + \left(\frac{\partial\vartheta}{\partial y} \right)^2 \right] \right. \\ & \left. + \sin^2\vartheta \left[\left(\frac{\partial\phi}{\partial x} \right)^2 + \left(\frac{\partial\phi}{\partial y} \right)^2 \right] \right\} \\ & - w_1 \cos\vartheta - \frac{1}{2} w_2 \cos^2\vartheta \\ & + \lambda \sin^2\vartheta \left(\cos\phi \frac{\partial\vartheta}{\partial x} + \sin\phi \frac{\partial\vartheta}{\partial y} \right) \Bigg) \mathrm{d}x \, \mathrm{d}y. \end{aligned} \tag{13}$$

Equation (13) is minimized by the $\mathbf{m}(x, y)$ field, or the $\vartheta(x, y)$ and $\phi(x, y)$ angles. Routine calculations give for the Euler–Lagrange equations satisfied by $\vartheta(x, y)$ and $\phi(x, y)$ [11]

$$\begin{aligned} & -K \left(\frac{\partial^2\vartheta}{\partial x^2} + \frac{\partial^2\vartheta}{\partial y^2} \right) + \sin\vartheta \cos\vartheta \\ & \times \left\{ w_2 + K \left[\left(\frac{\partial\phi}{\partial x} \right)^2 + \left(\frac{\partial\phi}{\partial y} \right)^2 \right] \right\} \\ & - w_1 \sin\vartheta - \lambda \sin^2\vartheta \left(\frac{\partial \cos\phi}{\partial x} + \frac{\partial \sin\phi}{\partial y} \right) = 0, \end{aligned} \tag{14a}$$

$$\begin{aligned} & -K \left(\mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} \right) \left[\sin^2\vartheta \left(\frac{\partial\phi}{\partial x} \mathbf{i} + \frac{\partial\phi}{\partial y} \mathbf{j} \right) \right] \\ & - \lambda \sin^2\vartheta \left(\sin\phi \frac{\partial\vartheta}{\partial x} - \cos\phi \frac{\partial\vartheta}{\partial y} \right) = 0. \end{aligned} \tag{14b}$$

By solving (14) we can obtain the tilt, $\vartheta(x, y)$ and twist,

Downloaded At: 09:32 26 January 2011

$\phi(x, y)$, angles formed by $\mathbf{m}(x, y)$ with $\mathbf{k}$ and with a given direction x.

The 'bulk' equations (14) have to be solved with the boundary conditions imposed on the border γ of the surface Σ. As is well known, these boundary conditions are obtained by means of a variational approach minimizing the total energy of the film. It is given by $F_T = F + F_\gamma$, where F is given by (13) and F_γ takes into account the energy contribution connected with the presence of the line γ. The quantity F_γ plays the same role as the surface tension when an interface between two different media is considered. In our case, we have two kinds of 'surface tension': the first one is connected to the interaction of the film with the substrate, described by w_1 and w_2 in equation (3), and the second is connected to the presence of the border γ, described by F_γ. In the following, we will suppose that $F_\gamma \ll F$. This condition is usually satisfied if Σ is large enough. In fact $F \propto R^2$ and $F_\gamma \propto R$, where R is a typical dimension of Σ. Consequently, $F_\gamma / F \propto 1/R$. This means that for large R, the above mentioned inequality is verified. In this case the total energy of the film practically coincides with F given by (13). This implies that the boundary conditions for the 'bulk' equations (14) are the transversality conditions [11]. By taking into account (13), these conditions can be written as

$$\left[K\left(\mathbf{i}\frac{\partial \vartheta}{\partial x} + \mathbf{j}\frac{\partial \vartheta}{\partial y}\right) + \lambda \sin^2 \vartheta (\mathbf{i}\cos\phi + \mathbf{j}\sin\phi)\right] \cdot \hat{\mathbf{v}} = 0, \tag{15a}$$

$$\sin^2 \vartheta \left(\mathbf{i}\frac{\partial \phi}{\partial x} + \mathbf{j}\frac{\partial \phi}{\partial y}\right) \cdot \hat{\mathbf{v}} = 0, \tag{15b}$$

where $\hat{\mathbf{v}}$ is a unit vector normal to γ, parallel to the (x, y)-plane.

