

Concentration dependence of the scalar order parameter in liquid-crystalline systems with variable molecular shape

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A theoretical model taking into account the photoisomerization influence on the nematic scalar order parameter is presented. An extension of the Maier-Saupe model is used to investigate the concentration dependence of the scalar order parameter. The evolution of the concentration of *cis-trans* isomers and of the scalar order parameter with the time of exposure to the illumination is investigated. Furthermore, it is shown that for sufficiently long exposition of the mesophase to the illumination the nematic phase can disappear. This phase transition takes place at a critical concentration of *cis* constituents.

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I. INTRODUCTION

In certain organic materials, which might exhibit liquid-crystalline phases, reversible transformations between different molecular structures can be induced by temperature variation as well as by adsorption of light. In some of these materials, like in the 4,*n*-alkyloxybenzoic acids, displaying nematic (*N*) and smectic-*C* (*S_C*) phases, the molecular structure changes with temperature between three states: cyclic (closed) dimers, open dimers, and monomers. These systems exhibit anomalies in the temperature dependence of the elastic constants [1], the electroconductivity [2], and the dielectric permittivity [3]. The temperature trends of these constants deviate from those of the classical nematics. It is reasonable to assume that this phenomenon is connected to the temperature variable form of the constituent molecules of the 4,*n*-alkyloxybenzoic acids. Consequently, to explain these behaviors it is necessary to take into account these changes in the molecular structure and to take into account also the relative concentrations of the different constituents forming the nematic phase [4]. In another type of material, like the azobenzene ones, the phenomenon of *trans-cis* photoisomerization takes place. This photoisomerization also results in drastic changes of the molecular shape, and, thus, also of the distribution of permanent dipole moments in the molecular structures [5,6]. These systems present photoinduced alterations leading to substantial changes of almost all material parameters characterizing the liquid-crystalline materials [7–9] and also a reversible light-induced anchoring transition due to the azobenzene moiety in the molecular structure [10].

For what concerns the bulk properties, the photoisomerization can also lead to a complete disappearing of the liquid-crystalline phase, replaced by the isotropic phase, when some critical concentration of constituents is reached. More precisely, under temperature change or under variation of time exposure to uv illumination the system undergoes a phase transition to the isotropic phase due to the strong variation in the concentration of the *cis* constituents.

In this paper we present a theoretical model to describe the behavior of the scalar order parameter and also of the macroscopic anisotropies with the concentration of the dif-

ferent molecular constituents characterizing the nematic state. The model takes into account the concentration dependence of the effective nematic potential acting on the molecules in the frame of a mean-field approximation. An extension of the Maier-Saupe model is considered in order to analyze the dependence of the nematic scalar order parameter vs the concentration of one of the constituents [11–13]. In particular we will discuss the case in which the system is formed by *trans* and *cis* isomers, where the chemical transformation of *trans* in *cis* is due to uv illumination.

II. THE SELF-CONSISTENT MODEL FOR TWO MISCIBLE NEMATOGENS

We will consider the liquid-crystalline system as formed by a mixture of two constituents, i.e., two miscible nematogens \mathcal{N}_1 and \mathcal{N}_2 . According to the system considered, these constituents can be *dimers* and *monomers*, if an energy to break the hydrogen bonding is considered [4], or *trans* and *cis* isomers in the case of azobenzene materials [5]. We suppose that the molecules forming \mathcal{N}_1 and \mathcal{N}_2 are rodlike. Let \mathbf{n} be the nematic director of the mixture. The angles formed by the molecular long axes of the molecules of \mathcal{N}_1 and \mathcal{N}_2 with \mathbf{n} will be indicated by θ_1 and θ_2 , respectively. In the mean-field approximation the total nematic potential is given by [11–13]

$$V(\theta_1, \theta_2) = \sum_{i,j} V_{ij} = V_{11} + V_{22} + V_{12} + V_{21}, \quad (1)$$

