

Nonlinear bending of molecular films by polarized light

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A theory of photoinduced directed bending of non-crystalline molecular films is presented. Our approach is based on elastic deformation of the film due to interaction between molecules ordered through polarized light irradiation. The shape of illuminated film is obtained in the frame of the nonlinear elasticity theory. It is shown that the shape and the curvature of the film depend on the polarization and intensity of the light. The curvature of an irradiated film is a non-monotonic function of the extinction coefficient.

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I. INTRODUCTION

Polymer films and solids containing light-sensitive molecules have the remarkable property to change their shape and size when irradiated with light. Certain polymer films containing azobenzene chromophores in the main and side chains exhibit strong surface relief features under illumination: trenches under the action of linearly polarized light and mounds or wells under the action of circularly polarized light \cite{1, 2}. Circular azobenzene polyester films freely lying on a water surface become elliptically deformed under the influence of linearly polarized light \cite{3}. Large, reversible shape changes can be induced optically by photoisomerization of nematic elastomers \cite{4}. Anisotropic bending and unbending behavior of molecular liquid-crystalline films containing azobenzene chromophores has been discovered and studied in Refs. \cite{5, 6} where it was shown that the films can be repeatedly and precisely bent along any chosen direction by using linearly polarized light. Fast (on the timescale of $10^{-2}$ s) light induced bending of monodomain liquid crystal elastomers has been observed observed in \cite{5}. Shape-memory effects in polymers containing cinnamic groups induced by ultraviolet light illumination were reported quite recently in Ref. \cite{6}. The possibility of coupling between orientational and translational degrees of freedom in liquid crystals was first raised by de Gennes \cite{9} and extended to nematic elastomers in \cite{10}. Based on this idea a phenomenological theory of photoinduced deformations of nematic elastomers was proposed in \cite{11}. A microscopic theory of photoinduced deformation of non-crystalline molecular films was developed in \cite{12}. The physical reason for surface-relief formation presented in \cite{12} is that azo-dyes have two isomeric states: cis and trans. The molecules in these two states have significantly different shapes. For example, in the case of azobenzene chromophores the trans-isomer is highly anisotropic whereas the cis-isomer is approximately isotropic \cite{12}, so the multipole moments and sizes may differ significantly. It was shown that there are two contributions to the photoelastic interaction: from the orientational interaction between molecules and from the interaction which is due to the change of the van der Waals interaction energy between a molecule and all surrounding molecules in its transition to the cis-isomer state. The former causes the film deformation under the action of linearly polarized light while the latter (together with the orientational interaction) is responsible for the surface relief formation under the action of circularly polarized light. The possibility of creation of wells and humps on the film surfaces under the action of circularly polarized light was discussed. It is worth noting that in the frame of this approach neither orientational order nor orientational in-plane anisotropy of the film in the absence of irradiation was assumed. One can say that the absorption of linearly polarized light creates an orientational order in the film which in turn produces anisotropic deformation. Quite recently, based on the idea of isomeric states, a theory of the polarization-dependent photocontractions of polydomain elastomers due to light-induced director rotation, was proposed in \cite{13}.

The aim of the present report is to apply this approach to anisotropic bending of molecular films by polarized light. We present an elastic energy of the film in the presence of polarized light and solving equations of equilibrium, we show that a change in the polarization direction of light causes a corresponding change of the shape of the film. We also show that the curvature of an irradiated film is a non-monotonic function of the extinction coefficient.

II. ELASTIC ENERGY OF MOLECULAR FILM

We consider a film containing molecules with two different isomeric states. Let the middle surface of the film coincide with the $x,y$-plane so that the undeformed film occupies the region: $|z| \leq \frac{h}{2}$, $x, y \in \Omega$. The film is irradiated by a linearly polarized electromagnetic wave which propagates along the $z$-axis. Its electric component has
the form
\[ \tilde{E}(\vec{r}, t) = \tilde{E} \cos(kz - \omega t). \]
where \( \omega \) is the frequency, \( k = \omega/c \) is the wave number \( (c \) is the speed of light) and
\[ \tilde{E} = E (\cos \psi, \sin \psi, 0) \]
is the amplitude. The angle \( \psi \) determines the polarization of the electromagnetic wave.