It should be stressed that among the solutions of the non-linear partial differential equations (14) and the boundary condition (15), there is the exact solution in which the twist angle $\phi(x, y)$ is constant and the tilt angle $\vartheta(x, y)$ depends in a simple manner on x and y. In fact in the case

$$\vartheta = \vartheta(\xi), \quad \text{where } \xi = \mathbf{q}_\perp \mathbf{r}_\perp = q_x x + q_y y, \tag{16}$$

one obtains from (15)

$$tg\,\phi = \left(\frac{\partial \vartheta}{\partial y}\right) \Big/ \left(\frac{\partial \partial}{\partial x}\right) = \frac{q_y}{q_x} = \text{const}, \tag{17}$$

i.e. $\phi = \text{const}$ [7]. In this case, the boundary condition (15 *b*) is identically satisfied, whereas (15 *a*) becomes

$$\left(K\frac{\mathrm{d}\vartheta}{\mathrm{d}\xi} + \lambda \sin^2 \vartheta\right) \mathbf{q} \cdot \hat{\mathbf{v}} = 0.$$

From now on the γ-line will be supposed to be of rectangular shape with two sides parallel to $\mathbf{q}$. In this case, the above mentioned boundary condition is identically satisfied on the two sides parallel to $\mathbf{q}$, because $\mathbf{q} \cdot \hat{\mathbf{v}} = 0$. On the other sides, it writes as

$$K\frac{\mathrm{d}\vartheta}{\mathrm{d}\xi} + \lambda \sin^2 \vartheta = 0, \text{ on the two sides normal to } \mathbf{q}. \tag{15a'}$$

This equation clearly shows that λ is equivalent to a finite anchoring energy. Equation (15 *a'*) indicates that if $\lambda \neq 0$, $|(\mathrm{d}\vartheta/\mathrm{d}\xi)_\gamma| = (\lambda/K)\sin^2 \vartheta$. This means that the system tries to be distorted over Σ.

We point out that when the substrate is assumed to be isotropic, neither the value of ϕ, nor $\mathbf{q}_\perp = q_x \mathbf{i} + q_y \mathbf{j}$ can be determined. On the contrary, when the substrate is characterized by an azimuthal anisotropy, ϕ is determined by the associated anisotropy-energy (connected with the easy azimuthal axis). In this case, the wave vector $\mathbf{q}_\perp$ is parallel to the azimuthal easy axis. Let us suppose, as before, that the substrate is flat and isotropic. The previous discussion shows that the function $\vartheta(\xi)$ given by (16) is determined by equation (14), which in the present case is written

$$-Kq^2 \frac{\mathrm{d}^2 \vartheta}{\mathrm{d}\xi^2} + w_2 \sin \vartheta \cos \vartheta + w_1 \sin \vartheta = 0, \tag{18}$$

q^2 being defined as $q^2 = q_x^2 + q_y^2$. The 'bulk' equation (18) has to be solved with the boundary condition (15 *a'*). However, in the present case it is simpler to follow an alternative method. It consists of writing the first integral of (18). In this manner an integration constant, connected to the total energy, appears in the problem. This integration constant is then found by minimizing the total energy of the system, given by (13) with respect to this quantity. The first integral of (18) is

$$-\frac{1}{2}Kq^2\left(\frac{\mathrm{d}\vartheta}{\mathrm{d}\xi}\right)^2 + \frac{1}{2}w_2 \sin^2 \vartheta - w_1 \cos \vartheta = -\frac{1}{2}E, \tag{19}$$

where E is the integration constant to be determined. As follows from (19), E is related to the total energy density connected with the ϑ-deformation (see also equation (13)). The solution of (18), or of (19), depends on w_1 and w_2, characterizing the uniform portion of the surface energy f_0. For the sake of simplicity, in the following, we will limit our investigation to the case $w_1 = 0$. In this sub-case, the solution of (19) is

$$\sin \vartheta = \mathrm{sn}\left[\left(\frac{Kq^2}{E}\right)^{-1/2} \xi \,|\, -k\right], \tag{20}$$

where $\mathrm{sn}(u/m)$ is the Jacobian elliptical function and m is the parameter of this function [12]. In (20), $k = w_2/E$.

