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KINETICS OF DIFFRACTION GRATINGS IN A POLYMER MATRIX CONTAINING AZOBENZENE CHROMOPHORES: EXPERIMENT AND MONTE CARLO SIMULATIONS

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We propose a simple kinetic model of diffraction gratings recording in a polymer matrix doped with azobenzene chromophores under the illumination with spatially modulated and linearly polarized light. The model, based on a polymer matrix controlled two-state, three-channel kinetics of trans-cis type photoisomerization cycles, is studied using kinetic Monte Carlo simulations on a lattice. Semi-quantitative agreement between experimental data (two-wave mixing method) for diffraction efficiency and the modeling is found. Fast and slow cis-particle kinetic processes responsible for experimentally observed two-exponential functional dependence of diffraction efficiency as function of time are identified.

Keywords: azobenzene; diffraction efficiency; Monte Carlo; photoisomerisation; polymer

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I. OUTLINE OF THE PROBLEM

In this paper we address the problem of a kinetic modeling of photoresponsive features of polymer matrices doped with photochromic molecules. Such the systems are investigated in search of materials for all optical switching elements, real-time holography or three-dimensional optical memories [1–6]. Azobenzene derivatives incorporated into polymeric matrices are of particular interest [7–11]. The mechanism of light induced dichroism and birefringence in these materials is well recognized [11–16]. The azo chromophores are strongly anisotropic, absorbing light if its polarization is parallel to the dipolar transition moment. In this process the cigar-shaped *trans* molecules change the conformation to *cis* form which is usually unstable; *cis* molecules relax into initial *trans* form through a non radiative channel. The photoisomerization cycles *trans*–*cis* lead to an induced optical anisotropy (angular hole burning); its decay rate depends on matrix rigidity and the specific nature of molecular interactions between azobenzene compounds and polymer chains [15].

This intuitively clear phenomenological scenario does not give, however, any information about the sequence of microscopic events and their characteristic time scales, the shape of gratings and quality and non-linearity of mapping of light intensity patterns into refractive or absorption index. This information is of primary importance in view of applications of photochromic polymers for real-time holography, optical phase conjugation or polarization holography. The system polymer-chromophores-light is a very complex one. Its treatment is difficult mainly because of a large variety of involved physical phenomena. Some of them can be treated, under some circumstances, in a standard framework of an equilibrium statistical mechanics. This refers to polymer-matrix self-interaction, polymer-chromophore and chromophore–chromophore interactions. Other processes, like orientational and spatial diffusion of the chromophores, belongs to the field of non-equilibrium statistical mechanics. On the other hand, an interaction of the chromophores with light has to be treated purely on a kinetic ground, because light cannot be treated, in our case, as a dynamic variable. Moreover, the kinetics of transitions between ground and excited *trans* and *cis* states is quantum in its nature. Last but not least, our knowledge about details of those interactions is often unsatisfactory.

The fundamental question which has to be answered is whether the kinetics of this complex system allows a systematic approach starting from a simple but reliable kinetic model, capable of reproducing main experimental facts concerning diffraction efficiency during recording/erasure processes. The other possibility is that the physics of the system

is governed to a large extent by specific interaction and a simple kinetic model under question does not exist.

The aim of this paper is to propose a simple kinetic model of diffraction gratings recording (formation), to simulate the model using kinetic Monte Carlo method and to compare its predictions with experimental results.

The paper is organized as follows. In the next Section the experimental setup (two-wave mixing method) is briefly described. In Section III the kinetic model is introduced and its Monte Carlo implementation is discussed. In particular a method for Monte Carlo-based calculation of diffraction efficiency is proposed. Section IV is devoted to Monte Carlo study of kinetics of diffraction grating recording under conditions typical for real experiments. A comparison with experimental results is given. Section V offers a discussion of the results, oriented onto applications to grating recording/erasure in photochromic polymers.

