Modelling the Dynamical Behaviour of Holographic Gratings with Nematic Film-Polymer Slice Sequence Structure

Sergii M. Shelestiuk [a] , Victor Yu. Reshetnyak [a] ,
Giancarlo Abbate [b] , Antigone Marino [b] & Francesco
Vita [c]

[a] Physics Faculty, Kyiv Taras Shevchenko National
University, Kyiv, Ukraine

[b] CNR-INFM and Dipartimento di Scienze Fisiche,
Universitá di Napoli Federico II, Napoli, Italy

[c] Dipartimento FIMET, Universitá Politecnica delle
Marche, Ancona, Italy

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Sergii M. Shelestiuk[1], Victor Yu. Reshetnyak[1], Giancarlo Abbate[2], Antigone Marino[2], and Francesco Vita[3]

[1]Physics Faculty, Kyiv Taras Shevchenko National University, Kyiv, Ukraine
[2]CNR-INFM and Dipartimento di Scienze Fisiche, Universitá di Napoli Federico II, Napoli, Italy
[3]Dipartimento FIMET, Universitá Politecnica delle Marche, Ancona, Italy

In recent years there has been much interest in the physics and possible technological applications of liquid crystal-based tuneable Bragg gratings. Such optical devices can be realised using special composite materials based on a sequence of polymeric sheets alternated by layers containing only liquid crystal, sometimes known as Policryps and Poliphem.

Recent experiments have clearly demonstrated a peculiar dependence of relaxation times on actual external field applied (both amplitude and duration) after switching off the operating voltage. We propose a theoretical model of director reorientation in such composites, in which both bulk behaviour in the LC stripes and interfacial polymer-LC interaction is taken into account. Within this model we explain the dynamical behaviour of holographic gratings characterized by a nematic film-polymer slice sequence structure, as well as other polymer-LC phase separated composites.

Address correspondence to Victor Yu. Reshetnyak, Physics Faculty, Kyiv Taras Shevchenko National University, Prosp. Glushkova 2, build. 1 Kyiv, 03680, Ukraine. E-mail: reshet@iop.kiev.ua

1. INTRODUCTION

In recent years there has been much interest in the physics and possible technological applications of liquid crystal (LC)-based switchable/tunable Bragg gratings. Such optical devices can be realized using composite materials based on polymer and LC. Holographic Polymer Dispersed LCs (H-PDLCs), in particular nano-sized H-PDLCs, and a recent composites known as Policryps and Poliphem, are particularly suited for photonic applications [1–3].

H-PDLCs consist in a spatially periodic distribution of nano-sized LC droplets embedded in a polymer matrix. An efficient diffraction grating is so obtained due to the mismatch between polymer and LC refractive indices. The grating diffraction efficiency can be switched or tuned by applying an electric field which reorients the LC molecules, thus changing the refractive index modulation perceived by the impinging light.

Policryps and Poliphems are two new types of LC-based gratings, both characterized by an alternated sequence of homogeneous polymer and LC sheets. In these structures the formation of LC droplets is avoided through the adoption of particular materials and fabrication processes [3]. Thus, by their intrinsic nature they are realized in form of grating. As a result, these gratings exhibit higher diffraction efficiency, higher transparency and lower switching voltage in comparison to traditional H-PDLCs.

Optical characterization of Policryps/Poliphem gratings in different wavelength ranges and theoretical modelling of their behaviour are mandatory for material optimization in view of real applications.

The electro-optical characterization of Policryps gratings has shown a peculiar dynamical response [4]. The relaxation time, i.e., the response time measured after the electric field is switched off, is dependent on the actual field applied (amplitude and pulse duration). Moreover, the time behaviour of the optical signal after removal of the electric field cannot be fitted in any case by a single exponential function and requires a two-parameter function for a good fit.

These results suggest two different phenomena responsible for LC director reorientation, hence the optical response of a Policryps grating. These are bulk elastic forces of LC deformation and interfacial interaction of polymer chains with LC molecules.