Downloaded At: 09:32 26 January 2011

Downloaded At: 09:32 26 January 2011

From (20) we obtain

$$\vartheta(x,y)=\mathrm{am}\left[\left(\frac{Kq^2}{E}\right)^{-1/2}\xi\,|-k\right]$$

where $\mathrm{am}(u)$ is the amplitude of the Jacobian elliptical function. By substituting (20) into (13), after integration, one obtains $F=F(E)$. Consequently, the E-parameter may be determined by minimizing F with respect to E. The period L of the space modulated structure (SMS) is determined, from (19), and it is found to be [9]

$$L=4K(k) \tag{21}$$

where $K(k)$ is the so-called real quarter period of the Jacobian function [12] (or the elliptical integral of the first kind between 0 and 2π). In the asymptotic case in which $k=w_2/E\ll 1$, the Jacobian elliptical function introduced in (20) can be approximated by [12]

$$\mathrm{sn}\,(u/-k)\approx\sin u=\sin\left[\left(\frac{Kq^2}{E}\right)^{-1/2}\xi\right]\approx\sin\xi, \tag{22}$$

because in our approximation $E=Kq^2$. It follows from (20) that one has

$$\vartheta(x,y)=\xi=q_x x+q_y y. \tag{23}$$

By substituting (23) and (17) into (13), straightforward calculations give, for the total energy of the monomolecular film, per unit area and per ϑ-period, the expression

$$F=\tfrac{1}{2}Kq^2-\tfrac{1}{2}\lambda q+\tfrac{1}{4}w_2. \tag{24}$$

The q-value minimizing (24) is

$$q=\lambda/2K, \tag{25}$$

fixing the period of the SMS. It may be simply verified that the differential system (14) and (15) also admits the trivial solution

$$\partial(x,y)=0 \quad\text{and}\quad \phi(x,y)=\text{const}, \tag{26}$$

corresponding to a homogeneous state (HS). It may be instructive to compare the total energy of the homogeneous state with that of the SMS. A simple calculation gives

$$\Delta F=F_{\mathrm{SMS}}-F_{\mathrm{HS}}=-\frac{1}{8}\frac{\lambda^2}{K}+\frac{1}{4}w_2, \tag{27}$$

from which we can derive that the SMS is energetically favourable, i.e. $\Delta F<0$, only if

$$\lambda>\lambda_c=(2w_2K)^{1/2}. \tag{28}$$

For $\lambda<\lambda_c$ the HS corresponds to the stable configuration.

In the framework $w_1\neq 0$, but $w_1\ll(\lambda^2/2K)$, the previous analysis remains almost unchanged. Therefore, this case will not be considered further.

4. Molecular estimation of the elastic constant connected to the Lifchitz-invariant

In the previous section, we have shown that if $\lambda>\lambda_c$, given by equation (28), $F_{\mathrm{SMS}}<F_{\mathrm{H}}$. This implies that the ground state is periodically distorted, and its period is given by $2\pi/q=4\pi K/\lambda$, according to (25). This situation, in some respects, is similar to that corresponding to cholesteric liquid crystals [11]. In that case, a linear term in the deformation tensor is present, due to the chirality of the molecules forming the phase under consideration. The main difference between the two cases is that an unbounded cholesteric liquid crystal sample displays a periodic deformation, for all values of the elastic constant associated to the linear term (spontaneous twist). On the contrary, in the present case, there exists a critical value of the relevant elastic constant, such that for smaller values, the HS structure is energetically favoured. As discussed elsewhere [13], it is possible to connect the elastic constants characterizing the monomolecular, orientationally ordered film to the intermolecular interaction energy. In this section this will be done for the elastic constant λ connected to the Lifchitz invariant.

Let $g(\mathbf{m},\mathbf{m}',\mathbf{r})$ be the intermolecular interaction energy between the surface elements $\mathrm{d}\Sigma$ and $\mathrm{d}\Sigma'$ at $\mathbf{R}$ and $\mathbf{R}'=\mathbf{R}+\boldsymbol{\rho}$, where the direction of the molecular major axes are $\mathbf{m}$ and $\mathbf{m}'$ (see figure 2). In general $g(\mathbf{m},\mathbf{m}',\mathbf{r})$ may be expanded in power series of $\mathbf{m}\cdot\mathbf{r}$, $\mathbf{m}'\cdot\mathbf{r}$ and $\mathbf{m}\cdot\mathbf{m}'$ in the following manner

