ABSTRACT
Twist grain boundary (TGB) phases represent liquid crystalline systems with a regular array of defects. In our research, we studied a compound with a stable TGBC phase and pursued its structure using various experimental techniques. Using AFM microscope, we observed the surface of the smectic film and detected a periodic relief. We found that the displacement amplitude is a few nanometres, with a periodicity of about 500 nm. Such periodicity is in accordance with the periodicity of the TGBC blocks’ rotation estimated by polarising microscopy. The surface modulation is explained by the deformation of the TGBC structure, which is created on TGBC films. A simplified model interpreting the observed smectic surface displacement as the consequence of rotating TGBC blocks inside the sample is proposed. TGBC blocks deform differently depending on their orientation with respect to the force acting by the tip of the AFM microscope cantilever probing the smectic surface.

Introduction
Twist grain boundary (TGB) phases are an example of liquid crystalline (LC) mesophases, revealing a frustration connected with their chirality [1,2] in an interplay with other molecular forces. TGB phases mostly appear as an intermediate state between cholesteric (Ch) and smectic phases. They had been theoretically described by Renn and Lubensky [3–5] and later proved experimentally by Goodby et al. [6]. TGB phases are examples of lamellar (smectic) phases with a regular defect structure consisting of parallel screw dislocations that separate smectic blocks (grains). The layer normal of smectic grains rotates across each grain boundary and creates a helical superstructure with an axis parallel to the smectic layers. In the TGB phase, there is a competition between chiral forces, twist of molecules and their tendency to pack into layers. These LC phases exhibit specific structural features, and their observations in a polarised light microscope (POM) show variable textures. We are speaking about the TGBA phase if the molecules in the smectic blocks are parallel to the layer normal. In the case of the molecules tilted with respect to the layer normal, we can obtain the TGBC phase and there is a variety of different modifications. For the first time, the TGBC phase has been proved experimentally by Nguyen et al. [7], and later several kinds of TGB phases with different local smectic structures were described [8–10]. While the structure of the TGBA phase seems to be well understood, the character and properties of tilted variants (TGBC phases) are still subjects of intensive research [11–13].

During our research of LC molecules with a lactic acid unit as a chiral moiety, we have found several compounds with TGB mesophases [14–22]. We studied...
and theoretically described the nucleation of filaments in the TGBA phase under different conditions [23,24]. Recently, we synthesised and studied the mesomorphic behaviour of new lactic acid derivatives designed as nKDDL and found the presence of TGB phases persisting at room temperatures [25]. For one homologue 12KDDL with n = 12 (dodecyl in the non-chiral alkyl chain), the cholesteric–TGBA–TGBC phase sequence was found on cooling from the isotropic phase. The optical and dielectric properties of nKDDL compounds were studied, and the effect of an electric field was analysed [25].

In this contribution, we pursued homologue 12KDDL using AFM microscopy, and other experimental studies were accomplished to gain more information on the structure of the TGBC phase. By applying AFM technique, we succeeded to visualise a defect structure in detail. In addition, we propose a model for describing our experimental data. We take into consideration the description of a relative displacement on the sample surface during AFM measurements. We will interpret the AFM data using a simplified elastic model that characterises the influence of probing apex of AFM tip on the liquid crystalline sample surface in the TGBC phase.

**Experimental**

Previously, the synthesis of the studied compound 12KDDL was presented [25], and the cholesteric (Ch)-TGBA-TGBC phase sequence was established on cooling from the isotropic phase (Iso). We established the following values: 83°C for Iso-Ch, 73°C for Ch-TGBA and 42°C for TGBA-TGBC phase transition temperature. The melting point (mp) was was determined to be 49°C, and the compound crystallised at 14°C during DSC measurements. Our observations with a polarising optical microscope (POM) in the TGBA phase in planar geometry revealed features of the upper-temperature cholesteric phase, with typical oily-streak textures. A stripe or grid texture was discovered in the TGBC phase (Figure 1), with a periodicity estimated to be around 0.5 µm.

