Supporting Material: Simulations of Orientational Hole Burning Dynamics in Azo-SAMs

Guanjiu Fang, Yue Shi, Joseph E. Maclennan, and Noel A. Clark
Department of Physics and Liquid Crystal Materials Research Center,
University of Colorado, Boulder, CO 80309, USA

Matthew J. Farrow and David M. Walba
Department of Chemistry and Biochemistry and the Liquid Crystal Materials Research Center,
University of Colorado, Boulder, CO 80309, USA

Numerical simulations of photo-alignment of self-assembled monolayers of azobenzene molecules are described. The two-dimensional model accounts for orientational hole burning, Brownian rotational diffusion, and for mean field effects. Photo-buffing with linearly or circularly polarized light leads to changes in the orientational order and hence in the sample birefringence.

I. INTRODUCTION

We have performed numerical simulations of the optically induced reorientation of azo-SAMs on glass substrates. We have computed the temporal evolution of the orientational distributions of the excited- and ground-state molecules in the presence of either linearly or circularly polarized light, which in turn allows us to calculate orientational order parameters and the time dependence of such optical properties as the absorbance and the photo-induced birefringence.

II. MODEL DESCRIPTION

The theoretical treatment uses elements of models developed by Jánossy [1] and Pedersen et al. [2]. Pedersen's model is based on work by Palto [3], who in turn cites Barnik [4] and references therein. We consider that the ground state (*trans*) and excited state (*cis*) populations are determined by three basic processes:

1. orientational hole burning (*cis → trans* or *trans → cis*), leading to a depletion in chromophores with transition moments oriented around ϕ_0, the polarization direction of the linearly polarized incident light beam;

2. repopulation of each state, assuming that each optically induced *cis* or *trans* molecule is created with a random orientation, i.e., that the change in molecular orientation is indeterminate; and

3. orientational diffusion, which represents the rotational Brownian motion of the molecules.

Process 1 (depletion) is central to all theories of optically-induced anisotropy published in the literature. Process 2 (repopulation)is included by Pedersen et al. At long times in the absence of excitation, one would expect that the angular distributions of *cis* and *trans* isomers would become orientationally isotropic. Here we follow Jánossy and use a diffusion term (Process 3), which smooths out any "bumps" in the distribution. A similar effect is achieved by Pedersen et al. using a simple linear correction term.

Spontaneous transitions (in particular thermal relaxation of *cis* to *trans* states) are ignored. The molecular reorientation is limited to the plane of the sample, with orientations of the transition moments given by the azimuth ϕ.

We thus consider the dynamics of two species, the *trans* and *cis* isomers, described respectively by the 2D orientational probability distributions $f(\phi)$ and $g(\phi)$. We start with distributions such that

$$\int_0^{2\pi} (f(\phi) + g(\phi))\, d\phi = \bar{f} + \bar{g} = 1 \,, \tag{1}$$

where $\bar{f}$ and $\bar{g}$ represent the total fractions (average probability densities) of each optical isomer. The total number of molecules in the simulations is conserved. The reorientation dynamics are described by the coupled rate equations

$$\frac{\partial f(\phi)}{\partial t} = D_1 \nabla^2 f(\phi) - \frac{1}{\tau_1} f(\phi) \cos^2(\phi - \phi_0)$$

$$+ \frac{1}{2\pi\tau_2} \int_0^{2\pi} g(\phi) \cos^2(\phi - \phi_0) \, d\phi \qquad (2a)$$

$$\frac{\partial g(\phi)}{\partial t} = D_2 \nabla^2 g(\phi) - \frac{1}{\tau_2} g(\phi) \cos^2(\phi - \phi_0)$$

$$+ \frac{1}{2\pi\tau_1} \int_0^{2\pi} f(\phi) \cos^2(\phi - \phi_0) \, d\phi \qquad (2b)$$

where D_1 and D_2 are orientational diffusion constants, and τ_1 and τ_2 correspond to the characteristic times for excitation from *trans* → *cis* and *cis* → *trans* respectively.

III. ORIENTATIONAL ORDER PARAMETER

In general, the orientational order parameter of the azo-SAM changes whenever the sample is illuminated by light. Consider the particular case of photo-buffing an oriented azo-SAM with light linearly polarized at $45°$ to the previous orientation, which causes the average orientation of the sample to rotate through $45°$. The simulations show that there is always a temporary reduction in the orientational order parameter S during this reorientation, with the amount depending on the value of the diffusion constant D, as shown in Fig. 1.
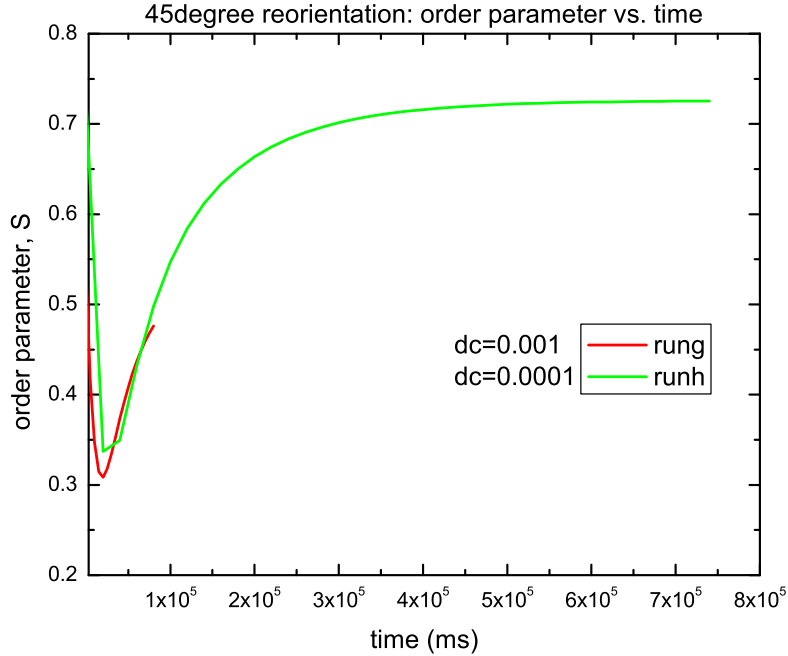

FIG. 1: Photo-buffing using linearly polarized light. When the direction of incident polarized light is rotated $45°$ from the initial orientation (at $t = 0$), the azo-SAM director reorients through $45°$. The orientational order parameter S of the initial and final states is identical but decreases temporarily during reorientation, shown here for two values of the orientational diffusion constant, $D_1 = 0.001$ (red) and $D_1 = 0.0001$ (green).

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