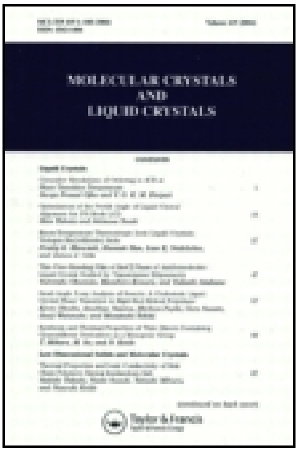

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Available online: 12 Jan 2012

Mol. Cryst. Liq. Cryst., Vol. 554: pp. 56–64, 2012

ISSN: 1542-1406 print / 1563-5287 online
DOI: 10.1080/15421406.2012.633026

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Recently the effect of photoinduced molecular reorientation of nematic liquid crystal molecules originating from dispersed gold nanoparticles (NP) in twisted geometry above the Freedeericksz threshold was reported experimentally via optical Kerr effect studies [1]. In this paper we work out the Monte Carlo approach suitable for modelling of this effect using standard Lebwohl–Lasher–Rapini model with an additional term responsible for photoinduced molecular reorientation. The influence of local electric field enhancement on transmission coefficient is studied for chosen cases.

Keywords Light transmission; monte carlo; optical kerr effect; twisted nematic liquid crystals

I. Introduction

Nematic liquid crystals (NLC) made of calamitic mesogenes confined in a cell with orienting layers form an interesting class on nonlinear optical materials by offering a possibility of a local change of their refractive index by external electromagnetic fields or internal interactions. The former can be triggered optically by light interaction with photochromic molecules exhibiting conformational modification upon light absorption and/or by metallic nanoparticles strongly interacting with light of wavelength being close to their surface plasmon polariton (SPP) excitiation energy. Both phenomena can lead to an effective reorientation of long molecular axes of NLC molecules and refractive index changes, respectively. These nonlinear optical effects form a basis for novel applications of NLC cells in the field of photonics. Light–enhanced refractive index changes enable to make materials suitable for dynamic holography, which opens route for construction of all–optical light modulators, phase conjugate mirrors, optical amplifiers, optical correlators and others. It is well known that a change of an external electric field E applied to the NLC cell can modify the phase and polarization state of light propagating through it. This effect is used in a twisted NLC cell having direct application in display technologies. In a 90°

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twisted NLC (TNLC) cell the rubbing directions on its opposite walls make an angle $\pi/2$, so transmitted light turns its polarization by 90° during passage through the cell with no applied field.

In this paper we focus our attention on the light transmission through TNLC cell accounting for molecular reorientation caused by the presence of metallic nanoparticles or optically bistable dyes excited by external light pulses. The interest in this topic is motivated by recent experimental studies [1], see below. Consider a normal incidence of a weak intensity linearly polarized light beam on the LC cell, having its polarization along the rubbing direction of the cell entrance plate. The laser light transmission through the cell will crucially depend on the amplitude of constant electric field E applied to the cell's transparent ITO electrodes, i.e. along the direction of light propagation. In this case, for small field amplitudes, below the Freedericksz threshold $E < E_F$, the incoming light polarization plane rotates by 90° and light fully passes through an output polarizer oriented at 90° with respect to the input light polarization, i.e. along the second rubbing direction. For electric fields above the Freedericksz threshold $E > E_F$, LC molecules change orientation of their long axes toward electric field lines and the rotation of the light polarization plane becomes hindered, resulting in the decrease of light transmission through the system. At sufficiently high values of applied electric field the panel becomes opaque. LC molecules, located in the center of LC cell, at external electric field just above the Freedericksz threshold are extremely susceptible to local environmental changes such as e.g., change of electric dipole of metallic nanoparticle or dyes due to their excitation by suitable light pulses. Such phenomena can be observed in LC mixtures with small amount of dye molecules ($<$1%) and still smaller amount of metallic nanoparticles ($<$0.01%) using optical Kerr effect experimental setup [1].

Those effects can be studied analytically via Landau–like approach [2]. This variational method yields the profiles of inhomogeneous (position dependent) orientation ordering of NLC molecules, which can be used to calculate the effective rotation of the polarization plane and transmission coefficient in the formalism of Jones matrices [3,4]. This approach bases, however, on an elastic continuum medium approximation and becomes unjustified for very thin LC layers, say below 1 μm. Moreover, as a rule, the infinitely strong anchoring forces for LC molecules at the surfaces are assumed for the sake of mathematical simplicity. On the other hand, it is known that finite (and sometimes weak) anchoring forces are present in those systems [5]; moreover, they can be of practical importance [6]. Finally, thermal fluctuations are not taken into account.