where V_{11} and V_{12} are the mean-field potentials acting on a molecule of \mathcal{N}_1 due to the other molecules of \mathcal{N}_1 and due to the molecules of \mathcal{N}_2 , respectively. A similar meaning has V_{22} and V_{21} . The partial nematic mean-field potentials V_{ij} in the Maier-Saupe approximation are given by [11–13]

$$V_{ij} = -\alpha_{ij} P_2(\theta_i) \langle P_2(\theta_j) \rangle, \quad (2)$$

where α_{ij} are coupling constants that depend on the distance between the center of mass of the molecules, on a molecular property, and also on the concentration of one of the con-

stituents in the system [4]. From the expressions reported above the total nematic potential can be written as

$$V(\theta_1, \theta_2) = V_1(\theta_1) + V_2(\theta_2), \quad (3)$$

where

$$V_i(\theta_i) = -[\alpha_{ii}S_i + \alpha_{ij}S_j]P_2(\theta_i), \quad (4)$$

if we define $S_i = \langle P_2(\theta_i) \rangle$ as the scalar order parameters of the molecules of \mathcal{N}_i . The total partition function Z_T is then factorized as follows:

$$\begin{aligned} Z_T &= \int_0^1 d(\cos \theta_1) \int_0^1 d(\cos \theta_2) e^{-(V_1+V_2)/k_B T} \\ &= \int_0^1 d(\cos \theta_1) e^{-V_1/k_B T} \int_0^1 d(\cos \theta_2) e^{-V_2/k_B T} \\ &= Z_1 Z_2. \end{aligned} \quad (5)$$

The behavior of the scalar order parameters is determined by imposing self-consistency, which furnishes the set of coupled equations

$$S_i = \frac{\int_0^1 d(\cos \theta_i) P_2(\theta_i) e^{-\beta V_i}}{Z_i} \quad (6)$$

for $i=1,2$, which can be faced in a numerical way. The above set of coupled equations depends on the temperature T and on the quantities α_{ij} entering in the partial nematic potential. The latter quantities, in turn, contain the strengths of the (mean-field) interaction among the molecules forming the nematic \mathcal{N}_1 , among the molecules forming the nematic \mathcal{N}_2 , and among the molecules of \mathcal{N}_1 and those of \mathcal{N}_2 . The concentration dependence of these quantities is determined by assuming that

$$\alpha_{ij} = u_{ij} n_j, \quad (7)$$

where $u_{ij} = u_{ji}$ and $n_i = N_i / (N_1 + N_2)$, with N_i being the number of molecules of the nematic \mathcal{N}_i [4].

The free energy of the mixture is given by

$$F = - \sum_i [N_i k_B T \ln Z_i + \frac{1}{2} N_i \langle V_i \rangle], \quad (8)$$

where, as it follows from Eqs. (4) and (6),

$$\langle V_i \rangle = - \sum_j \alpha_{ij} S_j S_i. \quad (9)$$

Note that, since α_{ij} are given by Eq. (7), from Eq. (8) we obtain that the conditions $\partial F / \partial S_i = 0$ are equivalent to Eq. (6). Putting $u_{12} = u_{21} = v$ the free energy density of the mixture is given by

$$F = N \left\{ - \sum_i \left[n_i k_B T \ln Z_i + \frac{1}{2} n_i^2 u_{ii} S_i^2 \right] + v n_1 n_2 S_1 S_2 \right\}, \quad (10)$$

where $N = N_1 + N_2$. We can also define a macroscopic anisotropy $\Delta X = X_{\parallel} - X_{\perp}$, where \parallel and \perp refer to the nematic director of a second order tensor X_{ij} . As it is well known, in the case of a pure compound, if $\Delta X^{(m)}$ is the molecular anisotropy and S the scalar order parameter, the macroscopic anisotropy is $\Delta X = S \Delta X^{(m)}$ [14]. In the case under consideration, where the nematic is a mixture of two nematogens, we have

$$\Delta X = n_1 S_1 \Delta X_1^{(m)} + n_2 S_2 \Delta X_2^{(m)}, \quad (11)$$

where $\Delta X_1^{(m)}$ and $\Delta X_2^{(m)}$ are the molecular anisotropies of the \mathcal{N}_1 and \mathcal{N}_2 , respectively.