The total elastic energy of irradiated thin film may be written as follows
\[ W = W_{el} + W_g + W. \] (3)
Here the first term represent the elastic energy of the non-irradiated film
\[ W_{el} = \frac{E}{2(1 - \sigma^2)} \int_{-h/2}^{h/2} dz \int_{\Omega} dxdy \left[ \epsilon_{xx}^2 + \epsilon_{yy}^2 \right] \]
\[ + 2\sigma \epsilon_{xx} \epsilon_{yy} + 2(1 - \sigma) \epsilon_{xy}^2, \]
where \( E \) and \( \sigma \) are Young’s modulus and Poisson’s ratio, respectively [12] and \( \epsilon_{\alpha\beta} \) is the strain tensor \( (\alpha, \beta = x, y) \). We assumed here that that the non-irradiated film is neither orientationally nor translationally ordered in the middle plane and therefore we modeled its elastic properties by using the isotropic energy [12]. The term
\[ W_g = P \int_{\Omega} dxdy w \] (5)
in Eq. (5) presents the potential energy of the film in the gravitational field. Here \( P = a_{gr} \rho_f h \) is the gravity force with \( \rho_f \) being the film density and \( a_{gr} \) being the acceleration of free fall. The last term in Eq. (3) gives the change of the elastic energy due to the interaction between the electromagnetic wave [11] and the film. It has the form [12]
\[ W = W_1 + W_2, \] (6)
where
\[ W_1 = -V_a \int_{-h/2}^{h/2} dz \int_{\Omega} dxdy N(\vec{r}) \left[ (\epsilon_{xx} - \epsilon_{yy}) \cos(2\psi) \right] \]
\[ + 2\epsilon_{xy} \sin(2\psi) \] (7)
represents the anisotropic part of the photoelastic interaction which describes the coupling of the shear deformation of the film to the incoming light and
\[ W_2 = -V_i \int_{-h/2}^{h/2} dz \int_{\Omega} dxdy N(\vec{r})(\epsilon_{xx} + \epsilon_{yy}) \] (8)
determines the isotropic in-plane deformations. In Eqs. (7)-(8) the parameter of the photoelastic interaction \( V_a \) is due to the orientational \( (e.g., \) dipole-dipole) part of intermolecular interaction while the parameter \( V_i \) is due to isotropic part of the intermolecular interaction. For the sake of simplicity we assume them space independent. The function \( N(\vec{r}) \) gives the population of cis-isomers for a given value of the radiation power \( E^2 \) [12]. Following the Bouguer-Lambert-Beer law which determines how the intensity of light decreases under its propagation inside an absorbing medium, we shall model the function \( N(\vec{r}) \) as follows
\[ N(\vec{r}) = N_0 \exp \left\{ \frac{(z - h/2)}{\xi} \right\}, \] (9)
where \( N_0 \) is the maximum population of the cis-isomers for a given power \( E^2 \) and \( \xi \) is the extinction length of the light which provides transition of chromophores from trans- to cis-isomeric state \( (\) in the experiments [3-6] it was the light with the wavelength 366 nm); other distribution can of course be used, depending on the actual arrangement of azo-dyes. Note that in Eq. (9) we neglected the fact that upon bending the normal to the film surface deviates from the \( z \)-direction which is legitimate when bending is small.

Note that in the case of circularly polarized light when instead of Eqs. (1), (2) we have
\[ \tilde{E}(\vec{r}, t) = \tilde{E} \cos(kz - \omega t), \sin(kz - \omega t), 0 \] (10)
and therefore the contribution [11] vanishes; the energy of photoelastic interaction is solely determined by Eq. (5).

Following the usual derivation of Föppl–von Karman equations for bending of a thin plate \( (\) see, e.g., [16], \) we write the strains as a linear expansion in \( z \) from the middle plane and get
\[ \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} \\
\epsilon_{xy} & \epsilon_{yy} \end{pmatrix} = \begin{pmatrix} u_{xx} & u_{xy} \\
u_{xy} & u_{yy} \end{pmatrix} + z \begin{pmatrix} \partial_{xx} w & \partial_{xy} w \\
\partial_{yx} w & \partial_{yy} w \end{pmatrix} \] (11)
where
\[ u_{\alpha\beta} = \frac{1}{2} (\partial_{\beta} u_{\alpha} + \partial_{\alpha} u_{\beta}) + \frac{1}{2} \partial_{\alpha} w \partial_{\beta} w \] (12)
are the components of the two-dimensional nonlinear deformation tensor and \( \partial_{\alpha} \) denotes differentiation with respect to the coordinate \( x_{\alpha} = x, y \). Referred to these coordinates, the components of displacement are \( u_{\alpha} = u_x, u_y, w \) where we have named the vertical displacement \( u_z = w \). Introducing these equations into Eq. (3) we can represent the elastic energy of an irradiated film in the form
\[ F = F_b + F_s + W. \] (13)
The bending energy is written as
\[ F_b = \frac{D}{2} \int_{\Omega} dxdy \left\{ \left( \Delta w \right)^2 \right\} \]
\[ + 2(1 - \sigma) \left[ \left( \partial_{xy} w \right)^2 - \partial_{x}^2 w \partial_{y}^2 w \right], \] (14)
where \( \Delta = \partial_x \partial_y \) is the two-dimensional Laplace operator and

\[
D = \frac{E h^3}{12(1 - \nu^2)}
\]

is the flexural rigidity of the film. For the stretching energy one has

\[
F_s = \frac{h}{2} \int_\Omega \left( \sigma_{xx} u_{xx} + \sigma_{yy} u_{yy} + 2\sigma_{xy} u_{xy} \right) \, dx dy
\]

