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Nonlinear bending of molecular films by polarized light

Yu.B. Gaididei [a], A.P. Krekhov [b,*], H. Büttner [b]

[a] Bogolyubov Institute for Theoretical Physics, 03143 Kiev, Ukraine
[b] Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany

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ABSTRACT

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.

1. 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 linear polarized light and mounds or wells under the action of circularly polarized light [1,2]. Circular azobenzene polyester films freely lying on a water surface become elliptically deformed under the influence of linearly polarized light [3]. Large, reversible shape changes can be induced optically by photoisomerization of nematic elastomers [4]. Anisotropic bending and unbending behavior of molecular liquid-crystalline films containing azobenzene chromophores has been discovered and studied in Refs. [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 in [7]. Shape-memory effects in polymers containing cinnamic groups induced by ultraviolet light illumination were reported quite recently in Ref. [8]. The possibility of coupling between orientational and translational degrees of freedom in liquid crystals was first raised by de Gennes [9] and extended to nematic elastomers in [10]. Based on this idea a phenomenological theory of photoinduced deformations of nematic elastomers was proposed in [4]. The case of inhomogeneous illumination was considered in [11]. A microscopic theory of photoinduced deformation of non-crystalline molecular films was developed in [12]. The physical reason for surface-relief formation presented in [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 [13], 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 [14].

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

* Corresponding author.
E-mail address: alexei.krekhov@uni-bayreuth.de (A.P. Krekhov).

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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.

2. 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 xy-plane so that the undeformed film occupies the region: $|z| \leqslant h/2$, $x, y \in \Omega$. The film is irradiated from above by a linearly polarized electromagnetic wave which propagates along the z-axis. Its electric component has the form

$$\vec{E}(\vec{r},t) = \vec{\mathcal{E}}\cos(kz+\omega t), \quad \vec{\mathcal{E}} = \mathcal{E}(\cos\psi, \sin\psi, 0), \tag{1}$$

where ω is the frequency, $k = \omega/c$ is the wave number (c is the speed of light) and the angle ψ determines the polarization of the electromagnetic wave.

The total energy of irradiated thin film may be written as follows

$$F = F_{el} + W_g + W. \tag{2}$$

Here the first term represent the elastic energy of thin film

$$F_{el} = \frac{E}{2(1-\sigma^2)} \int\limits_{-h/2}^{h/2} dz \int\limits_{\Omega} dx\,dy \left[\epsilon_{xx}^2 + \epsilon_{yy}^2 + 2\sigma\epsilon_{xx}\epsilon_{yy} + 2(1-\sigma)\epsilon_{xy}^2\right], \tag{3}$$

where E and σ are Young's modulus and Poisson's ratio, respectively [15] and $\epsilon_{\alpha\beta}$ is the strain tensor ($\alpha, \beta = x, y$). We assume here that the non-irradiated film is neither orientationally nor translationally ordered in the xy-plane and therefore we model its elastic properties by using the isotropic energy (3). The term

$$W_g = P \int\limits_{\Omega} dx\,dy\, w \tag{4}$$

in Eq. (2) presents the potential energy of the film in the gravitational field. Here $P = a_{gr}\rho_f h$ is the gravity force with ρ_f being the film density, a_{gr} being the acceleration of free fall, and w represents the vertical displacement of the film. The last term in Eq. (2) gives the change of the total energy due to the interaction between the electromagnetic wave (1) and the film. It has the form [12]

$$W = W_1 + W_2, \tag{5}$$

where

$$W_1 = -V_a \int\limits_{-h/2}^{h/2} dz \int\limits_{\Omega} dx\,dy\, \mathcal{N}(\vec{r})\left[(\epsilon_{xx} - \epsilon_{yy})\cos(2\psi) + 2\epsilon_{xy}\sin(2\psi)\right] \tag{6}$$

represents the anisotropic part of the photoelastic interaction which describes the coupling of the shear deformation of the film to the incoming light and

$$W_2 = -V_i \int\limits_{-h/2}^{h/2} dz \int\limits_{\Omega} dx\,dy\, \mathcal{N}(\vec{r})(\epsilon_{xx} + \epsilon_{yy}) \tag{7}$$

determines the isotropic in-plane deformations. In Eqs. (6), (7) 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 spatially independent. The function $\mathcal{N}(\vec{r})$ gives the population of *cis*-isomers for a given value of the radiation power $\mathcal{E}^2$ [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 $\mathcal{N}(\vec{r})$ as follows

$$\mathcal{N}(\vec{r}) = \mathcal{N}_0 \exp\left\{\frac{(z-h/2)}{\xi}\right\}, \tag{8}$$

where $\mathcal{N}_0$ is the maximum population of the *cis*-isomers for a given power $\mathcal{E}^2$ and ξ is the extinction length of the light which provides transition of chromophores from *trans*- to *cis*-isomeric state (in the experiments [5,6] 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. (8) 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 Eq. (1) we have

$$\vec{E}(\vec{r},t) = \mathcal{E}\left\{\cos(kz+\omega t),\ \sin(kz+\omega t),\ 0\right\} \tag{9}$$

and therefore the contribution (6) vanishes; the energy of photoelastic interaction is solely determined by Eq. (7).