Let us now consider the case in which one of the constituents do not contribute to the nematic order, as in the problem of *trans-cis* isomerization. In this framework we will consider that only the *trans* isomers (that have cylindrical symmetry) can build a nematic order, whereas the *cis* isomers will tend to reduce this order. This assumption follows from the experimental evidence that the molecules of the *cis* isomer are of ‘‘banana’’ shape. According to recent investigations this ‘‘banana’’ shape can be approximated by two linear parts forming an angle between them not very far from $\pi/2$ [10]. In this situation, due to the spinning and tumbling motions of thermal origin, the molecules of the *cis* isomer behave as spherical objects. Consequently in the liquid state they can originate just an isotropic phase. In this framework the molecules of *cis* isomer give rise to a kind of neutral background, where the molecules of *trans*-isomer are responsible for nematic order. Furthermore, we will assume that at zero temperature our system is made by $N_{trans} = N$ isomers. At a given temperature T we have

$$n_{trans} + n_{cis} = 1, \quad (12)$$

where $n_{trans} = N_{trans}(T)/N$ and $n_{cis} = N_{cis}(T)/N$ are the equilibrium concentration of *trans* and *cis* isomers. The couplings α_{ij} are then reduced to the case of *trans* isomer–*trans* isomer interactions, i.e., $\alpha_{ij} = \alpha_{trans}$ and $\alpha_{trans} = u n_{trans}$ [4].

In the special case of one component considered above, $S = \langle P_2(\theta) \rangle$ will be the scalar order parameter of *trans* isomers, and the partition function can be easily written as

$$Z = \int_0^1 d(\cos \theta) e^{-V(\theta)/k_B T}, \quad (13)$$

and the free energy is reduced to

$$F = -N_{trans} k_B T \ln Z + \frac{1}{2} N_{trans} \alpha_{trans} S^2. \quad (14)$$

Consequently, the order parameter can be obtained by solving just one self-consistent equation

$$S(T, n_{trans}) = \frac{\int_0^1 d(\cos \theta) P_2(\theta) e^{-\beta V(\theta)}}{Z}, \quad (15)$$

where we have indicated the explicit dependence on the concentration of the *trans* isomers. Our model is then reduced to the usual Maier-Saupe model, but now with a new ingredient represented by temperature-dependent concentration. This

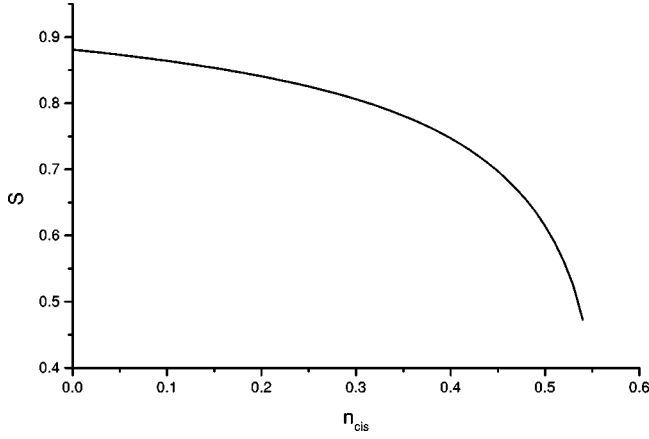


FIG. 1. Scalar order parameter vs the concentrations of *cis* isomers for a fixed, reduced temperature $T_R=0.1\nu/k_B$. The trend of the scalar order parameter follows a law of the kind $S^{6\propto}(1 - n_{cis}/n_{cis}^*)$.

dependence plays a distinct role from the one represented by the concentration dependence characteristic of the excluded volume theories of Onsager type [15,16]. In fact, in the classical Onsager model the number of particles is fixed. In this framework the critical density, below which the isotropic phase is stable, follows from a balance between the energy connected with the excluded volume and the thermal energy. On the contrary, according to our model also the number of particles responsible for the nematic phase depends on the temperature. In Onsager's model this is equivalent to having an excluded volume that is temperature dependent.

