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Temperature dependence and characteristics of relaxation modes in achiral polar smectic phases

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ABSTRACT

The paper studies relaxation modes and their corresponding amplitudes in antiferroelectric polar smectic phases made of achiral bent-core compounds. The analysis identifies two types of modes in the orthogonal $SmAP_A$ phase. The nature of these modes is either pure polar or quasi tilt, but they are split into phase and amplitude modes. One of the amplitude tilt modes is a soft mode and the corresponding relaxations time becomes infinite at the transition to the tilted phase. In tilted phases, characteristic modes change the phase of equilibrium order parameters, the amplitude or both simultaneously. Of these modes, two are predominately polar, soft mode and Goldstone mode are predominately tilt modes and the rest are mixed. The nature of characteristic modes is temperature independent in all studied phases.

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Fluctuation amplitudes; order parameters; polar smectics; relaxation modes

Introduction

Banana molecules, as they are trivially named because of their bent-core shape, have been widely studied after the realization that they can form antiferroelectric and ferroelectric phases, in spite of achiral molecular constituents [1]. Although bananas form a rich variety of phases [2], this paper focuses on antiferroelectric polar smectics, in which polarity originates from biaxial packing of molecule cores.

In the section 'The model', we present stable solutions derived from the minimization of free energy expressed in terms of polar and tilt order parameters. The section 'Relaxation modes' contains an analysis of the non-equilibrium free energy expressed in a matrix form. The matrix form allows for straightforward analysis of the dynamic properties of the system. Finally, we discuss the nature of obtained characteristic modes and the amplitudes of their fluctuations.

The model

In achiral smectic phases made of bent-core molecules, the degree of order is measured in two order parameters, the two-dimensional tilt and polarization vectors. Polarization order parameters can appear independently of the tilt as in the studied orthogonal polar $SmAP_A$ phase. More common, they appear simultaneously as in the studied tilted and polar SmC_SP_A and SmC_AP_A phases.

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Tilt order parameter is defined with respect to the j-th layer director

$$\vec{\xi}_j = \{n_{j,x}n_{j,z}, -n_{j,y}n_{j,z}\} \tag{1}$$

where n_x, n_y and n_z are components of the director $\vec{n}$.

Order parameter polarization describes the average orientation of the bent core, and average polarization of molecules is either parallel or anti-parallel to this direction

$$\vec{P}_j = \{P_{j,x}, P_{j,y}\} \tag{2}$$

Free energy of achiral smectic system made of bent-core molecules, expressed in order parameters is [3]

$$\begin{aligned} G = \sum_j & \frac{1}{2}a_{0p}P_j^2 + \frac{1}{4}b_{0p}P_j^4 + \frac{1}{2}a_{0t}\xi_j^2 + \frac{1}{4}b_{0t}\xi_j^4 + \frac{1}{2}\Omega(\vec{\xi}_j \times \vec{P}_j)_z^2 + \frac{1}{4}a_{1p}P_j(\vec{P}_{j-1} + \vec{P}_{j+1}) \\ & + \frac{1}{4}a_{1t}\xi_j(\vec{\xi}_{j-1} + \vec{\xi}_{j+1}) \end{aligned} \tag{3}$$

First four terms give energy contributions because of the polarization and tilt order caused by van der Waals forces. $\boldsymbol{a_{0p} = T - T_0}$ is the only temperature-dependent coefficient. Next term, with the negative coefficient Ω, describes the intralayer interaction between tilt and polarization, which favours mutual perpendicular orientation. Couplings between polarizations and tilts in the neighbouring layers are given by last two terms. For the purpose of this study, we choose the positive value of the coefficient a_{1p}, characteristic of antiferroelectric ordering in polarization. The coefficient a_{1t} is negative for preferred synclinic, or positive for anticlinic ordering of tilts in neighbouring layers.

The structures are described in a coordinate system, where the z-axis corresponds to the layer normal, the y-axis is parallel to the polarization order parameters and the x-axis is parallel to the tilt order parameters. In general, order parameters vary in direction from one layer to the other, but they have constant magnitudes. In order to minimize the free energy, the following Ansatzes for structures were used:

$$\begin{array}{ccc} SmAP_A & SmC_SP_A & SmC_AP_A \\ \vec{\xi}_0 = 0 & \vec{\xi}_{0j} = \theta_0\{1,0\} & \vec{\xi}_{0j} = \theta_0\{1,0\} \\ \vec{P}_{0j} = P_0\{0,1\} & \vec{P}_{0j} = P_0\{0,1\} & \vec{P}_{0j} = P_0\{0,1\} \\ \vec{P}_{0j+1} = P_0\{0,-1\} & \vec{\xi}_{0j+1} = \theta_0\{1,0\} & \vec{\xi}_{0j+1} = \theta_0\{-1,0\} \\ & \vec{P}_{0j+1} = P_0\{0,-1\} & \vec{P}_{0j+1} = P_0\{0,-1\} \end{array} \tag{4}$$