II. EXPERIMENT

The experimental results presented in the paper were obtained for a polymer belonging to polyimide family and containing Disperse Red dye [13,14] (2% to 0.1% by weight). Typical polymer foil thickness amounted to $30\text{ }\mu\text{m}$. For grating recording we employed a two-wave mixing technique (see Fig. 1) using a He-Ne laser ($\lambda = 632.8\text{ nm}$, 25 mW cw) as an excitation source with light intensity of incident beams $2I_0 \approx 500\text{ mW/cm}^2$. The state

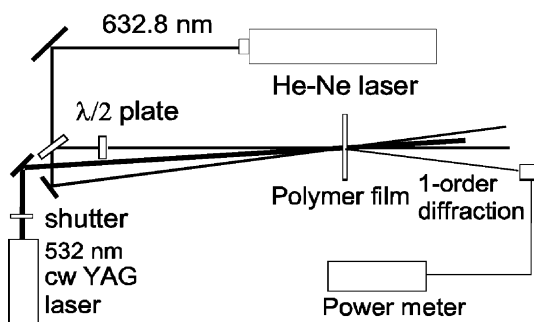


FIGURE 1 Scheme of the two-wave mixing experiment used for grating recording with orthogonal linear light polarizations. A cw He-Ne (632.8 nm) or/and Nd:YAG (532 nm) lasers were used as coherent light sources.

of polarization of the total optical field changes spatially in its magnitude and orientation. In the simplest case of s-s polarization (when two beams are linearly polarized with their electric field vectors perpendicular to the incidence plane) and at symmetrical geometry (the Bragg's planes are perpendicular to the films) the phase variation between the beams produces intensity fringe pattern of the form:

$$I(x) = 2I_0(1 + \sin(qx)), \quad (1)$$

where I_0 denotes the intensity of each of the incoming beams and q stands for the wave-vector of the created grating.

III. KINETIC MODEL AND MONTE CARLO SIMULATIONS

Two-state Three-channel Kinetic Model

Below, we present a simple kinetic model of *trans*–*cis* photoisomerization phenomena for azobenzene chromophores in a polymer matrix. Its possible extensions are discussed in Section V.

We start from the four state model of Dumont *et al.* [12] and consider only a two-level system of ground *trans* and *cis* states, neglecting the excited states. The light stimulated transition probability (per unit of time) $p(\text{trans} \rightarrow \text{cis})$ is proportional to the square of the cosine of the angle θ the *trans* molecule makes with polarization direction [14]:

$$p(\text{trans} \rightarrow \text{cis}) = I(x)p_{\text{trans} \rightarrow \text{cis}} \cos^2 \theta. \quad (2)$$

Here, $I(x)$ denotes the light intensity and $p_{\text{trans} \rightarrow \text{cis}}$ is a probability of an absorption of a photon in a single act of interaction chromophore–light.

For an inverse process *cis* \rightarrow *trans* two channels are used. The first is also light-induced:

$$p(\text{cis} \rightarrow \text{trans}) = I(x)p_{\text{cis} \rightarrow \text{trans}} \equiv I(x)R^{-1}p_{\text{trans} \rightarrow \text{cis}}. \quad (3)$$

Here, $p_{\text{cis} \rightarrow \text{trans}}$ determines the probability of a transition of a *cis* chromophore molecule to *trans* state in a single act of its interaction with light quantum. Parameter $R = p_{\text{trans} \rightarrow \text{cis}}/p_{\text{cis} \rightarrow \text{trans}}$ describing the ratio of time constants corresponding to those two elementary processes plays an important role in the kinetic description of the system. The independence of $p(\text{cis} \rightarrow \text{trans})$ on θ results from the assumed absorption isotropy of *cis* molecules. The second channel of *cis* \rightarrow *trans* reaction is due to the thermal relaxation and is thus independent on the intensity of incident light. The simplest choice for the transition probability (per unit of time) is

$$p(\text{cis} \rightarrow \text{trans})_{\text{thermal}} = \text{const}. \quad (4)$$

The above description corresponds to a *single* chromophore molecule. In the polymer matrix some restrictions appear due to an interaction polymer–dye. The thermal motion of the polymer leads to a constant change of a local environment of *cis* particle and thus influences an instantaneous class of allowed return positions during de-isomerization *cis* \rightarrow *trans*. The most important factors which determine allowed return orientations are steric effects. We model this complex problem in the limit of high mobility of the polymer (i.e., for a low glass transition temperature), by assuming that during the residence of a molecule in *cis* state its local environment changes strongly, leading to a random possible return *trans* orientations.