Following the usual derivation of Föppl–von Karman equations for bending of a thin plate (see, e.g., [15,16]), we write the strains as a linear expansion in z from the middle plane and get

$$\begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} \\ \epsilon_{xy} & \epsilon_{yy} \end{pmatrix} = \begin{pmatrix} u_{xx} & u_{xy} \\ u_{xy} & u_{yy} \end{pmatrix} + z \begin{pmatrix} \partial_{xx} w & \partial_{xy} w \\ \partial_{xy} w & \partial_{yy} w \end{pmatrix}, \tag{10}$$

where

$$u_{\alpha\beta} = \frac{1}{2}(\partial_\beta u_\alpha + \partial_\alpha u_\beta) + \frac{1}{2}\partial_\alpha w \partial_\beta w \tag{11}$$

are the components of the two-dimensional nonlinear deformation tensor and ∂_α 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 $u_z = w$. Note, that in the framework of the Föppl–von Karman approach the x, y-components of the strain tensor linearly depend on the vertical coordinate z [15]. This means that when the illuminated side of the plate contracts the opposite side of the plate extends and vice versa. Introducing Eqs. (10), (11) into (2) we can represent the elastic energy of the thin film in the form

$$F_{el} = F_b + F_s. \tag{12}$$

The bending energy is written as

$$F_b = \frac{D}{2} \int\limits_{\Omega} dx\,dy \left\{(\Delta w)^2 + 2(1-\sigma)\left[(\partial_{xy} w)^2 - \partial_x^2 w \partial_y^2 w\right]\right\}, \tag{13}$$

where $\Delta = \partial_\alpha \partial_\alpha$ is the two-dimensional Laplace operator and $D = Eh^3/[12(1-\sigma^2)]$ is the flexural rigidity of the film. For the stretching energy one has [15]

$$F_s = \frac{h}{2} \int\limits_{\Omega} dx\,dy\, (\sigma_{xx}u_{xx} + \sigma_{yy}u_{yy} + 2\sigma_{xy}u_{xy}), \tag{14}$$

where $u_{\alpha\beta}$ are defined by Eq. (11) with the longitudinal stresses

$$\sigma_{xx} = \frac{E}{1-\sigma^2}(u_{xx} + \sigma u_{yy}), \qquad \sigma_{yy} = \frac{E}{1-\sigma^2}(u_{yy} + \sigma u_{xx}),$$
$$\sigma_{xy} = \frac{E}{1+\sigma} u_{xy}. \tag{15}$$

In Eq. (2) the light-film interaction energy becomes

$$W = W_b + W_s \tag{16}$$

with the bending contribution $W_b = W_{b1} + W_{b2}$, where

$$W_{b1} = -h^2 \int\limits_{\Omega} dx\,dy \left\{ A_i \Delta w + A_a \left[\left(\partial_x^2 w - \partial_y^2 w\right) \cos(2\psi) + 2\partial_{xy} w \sin(2\psi) \right] \right\} \tag{17}$$

describes a linear interaction with bending deformation while the term

$$W_{b2} = -\frac{h}{2} \int\limits_{\Omega} dx\,dy \left\{ B_a \left[\left((\partial_x w)^2 - (\partial_y w)^2\right) \cos(2\psi) + 2\partial_x w \partial_y w \sin(2\psi) \right] + B_i \left[(\partial_x w)^2 + (\partial_y w)^2 \right] \right\} \tag{18}$$

is due to the nonlinear character of the two-dimensional deformation tensor (11). The stretching contribution in Eq. (16) is

$$W_s = -h \int\limits_{\Omega} dx\,dy \left\{ B_a \left[(u_{xx} - u_{yy}) \cos(2\psi) + 2u_{xy} \sin(2\psi) \right] + B_i (u_{xx} + u_{yy}) \right\}, \tag{19}$$

and the new light-film interaction parameters in Eqs. (17)–(19) are

$$A_i = V_i \overline{z\mathcal{N}}, \qquad A_a = V_a \overline{z\mathcal{N}}, \qquad B_i = V_i \overline{\mathcal{N}}, \qquad B_a = V_a \overline{\mathcal{N}}. \tag{20}$$

The mean value of *cis*-isomers in the film is given by

$$\overline{\mathcal{N}} \equiv \frac{1}{h} \int\limits_{-h/2}^{h/2} \mathcal{N}(z)\,dz = \mathcal{N}_0 \frac{\xi}{h} \left(1 - e^{-h/\xi}\right), \tag{21}$$

and the asymmetry of the *cis*-isomer distribution in the film is characterized by

$$\overline{z\mathcal{N}} \equiv \frac{1}{h^2} \int\limits_{-h/2}^{h/2} z\mathcal{N}(z)\,dz = \frac{1}{2} \mathcal{N}_0 \frac{\xi}{h} \left[1 - 2\frac{\xi}{h} + \left(1 + 2\frac{\xi}{h}\right) e^{-h/\xi} \right]. \tag{22}$$