By inserting (4) in (3) and minimizing with respect to θ_0 and P_0, one obtains a time-independent solution for the parameters θ_0 and P_0 (Figure 1)

$$\begin{array}{ccc} SmAP_A & SmC_SP_A & SmC_AP_A \\ \theta_0 = 0 & \theta_0^2 = \dfrac{-a_{0t}\,b_{0p} - a_{1t}b_{0p} - a_{1p}\Omega + T\Omega}{b_{0p}b_{0t} - \Omega^2} & \theta_0^2 = \dfrac{-a_{0t}\,b_{0p} + a_{1t}b_{0p} - a_{1p}\Omega + T\Omega}{b_{0p}b_{0t} - \Omega^2} \\ P_0^2 = \dfrac{a_{1p} - T}{b_{0p}} & P_0^2 = \dfrac{a_{1p}\,b_{0t} + a_{0t}\Omega + a_{1t}\Omega - b_{0t}T}{b_{0p}b_{0t} - \Omega^2} & P_0^2 = \dfrac{a_{1p}\,b_{0t} + a_{0t}\Omega - a_{1t}\Omega - b_{0t}T}{b_{0p}b_{0t} - \Omega^2} \end{array}$$

Relaxation modes

A system that has been deviated from equilibrium relaxes through its characteristic modes. According to the Goldstone theorem, the characteristic frequency of one of these modes is zero if the phase

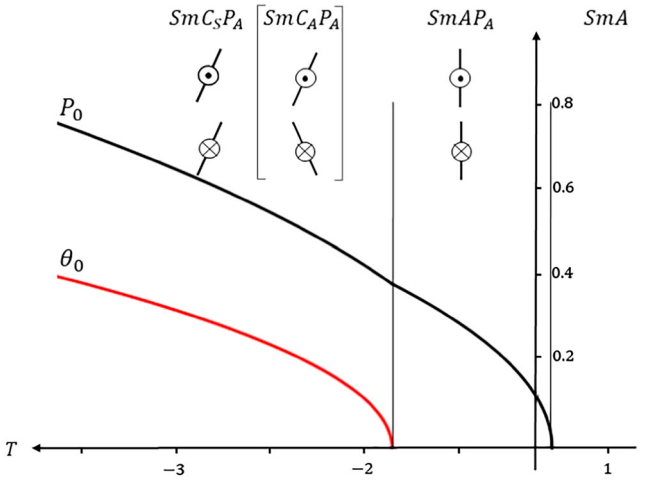

Figure 1. Theoretical dependence of polarization and tilt on the temperature. Set of parameters used for the model were $b_{0p} = 20$, $a_{0t} = 2$, $b_{0t} = 40$, $\Omega = -15$, $a_{1p} = 0.2$, $a_{1t} = \pm 0.5$. Thin vertical lines mark transitions between the phases. Structures of polar phases are symbolically presented above the graph. Arrow convention is used for indicating polarization direction.

transition is continuous [4]. A consequence of this zero-frequency mode is an energy non-changing coherent rotation of all molecules by the same angle when the liquid crystal is reoriented in a specific direction. In polar smectics, the Goldstone mode represents the rotation of the sample as a whole. For other continuous transitions below the *SmA*, the frequency of one of the other characteristic modes also approaches zero as the temperature reaches the phase transition [5]. Towards the transition, the pseudo forces returning the system to the equilibrium structure decrease, fluctuations increase and the system becomes softer. Therefore, this characteristic mode is called the soft mode; it condenses at the transition temperature and breaks the symmetry of the phase.

We begin the analysis of dynamic properties by inserting time-dependent tilt and polarization into free energy Equation (4):

$$\begin{aligned} \vec{\xi}(t) &= \vec{\xi}_0 + \delta\vec{\xi}(t) \\ \vec{P}(t) &= \vec{P}_0 + \delta\vec{P}(t) \end{aligned} \tag{5}$$

The time-dependent order parameter is a sum of a time-independent equilibrium order parameter and small fluctuations that can change its magnitude (subscript $\parallel$) or direction, that is, its phase (subscript $\perp$)

$$\begin{aligned} \vec{\xi}(t) &= \xi_0\vec{e}_\parallel + \delta\xi_\parallel\vec{e}_\parallel + \delta\xi_\perp\vec{e}_\perp \\ \vec{P}(t) &= P_0\vec{e}_\parallel + \delta P_\parallel\vec{e}_\parallel + \delta P_\perp\vec{e}_\perp \end{aligned} \tag{6}$$

where $\vec{e}_\parallel$ and $\vec{e}_\perp$ are unit vectors parallel or perpendicular to stable order parameters locally in each layer.