(16)

with the longitudinal stresses

\[
\sigma_{xx} = \frac{E}{1 - \nu^2} (u_{xx} + \nu u_{yy}) , \\
\sigma_{yy} = \frac{E}{1 - \nu^2} (u_{yy} + \nu u_{xx}) , \\
\sigma_{xy} = \frac{E}{1 + \nu} u_{xy} .
\]

(17)

In Eq.(13) the light-film interaction energy becomes

\[
W = W_b + W_s
\]

(18)

with the bending contribution

\[
W_b = W_{b1} + W_{b2} ,
\]

(19)

where

\[
W_{b1} = -h^2 \int_\Omega \left\{ A_i \Delta w + A_a \left[ (\partial_x^2 w - \partial_y^2 w) \cos(2\psi) + 2 \partial_x w \partial_y w \sin(2\psi) \right] \right\} ,
\]

(20)

describes a linear interaction with bending deformation while the term

\[
W_{b2} = -h^2 \int_\Omega \left\{ B_i \left[ (\partial_x^2 w - \partial_y^2 w) \cos(2\psi) \right] + B_i \left[ (\partial_x^2 w + \partial_y^2 w) \right] \right\}
\]

(21)

is due to the nonlinear character of the two-dimensional deformation tensor (12). The stretching contribution in Eq.(18) is

\[
W_s = -h \int_\Omega \left\{ B_i \left[ (u_{xx} - u_{yy}) \cos(2\psi) \right] + 2 u_{xy} \sin(2\psi) \right\} + B_i (u_{xx} + u_{yy}) \right\} ,
\]

(22)

and the new light-film interaction parameters in Eqs.(20)–(22) are

\[
A_i = V_i \frac{z}{N}, \\
A_a = V_a \frac{z}{N}, \\
B_i = V_i N, \\
B_a = V_a N.
\]

(23)

The function

\[
\overline{N} \equiv \frac{1}{h} \int_{-h/2}^{h/2} N(z) \, dz = N_0 \frac{\xi}{h} \left( 1 - e^{-h/\xi} \right)
\]

(24)

gives the mean value of cis-isomers in the film and

\[
\overline{zN} \equiv \frac{1}{h^2} \int_{-h/2}^{h/2} zN(z) \, dz
\]

\[
= \frac{1}{2} N_0 \frac{\xi}{h} \left[ 1 - 2 \frac{\xi}{h} \left( 1 + 2 \frac{\xi}{h} e^{-h/\xi} \right) \right]
\]

(25)

describes asymmetry of the cis-isomer distribution in the film.

By using Green’s formula for the two-dimensional integrals, Eqs.(20) and (22) can be presented in an equivalent form

\[
W_{b1} = -h^2 \oint_\ell \left\{ [A_i + A_a \cos(2(\psi - \theta))] \frac{\partial w}{\partial n} + A_a \sin(2(\psi - \theta)) \frac{\partial w}{\partial l} \right\},
\]

(26)

\[
W_s = -h \oint_\ell \left\{ B_i n \cdot \vec{u} + B_a \cos(2(\psi - \theta)) u_x \right. + B_a \sin(2(\psi - \theta)) u_y \left\},
\]

(27)

where \( \partial/\partial l \) is the derivative along the tangent \( \vec{l} \) to the contour and it has together with the normal derivative \( \partial/\partial n \) the form

\[
\frac{\partial}{\partial l} = \cos \theta \frac{\partial}{\partial y} - \sin \theta \frac{\partial}{\partial x} , \\
\frac{\partial}{\partial n} = \cos \theta \frac{\partial}{\partial x} + \sin \theta \frac{\partial}{\partial y} .
\]

(28)

where the angle \( \theta \) determines the direction of the outward normal to the boundary contour: \( \vec{n} = (\cos \theta, \sin \theta) \).

Eqs.(20) and (22) present two physically different mechanisms of film deflection. Eq.(22) describes the light-film interaction which causes the change of the film area. The intensity of the interaction is proportional to the mean value of cis-isomers in the film \( \overline{N} \) and as it is seen from Eq.(24), the action of light is equivalent to a uniformly distributed edge force applied in the plane of the film. In the presence of the interaction (22) with \( B_i > 0 \) the area of the film increases while the opposite sign corresponds to the compression of the film. On the other hand the interaction given by Eq.(20) is due to asymmetric distribution of cis-isomers in the film (23). As Eq.(20) shows, in this case the light produces a bending moment applied to the boundary contour.
III. DEFORMATIONS UNDER THE ACTION OF POLARIZED LIGHT