By using Green's formula for the two-dimensional integrals, Eqs. (17) and (19) can be presented in an equivalent form

$$W_{b1} = -h^2 \oint dl \left\{ \left[A_i + A_a \cos 2(\psi - \theta) \right] \frac{\partial w}{\partial n} + A_a \sin 2(\psi - \theta) \frac{\partial w}{\partial l} \right\}, \tag{23}$$

$$W_s = -h \oint dl \left\{ B_i \vec{n} \cdot \vec{u} + B_a \cos(2\psi - \theta) u_x + B_a \sin(2\psi - \theta) u_y \right\}, \tag{24}$$

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

$$\frac{\partial}{\partial l} = \cos\theta \partial_y - \sin\theta \partial_x, \qquad \frac{\partial}{\partial n} = \cos\theta \partial_x + \sin\theta \partial_y. \tag{25}$$

where the angle θ determines the direction of the outward normal to the boundary contour: $\vec{n} = (\cos\theta, \sin\theta)$. Eqs. (17) and (19) present two physically different mechanisms of film deflection. Eq. (19) 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 $\overline{\mathcal{N}}$ 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 (19) 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. (17) is due to asymmetric distribution of *cis*-isomers in the film (22). As Eq. (23) shows, in this case the light produces a bending moment applied to the boundary contour.

3. Deflections under the action of polarized light

The Euler–Lagrange equations for the functional (2) [with (12)–(14), (16)–(19)] (Föppl–von Karman equations) have the form

$$D\Delta^2 w - h \frac{\partial}{\partial x_\beta} \sigma_{\alpha\beta} \frac{\partial w}{\partial x_\alpha} + hB_i \Delta w + hB_a \left[\left(\partial_x^2 w - \partial_y^2 w\right) \cos 2\psi + 2\partial_{xy} w \sin 2\psi \right] = -P, \tag{26}$$

$$\frac{\partial}{\partial x_\beta} \sigma_{\alpha\beta} = 0. \tag{27}$$

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 δw and its normal derivative $\partial(\delta w)/\partial n$ on the edge are arbitrary. This gives the following set of equations

$$D \left[\frac{\partial}{\partial n} \Delta w + (1 - \sigma) \frac{\partial}{\partial l} \left\{ \sin\theta \cos\theta \left(\partial_y^2 w - \partial_x^2 w\right) + \cos 2\theta \partial_{xy} w \right\} \right] - h^2 A_a \frac{\partial}{\partial l} \sin 2(\psi - \theta) = 0, \tag{28}$$

$$D \left[\Delta w - (1 - \sigma) \left\{ \sin^2\theta \partial_x^2 w + \cos^2\theta \partial_y^2 w - \sin 2\theta \partial_{xy} w \right\} \right] - h^2 \left[A_i + A_a \cos 2(\psi - \theta) \right] = 0, \tag{29}$$

$$\sigma_{x\beta} n_\beta - (B_i + B_a \cos 2\psi) \cos\theta - B_a \sin 2\psi \sin\theta = 0,$$

$$\sigma_{y\beta} n_\beta - (B_i - B_a \cos 2\psi) \sin\theta - B_a \sin 2\psi \cos\theta = 0. \tag{30}$$

By introducing the Airy potential $\chi(x, y)$, so that Eqs. (27) are automatically satisfied:

$$\sigma_{xx} = \partial_y^2 \chi, \qquad \sigma_{yy} = \partial_x^2 \chi, \qquad \sigma_{xy} = \sigma_{yx} = -\partial_{xy} \chi, \tag{31}$$

and presenting the Airy potential as a sum

$$\chi(x, y) = \frac{1}{2}(B_i - B_a \cos 2\psi) x^2 + \frac{1}{2}(B_i + B_a \cos 2\psi) y^2 - B_a \sin 2\psi xy + T(x, y), \tag{32}$$

we rewrite the Föppl–von Karman equation (26) in the form

$$D\Delta^2 w - h\left(\partial_x^2 T \partial_y^2 w + \partial_y^2 T \partial_x^2 w - 2\partial_{xy} T \partial_{xy} w\right) = -P. \tag{33}$$

This equation is to be completed by the compatibility condition [15]

$$\Delta^2 T + E\left[\partial_x^2 w \partial_y^2 w - (\partial_{xy} w)^2\right] = 0. \tag{34}$$

Note that owing to the fact that we extracted from the Airy potential $\chi(x, y)$ the parabolic contribution, the Föppl–von Karman equation (33) does not contain light-induced driving terms. Introducing Eqs. (31), (32) into (30), we obtain that the boundary conditions for the potential $T(x, y)$ have particularly simple form

$$\partial_x^2 T \sin\theta - \partial_{xy} T \cos\theta = 0, \qquad \partial_y^2 T \cos\theta - \partial_{xy} T \sin\theta = 0. \tag{35}$$