In order to verify this assumption, we propose a theoretical model of gratings with nematic film-polymer slice sequence structure, in which the complex problem of the director reorientation in such composite

systems is afforded. We take into account on one side the bulk behaviour in the LC stripes and from the other side the interaction at the polymer-LC interface.

The theoretical model is developed under the following assumptions. As indicated by the experiments, we consider the LC molecules aligned homeotropically with respect to the confining polymer walls if no external field is applied. We suppose polymeric chains are fixed at the polymer-LC interface due to polymer elastic forces, which are assumed to be the same as for slightly bent thin rod. To avoid some complications in the solution, we also neglect LC conductivity and assume homogeneous electric field over the cell.

First, we construct a free energy functional of a LC cell. The effect of the LC-polymer interface is modelled by means of polymer chains protruding into the LC sheet and interacting with the LC molecules in the form of Rapini-Papoular potential, which is treated as an easy axis anchoring. In what follows, we minimize the total free energy with respect to relevant variables and then obtain the equations of dynamics for polymer chain and LC director distribution. Using the numerical simulation technique, we obtain the solution of a problem on dynamics of Policryps grating components and compare the results with experimental findings.

Our report has the following structure. We derive basic equations of dynamics in Sec. 2. Some estimations and numerical simulation is presented in Sec. 3. Here we also discuss the obtained results, which are compared with the experimental findings. In Sec. 4 we derive our conclusions and sketch the way for model improvement.

2. EQUATIONS OF DYNAMICS

The peculiar optical response of a Policryps diffraction grating is a result of LC molecules reorientation under the influence of an externally applied voltage. Thus, one needs to investigate the dynamics of such reorientation. In this section we derive the basic equations of dynamics for the components of a Policryps grating.

Since a grating is periodic, it is enough to study the dynamical behaviour of an arbitrary grating period, i.e., the LC cell represented in Figure 1. In contrast to ordinary LC cells, such system is confined on four sides, by both the polymer walls and the glass surfaces. However, we can neglect the LC-glass interaction because a) the glass surface does not undergo any aligning treatment, and b) the grating thickness d is at least one order of magnitude higher than the width L of the LC sheet.
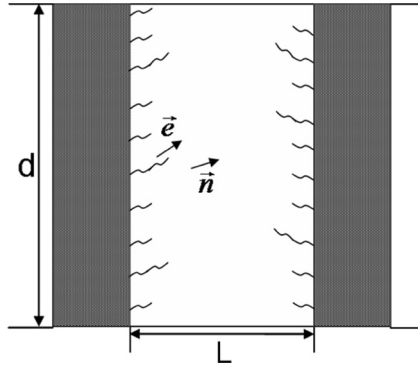
FIGURE 1 Diffractive grating period. LC layer of a width L contains polymeric chains, which are fixed at the polymer-LC interface.

Experimental data suggest there is no complete material separation. In other words, a certain fraction of the LC remains trapped within the polymer, thus reducing the refractive index contrast of the grating. This also leads to LC layer narrowing. Since we are focused on the analysis of LC layer processes, let us assume polymeric chains of a volume fraction $f(x)$ are diluted within LC film.

The external field E is applied across the cell, orthogonally to the glass substrates and to the undistorted LC alignment direction. For the sake of simplicity we neglect conductivity of LC and non-homogeneous electric field distribution over the cell, hence $E \approx V/d$. Here V is the applied voltage, d is a grating thickness. External field is applied for a time t_{pulse}:

$$E = \begin{cases} V/d, & t < t_{pulse}, \\ 0, & t \geq t_{pulse}. \end{cases} \tag{1}$$

In order to derive the equations of dynamics, we construct the free energy functional for the arbitrary LC cell and minimize it with respect to relevant variables. The total free energy functional of the LC cell includes both LC and polymer elastic terms, interaction of LC molecules with external electric field term and interaction of LC molecules with polymer chains term. The total free energy takes the form:

$$\mathbf{F} = \mathbf{F}_{LCel} + \mathbf{F}_E + \mathbf{F}_{pol-LC} + \mathbf{F}_{pol.el} \tag{2}$$