The Euler-Lagrange equations for the functional 13, 14, 15, 18, 22 (Föppl-von-Karman equations) have the form

\[ D \Delta^2 w - h \frac{\partial}{\partial x_\beta} \sigma_{\alpha \beta} \frac{\partial w}{\partial x_\alpha} + h B_i \Delta w \]
\[ + h B_n \left[ (\partial_x^2 w - \partial_y^2 w) \cos 2\psi + 2 \partial_{xy} w \sin 2\psi \right] = -P , \quad (29) \]
\[ \frac{\partial}{\partial x_\beta} \sigma_{\alpha \beta} = 0 . \quad (30) \]

The boundary conditions for these equations may be obtained in the same way as it was done in 15 and in the case of free boundary (the edge of the film is free) the variations of the vertical component \( \delta w \) and its normal derivative \( \partial \delta w / \partial n \) on the edge are arbitrary. This gives the following set of equations

\[ D \left[ \frac{\partial}{\partial n} \Delta w + (1 - \sigma) \frac{\partial}{\partial t} \left( \sin \theta \cos \theta \left( \partial_y^2 w - \partial_x^2 w \right) + \cos 2\theta \partial_{xy} w \right) \right] - h^2 A_n \frac{\partial}{\partial \theta} \sin (2\psi - \theta) = 0 , \quad (31) \]
\[ D \left[ \Delta w - (1 - \sigma) \sin^2 \theta \partial_x^2 w + \cos^2 \theta \partial_y^2 w - \sin 2\theta \partial_{xy} w \right] - h^2 \left[ A_i + A_n \cos (2\psi - \theta) \right] = 0 , \quad (32) \]
\[ \sigma_{x \beta} n_\beta - (B_i + B_n \cos 2\psi) \cos \theta - B_n \sin 2\psi \sin \theta = 0 , \quad (33) \]
\[ \sigma_{y \beta} n_\beta - (B_i - B_n \cos 2\psi) \sin \theta - B_n \sin 2\psi \cos \theta = 0 . \quad (34) \]

By introducing the Airy potential \( \chi(x, y) \), so that Eqs. (30) are automatically satisfied:

\[ \sigma_{xx} = \partial_x^2 \chi , \quad \sigma_{yy} = \partial_y^2 \chi , \quad \sigma_{xy} = \sigma_{yx} = -\partial_{xy} \chi , \quad (35) \]

and presenting the Airy potential as a sum

\[ \chi(x, y) = \frac{1}{2} \left( B_i - B_n \cos 2\psi \right) x^2 + \frac{1}{2} \left( B_i + B_n \cos 2\psi \right) y^2 - B_a \sin 2\psi xy + T(x, y) , \quad (36) \]

we obtain the Föppl-von-Karman equation 29 in the form

\[ D \Delta^2 w - h \left( \partial_x^2 T \partial_y^2 w + \partial_y^2 T \partial_x^2 w - 2 \partial_{xy} T \partial_{xy} w \right) = -P . \quad (37) \]

This equation is to be completed by the compatibility condition 15

\[ \Delta^2 T + E \left[ \partial_x^2 w \partial_y^2 w - (\partial_{xy} w)^2 \right] = 0 . \quad (38) \]

Note that owing to the fact that we extracted from the Airy potential \( \chi(x, y) \) the parabolic contribution, the Föppl-von-Karman equation 30 does not contain light-induced driving terms. Introducing Eqs. (34), (35) into Eqs. (33), we obtain that the boundary conditions for the potential \( T(x, y) \) have particularly simple form:

\[ \partial_x^2 T \sin \theta - \partial_{xy} T \cos \theta = 0 , \]
\[ \partial_y^2 T \cos \theta - \partial_{xy} T \sin \theta = 0 . \quad (39) \]

IV. BENDING OF CIRCULAR FILM

We consider the photoinduced bending of a circular film of radius \( R \). In the polar coordinates

\[ x = \rho R \cos \theta , \quad y = \rho R \sin \theta , \quad (39) \]

where \( \rho = r/R \), \( (r = \sqrt{x^2 + y^2}) \) is a dimensionless radial coordinate and \( \theta \) is the azimuthal angle we obtain from Eqs. (36) and (37) that equations for new dimensionless dependent variables

\[ \zeta = \frac{w}{h} , \quad \tau = \frac{h}{D} T \]

take the following form

\[ \Delta^2 \zeta - \frac{1}{\rho^2} \left\{ \left( \partial_\theta^2 \zeta + \rho \partial_\rho \zeta \right) \partial_\rho^2 \tau + \left( \partial_\theta^2 \tau + \rho \partial_\rho \tau \right) \partial_\rho^2 \zeta \right\} \]
\[ - \frac{2}{\rho^2} \left( \partial_\theta \tau - \rho \partial_\rho \tau \right) \left( \partial_\theta \zeta - \rho \partial_\rho \zeta \right) = 0 . \quad (40) \]