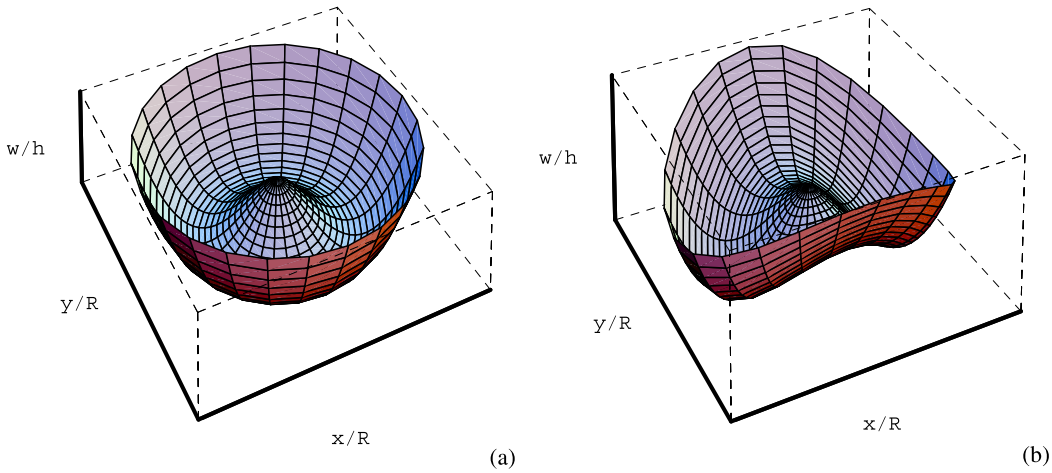

Fig. 1. Typical shape of the circular film illuminated by a circularly polarized light (a) and by a linearly polarized light (b). The vertical scale is expanded compared with the horizontal scale.

4. Bending of circular film

We consider the photoinduced bending of a circular film of radius R. In the polar coordinates $\rho R(\cos\theta, \sin\theta)$, where $\rho = r/R$ ($r = \sqrt{x^2+y^2}$) is a dimensionless radial coordinate and θ is the azimuthal angle we obtain from Eqs. (33), (34) that equations for new dimensionless variables $\zeta = w/h$, $\tau = Th/D$ take the following form

$$\Delta^2\zeta - \frac{1}{\rho^2}\Big\{\big(\partial_\theta^2\zeta + \rho\partial_\rho\zeta\big)\partial_\rho^2\tau + \big(\partial_\theta^2\tau + \rho\partial_\rho\tau\big)\partial_\rho^2\zeta - \frac{2}{\rho^2}(\partial_\theta\tau - \rho\partial_{\rho\theta}\tau)(\partial_\theta\zeta - \rho\partial_{\rho\theta}\zeta)\Big\} = -f, \tag{36}$$

$$\Delta^2\tau + 12\big(1-\sigma^2\big)\frac{1}{\rho^2}\Big\{\big(\partial_\theta^2\zeta + \rho\partial_\rho\zeta\big)\partial_\rho^2\zeta - \frac{1}{\rho^2}(\partial_\theta\zeta - \rho\partial_{\rho\theta}\zeta)^2\Big\} = 0, \tag{37}$$

where $f = PR^4/(hD)$ is a dimensionless gravity force. The boundary conditions (28), (29), and (35) at $\rho = 1$ ($r = R$) become

$$\Big[\partial_\rho\Delta\zeta + \frac{1-\sigma}{\rho}\partial_\rho\Big(\frac{1}{\rho}\partial_\theta^2\zeta\Big)\Big] - \frac{2}{\rho}a_a\cos 2(\psi-\theta) = 0, \tag{38}$$

$$\Big[\partial_\rho^2\zeta + \sigma\Big(\frac{1}{\rho}\partial_\rho\zeta + \frac{1}{\rho^2}\partial_\theta^2\zeta\Big)\Big] - \big[a_i + a_a\cos 2(\psi-\theta)\big] = 0, \tag{39}$$

$$(1-\rho\partial_\rho)\partial_\theta\tau = 0,\ \rho\partial_\rho\tau + \partial_\theta^2\tau = 0. \tag{40}$$

Here dimensionless parameters $a_i = A_i hR^2/D$, $a_a = A_a hR^2/D$ 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.

4.1. Circularly polarized light

In this subsection we consider the case of photoinduced film deformation when the light is circularly polarized (9) [the parameter a_a is set to zero in Eqs. (38), (39)]. Assuming azimuthal symmetry of solutions ($\partial_\theta\zeta = \partial_\theta\tau = 0$) from Eqs. (36)–(40) one can obtain approximately (see Appendix A for details) that the dimensionless vertical displacement of an irradiated film fixed in the center [$\zeta(\rho = 0) = 0$] is determined by the expression

$$\zeta_0(\rho) = \frac{\rho^2}{2}\Big\{\frac{a_i}{1+\sigma} - \Big(\frac{3+\sigma}{2(1+\sigma)} + \frac{\rho^2}{4} - 2\ln\rho\Big)\frac{f}{8}\Big\}. \tag{41}$$

Typical shape of the film given by Eq. (41) is shown in Fig. 1(a). The distinctive shape of the film results from the competition between the photoinduced deformation (term proportional to a_i) and the gravity force (term proportional to f).