$$g(\mathbf{m},\mathbf{m}',\mathbf{r})=\sum_{abc}\tilde{C}_{abc}(r)(\mathbf{m}\cdot\mathbf{m}')^a(\mathbf{m}\cdot\mathbf{r})^b(\mathbf{m}'\cdot\mathbf{r})^c, \tag{29}$$

where the expansion coefficients C_{abc} depend only on

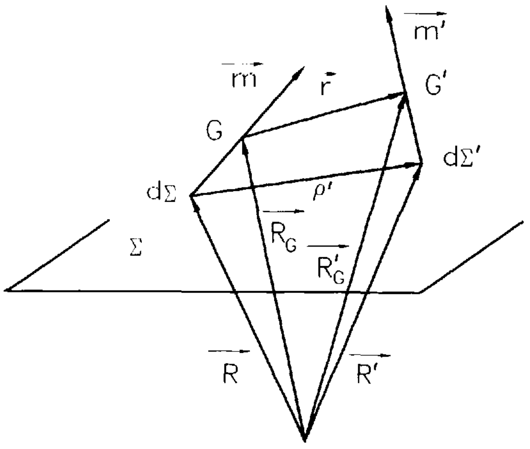

Figure 2. The geometrical parameters characterizing the interaction between the two surface elements $\mathrm{d}\Sigma$ and $\mathrm{d}\Sigma'$ in which the average molecular orientation is $\mathbf{m}$ and $\mathbf{m}'$. G and G' are the centres of the molecules. $\mathbf{r}=\mathbf{GG}'$ and $\boldsymbol{\rho}$ is the vector lying on the plane Σ from $\mathrm{d}\Sigma$ to $\mathrm{d}\Sigma'$.

Downloaded At: 09:32 26 January 2011

the modulus of $\mathbf{r}$. Since $g(\mathbf{m},\mathbf{m}',\mathbf{r})=g(\mathbf{m}',\mathbf{m},\mathbf{r})$, we derive $b=c$.

In the hypothesis that the interaction centre is localized in the middle of the molecules G, we have

$$\mathbf{R}_G=\mathbf{R}+\frac{l}{2}\mathbf{m} \quad \text{and} \quad \mathbf{R}'_G=\mathbf{R}'+\frac{l}{2}\mathbf{m}', \tag{30}$$

where l is the length of the molecule forming the Langmuir–Blodgett film, as follows from figure 2. By means of (30), one derives

$$\mathbf{r}=\mathbf{R}'_G-\mathbf{R}_G=\boldsymbol{\rho}+\frac{l}{2}\boldsymbol{\delta}\mathbf{m}, \tag{31}$$

where $\boldsymbol{\delta}\mathbf{m}=\mathbf{m}'-\mathbf{m}$. Since $\mathbf{m}\cdot\mathbf{m}=\mathbf{m}'\cdot\mathbf{m}'=1$, to the first order in $\boldsymbol{\delta}\mathbf{m}, \mathbf{m}$ and $\boldsymbol{\delta}\mathbf{m}$ are mutually orthogonal:

$$\mathbf{m}\cdot\boldsymbol{\delta}\mathbf{m}=0. \tag{32}$$

By substituting (31) into (19) and taking into account both (32) and the condition $|\boldsymbol{\delta}\mathbf{m}|\ll 1$ valid in the elastic limit, we obtain for the expansion coefficients to the first order in $|\boldsymbol{\delta}\mathbf{m}|$

$$\tilde{C}_{ab}(r)=\tilde{C}_{ab}(\rho)+\tilde{B}_{ab}(\rho)\frac{l}{2}\mathbf{u}\cdot\boldsymbol{\delta}\mathbf{m},$$

where

$$\tilde{B}_{ab}(\rho)=\left(\frac{\mathrm{d}\tilde{C}_{ab}}{\mathrm{d}r}\right)_{r=\rho},$$

and hence

$$\begin{aligned} g(\mathbf{m},\mathbf{m}',\mathbf{r})=\sum_{a,b}\bigg\{ & C_{ab(\rho)}(\mathbf{m}\cdot\mathbf{u})^{2b} \\ & +\left[bC_{ab}(\rho)+\frac{l}{2}B_{ab}(\rho)(\mathbf{m}\cdot\mathbf{u})\right] \\ & \times(\mathbf{m}\cdot\mathbf{u})^{2b-1}(\mathbf{u}\cdot\boldsymbol{\delta}\mathbf{m})\bigg\} \end{aligned} \tag{33}$$

