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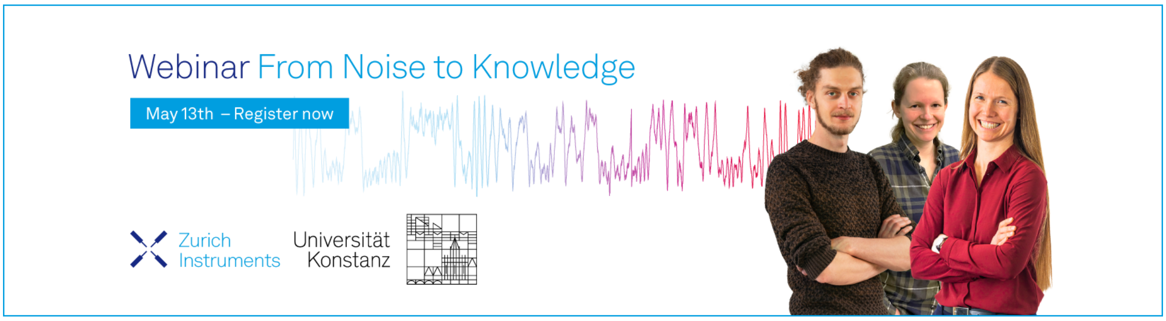

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Stochastic model for photoinduced surface relief grating formation through molecular transport in polymer films

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We use a stochastic model to study photoinduced surface relief grating (SRG) formation due to molecular transport in azobenzene polymer films. The model is shown to reproduce the essential experimental features of SRG formation. In particular, it predicts SRG formation under both p and s polarizations, and the double peaked topographies that can occur at early times of the process. The evolving molecular positions and orientations during exposure are also followed, providing a useful mechanistic picture of SRG dynamics. © *2008 American Institute of Physics*.
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Photoinduced mass transport in azobenzene-containing polymer films has been the subject of much discussion, with potential applications in optical lithography and data storage, for example.[1–5] In particular, studies of surface relief grating (SRG) formation under interferometric illumination have been instrumental in understanding the nature of the molecular motions associated with the phenomenon.[1,2,6–11]

We have developed a three-dimensional (3D) stochastic (Monte Carlo) approach for modeling such light-controlled molecular motion. Here we use this model to follow the detailed evolution of molecular positions and orientations, leading to an appealing and intuitive picture of the microscopic origins of SRG formation. Main features of the model will be described and commented through the present letter.

The photochemical system of interest is shown in Fig. 1(a). It consists of pseudostilbene-like azobenzene molecules grafted on a polymethyl methacrylate (PMMA) polymeric backbone.[1,2] Figure 1(b) gives a schematic of the *trans-cis-trans* isomerization cycle that is believed to be at the origin of the optically induced topography in the polymer.[1,2] Our model is based on a dense 3D spatial mesh of cubic cells. In the initial polymer part of the mesh, we randomly distribute molecules, one or zero per cell, consistent with a given grafting density. Each molecule has a transition moment vector $\boldsymbol{\mu}$ directed along its long axis. These vectors are randomly oriented in the cell. Each cell is also assigned to a local electric field vector, $\mathbf{E}$, based on an assumed existing field. There are several, physically based hypotheses in the model, and the two most important ones are as follows. First, the local probability of photon absorption is proportional to $|\boldsymbol{\mu}\cdot\mathbf{E}|^2$. In other words, molecules with transition moment vectors aligned parallel to $\mathbf{E}$ strongly absorb light while perpendicularly oriented molecules do not absorb any light (of course these are just the two extremes that can occur). Second, after photon absorption, the molecule undergoes a complete isomerization cycle, leading to a displacement parallel to its transition moment ("wormlike motion"[4]), by a distance roughly equal to the molecular length ($\sim$1.5 nm),[10] see Fig. 1(b) as an illustration. (We assume that the system is at a temperature near the glass transition, T_g, allowing us to neglect polymer rigidity.) While undergoing isomerization the molecules are allowed to slightly reorient. Each molecule's long axis is directed along one of 54 discrete directions. A system-defining parameter, P_r (in the 0–1 range), defines the probability for a random reorientation. A random number, r, is selected between 0 and 1 and if r is $\leq P_r$ then the reorientation occurs. This reorientation is randomly chosen in the $1.5-2$ sr range around the axis of the molecule. For high values of P_r the reorientation gets strong and tends to significantly reduce final topography because, in that case, the molecules quickly reorient perpendicular to the incident field. Additional hypotheses allow us to account for the nature of the copolymer. These include a joint probability for leaving one cell and reaching another (related to density and molecular diffusion), and also the short and long range interactions with both neighboring molecules and those grafted to the same chain. This permits modeling the local and nonlocal chromophore/chromophore and chromophore/PMMA mechanical interactions. Short range interactions—in particular, van der Waals interactions due to the strong dipolar momentum of the molecules—are accounted for with a random reorientation of the nearest neighbors in the direction of the