To gain more information about the TGB structure of 12KDDL, we prepared a film from the melted material. At room temperature, we studied its surface with an AFM microscope and observed a complex relief, as shown in Figure 2(a,b). At room temperature, AFM measurements were carried out on an ambient AFM (Bruker, Dimension Icon) in Peak Force Tapping mode using ScanAsyst Air tips (Bruker; k = 0.4 N/m; nominal tip radius 2 nm).

The textures observed by the AFM technique, which mark the surface relief of the sample, are in the form of surface stripes. Figure 2 shows two AFM figures with the depth profile of surface amplitudes in nanometres. We can precisely analyse the profile of the studied sample in the direction perpendicular to these stripes to obtain the plot of displacement over the surface. We expect that the revealed surface relief is created during measurement as a result of interaction between the sample elasticity and the force of the AFM cantilever applied on the sample surface. To orient the system of coordinates with respect to a modulation, we present a schematic representation of an array of TGB blocks in the TGBA and TGBC phases in Figure 3. This orientation will be necessary for the following theoretical description.

![Figure 1](image1.png)

**Figure 1.** Photo of the TGBC texture taken for the studied material at temperature T=30°C in the polarizing microscope with crossed polarizer (P) and analyser (A) positions. Measured topographies have 512 x 512 points resolution.
Deformation of the TGB structure

Herein, we will introduce a model that will describe our observations of surface displacement. Because the sample is prepared as a film spread on the glass plate, we expect that the molecules on the glass surface will prefer homogenous alignment. On the contrary, on the film surface with a borderline with air, we can suppose a homeotropic molecular arrangement. Let us consider that the surface of the film consists of a narrow smectic layer with a thickness $d_n$. The layers in the upper layer and in the interior of the film are organised in a helical structure characteristic of TGB phases (Figure 3). We expect that in the central part, the layers are relatively inclined to the glass surface and rotate around the rotation axis denoted as the $x$-axis (Figure 3). We can model the angle of layer inclination with respect to the $y$-axis as $\phi(x)$, see Figure 4. This angle is a function of the variable $x$, as previously shown [23]:

Based on AFM measurements, we can estimate that the surface displacement period is about 0.5 μm and the profile depth is 3–5 nm. We expect that the surface displacement corresponds to the TGB structure within the sample rather than the modulation of chiral smectic C director in the TGBC structure. The periodicity of a modulation in the same range of 500–600 nm was observed by the absorption spectroscopy of the film, showing an anomaly in this spectral region that can be attributed to selective reflection. Unfortunately, due to the resolution of this technique, a modulation of a defect array seen by POM observations (Figure 1) cannot be properly analysed. Therefore, we concentrated on AFM data, which are precise enough. In the next step, we will try to construct a model to explain the measured surface displacement using a description of the TGB structure inside the sample and, finally, to fit the experimental data obtained by the AFM technique.

**Figure 3.** (Colour online) Coordinate axes and schematic organisation of TGB blocks composed of molecular layers in the TGBA and TGB phases. Angle $\omega$ is the angle formed by relative rotation of neighbouring blocks of thickness $l_b$. In TGB phase vector, $n$ represents the molecular direction in smectic C layers, while $\theta$ represents the molecular tilt in smectic C layers.
Figure 4. Scheme of smectic layer orientation in the (y,z)-plane of TGB film at a border with air (upper part). Angle $\phi$ is the angle of inclination of smectic layers in TGBA structures from the y-axis and describes the rotation of TGBA blocks along the x-axis (Figure 3). (a) Displacement $\delta$ is induced by the microscope tip on the sample surface, whereas $\delta'$ is the component of $\delta$ into the normal layers, inclined by an angle $\phi$. Parameter $d_i$ is the thickness of smectic layers forming the sample surface, which is perpendicular to the z-axis. The thickness $d_o$ describes this part of the sample where the layers are organised in the helical order of the TGB structure. (b) The layers in the neighbouring TGB block oriented along the x-axis are inclined by angle $\phi' = \phi + \omega$.

\[ \phi(x) = \frac{\omega}{2} + \frac{\omega}{l_b} x. \]  

where $l_b$ is the dimension of the TGB block along the x-axis. Let $P$ be the helical pitch along the x-axis. Then the angle $\omega$ is the angle of relative rotation of the neighbouring TGB blocks (Figure 3). It can be determined as $\omega = 2\pi l_b/P$.