Free energy is then developed around equilibrium. The contribution of fluctuations to free energy is

$$\boldsymbol{\delta G} = \frac{1}{2}\boldsymbol{\chi_i}\underline{\boldsymbol{G}_2}\boldsymbol{\chi_i} \tag{7}$$

Here, $\vec{\chi}$ is an eight-component vector of collective fluctuations

$$\vec{\chi} = \{\delta\xi_{j,\parallel}, \delta\xi_{j,\perp}, \delta P_{j,\parallel}, \delta P_{j,\perp}, \delta\xi_{j+1,\parallel}, \delta\xi_{j+1,\perp}, \delta P_{j+1,\parallel}, \delta P_{j+1,\perp}\} \tag{8}$$

and $\underline{G_2}$ is time-dependent free energy equation written in a matrix form

$$G_2 = \begin{bmatrix} C & 0 & L & 0 & I & 0 & 0 & 0 \\ 0 & D & 0 & K & 0 & I & 0 & 0 \\ L & 0 & A & 0 & 0 & 0 & J & 0 \\ 0 & K & 0 & B & 0 & 0 & 0 & J \\ I & 0 & 0 & 0 & C & 0 & L & 0 \\ 0 & I & 0 & 0 & 0 & D & 0 & K \\ 0 & 0 & J & 0 & L & 0 & A & 0 \\ 0 & 0 & 0 & J & 0 & K & 0 & B \end{bmatrix} \tag{9}$$

with the elements

$$\begin{aligned} A &= 2a_{0t} + 6b_{0p}P_0^2 + 2\Omega\theta_0^2 & I &= \pm 2a_{1t} \\ B &= 2a_{0t} + 2b_{0p}P_0^2 & J &= 2a_{1p} \\ C &= 2a_{0t} + 6b_{0t}\theta_0^2 + 2\Omega P_0^2 & K &= 2\Omega\theta_0 P_0 \\ D &= 2a_{0t} + 2b_{0t}\theta_0^2 & L &= 4\Omega\theta_0 P_0 \end{aligned}$$

Note that element I has a negative sign for synclinic, and positive for anticlinic structure. Each thermodynamically induced fluctuation mode contributes equally to the free energy increase δG

$$\eta_i \frac{1}{2}(\delta a_i^2 \eta_i)\underline{G_2} = const. \tag{10}$$

where η_i is eigenvector that corresponds to the eigenvalue λ_i of the matrix $\underline{G_2}$ and δa_i is its amplitude. This allows for comparison of fluctuation amplitudes.

In the $SmAP_A$ phase, two types of modes exist, phase (marked with indexes 7, 6 and 4 in Figure 2) and amplitude. Nature of these modes is either pure polar or pure quasi tilt. Prefix 'quasi' is suggested

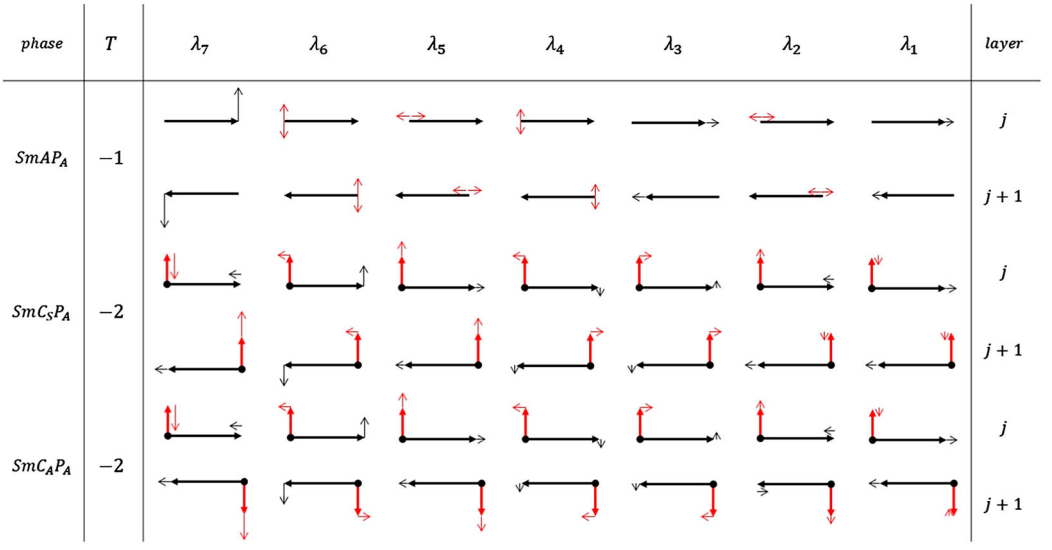

Figure 2. Relaxation modes of the studied phases in two neighbouring layers j and $j + 1$. Horizontal arrows represent equilibrium polarization and vertical arrows represent equilibrium tilt. Thin arrows represent amplitudes of fluctuations in relative mutual ratios calculated for the temperature.