where $C_{ab}(\rho)=\rho^{2b}\tilde{C}_{ab}(\rho)$, $B_{ab}(\rho)=\rho^{2b}\tilde{B}_{ab}$ and $\mathbf{u}=\boldsymbol{\rho}/\rho$. According to [13], the elastic tensor connected with the linear contribution in the deformation tensor is

$$A_{ij}=\frac{1}{2}\iint_{\Sigma_\infty}\chi_i(\boldsymbol{\rho})\rho_j\mathrm{d}\Sigma', \tag{34}$$

in the mean field approximation. In (34) $\chi_i(\boldsymbol{\rho})$ are defined by

$$\chi_i(\boldsymbol{\rho})=\left\{\frac{\partial g}{\partial(\delta m_i)}\right\}_{\boldsymbol{\delta}\mathbf{m}=0}, \tag{35}$$

and Σ_∞ means that the integration over ρ is extended over the range of intermolecular forces giving rise to the orientationally ordered monomolecular film. By substituting (33) into (35) one obtains

$$\chi_i(\boldsymbol{\rho})=\sum_{a,b}\left[bC_{ab}(\rho)+\frac{l}{2}B_{ab}(\rho)(\mathbf{m}\cdot\mathbf{u})\right](\mathbf{m}\cdot\mathbf{u})^{2b-1}u_i. \tag{36}$$

Consequently the tensor A_{ij} is found to be

$$\begin{aligned} A_{ij}=\frac{1}{2}\sum_{a,b}\bigg\{ & \iint_{\Sigma_\infty} bC_{abc}(\rho)(\mathbf{m}\cdot\mathbf{u})^{2b-1}u_iu_j\rho\mathrm{d}\Sigma' \\ & +\iint_{\Sigma_\infty}\frac{1}{2}B_{ab}(\rho)(\mathbf{m}\cdot\mathbf{u})^{2b}u_iu_j\rho\mathrm{d}\Sigma\bigg\}. \end{aligned} \tag{37}$$

A simple analysis shows that the first term on the right hand side of (37) is identically zero. To show this, let us consider a Cartesian reference frame in which $\mathbf{m}=(\sin\vartheta,0,\cos\vartheta)$ and $\mathbf{u}=(\cos\psi,\sin\psi,0)$, as shown in figure 3. In this case the term under consideration writes

$$T_{ij}=\frac{1}{2}\sum_{a,b}\iint_{\Sigma_\infty}C_{ab}(\rho)(\mathbf{m}\cdot\mathbf{u})^{2b-1}u_iu_j\rho\mathrm{d}\Sigma'. \tag{38}$$

In polar coordinates Σ_∞ is defined by: $\rho_0\leqslant\rho\leqslant\rho_\infty$ and $0\leqslant\psi\leqslant 2\pi$, where ρ_0 is of the order $1/\sigma^{1/2}$, where σ is the molecular surface density of the film. ρ_∞ is the range of the intermolecular forces. By using polar coordinates, (38) can be rewritten as

$$T_{ij}=\frac{1}{2}\sum_{a,b}bR_{ab}(\rho_0,\rho_\infty)(\sin\vartheta)^{2b-1}t_{ij}(b) \tag{39}$$

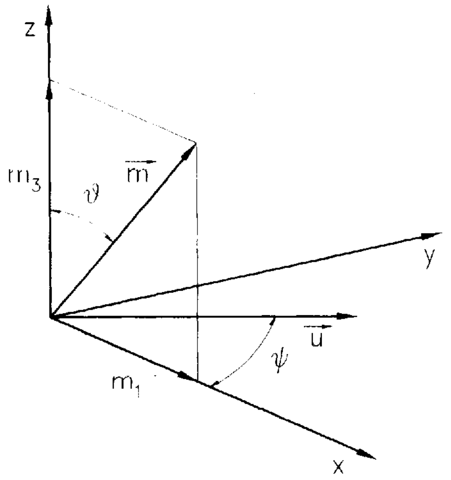

Figure 3. The Cartesian reference frame used to evaluate the integrals appearing in the pseudo-molecular model to estimate the elastic constant connected to the Lifchitz-invariant.

