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Deformation free energy and elastic description of a self-assembled system

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A continuum model is proposed to describe orientational states of a self-assembled system formed by rodlike molecules, in contact with an isotropic solid substrate. The total free energy is determined by taking into account the interactions between the molecules forming the film and between the molecules and the substrate. A phase diagram is presented, demonstrating that a critical surface molecular density exists, depending on the the ratio between the surface and the bulk free energy, separating homeotropic from tilted phases. The behavior of the elastic constants is investigated as a function of the surface molecular density. The elastic description leads to the presence of a linear term in the free energy, which accounts for the existence of possible spontaneous elastic distortions induced in the system.

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I. INTRODUCTION

Certain organic molecules orient themselves at the interface between a gaseous and a liquid phase (or between two liquid phases) forming a monomolecular film [1,2]. Such monolayer films at the air-water interface exhibit a rich variety of phases and constitute model systems for more complex biological membranes [3,4]. These systems attracted a lot of attention because molecular orientation at the interfaces is of importance in phenomena such as wetting, adhesion, lubrication, coating, catalysis, etc. [5,6]. They have been studied for over a half century by means of a great variety of experimental techniques [4–8] or, more recently, by investigation of dielectric properties both experimentally and theoretically [9–14]. From the theoretical side, the approaches were mostly concentrated on molecular dynamics [15,16] and Monte Carlo simulations [17–19]. Also simplified molecular models, based on cylindrical rods grafted on a two-dimensional lattice, have been considered since the pioneer work of Safran *et al.* [20], where a nonuniform tilt has been discussed. In general, modeling of these systems is a hard task because knowledge of intermolecular potentials is limited. Analytical results desirable but difficult to obtain in view of the very complex chemical structures of these molecules. Computer simulations seem to be a convenient tool to investigate the phase behavior, but have to be limited to a very small number of molecules.

In this paper we consider a continuous model in which the molecules are treated as rigid rods without internal degrees of freedom [3]. We extend to these systems the method employed in Ref. [21] to evaluate the elastic constants of a liquid crystalline media, starting from the intermolecular interaction. Analytical results are established, showing that the monolayer film can be characterized from the elastic point of view by an elastic energy density containing the usual quadratic part and a linear term in the deformation tensor. This term can be responsible for the ground state periodically deformed. We also establish the existence of a critical surface molecular density separating homeotropic from tilted phases, depending on the relative importance of the surface energy with respect to the bulk free energy.

II. TOTAL ENERGY

We consider a simple model in which the membrane is formed by identical rodlike molecules, of length L, having the direction of their long axes characterized by $\mathbf{m}$. The orientation of the molecules in the membrane is due to the interactions between the molecules forming the membrane itself and between the molecules of the membrane with the flat solid substrate. The reference frame is such that x and y axes are parallel to the substrate and the z axis is normal to it. The starting point for an elastic approach is to evaluate the deformation free energy of the membrane, by assuming that the molecular interactions are know. The interparticle potential is modeled by Lennard-Jones potential of the form

$$f(r) = -\epsilon_b\left[\left(\frac{R_0}{r}\right)^6 - \left(\frac{R_0}{r}\right)^{12}\right], \tag{1}$$

where R_0 is the lower cutoff of the order of the minimum distance between two neighbor molecules, such that $R_0 > 0$, and $\epsilon_b > 0$. The intermolecular interaction between two rigid rodlike molecules forming the membrane is then, by generalizing Eq. (1) to a continuous distribution of interacting points,

$$u_m(\mathbf{m},\mathbf{m}',\mathbf{R}) = \int_0^L \int_0^L f(r)\,d\ell\,d\ell', \tag{2}$$

where $\mathbf{m}$ and $\mathbf{m}'$ are the molecular orientations of the two interacting molecules and $\mathbf{R}$ is the position of $\mathbf{m}'$ with respect to $\mathbf{m}$ (see Fig. 1). Furthermore, r is defined in Fig. 2 and represents the distance between $d\ell$ and $d\ell'$. From Figs. 1 and 2 it follows that $r = r(\theta,\phi;\theta',\phi';R,\varphi;\ell,\ell')$ is given by

$$r = \sqrt{R^2 + \ell^2 + \ell'^2 + 2R\mathcal{R} - 2\ell\ell'\mathcal{L}}, \tag{3}$$

where $\mathcal{R} = \ell' \sin\theta' \cos(\phi' - \varphi) - \ell \sin\theta \cos(\phi - \varphi)$, and $\mathcal{L} = \cos\theta \cos\theta' + \sin\theta \sin\theta' \cos(\phi' - \phi)$.