Computer simulations, in particular Monte Carlo (MC) simulations, are devoid of those shortcomings and constitute a complementary, valuable tool for studies of various optical aspects of inhomogeneous ordering in NLC systems. This approach was applied to the study of electro–optic effects in NLC cells [6,7] and of nanosphere dispersed nematic liquid crystal metamaterial [8,9]. MC simulations using standard Metropolis algorithm [10,11] yield the profiles of inhomogeneous ordering of NLC molecules in thermal equilibrium at various realizations of external or internal electric fields

The aim of the paper is to work out Monte Carlo–based approach aimed at modelling of characteristics of probe light transmission through a TNLC system doped with metallic nanoparticles and/or photochromic molecules and excited with a strong pump light.

II. Modelling

A. Modified Lebwohl–Lasher–Rapini Model

The equilibrium orientational configurations of NLC molecules were sampled using Metropolis Monte Carlo simulations. The interactions are described by Lebwohl–Lasher hamiltonian [12] with Rapini term [13] H_{LLR} and an additional term H_{ph} which is responsible for the photoinduced order:

$$H = H_{LLR} + H_{ph}, \tag{1}$$

where

$$H_{LLR} = -\xi \sum_{<\vec{r},\vec{r}\,'>} P_2(\cos\beta(\vec{r},\,\vec{r}\,')) - E^2 \sum_{\vec{r}} P_2(\cos\beta(\vec{r})) + \alpha \sum_{\vec{r}_W} \sin^2\gamma(\vec{r}_W), \tag{2}$$

and

$$H_{ph} = -\tau \sum_{\vec{r}} P_2(\cos\psi'(\vec{r})). \tag{3}$$

Here P_2 denotes the second–order Legendre polynomial. Parameter ξ ($\xi = 25$) determines the strength of NLC–NLC orientational interaction, E stands for electric field and α describes the strength of anchoring forces acting on molecules located at the walls. $\beta(\vec{r},\,\vec{r}\,')$ is a relative angle between two molecules located at points $\vec{r}$, $\vec{r}\,'$, $\beta(\vec{r})$ denotes the angle which a molecule located at point $\vec{r}$ makes with electric field vector and $\gamma(\vec{r}_W)$ is the angle which a molecule at the wall makes with rubbing direction. More information about the model can be found in References [6–8].

The motivation for the specific choice of hamiltonian H_{ph}, Eq. (3), is as follows. The interaction of external pumping light with a dye or with a metallic nanoparticle creates an additional source of internal (local) electric field which exerts ordering forces on NLC molecules. In the former case a dipolar electric field appears with dipolar axis along some direction $\vec{s}$. Then, the molecules in close proximity of the nanoparticle get aligned along the lines of electric field. For the sake of simplicity we account here only for the lines parallel to $\vec{s}$ axis. Then, $\vec{s}$ serves as a direction of an additional electric field which can be taken into account in the hamiltonian in terms of function P_2. In Eq. (3) ψ' denotes the angle between the directions of $\vec{s}$ and of local director. The interaction constant τ determines the strength of reorientation and is dependent on the intensity of pumping beam and on the concentration as well as properties of dopants. Positive values of τ promote the parallel orientation of NLC molecules wrt. direction $\vec{s}$, while its negative values promote perpendicular orientation, see Fig. 1. In this paper we discuss only the case $\tau > 0$.

B. Monte Carlo–Based Calculation of Transmission Coefficient

In the model cell NLC molecules occupy the sites of a cubic lattice $50 \times 50 \times n_k$, where n_k denotes the number of molecules along z–axis, chosen as a direction of the propagation of probing light. The relation between the thickness D of TNLC cell and thickness d of a single molecular layer reads $D = d\,n_k$. An orientation of a long axis of a NLC molecule in an external coordinate system is described by a pair of angles ϕ, θ. Angle ϕ (twist) sets an azimuth and angle θ (tilt) is a polar angle calculated from x–y plane. Upper and lower walls of the cell are rubbed. The geometry of the model cell, with the assumed rubbing directions, is shown in Fig. 2. Similarly as in earlier simulations [6,7] the equilibration took 3×10^4 Monte Carlo Steps (MCS) and sampling – 2.3×10^5 MCS.