Downloaded At: 09:32 26 January 2011

where

$$R_{ab}(\rho_0,\rho_\infty)=\int_{\rho_0}^{\rho_\infty} C_{ab}(\rho)\rho^2\mathrm{d}\rho$$

and (40)

$$t_{ij}(b)=\int_0^{2\pi}(\cos\psi)^{2b-1}u_iu_j\mathrm{d}\psi.$$

A straightforward calculation shows that $t_{ij}(b)\equiv 0$. Consequently, $T_{ij}\equiv 0$. It follows that the tensor A_{ij} we are looking for is given by

$$A_{ij}=\sum_{a,b}\frac{l}{4}\iint_{\Sigma_\infty} B_{ab}(\rho)u_iu_j(\mathbf{m}\cdot\mathbf{u})^{2b}\rho\mathrm{d}\Sigma'. \qquad (41)$$

To deduce the explicit expressions for $\lambda=A_3$, it is necessary to reconsider the expansion (6). From it one easily obtains

$$\left.\begin{aligned}
A_{ii}&=3A_1+A_2+A_3P+A_4+A_5P,\\
m_iA_{ij}m_j&=A_1+A_2P^2+A_3P+A_4+A_5P,\\
k_iA_{ij}k_j&=A_1+A_2+A_3P+A_4P^2+A_5P,\\
k_iA_{ij}m_j&=A_1P+A_2P+A_3+A_4P+A_5P^2,\\
m_iA_{ij}k_j&=A_1P+A_2P+A_3P^2+A_4P+A_5,
\end{aligned}\right\} \qquad (42)$$

where $P=\mathbf{m}\cdot\mathbf{k}=\cos\vartheta$. A simple analysis shows that

$$k_iA_{ij}k_j=k_iA_{ij}m_j=m_iA_{ij}k_j=k_iA_{ij}m_j=0, \qquad (43)$$

because $\mathbf{k}\cdot\mathbf{u}=0$. By taking into account (43), we obtain from (42) the following expression for the elastic constant connected to the Lifchitz invariant

$$A_3=\lambda=P\frac{(1-P^2)A_{ii}\times 2m_iA_{ij}m_j}{(1-P^2)^2}. \qquad (44)$$

It should be noted that in the case $b=0$, it follows from (41) that

$$\left.\begin{aligned}
A_{ii}(b=0)&=\sum_a\frac{l}{4}2\pi\int_{\rho_0}^{\rho_\infty}B_{a0}(\rho)\rho^2\mathrm{d}\rho\\
m_im_jA_{ij}(b=0)&=\sum_a\frac{l}{4}2\pi\int_{\rho_0}^{\rho_\infty}B_{a0}(\rho)\rho^2\mathrm{d}\rho\\
&\quad\times\int_0^{2\pi}\sin^2\vartheta\cos^2\psi\mathrm{d}\psi\\
&=(1-P^2)\frac{1}{2}A_{ii}(b=0).
\end{aligned}\right\} \qquad (45)$$

Consequently $\lambda(b=0)=0$. This is consistent with equation (41). In fact, if $b=0$ the tensor of elements A_{ij} is given by

$$A_{ij}(b=0)=\sum_a\frac{l}{4}\int_{\rho_0}^{\rho_\infty}B_{a0}(\rho)\rho^2\mathrm{d}\rho\int_0^{2\pi}u_iu_j\mathrm{d}\psi.$$

By taking into account that

$$\int_0^{2\pi}u_iu_j\mathrm{d}\psi=\frac{\pi}{2}\delta_{ij},$$

we obtain $A_{ij}(b=0)=A_1(b=0)\delta_{ij}$, where

$$A_1(b=0)=\frac{\pi}{8}l\sum_a\int_{\rho_0}^{\rho_\infty}B_{a0}(\rho)\rho^2\mathrm{d}\rho.$$