Athermal Approximation and Monte Carlo Simulation

The properties of real systems are temperature-dependent. In our approach the interaction chromophore–matrix has athermal character (steric effects) which, in turn, does not depend on a particular polymer configuration. Thus, the polymer–polymer interaction plays no role in our approach. Moreover, the chromophore–chromophore interaction can be neglected because of a small concentration of the dye. As the result of the approximations made our model becomes athermal in its nature. It can be studied using a standard Monte Carlo simple sampling method [17,18]. The details look as follows.

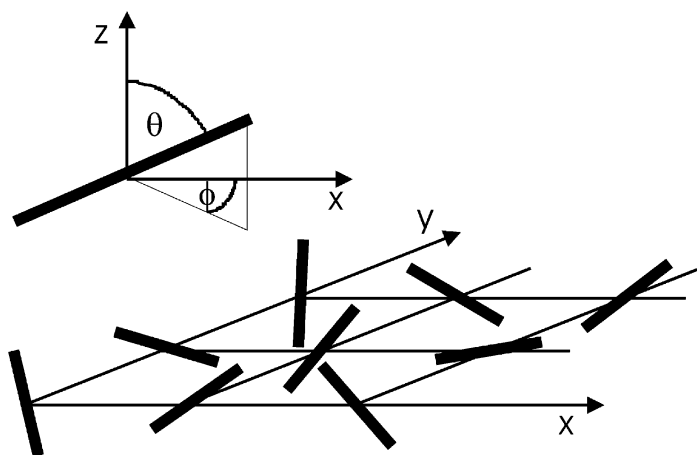


FIGURE 2 *Trans* chromophores distributed over the square lattice used to model the real system. Coordinates and the angles the molecules form with the *z* and *x* axes are also shown.

The geometry of the system mimics that of an interacting system: the chromophores are confined to a square lattice in the x - y plane, their long axes can take any orientation in three-dimensional space (Fig. 2). There are 90 chromophores along the x direction, influenced by light within a full period of intensity modulation, see formula (1) with $I_0 = 1$ and polarization along z -axis. The number of particles along the medium thickness (y -axis) is 10^4 . In each consecutive single Monte Carlo step (MCS) the states of each *trans* and *cis* molecules are changed according to the above introduced transition probabilities. The role of the natural "time unit" is played by one MCS. The rate constants $p_{trans \rightarrow cis}$, $p_{cis \rightarrow trans}$ set the time scales of the corresponding processes with respect to one MCS. In the simulations we use $p_{trans \rightarrow cis} = 0.01$. The thermal relaxation transition rate is chosen as 10^{-4} and plays a minor role in the early stages of grating recording. On the basis of the configurations obtained from Monte Carlo simulations various physical parameters can be studied. Below, we describe a method for a calculation of diffraction efficiency from Monte Carlo data.

Calculation of Diffraction Efficiency

Under a small signal approximation the diffraction efficiency of a periodic sinusoidal grating having amplitude Δn of refractive index is proportional to its square:

$$\eta \propto (\Delta n)^2. \quad (5)$$

Calculation of Δn in a system of anisotropic molecules encounters technical problems. In our approach the tensor of refractive indices is calculated using Kuzyk's approach [18] for a linear susceptibility of a polymer and dopant in the case of a low chromophore concentration. This requires averaging of polarizability tensor of chromophore molecules over all orientations. Assuming uniaxial ordering induced by linearly polarized (along z -axis) light, the averages can be expressed via orientational order parameter $\langle P_2 \rangle$ (P_2 stands for a second rank Legendre polynomial) [19]. When the probing light is s-polarized it "sees" effectively the refractive index n_{zz} and then $\eta \propto (n_{zz}^{\max} - n_{zz}^{\min})^2$. We obtain

$$\eta \propto [N_d^{trans}(x_{\max})(1 + 2\langle P_2 \rangle(x_{\max})) - N_d^{trans}(x_{\min})(1 + 2\langle P_2 \rangle(x_{\min}))]^2. \quad (6)$$