We deal with the TGB phase, which involves tilting smectic molecules in layers to form a helicoidal molecular arrangement with molecules rotating in the direction of the layer normal. However, as AFM probing induces layer deformations, we neglect the smectic C director structure for simplicity and describe smectic deformation using the mectic A elastic model. Therefore, we will describe the layer deformation of a smectic liquid crystal by the free energy density $\rho_f$ in the form:

\[ \rho_f = \frac{K}{2} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2 + \frac{B}{2} \left( \frac{\partial u}{\partial z} \right)^2. \]  

$K$ and $B$ are the mean Frank elastic constants characterising the layer curvature and compression modulus, respectively. The layer displacement in the direction of the layer normal is denoted as $u$. The free energy density yields the following equilibrium equation:

\[ \lambda^2 \Delta u = \frac{\partial^2 u}{\partial z^2}, \]  

where $\lambda = \sqrt{\frac{E}{\rho}} = \sqrt{\frac{B}{\rho}}$. We propose a model solution of (3) that is isotropic in the plane $(x,y)$ in cylindrical coordinates:

\[ u = \delta \left( \frac{2b_2^2}{r_o^2} \right) \left( \frac{r_o^2 - r^2}{2b_2^2} + \frac{z}{b_z} \right), \]  

with $r^2 = x^2 + y^2$. The solution (4) is defined for $r^2 \leq r_o^2$ and $0 \geq z \geq -d_z$. It means that (4) is non-zero within the volume $\pi r_o^2 d_z$, where $r_o^2 = d_o^2 + d_z^2$. Outside of this volume, we take $u = 0$. Parameters $d_o$, $d_z$, and $b_z$ are the dimensions of the mentioned volume in x-, y- and z-directions. Parameters $b_r$ and $b_z$ are lengths over which derivatives of the displacement $u$ change along radius $r$ and along z-direction, respectively. The volume $\pi r_o^2 d_z$ is situated under the sample surface at the position where the tip of AFM microscope cantilever is applied. As for the boundary conditions of (4), we have $u = 0$ at $r^2 = r_o^2$ and $z = 0$. At $r = 0$, it is $u = \delta$. The parameter $\delta$ is the amplitude of displacement in the z-direction induced by the AFM probing tip on the sample surface. According to experimental data, it follows that the order of $|\delta|$ is about a smectic layer thickness value. On other surfaces of the volume $\pi r_o^2 d_z$, the displacement $u$ could have a jump-like character for about $\delta$ with respect to a non-deformed medium outside this volume. In this sense, the solution of (4) is an approximate description of the problem. In the following paragraph, parameters will be determined by fitting $\delta$ to the experimental curve (Figure 5). The thickness $d_z$ is the sum $d_z = d_o + d_1$. We have already denoted the thickness $d_o$ as the thickness of the sample near its surface where smectic layers are perpendicular to the direction of the force of the AFM tip. The thickness $d_1$ describes the area of the sample where layers are organised in the helical order of the TGB structure.
The elasticity of this part of the sample can be describe by the free energy density of (2) in the coordinate system \((x, y', z)\), which is rotated with respect to the coordinate system \((x, y, z)\) by an angle \(\phi\) around the rotation x-axis. However, the displacement (4) will have the same form in new coordinates. For simplicity, we will take the parameters \(b_x\) and \(b_z\) the same in both coordinate systems. On the other hand, \(\delta' = \delta \cos \phi\) (see Figure 4). The parameter \(\delta'\) is the component of \(\delta\) perpendicular to the smectic layer and inclined from the y-axis by an angle \(\theta\). There is also the component of \(\delta\) along smectic layers. Nevertheless, this component is not taken in account as it does not contribute to the elasticity of smectic liquid crystal.