In the uniform state, where $\theta = \theta'$ and $\phi = \phi'$, r reduces to

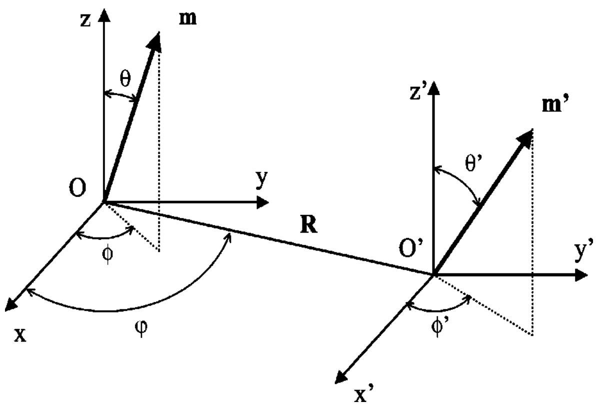

FIG. 1. Orientations of two rodlike molecules, of length L, whose long axes are $\mathbf{m}$ and $\mathbf{m}'$. The Cartesian axes x and y are parallel to the flat solid substrate. θ is the angle by which a molecule of the membrane may bend under the action of the interactions.

$$r_0 = \sqrt{R^2 + (\ell' - \ell)^2 + 2R(\ell' - \ell)\sin\theta\cos(\phi - \varphi)}. \quad (4)$$

To obtain the elastic energy density of the membrane, we assume, as usual, that $\mathbf{m}' = \mathbf{m}(\mathbf{R}) = \mathbf{m}(0) + \delta\mathbf{m}(\mathbf{R})$, where $|\delta\mathbf{m}(\mathbf{R})| \ll 1$. To save space, in this section we identify $\psi_1 = \theta$ and $\psi_2 = \phi$ [21]. In this manner the previous conditions read $\psi_i' = \psi_i + \delta\psi_i$, with $|\delta\psi_i| \ll 1$, $i = 1, 2$.

In this framework the intermolecular interaction, given by Eq. (2), can be expanded in power series of $\delta\psi_1$ and $\delta\psi_2$ as follows:

$$u_m(\psi_1, \psi_2; \psi_1', \psi_2'; R, \varphi) = u_m(\psi_1, \psi_2; R, \varphi) + A_i \delta\psi_i + \frac{1}{2} B_{ij} \delta\psi_i \delta\psi_j, \quad (5)$$

where the summation convention has been adopted. In Eq. (5) we have

$$u_m(\psi_1, \psi_2; R, \varphi) = \int_0^L \int_0^L f(r_0)\, d\ell\, d\ell', \quad (6)$$

$$A_i = \int_0^L \int_0^L \left(\frac{df}{dr}\right)_0 \left(\frac{\partial r}{\partial \psi_i'}\right)_0 d\ell\, d\ell', \quad (7)$$

and

$$B_{ij} = \int_0^L \int_0^L \left[\frac{d^2 f}{dr^2}\left(\frac{\partial r}{\partial \psi_i'}\frac{\partial r}{\partial \psi_j'}\right) + \frac{df}{dr}\frac{\partial^2 r}{\partial \psi_i' \partial \psi_j'}\right]_0 d\ell\, d\ell'. \quad (8)$$

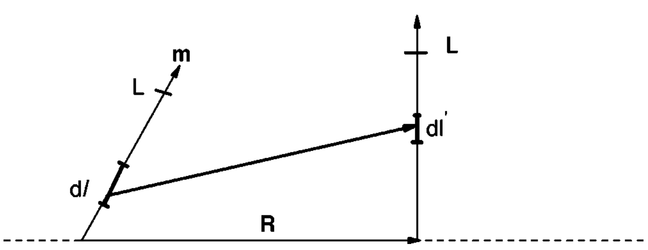

FIG. 2. Definition of the interparticle distance $\mathbf{r}$ and of the integration elements $d\ell$ and $d\ell'$ relative to two identical molecules of length L, whose long axes are $\mathbf{m}$ and $\mathbf{m}'$.

In Eqs. (7) and (8) the subscript 0 means that all the quantities have to be evaluated for $\psi_1 = \psi_1'$ and $\psi_2 = \psi_2'$. In the elastic approximation, $\delta\psi_i$ can be expanded as

$$\delta\psi_i = x_\alpha \frac{\partial \psi_i}{\partial x_\alpha} + \frac{1}{2} x_\alpha x_\beta \frac{\partial^2 \psi_i}{\partial x_\alpha \partial x_\beta}, \quad (9)$$

for $\alpha, \beta = 1, 2$, with $x_1 = x$, $x_2 = y$. The elastic energy density is given by

$$F = \frac{\sigma^2}{2} \int_{R_0}^{\infty} \int_0^{2\pi} u_m(\psi_1, \psi_2; \psi_1', \psi_2'; R, \varphi) R\, dR\, d\varphi, \quad (10)$$

where σ is the surface molecular density. By substituting Eq. (9) into Eq. (5) and the result into Eq. (10) we obtain

$$F = F_0 + F_1 + F_2, \quad (11)$$

where F_0 is the uniform part of the interaction energy and F_1 is the elastic contribution linear in the first and second derivatives of ψ_1 and ψ_2, whereas F_2 is the elastic contribution quadratic in the first-order derivatives of ψ_1 and ψ_2.

As follows from the discussion reported above, F_0 is given by

$$F_0(\psi_1, \psi_2) = \frac{\sigma^2}{2} \int_{R_0}^{\infty} \int_0^{2\pi} u_m(\psi_1, \psi_2; R, \varphi) R\, dr\, d\varphi \quad (12)$$

and can be evaluated numerically. Notice that F_0, as given by Eq. (12), does not depend, obviously, on $\psi_2 (= \phi)$. As will be discussed in the following, since the molecules interact also with the substrate, the uniform part of the energy has to contain, besides $F_0(\psi_1, \psi_2)$, also another contribution.