Here $N_d^{trans}(x)$ stands for a concentration of *trans* molecules at row x and $\langle P_2 \rangle(x)$ denotes the average of $P_2(\cos \theta)$ over *trans* molecules in row x . x_{\max} , x_{\min} denote respectively the rows where the product $N_d^{trans}(x)(1 + 2\langle P_2 \rangle(x))$ reaches maximum and minimum. For abbreviation,

the r.h.s. of Eq. (6) is denoted as Δ^2 , thus $\eta \propto \Delta^2$. The parameter $\langle P_2 \rangle(x)$ is calculated from Monte Carlo simulations. More details will be published elsewhere [20].

IV. RECORDING OF DIFFRACTION GRATINGS: FAST AND SLOW PROCESSES

In this Section we describe the Monte Carlo kinetics of diffraction grating recording stimulated by two s-polarized beams, resulting in a grating pattern given by formula (1) and compare the results with experiment.

Plot of the Monte Carlo time evolution of order parameter $\langle P_2 \rangle(x)$ calculated for $R = 0.6$ is shown in Figure 3. Using the data $N_d^{trans}(x)$ we calculate the r.h.s. of Eq. (3). The results for a few values of R are shown in Figure 4(a). Three different time regimes are found. Diffraction efficiency grows rapidly in the initial phase of the recording; later this behavior is replaced by a much slower increase towards a saturation value. At much longer times a slow decay of η sets in due to the slow thermal relaxation process. In this paper we analyze only the early stages of the recording. Figure 4(b)

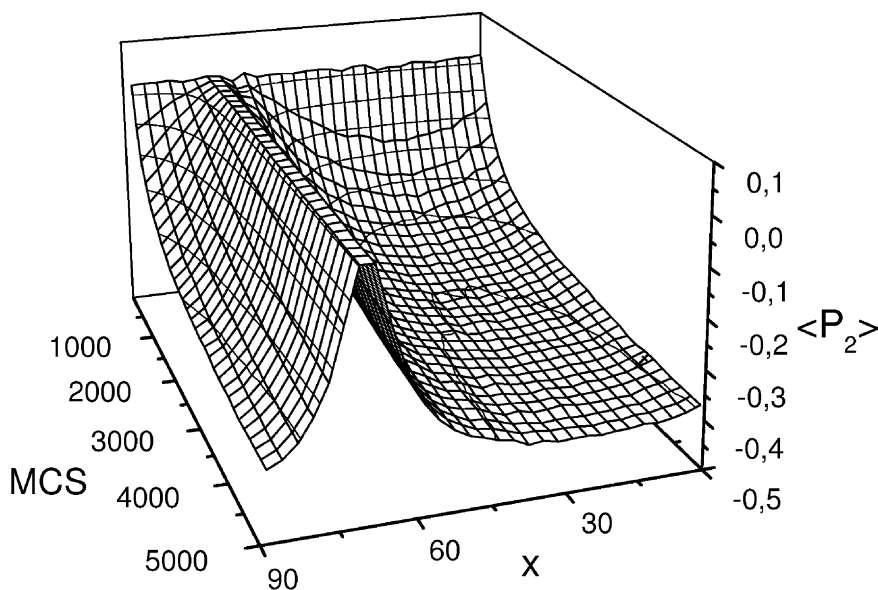


FIGURE 3 Plot of the evolution of the order parameter along the single grating period as obtained from MC simulation under constant in time “illumination”. $\langle P_2 \rangle(x)$ has been calculated for each row during grating recording process where MCS replace time units, $R = 0.6$.