The boundary conditions (31), (32) and (38) at \( \rho = 1 \) \((r = R)\) become

\[ \left[ \partial_\rho \Delta \zeta + \frac{1}{\rho} - \frac{\sigma}{\rho} \left( \frac{1}{\rho} \partial_\rho^2 \zeta \right) \right] \]
\[ - \frac{2}{\rho} a_n \cos 2(\psi - \theta) = 0 , \quad (41) \]

\[ \left[ \partial_\rho^2 \zeta + \frac{\sigma}{\rho} \left( \frac{1}{\rho} \partial_\rho \zeta + \frac{1}{\rho^2} \partial_\rho^2 \zeta \right) \right] \]
\[ - \left[ a_i + a_n \cos 2(\psi - \theta) \right] = 0 , \quad (42) \]

\[ \left( 1 - \rho \partial_\rho \right) \partial_\theta \tau = 0 , \]
\[ \rho \partial_\theta \tau + \partial_\rho^2 \tau = 0 , \quad (43) \]

where \( f = PR^4/(hD) \) is a dimensionless gravity force and dimensionless parameters

\[ a_i = A_i \frac{hR^2}{D} , \quad a_n = A_n \frac{hR^2}{D} \]
characterize the intensity of the light-film interaction.

To have some insight we consider first the case of weak light-film interaction: \( a_i < 1, a_a < 1 \). Then we compare these results with numerics.

### A. Circularly polarized light

In this subsection we consider the case of photoinduced film deformation when the light is circularly polarized \(^{(10)}\) (the parameter \( a_a \) is set to zero). Assuming the radial symmetry of solutions \( \partial_\theta \zeta = \partial_\theta \tau = 0 \) from Eqs.\(^{(41)-(45)}\) one can obtain approximately (see Appendix for details) that the shape of an irradiated film is determined by the expression

\[
\zeta_0(\rho) = \frac{\rho^2}{2} \left\{ \frac{a_i}{1 + \sigma} - \left( \frac{3 + \sigma}{2(1 + \sigma)} + \frac{\rho^2}{4} - 2 \ln \rho \right) \frac{f}{8} \right\} \tag{47}
\]

(see Fig. 1).

In order to verify the range of validity of the approximate solution \(^{(47)}\), full numerical simulations of Eqs.\(^{(41)-(45)}\) have been performed for the case of radial symmetry. We used finite difference method solving the resulting set of nonlinear algebraic equations by Newton iterations. The results of numerical calculations for the shape of irradiated film \( \zeta(\rho) \) are shown in Fig. 2 for the different values of the dimensionless gravity force \( f \) and the parameter \( a_i \) together with the approximate dependence \(^{(47)}\). Even for large value of parameter \( a_i \) the relative difference between numerical solution and the approximation \(^{(47)}\) does not exceed 25\% for \( a_i = 10 \) and becomes smaller for smaller \( a_i \). For \( a_i = 1 \) the numerical and approximate solutions are indistinguishable in the Fig. 2.

### B. Linearly polarized light

Let us consider now the case of photoinduced film deformation caused by the linear polarized light \(^{(11)}, (2)\). Expanding solutions of Eqs.\(^{(41)-(45)}\) in a Fourier series

\[
\zeta(\rho, \theta) = \sum_{n=0}^{\infty} \zeta_n(\rho) \cos \left[ 2n \left( \psi - \theta \right) \right] , \\
\tau(\rho, \theta) = \sum_{n=0}^{\infty} \tau_n(\rho) \cos \left[ 2n \left( \psi - \theta \right) \right] , \tag{48}
\]

and assuming the weak light-film interaction \( a_i < 1, a_a < 1 \) [the condition \( a_a < 1 \) allows to take into account only the zeroth and the first components in the Fourier series \(^{(48)}\)] one finds

\[
\zeta(\rho, \theta) = \zeta_0(\rho) - a_a \frac{\rho^2 (3 - 2 \rho^2)}{6(3 + \sigma)} \cos 2(\psi - \theta) \tag{49}
\]

for the vertical component of the displacement (see Fig. 3).

For comparison full numerical simulations of Eqs.\(^{(11)}-(45)\) have been performed by use of finite difference method. The results of calculations are shown in Fig. 4.
FIG. 3: The shape of the circular film illuminated by a linearly polarized light.

For small values of parameter $a_\alpha$ the high order terms $\zeta_n, \tau_n$ in the expansion (48) decrease for $n > 1$ and the numerical solution for $\zeta(\rho, \theta)$ practically coincide with approximation (49).