In order to verify the range of validity of the approximate solution (41), full numerical simulations of Eqs. (36)–(40) have been performed for the case of azimuthal 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 (41). For large values of parameter a_i the relative difference between numerical solution and the approximation (41) 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 undistinguished in Fig. 2.

4.2. Linearly polarized light

Let us consider now the case of photoinduced film deformation caused by the linear polarized light (1). Expanding solutions of Eqs. (36)–(40) in a Fourier series

$$\zeta(\rho,\theta) = \sum_{n=0}^{\infty}\zeta_n(\rho)\cos\big[2n(\psi-\theta)\big],$$
$$\tau(\rho,\theta) = \sum_{n=0}^{\infty}\tau_n(\rho)\cos\big[2n(\psi-\theta)\big], \tag{42}$$

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 terms in the Fourier series (42)] one finds

$$\zeta(\rho,\theta) = \zeta_0(\rho) - a_a\frac{\rho^2(3-2\rho^2)}{6(3+\sigma)}\cos 2(\psi-\theta) \tag{43}$$

for the vertical component of the displacement [see Fig. 1(b)].

For comparison full numerical simulations of Eqs. (36)–(40) have been performed by use of finite difference method. The results of calculations are shown in Fig. 3. For small values of parameter a_a the high order terms ζ_n, τ_n in the expansion (42) decrease for $n > 1$ and the numerical solution for $\zeta(\rho,\theta)$ practically coincide with approximation (43). For large values of parameter a_a the difference between approximation (43) and full numerical solution

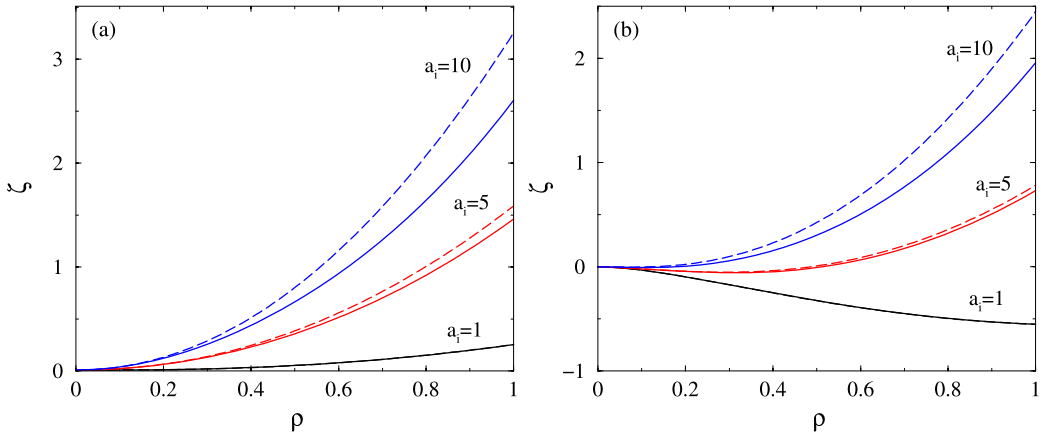

Fig. 2. Dimensionless displacement $\zeta(\rho)$ of the circular film illuminated by a circularly polarized light. Numerical (solid lines) and approximate (dashed lines) solutions for $\sigma = 0.5$ and $f = 1$ (a), $f = 10$ (b), and different values of a_i.

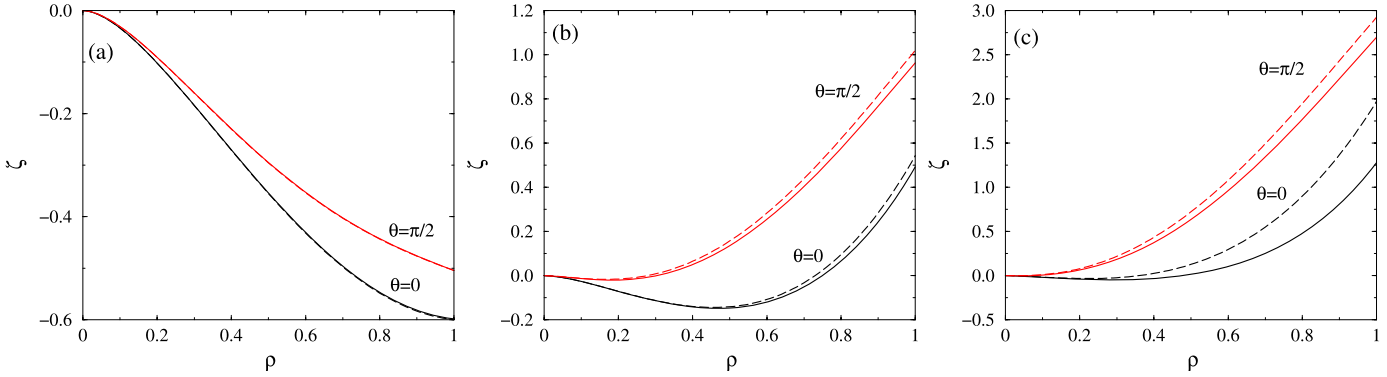

Fig. 3. Dimensionless displacement $\zeta(\rho)$ of the circular film illuminated by a linearly polarized light for $\psi = 0$ in the cross sections $\theta = 0$ and $\theta = \pi/2$. Numerical (solid lines) and approximate (dashed lines) solutions for $\sigma = 0.5$ and $f = 10$: $a_i = a_a = 1$ (a), $a_i = a_a = 5$ (b), and $a_i = a_a = 10$ (c).

increases and for $a_a = 10$ the maximal inaccuracy of Eq. (43) is observed for the cross section $\theta = 0$ at the edge of the film ($\rho = 1$).