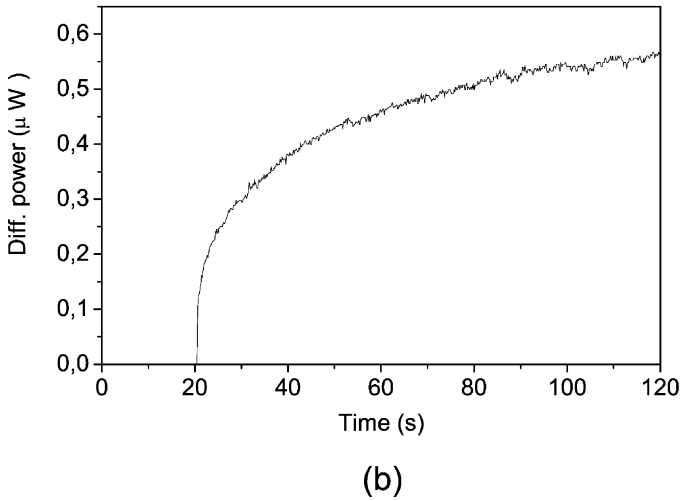
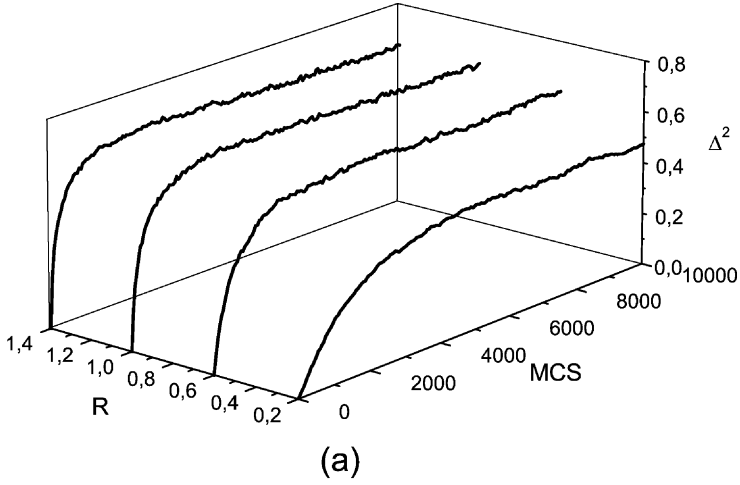


FIGURE 4 Plots of $\Delta^2 \propto \eta$ (cf. Eq. 6), which is directly proportional to $\eta_s(R, t)$, for a few values of parameter R : 1.4, 1.0, 0.6 and 0.2 versus time measured in MCS (a). Example of temporal evolution of light diffraction into first order measured for polyimide foil during the grating recording with He-Ne laser light (b). For $\eta_s = 0.1\%$ and for the 20 μm thick polymeric foil with a reading light wavelength $\lambda = 0.6328 \mu\text{m}$ the sinusoidal grating amplitude is $\Delta n_{zz} \approx 3.2 \times 10^{-4}$.

shows the real time evolution of η in a two-wave mixing experiment. Function $\eta(t)$ was successfully approximated by a superposition of two exponentials $\exp(-t/\tau)$, with time constants $\tau_A = 2.1s \ll \tau_B = 90s$ [21]. This results suggests an existence of some fast and slow processes in the system.

Two-exponential behavior is also found in Monte Carlo simulations. We have fitted the Δ^2 data, proportional to the diffraction efficiency, in the time interval from 0 to 2×10^4 MCS ($R = 0.6$):

$$\Delta^2 = a(2 - e^{-t/\tau_1} - e^{-t/\tau_2}) \quad (7)$$

(one-exponential fit fails). The fit with estimated parameters $a = 3$, $\tau_1 = 1010 \pm 282$ MCS, $\tau_2 = 309 \pm 25$ MCS reproduces nicely the Monte Carlo data (Fig. 5). Clearly, two time scales are present in the system.