In Fig. 1 we show the nematic scalar order parameter S vs the concentration of the *cis* isomers in the system for a typical value of the reduced temperature ($T_R=0.1\nu/k_B$). The system exhibits a phase transition to the isotropic phase for $n_{cis}^c=0.55$. One observes that near the critical concentration the behavior of the order parameter can be well approximated by

$$S(n_{trans}) \approx S_0 \left(1 - \frac{n_{cis}}{n_{cis}^*} \right)^{1/6}, \quad (16)$$

where, for the case depicted in Fig. 1, $S_0 \approx 0.93$, and n_{cis}^* is a concentration slightly below n_{cis}^c . In Fig. 2 we present a phase diagram of temperature vs concentration of *cis* component for the system. One observes that the usual critical temperature for the Maier-Saupe model ($T_R=0.22019\nu/k_B$) [17] is reached just when $n_{cis}=0$, as expected, since in that model the concentration of the molecules giving rise to the nematic phase is fixed (which, in our model corresponds to the assumption that only *trans* isomers are present). This result is in very good agreement with the data reported in [11], relevant to the experimental determination of the nematic-isotropic temperature for mixtures of MBBA doped with a solute formed by quasispherical molecules. In fact, the experimental data, reported in Fig. 3 of [11], show that the critical temperature for the nematic-isotropic phase transition of the mixture is a linear function of the concentration of the solute, as predicted by our model (for details see also references quoted in [11]).

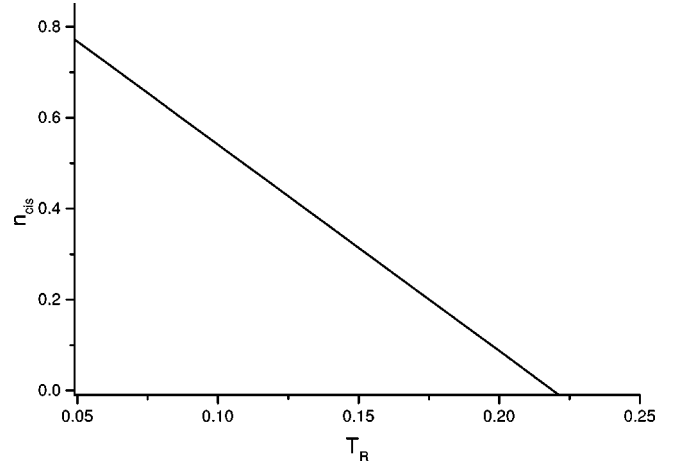


FIG. 2. Phase diagram in the reduced temperature vs *cis* concentration plane. The critical line represents the first order phase transition, nematic \rightarrow isotropic, induced by the variation in the concentration of *cis* isomers in the nematic medium.

III. THE EQUILIBRIUM *cis-trans* CONCENTRATIONS

At a given temperature T , the isomerization reaction follows the reaction scheme $[trans] \rightarrow [cis]$, depending on some rate constants that, in turn, depend on the intensity of the light in the illumination process [18,19]. The time evolution of the concentrations of the two constituents can be approximated by

$$n_{trans}(T,t) = cn_{trans}(T) + (1-c)n_{trans}(T)e^{-t/\tau}, \quad (17)$$

where τ is a characteristic time and c is a parameter to control the fraction of *trans-cis* isomers at a given temperature after the illumination (because some kind of recombination has to be taken into account). In fact, when $t=0$ one has $n_{trans}(T,0) = n_{trans}(T)$. From Eq. (12), stating the conservation of the total number of particles, and assuming for n_{trans} the approximate expression given by Eq. (17), it is easy to obtain