For what concerns F_1 it is of the kind

$$F_1 = a_\alpha^i \frac{\partial \psi_i}{\partial x_\alpha} + \frac{1}{2} a_{\alpha\beta}^i \frac{\partial^2 \psi_i}{\partial x_\alpha x_\beta}, \quad (13)$$

where

$$a_\alpha^i = \frac{\sigma^2}{2} \int_{R_0}^{\infty} \int_0^{2\pi} x_\alpha A_i R\, dR\, d\varphi \quad (14)$$

and

$$a_{\alpha\beta}^i = \frac{\sigma^2}{2} \int_{R_0}^{\infty} \int_0^{2\pi} x_\alpha x_\beta A_i R\, dR\, d\varphi, \quad (15)$$

with $i = \psi_1, \psi_2$. Finally, the usual quadratic part is given by

$$F_2 = \frac{1}{2} b_{\alpha\beta}^{ij} \frac{\partial \psi_i}{\partial x_\alpha} \frac{\partial \psi_j}{\partial x_\beta}, \quad (16)$$

where

$$b_{\alpha\beta}^{ij} = \frac{\sigma^2}{2} \int_{R_0}^{\infty} \int_0^{2\pi} x_\alpha x_\beta B_{ij} R\, dR\, d\varphi. \quad (17)$$

From the elastic point of view the membrane is characterized by the parameters a_α^i and $b_{\alpha\beta}^{ij}$. Since a_α^i are connected to the

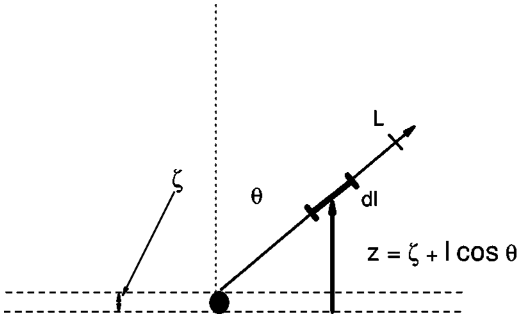

FIG. 3. Molecular orientation near the solid substrate. ζ is in the molecular scale of length.

linear terms in the deformation tensor, they can be responsible for spontaneous elastic deformations [22]. Furthermore, the $a^i_{\alpha\beta}$ give rise to elastic terms similar to the splay-bend elastic constant K_{13}. Finally, $b^{ij}_{\alpha\beta}$ are the equivalent of the usual Frank elastic constants of nematic liquid crystals [23].

A. Direct interaction of a molecule with the substrate

The interaction of a molecule (point) with a surface (half-space) is assumed to be

$$g(z) = -\epsilon_{\mathrm{s}}\left[\left(\frac{R_0}{z}\right)^3 - \left(\frac{R_0}{z}\right)^9\right], \tag{18}$$

where z is the distance of the molecule from the surface.

In the case under consideration where the molecule is rod like, in a first approximation, the direct interaction of a molecule with the substrate, supposed isotropic, can be easily obtained by generalizing Eq. (18). We have

$$u_{\mathrm{s}}(\theta) = \int_0^L g(z)\,d\ell, \tag{19}$$

where $z=\zeta+\ell\cos\theta$ and we assume that ζ is θ independent (Fig. 3). The integration indicated in Eq. (19) can be easily performed, giving

$$\frac{u_{\mathrm{s}}(\theta)}{\epsilon_{\mathrm{s}}} = \frac{R_0^3}{8\cos\theta}\left[\frac{R_0^6 - 4\zeta^6}{\zeta^8} + \frac{4(\zeta + L\cos\theta)^6 - R_0^6}{(\zeta + L\cos\theta)^8}\right]. \tag{20}$$

In Fig. 4 the behavior of the direct interaction of the molecule versus θ is shown. Homeotropic orientation corresponds to $\theta=0$. The surface part of the free energy is then minimized for $\theta\to\pi/2$, when $L/R_0 \gg 1$—i.e., for planar orientation.

B. Uniform part of the energy

The uniform part of the energy is given by

$$F_{\mathrm{u}}(\theta) = F_0(\theta) + F_{\mathrm{s}}(\theta), \tag{21}$$

where $F_0(\theta)$ is given by Eq. (12) and

$$F_{\mathrm{s}}(\theta) = \sigma u_{\mathrm{s}}(\theta). \tag{22}$$

Consequently,

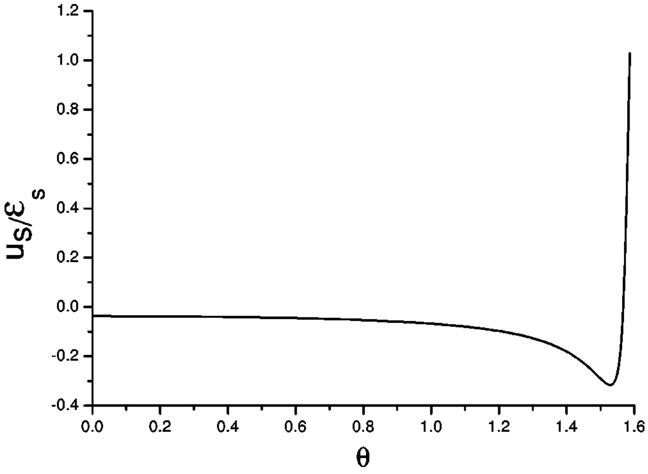

FIG. 4. Behavior of the direct interaction of the molecule vs θ for $L/R_0=10$ and $\zeta/R_0=1.0$.