The total elastic free energy \(F\) can be obtained using expressions (4) multiplied by the volumes of the corresponding volumes of considered structures:

\[
F = \left( d_o \pi r_o^2 \right) \frac{B}{2} \left[ \left( \frac{2b_x^2}{r_o^2} \right)^2 \left( \frac{2\delta}{b_x} \right)^2 + \left( \frac{\delta}{b_x} \right)^2 \right] + \left( d_1 \pi r_o^2 \right) \frac{B}{2} \left[ \left( \frac{2b_z^2}{r_o^2} \right)^2 \left( \frac{2\delta}{b_z} \right)^2 + \left( \frac{\delta}{b_z} \right)^2 \right] \cos^2 \phi
\]

\[(5)\]

The probing tip of the AFM microscope acts on the sample surface by the force \(-f_s\) per the surface \(S\) of the microscope tip, which gives the surface stress \(\sigma_s = -\frac{f_s}{S}\). The sign (-) means that the force is oriented in the opposite direction of the z-axis.

The equilibrium of forces in our model is given by the relation:

\[-\frac{\partial F}{\partial \delta} + \sigma_s \pi r_o^2 = 0\]

\[(6)\]

Force \(f_s\) is of the order of pN, but the surface of microscope cantilever is difficult to determine. Let us define a non-dimensional force parameter \(q = \left( \frac{w_o}{B} \right) \left( \frac{r_o^2}{2} \right)^2\) that will be determined later from the experimental dependence, as shown in Figure 5. Using formula (5), the equation (6) gives parameter \(\delta\) in the form:

\[
\delta = -\frac{q b_x^2 b_z^4}{\left( b_x^4 + 4\lambda^2 b_z^2 \right) \left( d_o + d_1 \cos^2 \phi \right)}
\]

\[(7)\]

Expression (7) shows a relatively simple dependence of the displacement amplitude \(\delta\) as the function of the angle of structure rotation along the rotation axis \(x\). The change of amplitude \(\delta\) in (7) is connected with the inclination \(\phi\) of TGB grains with respect to the acting force \(f_s\). When \(\phi\) is small, force \(f_s\) compresses smectic layers not only on the surface but also in smectic blocs under the surface and \(\delta\) is maximal. When \(\phi\) approaches \(\frac{\pi}{2}\), smectic layers in TGB blocks are not compressed and \(\delta\) is minimal.

**Discussion**

The absolute value of displacement or its sign, as measured by the AFM technique and shown in Figure 4, is related to some mean value of the surface position. Figure 5 shows the experimental data obtained using AFM, with the relative displacement of the sample surface adjusted to be positive. Parameter \(\delta\) together with other parameters in expression (7) can be fitted to the experimental data. As the differences of amplitude \(\delta\) are important, we modify (7) by a constant that shifts \(\delta\) to obtain \(\delta \geq 0\). Then, we take

\[
\delta = \frac{q b_x^2 b_z^4}{\left( b_x^4 + 4\lambda^2 b_z^2 \right) \left( d_o + d_1 \cos^2 \phi \right)} \left( \frac{1}{d_o} - \frac{1}{d_o + d_1 \cos^2 \phi} \right).
\]

\[(8)\]

For the purpose of fitting, we will modify the function \(\phi(x)\) (1) as follows:

\[
\phi(x) = \frac{2\pi}{\lambda} x - \frac{\pi}{2} + \phi_o.
\]

\[(9)\]

From (1), it is clear that \(x\) should change by jumps of the length \(l_b\). For simplicity, we use (9) in expression (8) continuously. Parameter \(\phi_o\) together with \(-\frac{\pi}{2}\) in (9) is the phase shift of the angle \(\phi(x)\), which permits the function \(\delta\) given by (8) to be adjusted to measured data. The reason is that we do not know the exact position of the coordinate origin. For the fit, we applied as the starting value the estimation \(\lambda = 4.5\) nm, which corresponds to the molecular length of 12KDDL at
a temperature of about 5 K below the temperature transition from TGBA to TGBC [25].