The first terms are given by [5]:

$$\mathbf{F}_{LCel} = \frac{1}{2} \int \left\{ K_1 (\mathrm{div}\vec{n})^2 + K_2 (\vec{n} \cdot \mathrm{curl}\vec{n})^2 + K_3 [\vec{n} \times \mathrm{curl}\vec{n}]^2 \right\} dV,$$

$$\mathbf{F}_E = \frac{-1}{2} \int \varepsilon_0 \hat{\varepsilon} \vec{E} \cdot \vec{E} \, dV,$$

here $\hat{\varepsilon}$ is the relative dielectric permittivity tensor.

For the sake of simplicity we may wish to use one-constant approximation, *i.e.*, $K_1 = K_2 = K_3 = K$. It is also convenient to rewrite the above expressions in terms of the LC director deviation angle θ by $\vec{n} = (\cos\theta, 0, \sin\theta)$.

We consider polymer "tails" interact with LC molecules in the bulk of a cell in the form of Rapini-Papoular anchoring energy [6]:

$$\mathbf{F}_{pol-LC} = \frac{-W_p}{2} \int f(x)(\vec{n} \cdot \vec{e})^2 dV. \tag{3}$$

Here we have introduced the polymer director $\vec{e} = (\cos\theta_p, 0, \sin\theta_p)$, which is analogous to LC director $\vec{n}$. The polymer director is a unit vector, parallel to an average polymeric chain direction at each point. $f(x)$ is the volume fraction of polymeric molecules in LC, W_p is the anchoring energy.

Experiments suggest polymer chains tend to homeotropic alignment at the walls, which may be the result of a diffusion-counterdiffusion process. Thus one needs to derive the elastic energy of the polymer deformation term. We assume the free energy of polymer chain deformation is the same as for a slightly bent thin rod. This energy per rod length has the form [7]:

$$\tilde{\mathbf{F}}_{pol.el} = \int \frac{z_r^2 E_p}{2R^2} dS, \tag{4}$$

here the integral is taken over the cross-section of a rod. R is a radius of curvature of a rod in (xz) plane, which is constant for slightly bent thin rod; z_r is a z-coordinate of a distorted rod (see Fig. 2); E_p is its Young's elastic modulus.

Taking into account undistorted polymeric chains are parallel to x-axis, the relation of coordinates of a distorted rod with those of a polymer chains is given by

$$x_r = R \sin\theta_p,$$

$$z_r = R(1 - \cos\theta_p),$$
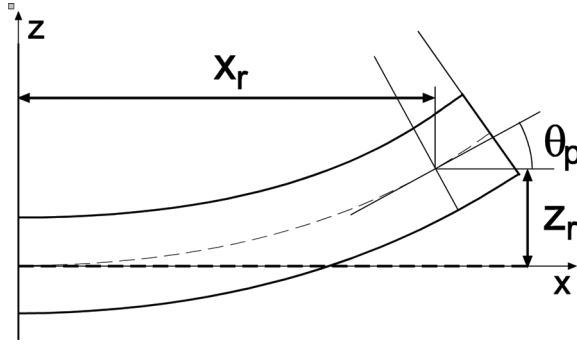
FIGURE 2 Polymeric chain deformation.

and finally, elastic free energy of such deformation has the form

$$\mathbf{F}_{pol.el} = \int \frac{E_p}{2} f(x)(1 - \cos\theta_p)^2 dV. \tag{5}$$

Volume fraction of dissolved polymeric chains in the bulk of LC depends on the x-coordinate. It reaches the maximum f_0 at the polymer slice wall, and sharply decreases to zero while moving to the centre of the LC layer. This suggests the volume fraction of polymeric molecules in LC $f(x)$ has the form:

$$f(x) = f_0\big(\exp(-x/\xi_L) + \exp(-(L-x)/\xi_L)\big), \tag{6}$$

here ξ_L is a characteristic length of polymeric chains.