5. 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 contributions). We will also neglect the action of the gravity force. As a solution to Eq. (26) we choose

$$w = \frac{1}{2}ax^2 + bxy + \frac{1}{2}cy^2, \tag{44}$$

where a, b, and c are some constants. These constants can be found by using the boundary condition (29). However a more simple way to find them is to introduce Eq. (44) into Eqs. (13), (17) and get

$$\frac{1}{L^2}F = \frac{D}{2}\big[(a+c)^2 + 2(1-\sigma)\big(b^2 - ac\big)\big] - h^2 A_i(a+c) - h^2 A_a\big[(a-c)\cos 2\psi + 2b\sin 2\psi\big]. \tag{45}$$

The elastic energy (45) has a minimum for

$$a = h^2\frac{A_i(1-\sigma) + (1+\sigma)A_a\cos 2\psi}{D(1-\sigma^2)},$$
$$c = h^2\frac{A_i(1-\sigma) - (1+\sigma)A_a\cos 2\psi}{D(1-\sigma^2)},$$
$$b = h^2\frac{A_a\sin 2\psi}{D(1-\sigma)}. \tag{46}$$

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

$$w = \frac{1}{2}\kappa_1(x\cos\psi + y\sin\psi)^2 + \frac{1}{2}\kappa_2(-x\sin\psi + y\cos\psi)^2, \tag{47}$$

which is characterized by the following two principal curvatures

$$\kappa_1 = h^2\frac{A_i(1-\sigma) + A_a(1+\sigma)}{D(1-\sigma^2)},$$
$$\kappa_2 = h^2\frac{A_i(1-\sigma) - A_a(1+\sigma)}{D(1-\sigma^2)}, \tag{48}$$

and has the equilibrium energy given by the expression

$$F = -\frac{h^4L^2}{D(1-\sigma^2)}\big[A_i^2(1-\sigma) + A_a^2(1+\sigma)\big]. \tag{49}$$

To characterize the global shape of the film it is convenient to introduce the mean curvature $H = (\kappa_1 + \kappa_2)/2$ 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 to a cylindric one. 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. Note that in [5] polymer films were anisotropic whereas we have considered isotropic non-crystalline film. When the light is polarized along the x-axis ($\psi = 0$) the bending occurs around the y-axis [Fig. 4(a)]. Under the action of light polarized along one of the film diagonals

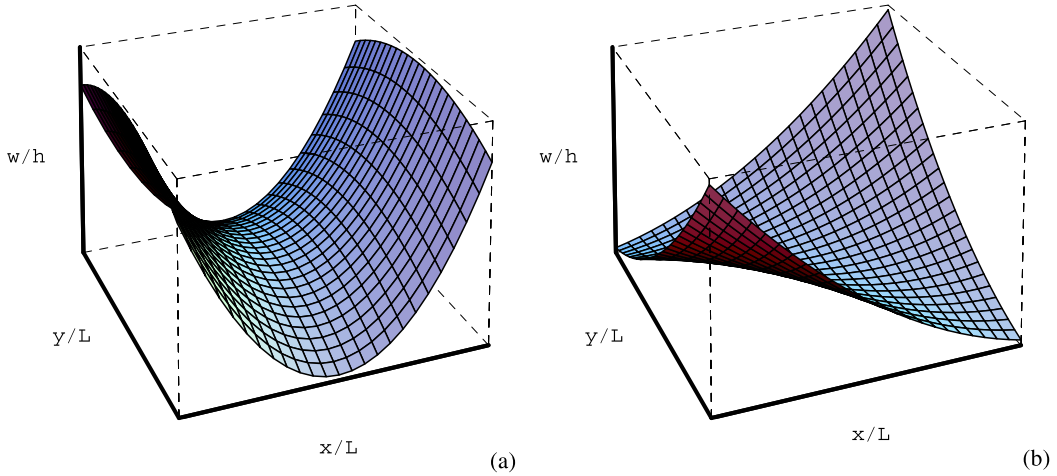

Fig. 4. Typical shape of the rectangular film with $A_a < A_i$ illuminated by a linearly polarized light for $\psi = 0$ (a) and for $\psi = \pi/4$ (b). The vertical scale is expanded compared with the horizontal scale.