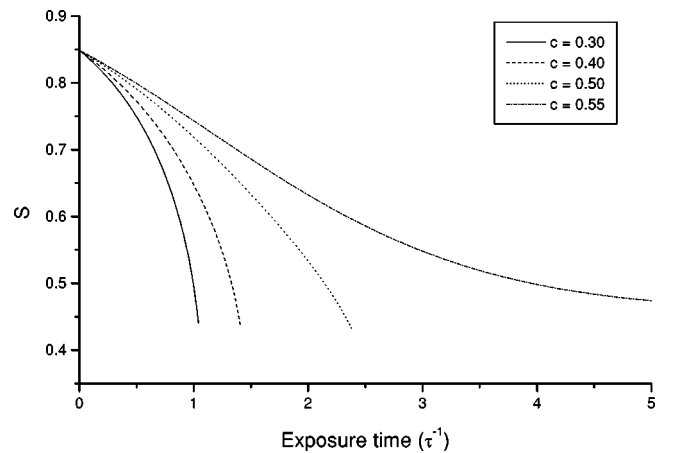


FIG. 3. Scalar order parameter vs the exposure time for uv illumination (τ is a characteristic time). Since the *cis* isomer concentration is strongly increasing with time, the system exhibits a phase transition to the isotropic phase at relatively low temperatures. Notice that for $c > 0.55$ there is no phase transition at this temperature ($T_R=0.1\nu/k_B$).

$$n_{cis}(T,t) = 1 - n_{trans}(T,t). \quad (18)$$

The time evolution proposed above takes into account the condition connected with Eq. (12) and also the experimental fact that with the exposure time to the illumination, the concentration of *cis* isomers increases, whereas the *trans* isomer concentrations decreases. However, in the limit of long time exposure, i.e., $t \rightarrow \infty$, the concentration of *trans* does not tend to zero, but to some fraction (controlled by the parameter c) of the equilibrium concentration $n_{trans}(T)$.

Let us now recall the equilibrium distribution of the concentrations of the different constituents forming the mixture. Let μ be the chemical potential of the mixture under consideration. At a given temperature T the equilibrium distributions of *cis* and *trans* isomers are, respectively, given by

$$n_{cis} = e^{-(\mu+E)/k_B T}, \quad \text{and} \quad n_{trans} = e^{-\mu/k_B T}, \quad (19)$$

subject to the condition (12), which implies that

$$e^{\mu/k_B T} = 1 + e^{-2E/k_B T}. \quad (20)$$

This relation defines the chemical potential in terms of an energy difference between the *trans* and *cis* states and of the temperature. It is important to stress, however, that this dependence on the energy difference between *cis* and *trans* states is not so crucial because $E \gg k_B T$. The limits for the above expressions are the following: $T \rightarrow 0$ gives $n_{cis} \rightarrow 0$, $n_{trans} \rightarrow 1$. On the other hand, for $T \rightarrow \infty$, $n_{cis} = n_{trans} = 1/2$. The temperature dependence of these constituents can be used to explain the experimental data relative to the concentrations of cyclic and open dimers, and monomers, in 4, *n*-alkyloxybenzoic acids [4]. Now, if the above results are

used in Eq. (15) it is possible to investigate the behavior of the order parameter with the exposure time to the illumination.

In Fig. 3 we show the scalar order parameter vs the exposure time for the reduced temperature of $T_R = 0.1v/k_B$. One observes the crucial role played by the parameter c that controls the concentration of *cis-trans* isomers for long exposure time. If $c > 0.55$ there is no phase transition induced by the time of exposure at the temperature considered. It is evident that the permanence of the liquid-crystalline phase is strongly dependent on the concentration of *cis* isomers in the system.

IV. CONCLUSIONS

We have proposed a simple model to account for the behavior of the scalar order parameter in liquid-crystalline systems made by more than one nematogen component. The model is an extension of the Maier-Saupe-model, which includes the concentration variation of the constituents forming the nematic medium. The approach can be successfully applied to distinct systems, like the one formed by cyclic dimers and monomers, and also to the systems where azobenzene compounds play a crucial role. Particular attention was devoted to these later systems where the illumination process gives rise to the appearance of new objects with different symmetries in the systems (photoisomerization). For these systems the theoretical predictions of the model are in very good agreement with the experimental data.

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