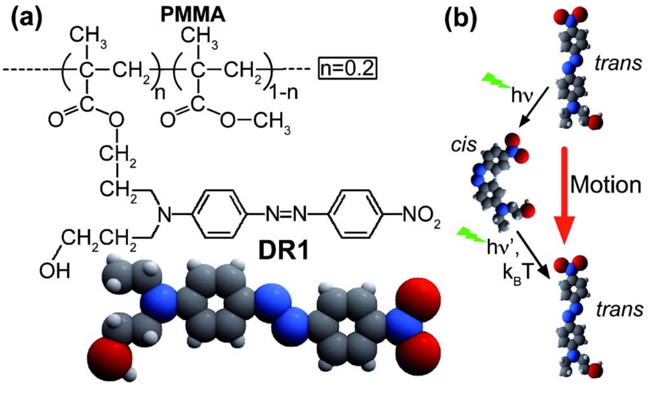

FIG. 1. (Color online) The azobenzene-containing polymer. (a) Chemical structure showing the azobenzene-like molecule grafted to a chain of PMMA. (b) Photoinduced motion via a *trans-cis-trans* isomerization cycle.

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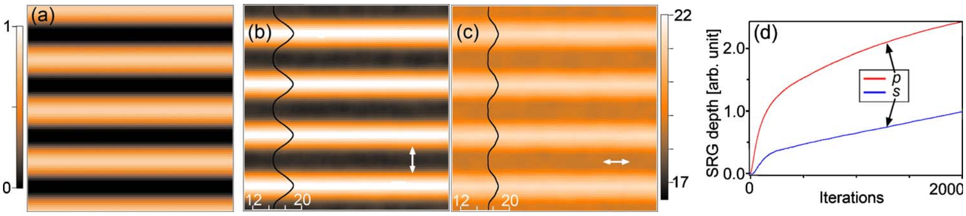

FIG. 2. (Color online) Simulation of SRG formation with the stochastic model. (a) The assumed optical interferometric electric field intensity distribution. [(b) and (c)] The resulting photoinduced topography after 2000 iterations. The axis refers to the height of the topography (arbitrary units, 0 corresponds to the substrate on which the polymer is deposited). (b) *p* polarization, (c) *s* polarization. White arrows represent the direction of the light field polarization. (d) Time evolution of the SRG depth.

moving molecule. This interaction strongly impacts molecular orientation, acting as counterbalance to the photoinduced reorientation. Concerning long range interactions, each time an azobenzene group moves, a random set of molecules grafted in the same polymer chain is selected. These molecules are then randomly reoriented in the direction of the moving molecule. Each iteration represents a stage in the evolution of the system, allowing us to map out the dynamics of SRG formation (transient regime). Equally important, the long time static regime can also be achieved, corresponding to zero probability for the molecules to absorb a photon. This occurs if every molecule is such that it is either perpendicular to its local field or its local field has zero magnitude (dark zone).