V. BENDING OF RECTANGULAR FILMS

Let us now consider the case of rectangular film: $x \in (-L/2, L/2), y \in (-L/2, L/2)$ interacting with a linearly polarized light. We will consider the case of weak light-film interaction and use the linear theory (neglect the stretching contribution). We will also neglect the action of the gravity force. As a solution to Eq. (29) we choose

$$w = \frac{1}{2} a x^2 + b x y + \frac{1}{2} c y^2 , \quad (50)$$

where $a$, $b$, and $c$ are some constants. These constants can be found by using the boundary condition (32). However a more simple way to find them is to introduce Eq. (50) into Eqs. (14) and (19) and get

$$\frac{1}{L^2} F = \frac{D}{2} \left[ (a + c)^2 + 2(1 - \sigma)(b^2 - ac) \right]$$

$$- h^2 A_i (a + c) - h^2 A_a [(a - c) \cos 2\psi + 2 b \sin 2\psi] . \quad (51)$$

The function (51) has a minimum for

$$a = h^2 \frac{A_i (1 - \sigma) + (1 + \sigma) A_a \cos 2\psi}{D(1 - \sigma^2)} ,$$

$$c = h^2 \frac{A_i (1 - \sigma) - (1 + \sigma) A_a \cos 2\psi}{D(1 - \sigma^2)} ,$$

$$b = h^2 \frac{A_a \sin 2\psi}{D(1 - \sigma)} . \quad (52)$$

Thus under the action of linearly polarized light (1), (2) an initially flat molecular film takes the shape

$$w = \frac{1}{2} \kappa_1 (x \cos \psi + y \sin \psi)^2$$

which is characterized by the following two principal curvatures

$$\kappa_1 = h^2 \frac{A_i (1 - \sigma) + A_a (1 + \sigma)}{D(1 - \sigma^2)} ,$$

$$\kappa_2 = h^2 \frac{A_i (1 - \sigma) - A_a (1 + \sigma)}{D(1 - \sigma^2)} . \quad (54)$$
and has the equilibrium energy given by the expression

\[ F = -\frac{h^4L^2}{D(1-\sigma^2)} \left[ A_i^2(1-\sigma) + A_a^2(1+\sigma) \right]. \tag{55} \]

To characterize the global shape of the film it is convenient to introduce the mean curvature

\[ H = \frac{\kappa_1 + \kappa_2}{2} \]

and the Gaussian curvature

\[ K = \kappa_1 \kappa_2. \]

When \( K > 0 \) the point \((x = 0, y = 0)\) is an elliptic one and the film has a paraboloid shape. For \( K = 0 \) it becomes cylinder-like. Let us assume first that \(|\kappa_1| > |\kappa_2|\), then an irradiated film takes a shape close a cylindric one. Note that this is probably the case in the experiments of Refs. [5, 6] where figures show that polymer films are bent in a cylinder-like fashion. In this case when the light is polarized along the \( x \)-axis (\( \psi = 0 \)) the bending occurs around the \( y \)-axis (see Fig. 5). Under the action of light polarized along one of the film diagonals (\( \psi = \pi/4, 3\pi/4 \)) the film bends around a diagonal (see Fig. 6). This behavior is in a full agreement with the results of the Refs. [5, 6]. When \( K < 0 \) the film takes a saddle-like shape and the corresponding shape profile is shown in Fig. 7. Note that this probably the case in the experiments of Ref. [7] where such of kind of deformation was observed for liquid-crystal elastomers with azo-dyes.

The principal curvatures of the film \( \kappa_1 \) and \( \kappa_2 \) are linearly proportional to the maximum population of the \textit{cis}-isomers in the film \( \mathcal{N}_0 \) and they are a non-monotonic function of the extinction length \( \xi \). In Fig. 8 we presented the normalized mean curvature \( H/H_m \) (\( H_m \) is the maximum value of the mean curvature) as a function of \( \xi \), restricted to \( \xi < 2h \) (\( h \) is the film thickness). The last statement may be considered as a microscopical explanation of the conclusion which was drawn in Ref. [11] in the frame of a phenomenological theory. Note also that it is clear from Eqs. (23), (25), and (44) that for a decreasing number of \textit{cis}-isomers in the film the curvature of the film becomes smaller and the film eventually returns to its initial shape. This is happening in the experiments of Refs. [5, 6] when the film is irradiated with light of the wavelength \( > 540 \) nm when the \textit{cis}-isomeric state is depopulated.

VI. CONCLUSION

In conclusion, we presented a nonlinear elastic theory which describes an anisotropic bending of molecular films under the absorption of polarized light. Solving equations of equilibrium, we showed that a change in the polarization direction of light causes a corresponding change of the shape of the film. We also showed that the curvature of an irradiated film is a non-monotonic function of the extinction coefficient.
FIG. 8: The normalized mean curvature \( H/H_m \) as function of scaled extinction length \( \xi/h \).