We have analyzed the R -dependence of τ_1 , τ_2 . The functions $\tau_1(R)$, $\tau_2(R)$ decrease with increasing R . The ratio $\tau_2(R)/\tau_1(R)$ follows a simple exponential law. Namely, the data in Figure 6 imply an approximate linear dependence of $\log[\tau_2(R)/\tau_1(R)]$ on R and thus

$$\tau_2 = \tau_1 e^{-\alpha R}, \quad (8)$$

where α is a constant. A short discussion of this observation is given in Section V.

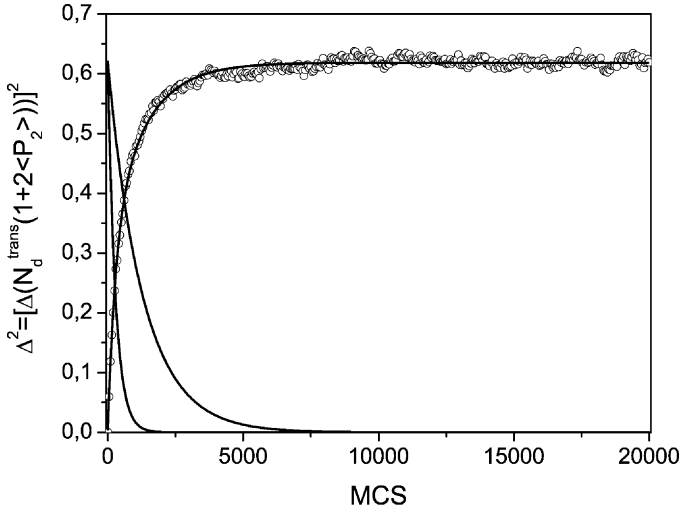


FIGURE 5 Bi-exponential fit to the Monte Carlo simulated diffraction efficiency. The exponentials appearing in the fit are shown separately. $R = 0.6$.

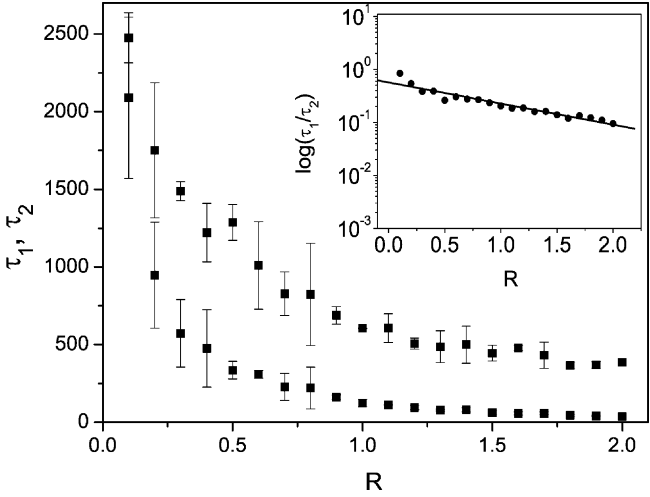


FIGURE 6 Plots of functions $\tau_2(R)$, $\tau_1(R)$ versus parameter R .

Monte Carlo simulations offer an unique possibility of a “microscopic” search for complex physical processes during the recording, related to various time scales. The time evolution of the distribution (empirical histogram) $\rho(\cos \theta)$ for *trans* molecules in row 22 (corresponding to the

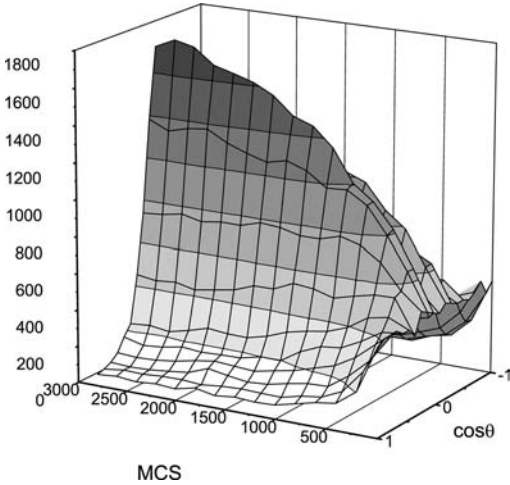


FIGURE 7 MC simulation of (non-normalized) distributions $\rho(\cos \theta(t))$ of *trans* molecules during the grating recording process at row 22 ($R = 0.6$). Vertical scale results from dividing $\cos \theta$ axis into 20 bins.