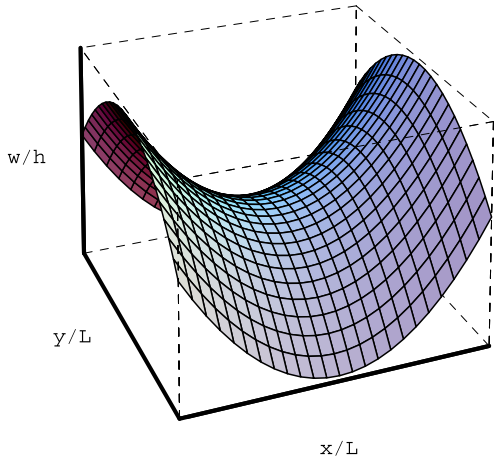

Fig. 5. Typical shape of the rectangular film with $A_a > A_i$ illuminated by a linearly polarized light for $\psi = 0$. The vertical scale is expanded compared with the horizontal scale.

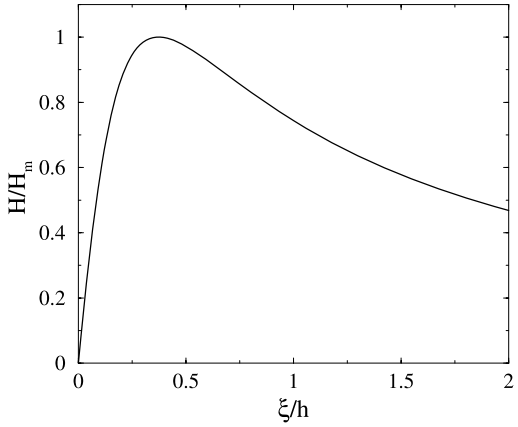

Fig. 6. The normalized mean curvature H/H_m as function of scaled extinction length ξ/h.

($\psi = \pi/4, 3\pi/4$) the film bends around a diagonal [Fig. 4(b)]. This behavior is in a full agreement with the results of the Ref. [6]. When $K < 0$ the film takes a saddle-like shape and the corresponding shape profile is shown in Fig. 5. Note that this is probably the case in the experiments of Ref. [7] where such kind of deformation was observed for liquid crystal elastomers with azo-dyes.

The principal curvatures of the film, κ_1 and κ_2, are linearly proportional to the maximum population of the *cis*-isomers in the film $\mathcal{N}_0$ and they are non-monotonic functions of the extinction length ξ. In Fig. 6 we present the normalized mean curvature H/H_m (H_m is the maximum value of the mean curvature) as a function of ξ, restricted to $\xi < 2h$ (h is the film thickness). The non-monotonic dependence of the mean curvature on the extinction length is similar to the one given in Ref. [11]. Note also that it is clear from Eqs. (20), (22) and (48) that for a decreasing number of *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 $\lambda > 540$ nm when the *cis*-isomeric state is depopulated.

6. Conclusion

In conclusion, we presented a nonlinear elastic theory which describes an anisotropic bending of molecular films under the absorption of polarized light. Photoinduced deformations of circular and rectangular films studied in detail. 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. Suitable approximate expressions for the shape of photoinduced deformation were obtained and compared with full numerical simulations in the framework of nonlinear elasticity theory. We also showed that the curvature of an irradiated film is a non-monotonic function of the extinction coefficient.

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Appendix A

We look for the solutions of Eqs. (36)–(40) in terms of Fourier series (42). Introducing Eqs. (42) into (36), (37) and taking into account only the first two terms in the expansions (42), we get

$$\Delta_\rho^2\zeta_0-\frac{1}{\rho}\frac{d}{d\rho}\left\{\frac{d\tau_0}{d\rho}\frac{d\zeta_0}{d\rho}+\frac{1}{2}\frac{d\zeta_1}{d\rho}\frac{d\tau_1}{d\rho}-2\frac{d}{d\rho}\left(\frac{1}{\rho}\tau_1\zeta_1\right)\right\}=-f, \tag{50}$$

$$\Delta_\rho^2\tau_0+12\left(1-\sigma^2\right)\frac{1}{2}\frac{1}{\rho}\frac{d}{d\rho}\left\{\left(\frac{d\zeta_0}{d\rho}\right)^2+\frac{1}{2}\left(\frac{d\zeta_1}{d\rho}\right)^2-2\frac{d}{d\rho}\left(\frac{1}{\rho}\zeta_1^2\right)\right\}=0, \tag{51}$$

$$\left(\Delta_\rho-\frac{4}{\rho^2}\right)^2\zeta_1-\frac{1}{\rho}\left[\frac{d}{d\rho}\left(\frac{d\zeta_0}{d\rho}\frac{d\tau_1}{d\rho}\right)+\frac{d}{d\rho}\left(\frac{d\tau_0}{d\rho}\frac{d\zeta_1}{d\rho}\right)-\frac{4}{\rho}\left(\zeta_1\frac{d^2\tau_0}{d\rho^2}+\tau_1\frac{d^2\zeta_0}{d\rho^2}\right)\right]=0, \tag{52}$$

$$\left(\Delta_\rho-\frac{4}{\rho^2}\right)^2\tau_1+12\left(1-\sigma^2\right)\frac{1}{\rho}\left[\frac{d}{d\rho}\left(\frac{d\zeta_0}{d\rho}\frac{d\zeta_1}{d\rho}\right)-\frac{4}{\rho}\zeta_1\frac{d^2\zeta_0}{d\rho^2}\right]=0, \tag{53}$$