In our model each of n_k layers represents a thin birefringent plate that causes a phase retardation of probing light depending on an averaged orientation of long axes of NLC molecules in a layer which represents the direction of a local optical axis [3]. Given this

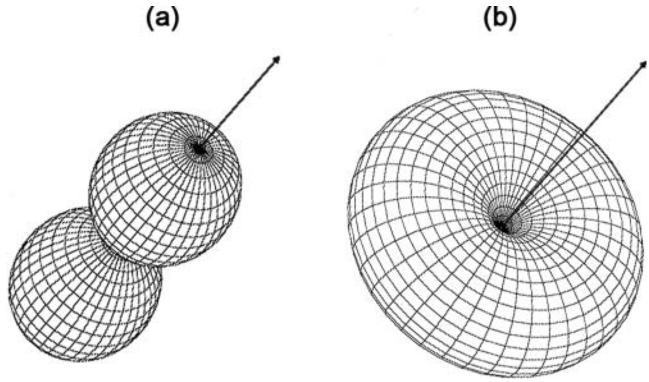

Figure 1. Schematically shown distribution of angular orientation of NLC molecules promoted by hamiltonian H_{ph}, Eq. (3): $\tau > 0$, axial ordering (a), and $\tau < 0$, anti–axial ordering (b).

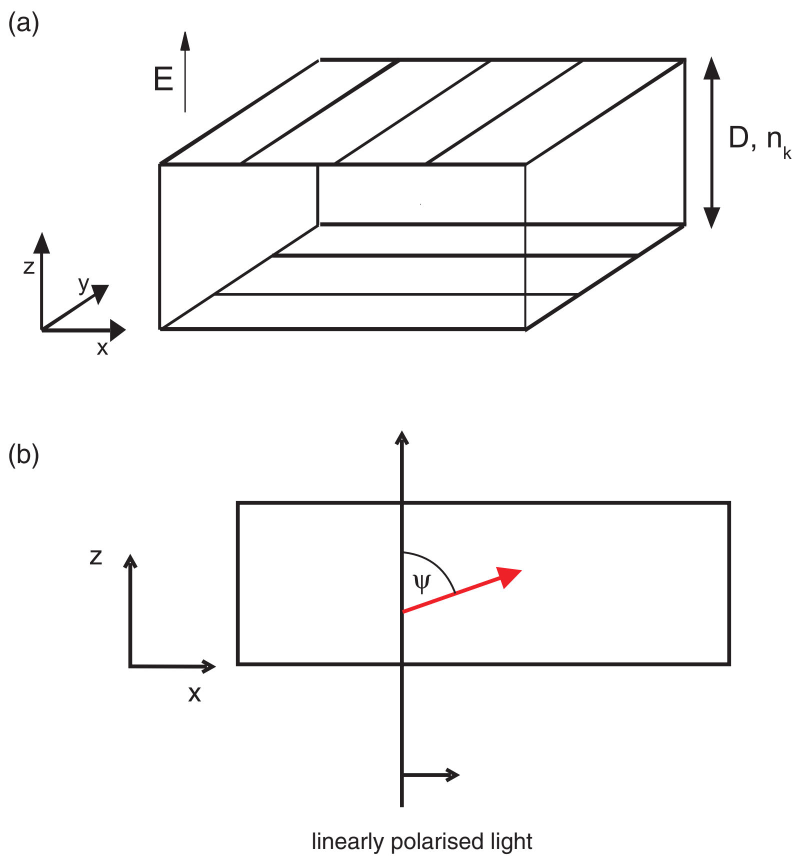

Figure 2. Geometry of the model twisted NLC cell used in Monte Carlo simulations. Rubbing directions are shown with straight lines (left). Probing light is incident along the z–axis. External pump light introducing molecular alignment at angle ψ is incident obliquely with respect to normal to the cell surface (right).

orientation it is straightforward to calculate the change of the polarization state of light passing through the system. In the Jones matrix approach a thin layer of a birefringent material with surfaces perpendicular to the incident light changes its polarization state: $\vec{J}^{out} = M\vec{J}^{in}$, where the time–independent Jones vector has the form:

$$\vec{J} = \begin{pmatrix} E_x \\ E_y \end{pmatrix} = \begin{pmatrix} m_x e^{i\delta_x} \\ m_y e^{i\delta_y} \end{pmatrix} = e^{i\delta_x} \begin{pmatrix} m_x \\ m_y e^{i\delta} \end{pmatrix}, \tag{4}$$