Substituting Eqs. (5) and (3) into (2), one gets the total free energy functional in the reduced form

$$\begin{aligned}
\mathbf{F}' = \int_0^L \int_0^d \Bigg\{ &\frac{K}{2}\left(\left(\frac{\partial\theta}{\partial x}\right)^2 + \left(\frac{\partial\theta}{\partial z}\right)^2\right) - \frac{1}{2}\varepsilon_0\varepsilon_a E^2\sin^2\theta \\
&- \frac{W_p f}{2}\cos^2(\theta - \theta_p) + \frac{E_p f}{2}(1 - \cos\theta_p)^2 \Bigg\} dxdz,
\end{aligned} \tag{7}$$

here ε_a is LC dielectric tensor anisotropy.

Minimizing free energy functional (7) with respect to relevant variables, and introducing the energy dissipation [5], one gets the following equations of dynamics:

$$\begin{cases}
\gamma_v \frac{\partial\theta}{\partial t} = K\Delta\theta + \varepsilon_0\varepsilon_a E^2\sin\theta\cos\theta - W_p f\cos(\theta - \theta_p)\sin(\theta - \theta_p); \\
\gamma_p \frac{\partial\theta_p}{\partial t} = W_p f\cos(\theta - \theta_p)\sin(\theta - \theta_p) - E_p f(1 - \cos\theta_p)\sin\theta_p
\end{cases} \tag{8}$$

here γ_v and γ_p are the bulk viscosity of LC and of polymeric chains, respectively.

For the problem to be closed, one needs to derive the boundary and initial conditions. Since there is no treatment on the glass surfaces, we apply Neumann boundary conditions on these surfaces. Polymer chains are fixed at the slice interface, as was discussed above. Here we use Dirichlet boundary conditions for polymer director on these surfaces. Interaction of LC molecules with polymer is taken into account in the bulk, thus we may neglect the surface inter-action energy contribution. In what follows, we obtain the boundary conditions:

$$\begin{cases} \frac{\partial\theta}{\partial z}(t,x,0) = \frac{\partial\theta}{\partial z}(t,x,d) = 0; \\ \frac{\partial\theta_p}{\partial z}(t,x,0) = \frac{\partial\theta_p}{\partial z}(t,x,d) = 0; \\ \frac{\partial\theta}{\partial x}(t,0,z) = \frac{\partial\theta}{\partial x}(t,L,z) = 0; \\ \theta_p(t,0,z) = \theta_p(t,L,z) = 0; \end{cases} \tag{9}$$

We also take into consideration the homeotropic initial configuration of LC and polymeric chains:

$$\theta(0,x,z) = \theta_p(0,x,z) = 0. \tag{10}$$

As a result, we have obtained the closed non-linear boundary-value problem (8)–(10), the solution of which gives us both LC director and polymer chain director distributions in the bulk of LC layer at each moment. However, this problem cannot be solved analytically without any additional approximations. Thus, we need to resort to some numerical simulation techniques in order to perform further analysis of Policryps gratings.

3. ESTIMATIONS AND NUMERICAL SIMULATION

At this point, we need to perform the comparison of the theoretical model, developed in Sec. 2, with the experimental data. The dynamical behaviour of holographic gratings with nematic film-polymer slice sequence structures is given by the non-linear boundary-value pro-blem (8)–(10). In order to obtain the solution of this problem, we resort to numerical simulation.

Some unknown parameters are obtained from performed experi-ments. In particular, LC layer width L is a fraction α of the grating pitch $\wedge$ and is given by

$$L = \alpha \wedge.$$

The fraction α is normally of the order of 0.1–0.2 [4], which is much less than the overall LC concentration in the grating ($f_{LC} = 30\%$), since not all the LC phase-separates from the polymer and a certain fraction of the LC remains trapped within the polymer, as was discussed above. Fitting the experimental data gives us LC sheet width to be $L = 0.15\,\mu m$ [4]. The grating sample thickness was $d = 8.8\,\mu m$, and applied field during the experiments was of amplitude $E = 9.3\,V/\mu m$ and of pulse duration $t_{pulse} = 100\,\mu s$.