Figure 2(a) shows an assumed $|\mathbf{E}|^2$ distribution consistent with a two-beam interferometric pattern. Figures 2(b) and 2(c) show the calculated surface topography obtained after 2000 iterations for *p* [Fig. 2(b)] and *s* [Fig. 2(c)] polarizations. We note two interesting features that are in agreement with previous experimental observations. First, molecules move from optically bright zones to dark zones,[1,2] i.e., the surface topography builds up over dark zones and dips near bright zones. Second, a SRG, although with lower contrast, is obtained even in s polarization where the field polarization direction is *perpendicular* to the field gradient.[9] This is because the initially randomly oriented molecules actually move along their own axis and not along the incident polarization. This underscores the fact that the field polarization only determines the probability that the molecule will move. This point is illustrated in Fig. 3 which shows that molecular displacement from bright to dark zones is generally tilted compared to the field gradient direction for *s* polarization, whereas it is generally straight for *p* polarization. This explains why the *s* polarization SRG has poor contrast and thus gives weaker diffraction efficiency.[1,2,11] This lower contrast is clear in Fig. 2(c) as compared to Fig. 2(b). It is also highlighted in Fig. 2(d) where the evolution of the relief depth for each polarization case is shown. For *p* polarization (red curve), the SRG initially grows much faster and then enters a slower growth regime where molecules oriented mainly along the fringes continue to escape slowly from the bright fringes. This is due to a low probability of light absorption and a displacement trajectory significantly tilted with regards to the gradient direction. This compares to the first, fast growing step involving primarily molecules oriented perpendicular to the fringes. These molecules escape quickly from the bright fringes with a high probability of absorption/isomerization and a short path to the dark regions of the interferometric pattern (see Fig. 3). For *s* polarized light (blue curve), the molecules with a high probability of absorption were not able to participate efficiently in the SRG formation because their movement direction is not along the shortest path to the dark regions of the interferometric pattern. The first growth step (until iteration ~200) results from molecules oriented mainly perpendicular to the fringes. Their direction is favorable to SRG formation. However, the associated absorption probability is extremely low, leading to weak dynamics and SRG formation efficiency. It is important to highlight the strong agreement between our calculated data of Fig. 2(d) and recently reported experimental data.[9,11]

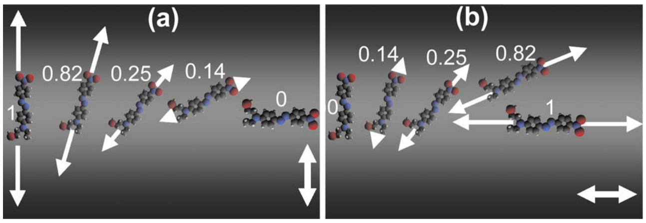

FIG. 3. (Color online) Illustration of SRG formation under *p*-polarized illumination vs SRG formation under *s*-polarized illumination. (a) *p* case and (b) *s* case. Numbers are normalized probabilities of absorption. Double thick arrows represent the direction of the light field polarization. Thin arrows represent magnitude and direction of the molecular displacement. In (a) and (b), the intensity distribution of one period of the incident interferometric pattern is represented.

Our model also allows us to describe the formation of the double peaked topography experimentally observed at early times in *p*-polarized SRG formation.[8] The left column of Fig. 4 shows the calculated SRG profile at iterations 100, 200, 500, 1000, and 2000. The right column shows the resulting molecular orientation at the top and bottom of the grating. Initially, a grating with period d with a $d/2$ overmodulation is seen. This corresponds to the accumulation of two families of molecules moving from two adjacent bright regions. These two sets of molecules do not significantly overlap for the moment. At iteration 500, the molecules start overlapping and the contrast of the d period grating increases while that of the $d/2$ period modulation decreases. By iteration number 1000 the $d/2$ period has vanished but the overlapping is not complete in the sense that the grating is not purely sinusoidal. By iteration number 2000 the SRG is purely sinusoidal and a steady state has been achieved. This example shows that our model describes the molecular displacement at transient regimes. It also shows that there is no need of subtle *s*-*p* configurations to obtain a double frequency SRG,[11] because the latter can be obtained with a *p*-*p* configuration, as shown in Ref. 8.