where $\delta = \delta_y - \delta_x$ and m_x, m_y are amplitudes of electric field components E_x i E_y. M denotes Jones matrix which for k–th layer takes the form:

$$M_k = R(-\phi_k)\ W_k R(\phi_k), \tag{5}$$

where R is the rotation matrix in two dimensions which transforms Jones vector from fixed external coordinate system to a coordinate system defined by eigenvectors of the optical element, in which the optical properties of the element are described by matrix W_k:

$$W_k = \begin{pmatrix} e^{-i\Gamma/2} & 0 \\ 0 & e^{i\Gamma/2} \end{pmatrix}, \tag{6}$$

where

$$\Gamma = \frac{2\pi d}{\lambda} \left(n_e^{eff}(\theta_k) - n_o \right). \tag{7}$$

Here n_o denotes the ordinary refractive index of the birefringent element and $n_e^{eff}(\theta)$ is the effective extraordinary refractive index of the k–th thin birefringent layer, which depends on the orientation angle θ_k of its optical axis and on extraordinary refractive index n_e:

$$n_e^{eff}(\theta_k) = \frac{n_e\, n_o}{\sqrt{n_e^2\, \sin^2\theta_k + n_o^2\, \cos^2\theta_k}}. \tag{8}$$

This approach is commonly used in the case of a perpendicular incidence of light onto the 90° TNLC cell [3,14]. Parameters ϕ_k and θ_k for k–th thin layer were calculated as averages over configurations of angles ϕ and θ of NLC molecules in this layer. The product of matrices M_k determines the polarization state of the light propagating through the system:

$$\vec{J}^{out} = \left\{ \prod_{k=1}^{n_k} M_k \right\} \vec{J}^{in}. \tag{9}$$

The incident light was linearly polarized along the x-direction; its Jones vector was $\vec{J}^{in} = \binom{1}{0}$. The light transmission coefficient T in a normally white mode geometry is then equal to the intensity of light passing through the TNLC layer and a polarizer oriented along the y-direction [3]:

$$T = m_y^2. \tag{10}$$

More details on Monte Carlo approach to the calculation of transmission coefficient in TNLC systems can be found in Ref. [15]

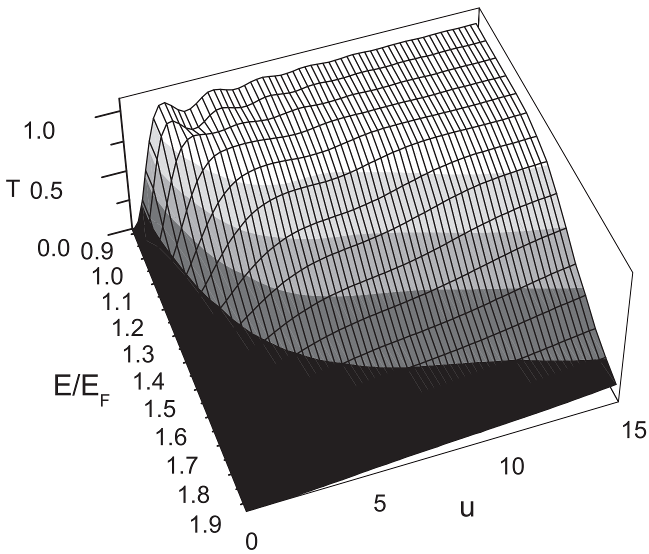

Figure 3. Transmission coefficient T of a twisted nematic cell with $n_k = 20$ layers, in the normally white mode, as a function of the normalized electric field E/E_F and $u = 2D\Delta n/\lambda$, for strong anchoring $\alpha = 50$, in the absence of photoinduced effects ($\tau = 0$).

III. Light Transmission: Chosen Cases

Let us present a few simple applications of the formalism introduced above. We assume, for the sake of simplicity, that the external pumping light introduces the direction of preferable orientation $\vec{s}$ of NLC molecules in the plane $z-x$ as shown in Fig. 2. Then, the orientation of vector $\vec{s}$ is given by a single angle ψ. The discussion of the dependence of the transmission