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. (42) into (38)–(40), we obtain the boundary conditions at $\rho=1$ for the zeroth harmonics in the form

$$\frac{d}{d\rho}\frac{1}{\rho}\frac{d}{d\rho}\rho\frac{d\zeta_0}{d\rho}=0,\qquad \frac{d^2\zeta_0}{d\rho^2}+\frac{\sigma}{\rho}\frac{d\zeta_0}{d\rho}-a_i=0,\qquad \frac{d\tau_0}{d\rho}=0, \tag{54}$$

and for the first Fourier harmonics in the form

$$\frac{d}{d\rho}\left(\Delta_\rho-\frac{4}{\rho^2}\right)\zeta_1+4\frac{1-\sigma}{\rho^3}\left(\zeta_1-\rho\frac{d\zeta_1}{d\rho}\right)-\frac{2}{\rho}a_a=0,\qquad \left(\Delta_\rho-\frac{4}{\rho^2}\right)\zeta_1+\frac{1-\sigma}{\rho^2}\left(4\zeta_1-\rho\frac{d\zeta_1}{d\rho}\right)-a_a=0, \tag{55}$$

$$\tau_1=0,\quad \frac{d\tau_1}{d\rho}=0. \tag{56}$$

As it is seen from Eqs. (55) the amplitude of the first harmonic ζ_1 is proportional to the light-film interaction parameter a_a. Assuming that $a_a<1$, we neglect all terms proportional a_a^n with $n\geqslant 2$. Under this assumption one can neglect the last two terms in Eqs. (50), (51) and obtain

$$\Delta_\rho^2\zeta_0-\frac{1}{\rho}\frac{d}{d\rho}\left\{\frac{d\tau_0}{d\rho}\frac{d\zeta_0}{d\rho}\right\}=-f,\qquad \Delta_\rho^2\tau_0+12\left(1-\sigma^2\right)\frac{1}{2}\frac{1}{\rho}\frac{d}{d\rho}\left\{\left(\frac{d\zeta_0}{d\rho}\right)^2\right\}=0. \tag{57}$$

Integrating each equation, we get

$$\rho\frac{d}{d\rho}\frac{1}{\rho}\frac{d}{d\rho}\rho\frac{d\zeta_0}{d\rho}-\frac{d\tau_0}{d\rho}\frac{d\zeta_0}{d\rho}=-\frac{1}{2}f\left(\rho^2-1\right),\qquad \rho\frac{d}{d\rho}\frac{1}{\rho}\frac{d}{d\rho}\rho\frac{d\tau_0}{d\rho}+12\left(1-\sigma^2\right)\frac{1}{2}\left(\frac{d\zeta_0}{d\rho}\right)^2=0, \tag{58}$$

where the condition of regularity at the center $d\zeta_0/d\rho=0$ and the boundary conditions (54) were used.

Eqs. (58) are simplified by introducing the new variables

$$g=\frac{1}{\rho}\frac{d\zeta_0}{d\rho},\qquad \alpha=\frac{1}{4}\frac{1}{\rho}\frac{d\tau_0}{d\rho},\qquad z=\rho^2. \tag{59}$$

Then Eqs. (58) become

$$\frac{d^2}{dz^2}(zg)-g\alpha=-\frac{f}{8}\left(1-\frac{1}{z}\right),\qquad \frac{d^2}{dz^2}(z\alpha)+\frac{3(1-\sigma^2)}{8}g^2=0. \tag{60}$$

The boundary conditions (54) at $z=1$ become

$$\frac{d^2}{dz^2}(zg)=0,\qquad 2z\frac{dg}{dz}+(1+\sigma)g-a_i=0,\qquad \alpha=0. \tag{61}$$

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

$$g=g_0+\epsilon g_1+\cdots,\qquad \alpha=\alpha_0+\epsilon\alpha_1+\cdots. \tag{62}$$

Inserting (62) into Eqs. (60) we get in zeroth order

$$\epsilon^0:\quad \frac{d^2}{dz^2}(zg_0)-g_0\alpha_0=-\frac{f}{8}\left(1-\frac{1}{z}\right),\qquad \frac{d^2}{dz^2}(z\alpha_0)=0. \tag{63}$$

In the same way the boundary conditions (61) at $z=1$ can be expressed as

$$\epsilon^0:\quad \frac{d^2}{dz^2}(zg_0)=0,\qquad 2z\frac{dg_0}{dz}+(1+\sigma)g_0-a_i=0,\qquad \alpha_0=0. \tag{64}$$

Solving Eqs. (63) with boundary conditions (64) one finds

$$g_0=\frac{a_i}{1+\sigma}-\frac{f}{8}\left\{\frac{1-\sigma}{2(1+\sigma)}+\frac{z}{2}-\ln z\right\},\qquad \alpha_0=0. \tag{65}$$

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