The numerical simulations of the one problem were performed using finite element method (FEM). For this purpose we used *FlexPDE* software by *PDE Solutions Inc*. Figures 3 and 4 represent polymer chain and LC director dynamical behaviour in the bulk of a cell and in the interfacial region, respectively.

A few actual unknown parameter sets were used for the simulation. However, a good qualitative agreement with experiments was obtained only in the case of relatively strong anchoring of LC molecules with polymer chains at the polymer-LC interface $W_p \geq 10^4\,J/m^3$. As a consequence, strong interaction energy leads to quite complicated LC relaxation (see Fig. 4). Here the dynamics is driven by the interfacial region of LC cell. Thus, the numerical simulation suggests the "surface" polymer-LC interaction is crucial in this process, as was predicted earlier [4].

To quantitatively compare our simulation with experimental data and to fit the latter using the developed theoretical model, further
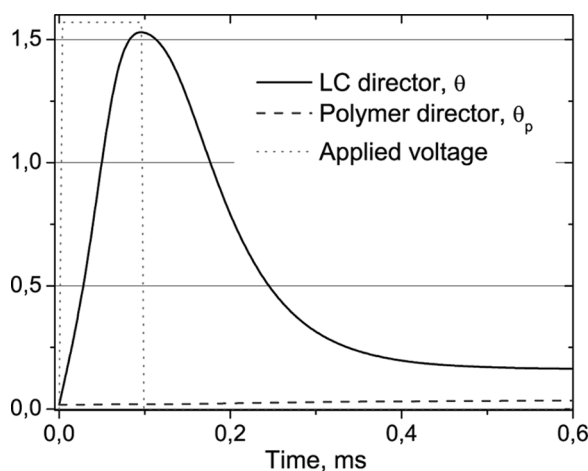
FIGURE 3 LC director θ and polymer chain director θ_p reorientation in the bulk of a LC cell.
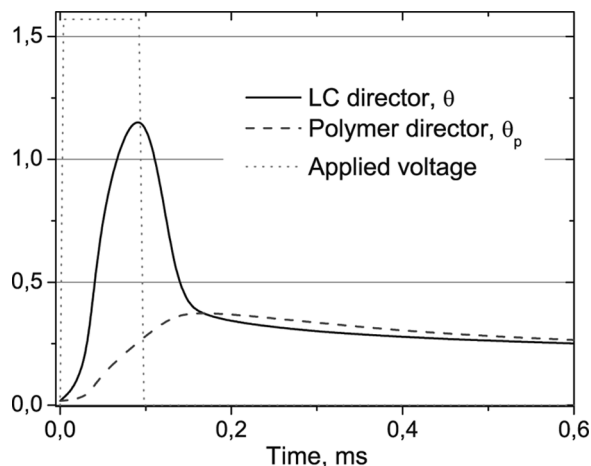
FIGURE 4 LC director θ and polymer chain director θ_p reorientation at the polymer-LC interface.

studies have to be done. In particular, a diffraction efficiency model, linked to the polymer and LC director orientations, has to be developed. In such a way it is possible to relate the dynamical behaviour of LC molecules with experimentally obtained optical response curves, which have a direct bearing on diffraction efficiency. We shall present elsewhere a more complete diffraction efficiency theory for holographic gratings with nematic film-polymer slice sequence structure.

4. CONCLUSIONS

In this paper we have analysed the dynamical behaviour of Policryps diffractive gratings. Here the switching times are strongly dependent on both amplitude and duration of the applied electric pulses. This was not expected for the elastic LC relaxation.

A theoretical model has been developed in order to describe the peculiar reorientation of LC molecules and Polymer chains after removal of the electric field. Within the theory we have found two different phenomena responsible for such a dynamical behaviour. These two are related to both bulk and surface interaction. Anchoring of LC molecules with polymer chains in the interfacial region gives a substantial contribution to the dynamics of such composites. The theory was compared with recent experimental findings, and a qualitative agreement was found.

Though the theory has been developed to explain the dynamics of Polycryps structures, it can also be useful to describe other similar separated or partially separated polymer-LC composites as well.

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