By comparing the expression for $A_{ij}(b=0)$ with expansion (6), we obtain $A_3(b=0)=\lambda(b=0)=0$, as deduced before. As a consequence of these results the Lifchitz invariant is connected to an intermolecular interaction depending on $(\mathbf{m}\cdot\mathbf{r})$ and $(\mathbf{m}'\cdot\mathbf{r})$. When these terms are absent, so that g depends only on the relative orientation $\mathbf{m}\cdot\mathbf{m}'$, λ is identically zero. Since $b\geqslant 1$, it is possible to rewrite (44) in the form

$$\begin{aligned}
\lambda=P\frac{l}{4}\sum_{a,b}(1-P^2)^{b-1}&\int_{\rho_0}^{\rho_\infty}B_{ab}(\rho)\rho^2\mathrm{d}\rho\\
\times&\int_0^{2\pi}(\cos\psi)^{2b}(1-2\cos^2\psi)\mathrm{d}\psi,
\end{aligned} \qquad (46)$$

showing that there are no divergences in the limit $P\to 1$.

As an example, let us now consider the simple case in which

$$g(\mathbf{m},\mathbf{m}',\mathbf{r})=G_0\mathrm{e}^{-(r/r_0)^2}(\mathbf{m}\cdot\mathbf{m}')^2(\mathbf{m}\cdot\mathbf{r})(\mathbf{m}'\cdot\mathbf{r}), \qquad (47)$$

where G_0 is the strength of the molecular interaction and r_0 a typical length, of the order of magnitude of the molecular dimensions. Expression (47) for $g(\mathbf{m},\mathbf{m}',\mathbf{r})$ is a generalization of that proposed by McMillan [14] for studying the smectic phase. By comparing (47) with (25) we deduce that

$$\tilde{C}_{ab}=G_0\delta_{a2}\delta_{b1}\mathrm{e}^{-(r/r_0)^2}, \qquad (48)$$

and hence

$$\tilde{B}_{ab}=\left(\frac{\mathrm{d}\tilde{C}_{ab}}{\mathrm{d}r}\right)_\rho=-2G_0\frac{\rho}{r_0^2}\mathrm{e}^{-(r/r_0)^2}\delta_{a2}\delta_{b1}. \qquad (49)$$

It follows that

$$B_{ab}(\rho)=\rho^{2b}\tilde{B}_{ab}=-2G_0\frac{\rho^3}{r_0^2}\mathrm{e}^{-(r/r_0)^2}\delta_{a2}\delta_{b1}. \qquad (50)$$

By substituting (50) into (46) a simple calculation gives

$$\lambda\approx\frac{\pi}{4}lG_0\frac{\rho_0^5}{r_0}P. \qquad (51)$$

Other more general models can be considered, as suggested recently by Binder *et al.* [15] and Safran *et al.* [16].

Downloaded At: 09:32 26 January 2011

5. Conclusions

An elastic description of an orientationally oriented monomolecular film has been proposed. By generalizing the well-known elastic theory proposed by Frank for a nematic liquid crystal, an expression for the elastic energy density of a Langmuir–Blodgett film has been obtained. We have shown that when the distortion is described by means of a tensor of a second order defined by $\partial m_i/\partial x_j$, where **m** is the average molecular orientation, the elastic energy density may contain a linear term in the deformation tensor. This term is known to people working in magnetism as the Lifchitz-invariant [9]. Our analysis has shown that the ground state of the Langmuir–Blodgett film may be distorted if the elastic constant connected to the Lifchitz-invariant [9] is larger than a critical value. We have also proposed a pseudo-molecular model to evaluate the elastic constants characterizing the Langmuir–Blodgett film. According to this model, the Lifchitz-invariant has to be taken into account in the elastic description every time the interaction among the molecules forming the film does not depend only on the relative orientation of the interacting molecules. A simple expression for the intermolecular interaction energy describing the interaction between conically shaped molecules has also been proposed. The analysis presented in this paper may be useful also to describe the alignment induced in nematic liquid crystals by surfaces coated by a Langmuir–Blodgett film [17]. In fact, according to Hiltrop and Stegemeyer [6, 17], the nematic orientation in samples aligned by means of Langmuir–Blodgett films is sometimes related to steric interaction. This means that the nematic liquid crystal molecules can enter into small holes existing in the film. The absorbed liquid crystal molecules are before forced into a preferred orientation which is transferred to the bulk director field through the elastic interaction. This model implies that the steric interaction is very large, and hence the nematic liquid crystal orientation near the Langmuir–Blodgett film is coincident with that of the film. The model has been recently used by the Göteborg group to interpret the temperature of surface transitions in nematic liquid crystal samples oriented by means of egg lecithin [18, 19]. The original model of Hiltrop and Stegemeyer has been recently generalized by Alexe-Ionescu *et al.* [20, 21], to describe the case where the steric interaction between both the nematic and the film is comparable with the dispersion interaction between both the nematic and the film and the nematic and the solid substrate. However, since the steric interaction between a nematic liquid crystal and the Langmuir–Blodgett film always plays an important role in the macroscopic orientation of the nematic sample, it is important to know the ground state of the orienting film. The analysis reported in our paper has shown that the latter can either be distorted or undistorted according to the importance of the Lifchitz invariant.