$$F_{\mathrm{u}}(\theta) = \frac{\sigma^2}{2}\int_{R_0}^{\infty}\int_0^{2\pi} u_{\mathrm{m}}(\theta,\phi;R,\varphi)R\,dR\,d\varphi + \sigma u_{\mathrm{s}}(\theta), \tag{23}$$

where, as stated above, the ϕ dependence disappears after integration over φ. Let us assume that $F_{\mathrm{u}}(\theta)$ has a minimum for $\theta=\theta_0$, defining a uniform state.

The behavior of $F_{\mathrm{u}}(\theta)$ vs θ was numerically investigated for different values of the ratio $\epsilon=\epsilon_{\mathrm{s}}/\epsilon_{\mathrm{b}}$ (giving the relative importance of the surface to bulk contribution to the uniform part of the total free energy). For each value of the surface molecular density σ, it was verified that, in fact, $F_{\mathrm{u}}(\theta)$ presents a minimum for $0\leqslant\theta\leqslant\pi/2$ as expected. In Fig. 5 the value θ_{c} for which $F_{\mathrm{u}}(\theta)$ is minimum is shown as a function of the dimensionless surface molecular density $\underline{\sigma}=\sigma R_0^2$. As follows from Fig. 5, there exists a critical value of the surface density σ, σ_c, such that for $\sigma>\sigma_c$ the homogeneous stable orientation is the one in which the rodlike molecules are normal to the substrate. This result can be easily understood. In fact, for $\sigma>\sigma_c$ the repulsive part of the Lennard-

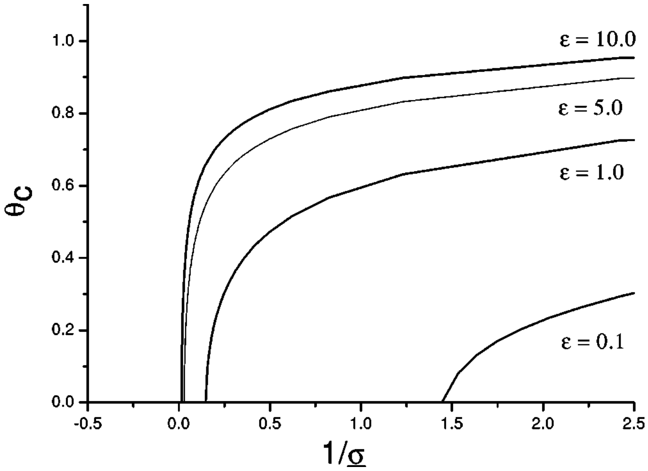

FIG. 5. Phase diagram exhibiting the value θ_{c} for which $F_{\mathrm{u}}(\theta)$ is minimum vs the inverse of the dimensionless surface molecular density $\underline{\sigma}=\sigma R_0^2$ (see the text).

Jones interaction dominates, and tilted orientations are forbidden. On the contrary, for small σ the interaction with the substrate, which favors the planar orientation, can induce a tilted orientation. For $\sigma \approx \sigma_c$ we have $\theta_c \propto (\sigma_c - \sigma)^{1/2}$, typical of second-order phase transitions. This suggests that the film with $\theta_c = 0$ and with $\theta_c \neq 0$ can be considered as two different phases of the film. This result is in agreement with the computer simulation analysis performed in Refs. [3,17].

III. EVALUATION OF THE ELASTIC CONSTANTS

By substituting Eq. (4) into Eq. (7) and taking into account that $\psi_1 = \theta$ and $\psi_2 = \phi$, we obtain

$$A_\theta = R \cos\theta \cos(\phi - \varphi) H,$$

$$A_\phi = -R \sin\theta \sin(\phi - \varphi) H, \tag{24}$$

where

$$H = H(\theta, \phi; R, \varphi) = \int_0^L \int_0^L \frac{\ell'}{r_0} \left(\frac{df}{dr}\right)_0 \mathrm{d}\ell \mathrm{d}\ell'. \tag{25}$$