Finally, we discuss the detailed evolution of *molecular orientations*. This microscopic level of our multiscale model is useful for understanding the mechanism of SRG forma-

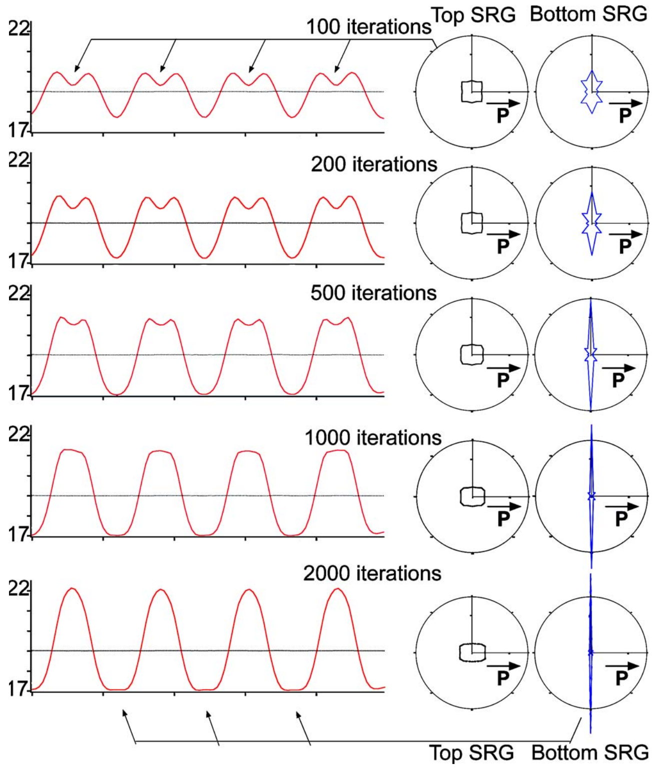

FIG. 4. (Color online) Transient polymer surface topography (left) and simultaneous molecular orientation (polar diagrams, right) of SRG formation for the case of *p* polarization. The polar diagrams represent the density of in-plane molecular orientation along directions in the [0°–360°] range.

tion. The right part of Fig. 4 shows calculated polar diagrams at two specific positions: at the bottom and top of the photoinduced surface grating. These diagrams represent the in-plane projection of the distribution of molecular orientations. They are calculated simultaneously with the evolving topographical profiles. Initially, the molecules are randomly oriented and both top and bottom diagrams look isotropic. At iteration 100, reorientation has started: the orientation distribution is still isotropic at the top of the grating but stretches along the fringes at the bottom of the topography grating where the incident light fringes are bright. This is because molecules oriented perpendicular to the incident polarization only weakly escape from bright fringes. They thus tend to stay within these bright zones. The strength of this effect increases as the system evolves (iterations 200, 500, 1000): the bottom diagram gets more and more elongated. Since molecules oriented parallel to the incident polarization contribute the most to SRG formation, one might expect to see just the opposite effect for the polarization of the molecules at the top of the grating, i.e., for the molecules to be oriented in the polarization direction. However, Fig. 4 shows that in this top case there is only a slight tendency for molecules to orient in the polarization direction: the polarization diagrams only slightly stretch along the polarization axis. This is because, during the molecular motion to the top of the grating, the model allows for further molecular orientation relative to the incident polarization. These results are in good agreement with published polarization analysis.[7] They illustrate well the origin of the photoinduced birefringence (more generally index anisotropy) in azo-polymers.[1,2] Figure 4 shows that anisotropy results from not only molecular reorientation but also from spatial sorting of molecules as a function of their initial orientation relative to both field gradient and polarization directions.

A stochastic model has been used to study SRG formation in azo-polymer films. Key experimentally observed phenomena such as SRG formation in both *s* and *p* incident polarization cases and transitory double topographic peaks were obtained. Inspection of the system evolution allowed us to see the molecular transport, reorientation, and orientation sorting effects that give rise to these phenomena. Future work will involve use of more complex illuminations (e.g., countercircularly polarized beams), and incorporation of mechanical effects (e.g., surface tension and polymer rigidity). We also plan to take into account photobleaching and the fact that the optical field is likely to be modified as the topography changes. This letter showed the capability of our model to describe the evolution of photoassisted molecular displacements with high resolution. This will be of prime importance for developing photoassisted molecular electronics, as well as new approaches of optical imaging, lithography, and data storage.

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