The fit of δ to experimental data is presented in Figure 5. Maxima of δ correspond to φ giving $\cos^2 \phi = 1$. The fitting yields the following parameter values: the pitch of TGB structure $P = 0.50 \, \mu m$, undefined $3 \, nm$, undefined $5 \, nm$, $d_c = 4.2 \, nm$, $d_1 = 11.6 \, nm$ and $\lambda = 4.61 \, nm$. The parameter of the phase shift $\theta_0 = -2.29$. Finally, the non-dimensional force parameter $q$ was determined as $q = 0.17$.

Let us discuss the values of the obtained parameters. Pitch $P$ is comparable to other TGB phases previously presented [1,23]. Let us point out that a similar value of pitch length was observed for another lactic acid derivative PHB(S) exhibiting the TGBA phase, which was studied previously [21]. Using our parameters, we can calculate the volume $\pi r_o^2 d_z$. The length $d_z$ can be written as $d_z = d_0 + d_1 \approx 14.5 \, nm$. This value is nearly equal to our fitted value $b_\perp = 15.2 \, nm$. Then we can expect that $d_z \approx d_y \approx b_\perp = 11 \, nm$. Therefore, $\pi r_o^2 \approx \pi \left( d_x^2 + d_y^2 \right)$ or $2 \pi b_\perp^2$. We also suppose that $d_z \approx l_y$. In Ref [1], the length $l_y$ for another type of the TGB material was estimated as $18.3 \, nm$, so we consider such a value as reasonable. The parameter $q = 0.17$ gives the relation between force $f_z$ on the surface $S$ of the sample and the compression modulus $B$. The value of $B$ is a function of the temperature, and it can be roughly estimated from the value $\lambda = 4.61 \, nm$ we obtained from the fitting procedure. If we utilise value $K \sim 10^{-11} \, N$, which is presented in the literature [1], we obtain $B = 4.7 \times 10^5 \, J/m^3$. This value is smaller than in a smectic A phase, which reflects the fact that we deal with a tilted smectic C structure, where $B$ is smaller with respect to smectic A phases.

**Conclusions**

In summary, we have pursued films of the lactic acid derivative 12KDDL in the TGBA phase by the AFM technique. Then we analysed our observations and tried to describe the structural parameters based on our experimental data. After a detailed analysis of AFM films, we prepared a simplified theoretical model that reflects the topology of the TGB phase as well as its elastic properties. We can conclude that our model of the TGB structure is composed of inclined layers with the TGB structure enveloped by a smectic layer to ensure homeotropic anchoring at a border with an air, which provides a reasonable background for fitting the experimental data. The model assumes equilibrium between the force of the microscope tip acting and probing the sample surface and the helicoidal TGB structure. The deformation of the TGB structure depends on the orientation of smectic layers in the TGB structure with respect to the orientation of acting force, which results in a change in relative displacement $\delta$. Therefore, it is important to note that the microscope probing the sample surface reveals the TGB structure under the sample surface. The fit of the measured surface displacement is in the concordance with the displacement obtained from our theoretical model. The observed stripe periodicity detected by AFM corresponds to the periodicity of the TGB structure inside the sample and offers us important information.

The values of the surface displacement amplitude $\delta$ that we fitted to our experimental data are in agreement with other microscopic and spectral observations on 12KDDL. Unfortunately, we are not able to establish the periodicity observed in the polarising microscope (Figure 1) at higher resolution. In addition, the spectroscopic measurements on the film detected the anomaly in a rather broad range of 500–600 nm, and it is difficult to establish the pitch value exactly based on this method. We can summarise that the AFM technique is very powerful and provides very precise information about pitch value. The first attempt to apply AFM measurements to establish the periodicity of a cholesteric phase with a short pitch-length was done by Škarabot et al. [26]. Nevertheless, to the best of our knowledge, TGB phases have not yet been characterised by this technique.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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**ORCID**

Vladimíra Novotná http://orcid.org/0000-0001-9960-4426

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