maximum of light intensity) is shown in Figure 7 ($R = 0.6$). The initial $\cos \theta$ -independent distribution transforms rapidly into a peaked form centered around $\cos \theta = 0$, which implies that the long axes of the molecules tend to align in the direction perpendicular to the polarization of the light. This effect corresponds to the angular hole burning mechanism discussed in the Introduction. The rapid change of the distribution occurs within few hundred MCS, i.e. in the time comparable to $\tau_2(R = 0.6) \approx 300$ MCS, while later on the evolution is governed by a time scale of an order of magnitude $\tau_1(R = 0.6) \approx 1000$ MCS. After a few thousands MCS the distribution reaches a stationary form, as in the case of η , see Figure 4(a).

The role of fast and slow processes is even more pronounced in the kinetics of *trans* and *cis* particles concentration ($c_{cis} = N_d^{cis}/N_d$), presented in Figure 8, for $R = 1.4$. For this value of R we have $\tau_1 = 500 \pm 119$, $\tau_2 = 81 \pm 14$. Consider again row 22 (maximum of illumination). In an initial phase (up to, say, 100 MCS) we observe an abrupt increase of c_{cis} which was successfully fitted using an exponential with relaxation time $\tau_s = 50$ MCS (Fig. 8(a)). After the maximum is reached, the concentration decreases with a larger time scale, of an order of magnitude of 1000 MCS.

From the above "microscopic" studies we conclude that the decisive role in recording of the gratings is played by the concentration of *trans* molecules reoriented along the polarization direction of light, because they can be photoisomerized into *cis* state with a high probability. The fast process in the kinetics of *cis* particles takes place when the concentration of such the *trans* molecules is large. The reaction *cis* \rightarrow *trans* is unimportant in this phase since $c_{cis} \ll 1$. Nevertheless, some of *cis* particles deisomerize into *trans* particles with $\theta \approx \pi/2$ which have a negligible probability of being re-excited. Thus, a number of potential candidates for *cis* particles continuously decreases, leading first to a slowdown in an increase of c_{cis} and then to a decrease of this concentration.

Taking into account the closeness of the times $\tau_s = 50$ and $\tau_2 = 80$, we conclude that the fast process leading to an abrupt increase of diffraction efficiency in experimental grating recording is due to the well-defined fast kinetic process which drives the concentration of *cis* particles c_{cis} towards its maximum.

V. CONCLUSIONS

We have proposed a simple lattice model of kinetics of diffraction gratings recording in a polymer matrix doped with azobenzene chromophores. Only *trans* - *cis* isomerization cycles and steric effects are taken into account. The model was studied using kinetic Monte Carlo simulations and the results were compared with experiment.