By substituting Eqs. (24) into Eqs. (14) and (15) one obtains

$$a_x^\theta = \cos\theta (\cos\phi I_{20} + \sin\phi I_{11}),$$

$$a_y^\theta = \cos\theta (\cos\phi I_{11} + \sin\phi I_{02}),$$

$$a_x^\phi = \sin\theta (\cos\phi I_{11} - \sin\phi I_{20}),$$

$$a_y^\phi = \sin\theta (\cos\phi I_{02} - \sin\phi I_{11}), \tag{26}$$

and

$$a_{xx}^\theta = \cos\theta (\cos\phi J_{30} + \sin\phi J_{21}),$$

$$a_{yy}^\theta = \cos\theta (\cos\phi J_{12} + \sin\phi J_{03}),$$

$$a_{xy}^\theta = \cos\theta (\cos\phi J_{21} + \sin\phi J_{12}),$$

$$a_{xx}^\phi = \sin\theta (\cos\phi J_{21} - \sin\phi J_{30}),$$

$$a_{yy}^\phi = \sin\theta (\cos\phi J_{03} - \sin\phi J_{12}),$$

$$a_{xy}^\phi = \sin\theta (\cos\phi J_{12} - \sin\phi J_{21}), \tag{27}$$

where

$$I_{mn} = \frac{\sigma^2}{2} \int_{R_0}^\infty \int_0^{2\pi} R^3 H \cos^m \varphi \sin^n \varphi dR d\varphi \tag{28}$$

and

$$J_{mn} = \frac{\sigma^2}{2} \int_{R_0}^\infty \int_0^{2\pi} R^4 H \cos^m \varphi \sin^n \varphi dR d\varphi. \tag{29}$$

Let us consider now the elastic parameters $b_{\alpha\beta}^{ij}$ defined by Eq. (17). By using Eq. (8) we obtain

$$B_{\theta\theta} = R^2 \cos^2\theta \cos^2(\phi - \varphi) L + M - R \sin\theta \cos(\phi - \varphi) H,$$

$$B_{\phi\phi} = R^2 \sin^2\theta \sin^2(\phi - \varphi) L + \sin^2\theta M - R \sin\theta \cos(\phi - \varphi) H,$$

$$B_{\theta\phi} = -R^2 \sin\theta \cos\theta \sin(\phi - \varphi) \cos(\phi - \varphi) L - R \cos\theta \sin(\phi - \varphi) H, \tag{30}$$

where H is defined by Eq. (25):

$$L = L(\theta, \phi; R, \varphi) = \int_0^L \int_0^L \frac{\ell'^2}{r_0^2} \left[\left(\frac{d^2 f}{dr^2}\right)_0 - \frac{1}{r_0} \left(\frac{df}{dr}\right)_0 \right] \mathrm{d}\ell \mathrm{d}\ell' \tag{31}$$

and

$$M = M(\theta, \phi; R, \varphi) = \int_0^L \int_0^L \frac{\ell' \ell}{r_0} \left(\frac{df}{dr}\right)_0 \mathrm{d}\ell \mathrm{d}\ell'. \tag{32}$$

Using now Eqs. (30) the elastic parameters we are looking for are given by

$$b_{xx}^{\theta\theta} = \cos^2\theta (P_{40} \cos^2\phi + P_{31} \sin 2\phi + P_{22} \sin^2\phi) + Q_{20} - \sin\theta (S_{30} \cos\phi + S_{21} \sin\phi),$$

$$b_{yy}^{\theta\theta} = \cos^2\theta (P_{22} \cos^2\phi + P_{13} \sin 2\phi + P_{04} \sin^2\phi) + Q_{02} - \sin\theta (S_{12} \cos\phi + S_{03} \sin\phi),$$

$$b_{xy}^{\theta\theta} = \cos^2\theta (P_{31} \cos^2\phi + P_{22} \sin 2\phi + P_{13} \sin^2\phi) + Q_{11} - \sin\theta (S_{21} \cos\phi + S_{12} \sin\phi), \tag{33}$$

$$b_{xx}^{\phi\phi} = \sin^2\theta (P_{40} \sin^2\phi - P_{31} \sin 2\phi + P_{22} \cos^2\phi) + Q_{20} \sin^2\theta - \sin\theta (S_{30} \cos\phi + S_{21} \sin\phi),$$

$$b_{yy}^{\phi\phi} = \sin^2\theta (P_{22} \sin^2\phi - P_{13} \sin 2\phi + P_{04} \cos^2\phi) + Q_{02} \sin^2\theta - \sin\theta (S_{12} \cos\phi + S_{03} \sin\phi),$$

$$b_{xy}^{\phi\phi} = \sin^2\theta (P_{31} \sin^2\phi - P_{22} \sin 2\phi + P_{13} \cos^2\phi) + Q_{11} \sin^2\theta - \sin\theta (S_{21} \cos\phi + S_{12} \sin\phi), \tag{34}$$

and

$$b_{xx}^{\theta\phi} = -\sin\theta \cos\theta [(P_{40} - P_{22}) \cos\phi \sin\phi - P_{31} \cos 2\phi] - \cos\theta (S_{30} \sin\phi - S_{21} \cos\phi),$$

$$b_{yy}^{\theta\phi} = -\sin\theta \cos\theta [(P_{22} - P_{04}) \cos\phi \sin\phi - P_{13} \cos 2\phi] - \cos\theta (S_{12} \sin\phi - S_{03} \cos\phi),$$

$$b_{xy}^{\theta\phi} = -\sin\theta \cos\theta [(P_{31} - P_{13}) \cos\phi \sin\phi - P_{22} \cos 2\phi] - \cos\theta (S_{21} \sin\phi - S_{12} \cos\phi), \tag{35}$$

where

$$P_{mn} = \frac{\sigma^2}{2} \int_{R_0}^\infty \int_0^{2\pi} R^5 L \cos^m \varphi \sin^n \varphi dR d\varphi,$$

$$Q_{mn}=\frac{\sigma^2}{2}\int_{R_0}^{\infty}\int_0^{2\pi}R^3M\cos^m\varphi\sin^n\varphi dRd\varphi,$$

$$S_{mn}=\frac{\sigma^2}{2}\int_{R_0}^{\infty}\int_0^{2\pi}R^4H\cos^m\varphi\sin^n\varphi dRd\varphi. \qquad (36)$$

Relations (26), (27), and (33)–(35) give the elastic parameters characterizing the monomolecular film for all molecular orientation (θ,ϕ).