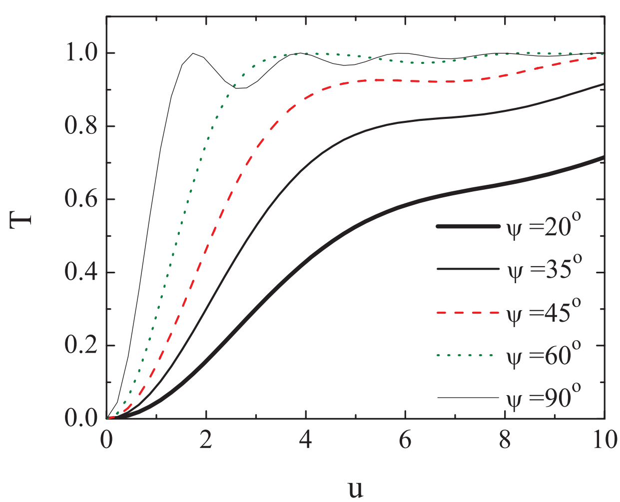

Figure 4. Transmission coefficient T of a twisted nematic cell with $n_k = 20$ layers for constant electric field above Freedericksz threshold ($E \simeq 1.2E_F$), for a few values of angle ψ and for reorientation strength $\tau = 0.5$

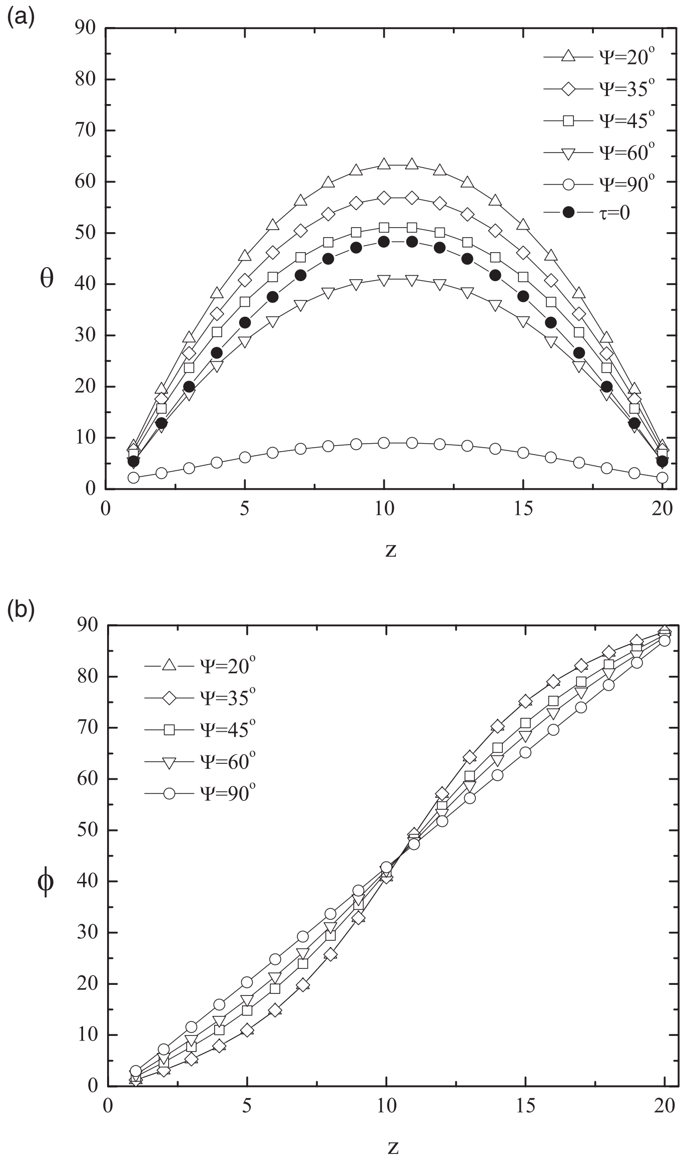

Figure 5. Profiles of angles θ (left) and ϕ (right) along z direction for a few values of angle ψ. $E \simeq 1.2E_F, \alpha = 50, \tau = 0.5$.

coefficient on various parameters is simplified by the fact that T depends on a scaled dimensionless variable u [3]:

$$u = \frac{2D\Delta n}{\lambda}, \tag{11}$$

where $\Delta n = n_e - n_o$ denotes the birefringence of NLC and λ is the incident probing light wavelength.

First, we calculate the transmission coefficient of the system consisting of $n_k = 20$ layers, as a function of the electric field E and variable u, for strong ($\alpha = 50$) anchoring in the absence of photoinduced orienting effects ($\tau = 0$). The results shown in Fig. 3 are in a fair agreement with well–known analytical results obtained for infinitely strong anchoring forces [3].