This work has been supported by the Ministero Università Ricerca Scientifica Tecnologica, the Istituto Nazionale Fisica della Materia (Genova) and through the Politecnico di Torino-Russian Academy of Sciences Scientific Collaboration, European Community. Many thanks are due to P. Allia for a critical revision of the manuscript.

References

[1] de Gennes, P. G., 1974, *The Physics of Liquid Crystals* (Oxford: Clarendon Press).
[2] Alexe-Ionescu, A. L., 1993, *Mod. Phys. Lett. B*, **7**, 307.
[3] Vertogen, G., 1983, *Physica A*, **117**, 227 and 1983, *Phys. Lett. A*, **89**, 448.
[4] Alexe-Ionescu, A. L., Barberi, R., Barbero, G., and Giocondo, M., 1994, *Phys. Lett. A*, **190**, 109.
[5] Barbero, G., Evangelista, L. R., Giocondo, M., and Ponti, S., 1994, *J. de Phys. II*, **4**, 1519; Faetti, S., and Nobili, M., *J. de Phys. II*, **4**, 1617.
[6] Hiltrop, K., and Stegemeyer, H., 1981, *Ber. Bunsenges, phys. Chem.*, **85**, 582; Hiltrop, K., and Stegemeyer, H., 1984, *Liq. Crystals Ord. Fluids*, **4**, 515.
[7] Popov, F., Zvezdin, A. K., Vorob'ev, G. P., Kadomtseva, A. M., Murashev, V. A., and Rakov, D. N., 1983, *Soviet Phys. Lett. JETP*, **57**, 69.
[8] Vertogen, G., Flapper, S. D., and Dullemond, C., 1982, *J. chem. Phys.*, **76**, 616.
[9] Sparavigna, A., Strigazzi, A., and Zvezdin, A. K., 1994, *Phys. Rev. B*, **50**, 2953.
[10] Kleman, M., 1977, *Points, Lignes, Porois*, (Les Edition de Physique Les Ulis) p. 81.
[11] Elsgolts, L., 1980, *Differential Equations and the Calculus of Variations* (Moscow: MIR).
[12] Gradshteyn, I. S., and Ryzhnik, I. M., 1965, *Table of Integrals, Series and Products* (New York: Academic Press).
[13] Alexe-Ionescu, A. L., Barbero, G., Gabbasova, Z., Sayko, G., and Zvezdin, A. K., 1994, *Phys. Rev. E*, **49**, 5354.
[14] McMillan, W. L., 1971, *Phys. Rev. A*, **4**, 1238.
[15] Scheringer, M., Hifer, R., and Binder, K., 1992, *J. chem. Phys.*, **96**, 2269.
[16] Safran, S. A., Robbins, M. O., and Garoff, S., 1986, *Phys. Rev. A*, **33**, 2186.
[17] Hiltrop, K., Hasse, J., and Stegemeyer, H., 1995, *Ber. Bunsenges. phys. Chem.*, **99**, 209.
[18] Flatischler, K., Komitov, L., Lagerwall, S. T., Stebler, B., and Strigazzi, A., 1991, *Molec. Crystals liq. Crystals*, **198**, 119.
[19] Komitov, L., Lagerwall, S. T., Sparavigna, A., Stebler, B., and Strigazzi, A., 1992, *Molec. Crystals liq. Crystals*, **223**, 197.
[20] Alexe-Ionescu, A. L., Barbero, G., Ignatov, A., and Miraldi, E., 1993, *Appl. Phys. A*, **56**, 453.
[21] Alexe-Ionescu, A. L., Barberi, R., Barbero, G., and Giocondo, M., *Appl. Phys. A* (to be published).