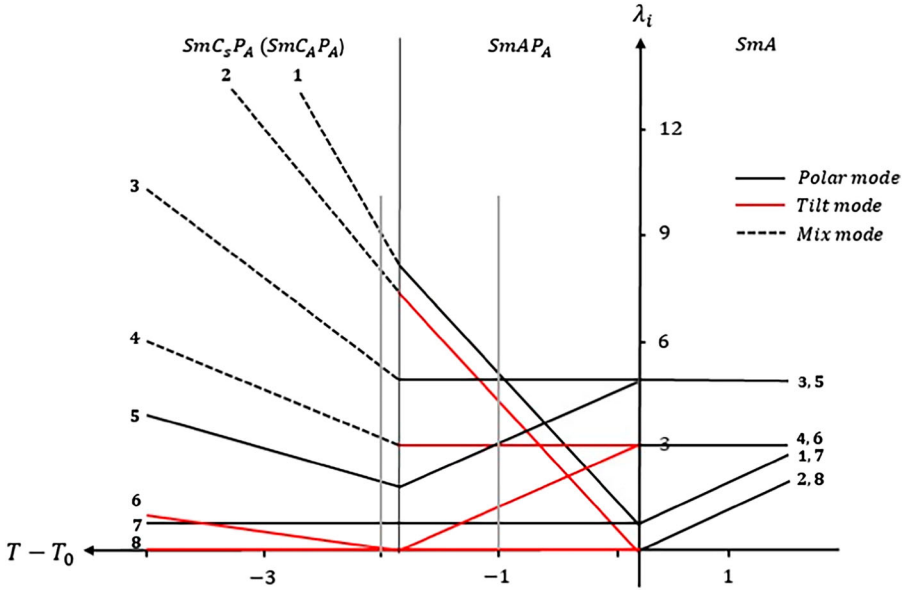

Figure 3. Characteristic modes in dependence of temperature. Full lines are polar and tilt modes and dashed lines are mixed modes. Numbering of modes corresponds to that in Figure 2, while Goldstone mode is marked with 8. Thin vertical lines highlight temperature values from Figure 2. Set of parameters used for the analysis is $b_{0p} = 20$, $a_{0t} = 2$, $b_{0t} = 40$, $\Omega = -15$, $a_{1p} = 0.2$, $a_{1t} = \pm 0.5$.

because there exist fluctuations that tend to tilt the molecule, but the equilibrium structure does not have a tilt.

In the studied *SmCP* cases, in the local system, two modes change only the amplitude of equilibrium order parameters (λ_7 and λ_5 in Figure 2), while modes λ_6, λ_4 and λ_3 change only their direction. The rest of the modes, where both order parameters change similarly, whether in phase, or simultaneously in phase and magnitude, are mixed. Among these modes, two are predominantly polar in nature (λ_7 and λ_5 in Figure 2), where the change of polarization is much greater than the change of tilt. The soft mode, i.e. λ_6 in Figure 2, is the only predominantly tilt mode, where the change of tilt is significantly greater than the change of polarization. As expected, the soft mode is of the same nature as Goldstone mode in all three studied phases, due to the fact that it splits in two modes at the phase transition point, from which one of them becomes the 'new' Goldstone mode in the following phase. Nature of these modes does not change with temperature, as marked by a colour code in Figure 3.

Conclusions

In the paper, the dynamic properties of antiferroelectric orthogonal $SmAP_A$ and tilted SmC_SP_A and SmC_AP_A phases made of achiral, bent-core molecules were analysed. We developed a procedure to find relaxation frequencies and corresponding eigenvectors for eight characteristic modes present in these systems. We analysed the types of modes, that is, amplitude modes that change the magnitudes of order parameters, and phase modes that change the direction of order parameters. The amplitudes of order parameters' fluctuations, estimated from the equipartition theorem, revealed the nature of these modes. There exist pure polar and quasi-tilt modes in the orthogonal phase. Titled phases have predominantly polar modes and the soft mode is predominantly tilt, while most modes are mixed. The nature of characteristic modes in studied cases does not depend on temperature.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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