The inclusion of photoinduced effects has a strong impact on light transmission. Fig. 4 shows the MC calculated transition coefficient T for constant electric field above the Freedericksz threshold $E \simeq 1.2E_F$, in function of u for a few values of angle ψ in the range from 20° to 90°; we have put $\tau = 0.5$. We find that for fixed value of u the increase of angle ψ is accompanied by an increase of coefficient T. For $\psi = \pi/2$ oscillations in $T(u)$ appear. There is some kind of equivalence between parameter ψ and reduced electric field E/E_F in that the increase of the latter has qualitatively similar effect on $T(u)$ as the decrease of the former.

Monte Carlo simulations offer an insight into "microscopic" mechanisms underlaying macroscopic effects through inspection of typical microscopic configurations. Figure 5 characterizes the orientation of local director along the z direction in terms of profiles of angles θ (left) and ϕ (right) for a few values of angle ψ. Again, a systematic dependence on ψ is found: the profile $\theta(u)$ becomes more and more flat as ψ increases. The profile corresponding to $\psi = \pi/4$ is close to the profile calculated in the absence of photoinduced effects ($\tau = 0$). On the other hand, a more flat profile corresponds (for $\tau = 0$) to lower values of electric field. Thus, we find again that the increase of angle ψ generates the answer of the system similar to that in a "pure" ($\tau = 0$) system when electric field decreases.

IV. Discussion and Conclusions

We have presented a Monte Carlo based method for modelling of optical transmission in twisted nematic liquid crystals, in the presence of dopant particles like photochromic dyes or metallic nanoparticles. Under illumination with laser light the dopants generate additional electric field which contributes to the local orientation of the director. We have made the first step towards modeling of this effect by adding a new term to standard Lebwohl–Lasher–Rapini model hamiltonian (it is worth noting that this term can be also used for the description of light–induced ordering of NLC molecules; this effect is, as a rule, weak). The transmission coefficient was calculated in the framework of Jones matrices, using averaged orientation of NLC molecules in thin LC layers calculated from MC simulations. We have found that the orientation of the exciting laser beam relative to the cell surface constitutes an important parameter which can effectively modify the transmission coefficient. The experimental studies of photoinduced effects in transmission are at progress now and will be published, together with Monte Carlo analysis, in future papers.

Acknowledgments

G.P. thanks Polish National Science Center for financial support under Grant NN507 322440.

References

[1] Karpinski, P., & Miniewicz, A. (2009). *Europhys. Lett.*, *88*, 56003.
[2] Stewart, I. W. (2004). *The static and dynamic continuum theory of liquid crystals*, Taylor & Francis: London and New York.
[3] Yeh, P., & Gu, C. (1999). *Optics of liquid crystal displays*, Wiley: New York.

[4] Khoo, I. C. (1994). *Liquid Crystals Physical Properties and Nonlinear Optical Phenomena*, Wiley Interscience: New York.
[5] Barbero, G., & Evangelista, L. G. (2006). *Adsorption phenomena and anchoring energy in nematic liquid crystals*, Taylor & Francis: Boca Raton.
[6] Komorowska, K., Pawlik, G., Mitus, A. C., & Miniewicz, A. (2001). *J. Appl. Phys.*, *90*, 1836.
[7] Pawlik, G., Mitus, A. C., & Miniewicz, A. (2000). *Opt. Commun.*, *182*, 249.
[8] Pawlik, G., Jarema, M., Walasik, W., Mitus, A. C., & Khoo, I. C. (2010). *J. Opt. Soc. Am. B*, *27*, 567.
[9] Pawlik, G., Jarema, M., Walasik, W., Mitus, A. C., & Khoo, I. C. (2011). *Opt. Matter.*, *33*, 1459.
[10] Allen, P., & Tildesley, D. (1987). *Computer Simulation of Liquids*, Clarendon Press: Oxford.
[11] Landau, D., & Binder, K. (2000). *A Guide to Monte Carlo Simulations in Statistical Physics*, Cambridge University Press: New York.
[12] Lebwohl, P. A., & Lasher, G. (1972). *Phys. Rev. A*, *6*, 426.
[13] Rapini, A., & Papoular, M. (1969). *J. Phys. (France)*, *30*, 54.
[14] Blanche, P.-A., Lemaire, Ph. C., Maertens, C., Dubois, P., & Jerome, R. (2000). *J. Opt. Soc. Am. B*, *17*, 729.
[15] Pawlik, G., Mitus, A. C., & Kajzar, F. (2005). *Proc. SPIE*, 5990, 59900F.