Small fluctuations near to a uniform state

For small fluctuations near to a uniform state, we can assume that $\phi=0$. In this case r_0, given by Eq. (4), can be written as $r_0(\theta,0;R,\varphi;\ell,\ell')$—i.e.,

$$r_0=\sqrt{R^2+(\ell'-\ell)^2+2R(\ell'-\ell)\sin\theta\cos\varphi}. \qquad (37)$$

From Eq. (37) it follows that

$$r_0(\theta,0;R,\varphi;\ell,\ell')=r_0(\theta,0;R,2\pi-\varphi;\ell,\ell'). \qquad (38)$$

In this case also the functions $H(\theta,0;R,\varphi)$, $L(\theta,0;R,\varphi)$, and $M(\theta,0;R,\varphi)$, introduced before, are such that

$$H(\theta,0;R,\varphi)=H(\theta,0;R,2\pi-\varphi),$$

$$L(\theta,0;R,\varphi)=L(\theta,0;R,2\pi-\varphi),$$

$$M(\theta,0;R,\varphi)=M(\theta,0;R,2\pi-\varphi). \qquad (39)$$

Consequently, from Eqs. (28), (29), and (36), it follows that if n is odd, I_{mn}, J_{mn}, P_{mn}, Q_{mn}, and S_{mn} are zero. From this observation it follows that near to a homogeneous state $(\theta=\theta_0,\phi=0)$ the elastic parameters are given by

$$a_x^{\theta}=\cos\theta_0 I_{20}(\theta_0),$$

$$a_y^{\theta}=0, \quad a_x^{\phi}=0,$$

$$a_y^{\theta}=\sin\theta_0 I_{02}(\theta_0), \qquad (40)$$

$$a_{xx}^{\theta}=\cos\theta_0 J_{30},$$

$$a_{yy}^{\theta}=\cos\theta_0 J_{12}(\theta_0),$$

$$a_{xy}^{\theta}=0, \quad a_{xx}^{\phi}=0,$$

$$a_{yy}^{\phi}=\sin\theta_0 J_{03},$$

$$a_{xy}^{\phi}=\sin\theta_0 J_{12}(\theta_0), \qquad (41)$$

and

$$b_{xx}^{\theta\theta}=\cos^2\theta_0 P_{40}(\theta_0)+Q_{20}(\theta_0)-\sin\theta_0 S_{30}(\theta_0),$$

$$b_{yy}^{\theta\theta}=\cos^2\theta_0 P_{22}(\theta_0)+Q_{02}(\theta_0)-\sin\theta_0 S_{12}(\theta_0),$$

$$b_{xy}^{\theta\theta}=b_{xy}^{\phi\phi}b_{xx}^{\theta\phi}=b_{yy}^{\theta\theta}=0,$$

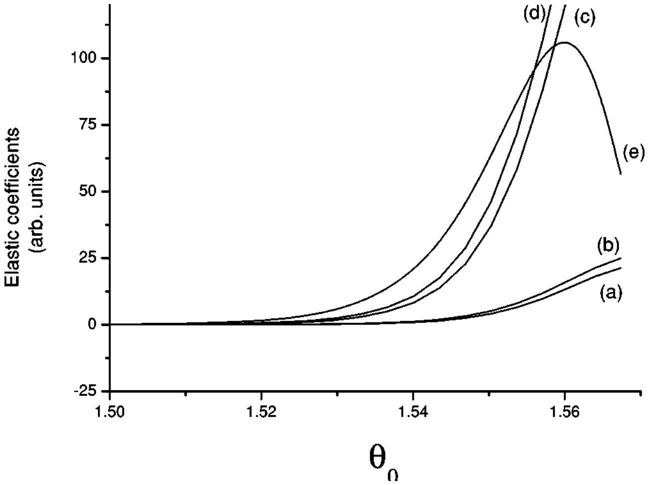

FIG. 6. Behavior of the elastic coefficients vs θ_0, for $\underline{\sigma}=0.1$. (a) $10^{-3}b_{yy}^{\phi\phi}$, (b) $10^{-3}b_{yy}^{\theta\theta}$, (c) $10^{-6}b_{xx}^{\phi\phi}$, (d) $10^{-6}b_{xx}^{\theta\theta}$, and (e) $10^{-3}b_{xy}^{\theta\theta}$. The scale is arbitrary just to show all the coefficients in the same plot. However, all the elastic coefficients are positive in the range $0\leqslant\theta_0\leqslant\pi/2$. The curves were depicted for $L/R_0=9.0$ and $\zeta/R_0=1.0$.