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APPENDIX

We will look for solutions of Eqs. (43)–(45) in terms of Fourier series (48). Introducing Eqs. (48) into Eqs. (43)–(45), and taking into account only the first two terms in the expansions (48), we get

\[
\Delta_{\rho} \zeta - \frac{1}{\rho} \frac{d}{d\rho} \left( \frac{d\tau_0}{d\rho} \frac{d\zeta_0}{d\rho} + \frac{1}{2} \frac{d\zeta_0}{d\rho} \frac{d\tau_1}{d\rho} \right) - 2 \frac{d}{d\rho} \left( \frac{1}{\rho} \tau_1 \zeta_1 \right) = -f , \tag{56}
\]

\[
\Delta_{\rho}^2 \tau_0 + 12(1 - \sigma^2) \frac{1}{2} \frac{d}{d\rho} \left( \begin{array}{c}
\frac{d\zeta_0}{d\rho} \\
\frac{d\tau_1}{d\rho}
\end{array} \right)^2
+ \frac{1}{2} \left( \frac{d\zeta_1}{d\rho} \right)^2 - 2 \frac{d}{d\rho} \left( \frac{1}{\rho} u_1^2 \right) = 0 , \tag{57}
\]

\[
\begin{align*}
\left( \Delta_{\rho} - \frac{4}{\rho^2} \right)^2 \zeta_1 &= \frac{1}{\rho} \frac{d}{d\rho} \left( \frac{d\zeta_0}{d\rho} \frac{d\tau_1}{d\rho} \right) \\
+ \frac{d}{d\rho} \left( \frac{d\tau_0}{d\rho} \frac{d\zeta_1}{d\rho} \right) - \frac{4}{\rho} \left( \zeta_1 \frac{d^2 \tau_0}{d\rho^2} + \tau_1 \frac{d^2 \zeta_0}{d\rho^2} \right) &= 0 , \tag{58}
\end{align*}
\]

where

\[
\Delta_{\rho} = \frac{1}{\rho} \frac{d}{d\rho} \rho \frac{d}{d\rho}
\]

is the radial part of the Laplace operator. Inserting Eqs. (48) into Eqs. (43)–(45), we obtain the boundary conditions at \( \rho = 1 \) for the zeroth harmonics in the form

\[
\frac{d}{d\rho} \left( \frac{d\zeta_0}{d\rho} \right) = 0 , \tag{60}
\]

\[
\frac{d^2 \zeta_0}{d\rho^2} + \frac{\sigma}{\rho} \frac{d\zeta_0}{d\rho} - a_1 = 0 , \tag{61}
\]

\[
\frac{d\tau_0}{d\rho} = 0 , \tag{62}
\]

and for the first Fourier harmonics in the form

\[
\frac{d}{d\rho} \left( \Delta_{\rho} - \frac{4}{\rho^2} \right) \zeta_1 + 4 \frac{1 - \sigma}{\rho^3} \left( \zeta_1 - \rho \frac{d\zeta_1}{d\rho} \right) - \frac{2}{\rho} a_1 = 0 , \tag{63}
\]

\[
\left( \Delta_{\rho} - \frac{4}{\rho^2} \right) \zeta_1 + \frac{1 - \sigma}{\rho^2} \left( 4 \zeta_1 - \rho \frac{d\zeta_1}{d\rho} \right) - a_1 = 0 , \tag{64}
\]

\[
\tau_1 = 0 , \frac{d\tau_0}{d\rho} = 0 . \tag{65}
\]

As it is seen from Eqs. (63), (64) the amplitude of the first harmonics is proportional to the light-film interaction parameter \( a_1 \). Assuming that \( a_1 < 1 \), we neglect all terms proportional to \( a_1^n \) with \( n \geq 2 \). Under this assumption one can neglect the last two terms in Eqs. (66), (67) and obtain

\[
\Delta_{\rho}^2 \zeta_0 - \frac{1}{\rho} \frac{d}{d\rho} \left( \frac{d\tau_0}{d\rho} \frac{d\zeta_0}{d\rho} \right) = -f , \tag{66}
\]

\[
\Delta_{\rho}^2 \tau_0 + 12(1 - \sigma^2) \frac{1}{2} \frac{d}{d\rho} \left( \begin{array}{c}
\frac{d\zeta_0}{d\rho} \\
\frac{d\tau_1}{d\rho}
\end{array} \right)^2
+ \frac{1}{2} \left( \frac{d\zeta_1}{d\rho} \right)^2 - 2 \frac{d}{d\rho} \left( \frac{1}{\rho} u_1^2 \right) = 0 , \tag{67}
\]

Integrating each equation, we get

\[
\rho \frac{d}{d\rho} \frac{d}{d\rho} \frac{d\zeta_0}{d\rho} \frac{d\tau_0}{d\rho} - \frac{d\tau_0}{d\rho} \frac{d\zeta_0}{d\rho} = \frac{1}{2} f (\rho^2 - 1) , \tag{68}
\]

\[
\rho \frac{d}{d\rho} \frac{d}{d\rho} \frac{d\tau_0}{d\rho} + 12(1 - \sigma^2) \frac{1}{2} \left( \frac{d\zeta_0}{d\rho} \right)^2 = 0 . \tag{68}
\]
where the condition of regularity at the center \( \frac{d \zeta_0}{d \rho} = 0 \) and the boundary conditions (60), (62) were used.