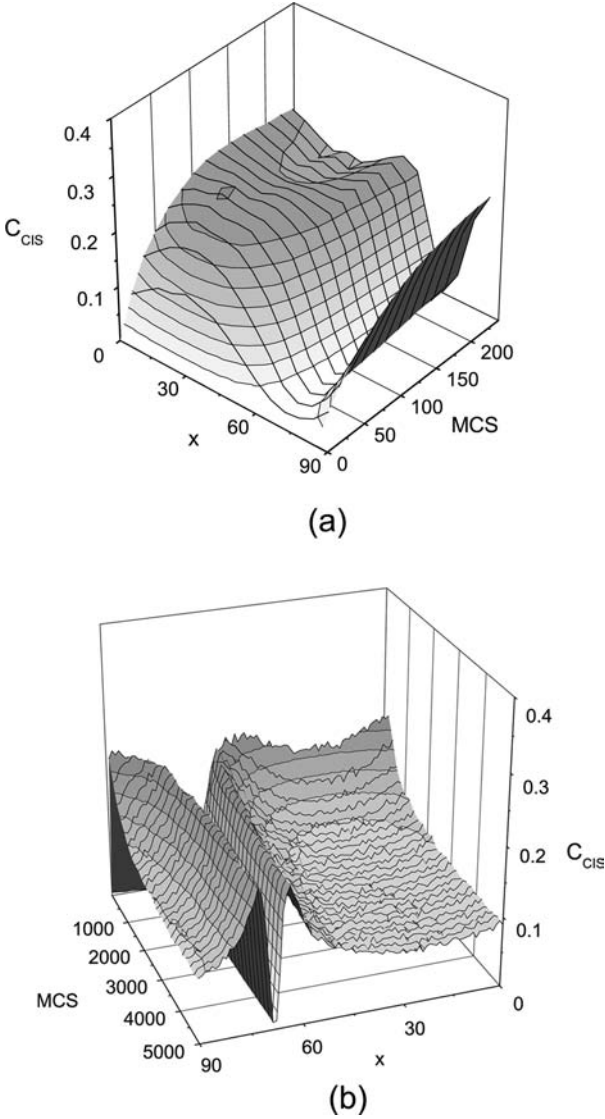


FIGURE 8 Spatial and temporal evolution of the concentration of *cis* molecules (C_{cis}) during the initial (0 to 240 MCS) (a) and the long time period (0 to 5000 MCS) (b) $R=1.4$.

The model reproduces a two-exponential kinetics of grating recording found in real experiments. As expected, angular redistribution of *trans* molecules was the main mechanism leading to appearance of the refractive index grating. Fast and slow processes found experimentally in time evolution of diffraction efficiency during grating recording were nicely interpreted in terms of short-time and long-time kinetic processes related to *cis* molecules. The time constants corresponding to slow and fast processes are related to each other via exponential relation (8). Taking into account that the ratio of times $\tau_A/\tau_B \approx 0.044$ (Section IV), we obtain an estimation for parameter $R \approx 3.5\text{--}4.0$. It is important to note that this value cannot be directly interpreted in terms of quantum yield [12], because we have neglected the excited *trans* and *cis* states. We point out that an appearance of fast and slow processes may lead to substantial mathematical simplifications in an analytical description of kinetics.

The model is capable of a satisfactory reproduction of experimental results for diffraction efficiency in the case of diffraction grating erasure and also recording in a presence of an additional offset field which is turned off and on again. To this end rotational diffusion (or rotational fluctuations) has to be taken into account. Also in those cases Monte Carlo simulations offer a possibility of a “microscopic” interpretation of the underlying physical processes. The details will be presented elsewhere [20].

Qualitative and semiquantitative agreement between an experiment (kinetics of grating recording) and kinetic Monte Carlo simulations clearly indicates that the model includes relevant degrees of freedom of the system under question. Our study shows that even simple Monte Carlo simulations are capable of a realistic description of (time-dependent) phenomena in material sciences, as found in our earlier analysis of electrooptical properties of nematic liquid crystals [26,27].

Further studies can be done in two directions. In the first one more realistic models can be studied via Monte Carlo simulations, including full four state model of photoisomerization processes, incorporation of translational and rotational diffusion or taking into account polymer dynamics. The later is of particular interest because of a possibility of controlling the recording of the grating by a sudden change of the temperature due to an impulse laser action. This promising idea comes from magnetooptic recording [22] and is now a subject of experimental studies. Here, a temperature-dependent study of polymer matrix is necessary; it can be done, e.g., using an importance-sampling Monte Carlo simulation for a lattice model with fluctuating bonds, introduced in papers [23–25]. This study is at progress now. Another actual topic is study of diffraction grating recording/erasure kinetics in polymers with side-chains chromophores; a modified model can also be used for their description.

On the other hand, the question of the role of particular assumptions made in modeling is of primary importance for an identification of basic and secondary effects. In this sense a simple exactly solvable analytical model of kinetics of diffraction gratings formation, capable of reproduction of main experimental effects, would serve as a starting point for a systematical incorporation of factors responsible for various interactions in the system. Such a model will be a subject of a separate paper.

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