$$b_{xx}^{\phi\phi}=\sin^2\theta_0 P_{22}(\theta_0)+Q_{20}(\theta_0)\sin^2\theta_0-\sin\theta_0 S_{30}(\theta_0),$$

$$b_{yy}^{\phi\phi}=\sin^2\theta_0 P_{04}(\theta_0)+Q_{02}(\theta_0)\sin^2\theta_0-\sin\theta_0 S_{12}(\theta_0),$$

$$b_{xy}^{\theta\theta}=\sin\theta_0\cos\theta_0 P_{22}(\theta_0)+\cos\theta_0 S_{12}(\theta_0). \qquad (42)$$

In Fig. 6 the behavior of the elastic coefficients $b_{\alpha\beta}^{ij}$ is shown as a function of θ_0. For the illustrative set of parameters we are using (L/R_0 and $\zeta/R_0=1.0$) the coefficients, for $\theta_0\simeq\pi/2$, are $b_{xx}^{\theta\theta}\approx 2\times 10^8$, $b_{yy}^{\theta\theta}\approx 3\times 10^5$, $b_{xx}^{\phi\phi}\approx 2\times 10^7$, $b_{yy}^{\phi\phi}\approx 2\times 10^4$, and $b_{xy}^{\theta\theta}\approx 6\times 10^4$. In Fig. 7 the same elastic coefficients are shown as a function of $\underline{\sigma}$ for $\theta_0\approx\pi/2$ for the same set of parameters as in Fig. 6. The important feature of

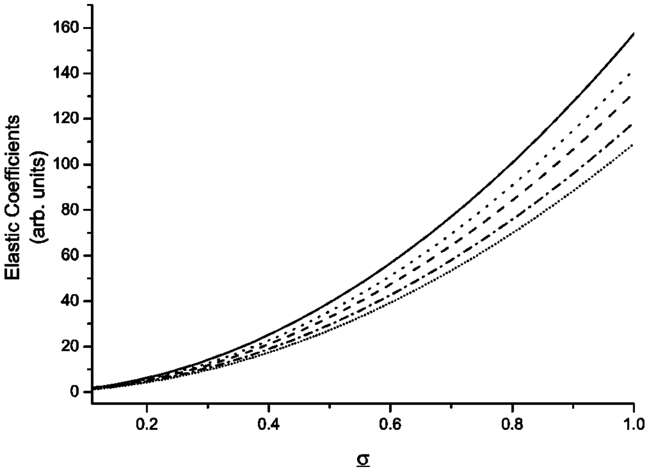

FIG. 7. Behavior of the elastic coefficients vs $\underline{\sigma}$ for $\theta_0=1.56$ rad. Solid line refers to $10^{-6}b_{yy}^{\theta\theta}$, dotted line to $10^{-8}b_{xx}^{\theta\theta}$, dashed line to $10^{-4}b_{yy}^{\phi\phi}$, dash-dotted line to $10^{-7}b_{xx}^{\phi\phi}$, and short-dotted line to $10^{-5}\times b_{xy}^{\theta\theta}$. The scale is arbitrary and the set of parameters is the same as in Fig. 6.

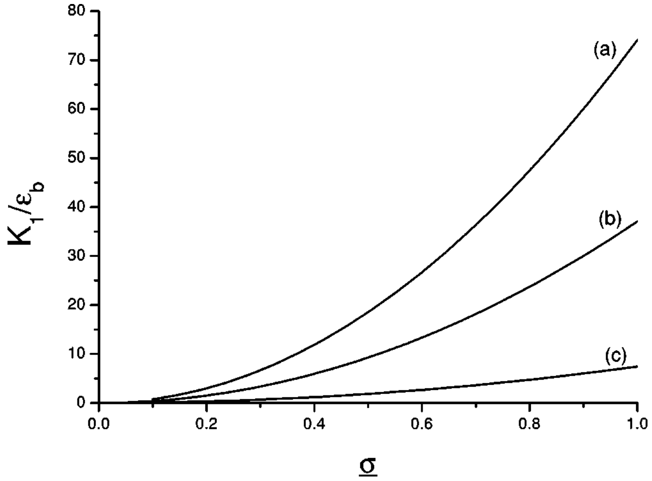

FIG. 8. Behavior of the elastic constant K_1 vs $\underline{\sigma}$. (a) $L/R_0=10$, (b) $L/R_0=20$, and (c) $L/R_0=100$.

these figures is the fact that the coefficients are always positive. This fact is an indication of the stability of the orientational states of the membrane, since $b^{ij}_{\alpha\beta}$, as discussed before, play a role analogous to the Frank elastic constants in liquid crystals [23]. Furthermore, according to our numerical calculations, $b^{\theta\theta}_{xx}/b^{\theta\theta}_{yy}\approx 10^3$ and $b^{\phi\phi}_{xx}/b^{\phi\phi}_{yy}\approx 10^3$. These results show that the deformations involving $\partial\theta/\partial x$ and $\partial\phi/\partial x$ are more expensive, from the point of view of elastic energy, than the ones involving the deformations $\partial\theta/\partial y$ and $\partial\phi/\partial y$.