Equations (68) are simplified by introducing the new variables

\[
g = \frac{1}{\rho} \frac{d \zeta_0}{d \rho}, \quad \alpha = \frac{1}{4 \rho} \frac{d \tau_0}{d \rho}, \quad z = \rho^2.
\]  

(69)

Then Eqs. (68) become

\[
\frac{d^2}{dz^2} \left( z g \right) - g \alpha = -\frac{f}{8} (1 - \frac{1}{z}),
\]

\[
\frac{d^2}{dz^2} \left( z \alpha \right) + \frac{3(1 - \sigma^2)}{8} g^2 = 0.
\]  

(70)

The boundary conditions (60)-(62) at \( z = 1 \) become

\[
\frac{d^2}{dz^2} \left( z g \right) = 0,
\]

\[
2z \frac{d g}{d z} + (1 + \sigma) g - a_i = 0,
\]

\[
\alpha = 0.
\]  

(71)

Assuming that \( \epsilon \equiv 3(1 - \sigma^2)/8 < 1 \) is a small parameter we expand the functions \( g(z) \) and \( \alpha(z) \) into series

\[
g = g_0 + \epsilon g_1 + \cdots,
\]

\[
\alpha = \alpha_0 + \epsilon \alpha_1 + \cdots.
\]  

(72)

Inserting (72) into Eqs. (71) we get

\[
\epsilon^0: \quad \frac{d^2}{dz^2} \left( z g_0 \right) - g_0 \alpha_0 = -\frac{f}{8} (1 - \frac{1}{z}),
\]

\[
\frac{d^2}{dz^2} \left( z \alpha_0 \right) = 0.
\]  

(73)

\[
\epsilon^1: \quad \frac{d^2}{dz^2} \left( z g_1 \right) - g_0 \alpha_1 - g_1 \alpha_0 = 0,
\]

\[
\frac{d^2}{dz^2} \left( z \alpha_1 \right) + g_0^2 = 0.
\]  

(74)

In the same way the boundary conditions (71) at \( z = 1 \) can be expressed as

\[
\epsilon^0: \quad \frac{d^2}{dz^2} \left( z g_0 \right) = 0,
\]

\[
2z \frac{d g_0}{d z} + (1 + \sigma) g_0 - a_i = 0,
\]

\[
\alpha_0 = 0.
\]  

(75)

\[
\epsilon^1: \quad \frac{d^2}{dz^2} \left( z g_1 \right) = 0,
\]

\[
2z \frac{d g_1}{d z} + (1 + \sigma) g_1 = 0,
\]

\[
\alpha_1 = 0.
\]  

(76)

From Eqs. (73) and (75) one finds

\[
g_0 = \frac{a_i}{1 + \sigma} - \frac{f}{8} \left\{ \frac{1 - \sigma}{2(1 + \sigma)} + \frac{z}{2} - \ln z \right\},
\]

\[
\alpha_0 = 0.
\]  

(77)

[1] S. Bian, L. Li, J. Kumar, D.Y. Kim, J. Williams, and S.K. Tripathy, Appl. Phys. Lett. 73, 1817 (1998).
[2] J. Kumar, L. Li, X.L. Liang, D.Y. Kim, T.S. Lee, and S. Tripathy, Appl. Phys. Lett. 72, 2096 (1998).
[3] D. Bublitz, M. Helgert, B. Fleck, L. Wenke, S. Hvilsted, and P.S. Ramanujam, Appl. Phys. B 70, 863 (2000).
[4] H. Finkelmann, E. Nishikawa, G.G. Pereira, and M. Warner, Phys. Rev. Lett. 87, 015501 (2001).
[5] T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, and A. Kanazawa, Adv. Mater. 15, 201 (2003).
[6] Y. Yu, M. Nakano, and T. Ikeda, Nature 425, 145 (2003).
[7] M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, and M. Shelley, Nature Materials 3, 307 (2004).
[8] A. Lendlein, H. Jiang, O. Jünger, and R. Langer, Nature 434, 879 (2005).
[9] P.G. De Gennes, C. R. Acad. Sci. Ser. B 281, 101 (1975).
[10] M. Warner and E.M. Terentjev, Liquid Crystal Elastomers (Clarendon Press, Oxford, 2003).
[11] M. Warner and L. Mahadevan, Phys. Rev. Lett. 92, 134302 (2004).
[12] Y.B. Gaididei, P.L. Christiansen, and P.S. Ramanujam, Appl. Phys. B 74, 139 (2002).
[13] T.G. Pedersen, P.S. Ramanujam, P.M. Johansen, and S. Hvilsted, J. Opt. Soc. Am. B 15, 2721 (1998).
[14] D. Corbett and M. Warner, Phys. Rev. Lett. 96, 237802 (2006).
[15] L.D. Landau and E.M. Lifshitz, Theory of Elasticity (Pergamon, Oxford, 1986).
[16] J.J. Stoker, Nonlinear Elasticity (Gordon and Breach, New York, 1983).