In particular, if $\theta_0=0$, r_0, as given by Eq. (37), is reduced to $r_0=\sqrt{R^2+(\ell'-\ell)^2}$. In this situation, $I_{mn}(0)$, $J_{mn}(0)$, $P_{mn}(0)$, $Q_{mn}(0)$, and $S_{mn}(0)$ vanish if m is odd. Consequently, for small fluctuations close to the homeotropic alignment, only the elastic coefficients

$$a^{\theta}_{x}=I_{20}(0)=K_1,$$

$$b^{\theta}_{xx}=P_{40}(0)+Q_{20}(0)=K_{2x},$$

$$b^{\theta}_{yy}=P_{22}(0)+Q_{02}(0)=K_{2y} \qquad (43)$$

are different from zero. In this case, at the second order in $\delta\theta=\theta$ the elastic energy density is given by

$$F=F_0+K_1\frac{\partial\theta}{\partial x}+\frac{1}{2}\left[K_{2x}\left(\frac{\partial\theta}{\partial x}\right)^2+K_{2y}\left(\frac{\partial\theta}{\partial y}\right)^2\right]. \qquad (44)$$

Notice that the existence of the linear term in the free energy density could be connected with a deformed ground state of the membrane [22]. It is the equivalent of the Lifchitz invariants. If the substrate is isotropic, as assumed above, $\theta=\theta(x)$ only, because the y dependence increases the free energy density. In this case the favored orientation is the distorted one, with a gradient given by

$$\frac{\partial\theta}{\partial x}=-\frac{K_1}{K_{2x}}.$$

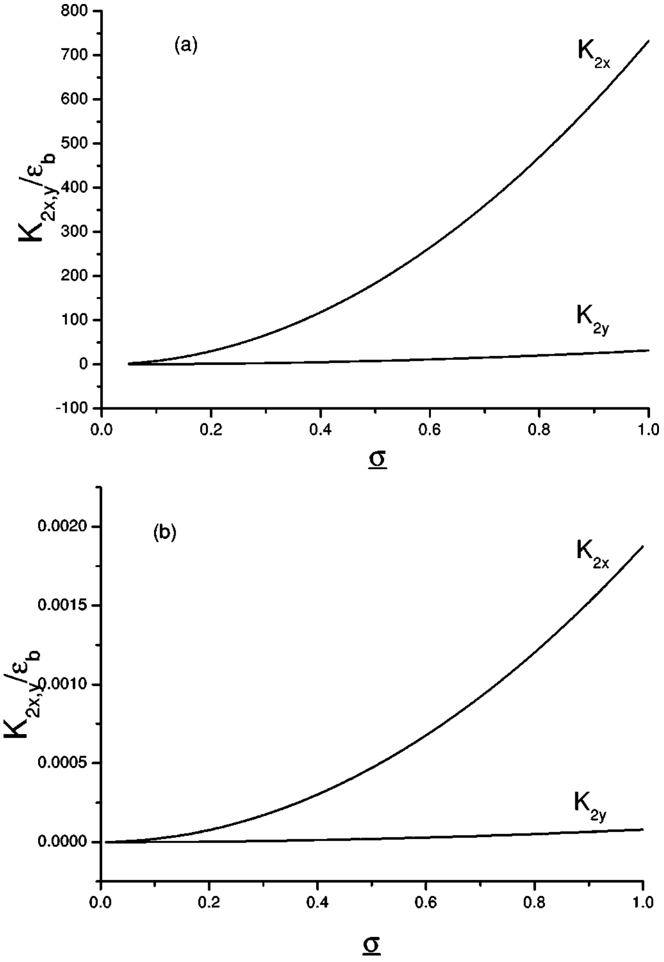

FIG. 9. Behavior of the elastic constant K_{2x} and K_{2y} vs $\underline{\sigma}$ for the case in which (a) $L/R_0=20$ and (b) $L/R_0=100$.

In Fig. 7 the dependence of the elastic parameters $b^{\alpha\beta}_{ij}$ vs the surface density is shown. As expected, they are monotonic functions of σ. In fact, as σ increases the attractive part of the Lennard-Jones potential favors homogeneous alignment, indicating that spatial deformations are very expensive from the point of view of the energy. In Fig. 8 we show the elastic constants K_1 vs $\underline{\sigma}$ for small deformation close to the homeotropic orientation, for a typical value of L/R_0, and in Fig. 9, K_{2x} and K_{2y} are shown for two illustrative values of the parameters. All these constants are positive increasing functions in the entire range of values of $\underline{\sigma}$.

IV. CONCLUSIONS

We proposed a continuum model of orientational ordering in dense self-assembled systems forming a monomolecular film. The molecules forming the film have been treated as rigid rods without internal degrees of freedom. By assuming a Lennard-Jones-like potential for the intermolecular interaction and for the molecule-substrate interaction, we have evaluated the elastic constants of the film. According to our analysis, the elastic energy density of a membrane formed by rodlike molecules contains, besides the usual terms quadratic in the deformation tensor, also linear terms in this quantity. These linear terms, known in magnetic theory as Lifchitz invariants, can be responsible for ground states that can be periodically deformed. We have also investigated the stability of the uniform orientation with respect to the surface density. Our results are in agreement with the ones obtained by means of computer simulation, but are mostly established in analytical manner.

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