Beyond the flexoelectric model of modulated nematics

Nataša Vaupotič,[1,2] Samo Curk,[1] Mikhail A. Osipov,[3] Mojca Čepič,[2,4] Hideo Takezoe,[5,6] Ewa Gorecka[6]

[1] Faculty of Natural Sciences and Mathematics, University of Maribor, Koroška 160, 2000 Maribor, Slovenia
[2] Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
[3] Department of Mathematics and Statistics, University of Strathclyde, 26 Richmond str., G1 Glasgow, United Kingdom
[4] Faculty of Education, University of Ljubljana, Kardeljeva ploščad 16, 1000 Ljubljana, Slovenia
[5] Toyota Physical and Chemical Research Institute, 41-1 Yokomichi, Nagakute, Aichi 480-1192, Japan
[6] Department of Chemistry, University of Warsaw, Zwirki i Wigury 101, 02-089 Warsaw, Poland

We show that the flexoelectric model of chiral and achiral modulated nematics predicts the compression modulus that is by orders of magnitude lower than the measured values. The descrepancy is much larger in the chiral modulated nematic phase, in which the measured value of the compression modulus is of the same order of magnitude as in achiral modulated nematics, even though the heliconical pitch is by an order of magnitude larger. The relaxation of a one-constant approximation in the biaxial elastic model used for chiral modulated nematics does not solve the problem. Therefore, we propose a new structural model of the modulated nematic phase, which is consistent with the current experimental evidence and can also explain large compression mudulus: the structure consists of short-range smectic clusters with a 4-fold symmetry and periodicity of 2 molecular distances. In chiral systems, chiral interactions lead to a helicoidal structure of such clusters.

I. INTRODUCTION

The spontaneous chiral symmetry breaking, particularly if it occurs in systems made of non-chiral molecules, is an intriguing phenomenon. Until recently it was believed that chiral self-segregation requires a solid state, because averaging of molecular interactions over all molecular positions weakens the chiral discrimination in liquid. Therefore spontaneous symmetry breaking observed in the nematic phase, the phase with orientational order and no long-range positional order, created a lot of interest. At the nematic-nematic phase transition the ordinary nematic phase, which is homogeneous in space, transforms into a modulated phase. The lower-temperature nematic phase is usually a twist-bend nematic (N_{TB}) phase, which is characterized by a helicical structure with the pitch of only few molecular distances (8-10 nm) [1–7]. So far the N_{TB} phase was observed only for two types of mesogenic molecules: dimers, in which two mesogenic units are connected by a linking group with an odd number of carbon atoms, and for rigid bent-core molecules. Recent studies addressed the influence of the molecular chirality on the N_{TB} phase. Surprisingly, for chiral bent dimers, the modulation pitch is of the order of magnitude larger [8, 9]. Despite the different pitch, the compression modulus of both chiral and achiral modulated nematics seems to be of the same order of magnitude [9].

Theoretically two types of the modulated nematic phase, the twist-bend (TB) and the splay-bend (SB), were predicted [10, 11]. Because in the bent-core systems the splay elastic constant is, in general, larger than the bend [12–19] and twist elastic constant [20, 21], the twist-bend structure is expected to be more frequent [11, 22]. For chiral dimers, however, multiple modulated structures were observed [8]. As a possible driving force for the formation of the modulated structures the flexoelectric effect was proposed [10, 22], which describes the appearance of a local electric polarization induced by a non-homogenous deformation of material. It was shown that the modulated structures are locally biaxial [22] with a low biaxial order parameter. So, a uniaxial continuum model including the flexoelectric terms was used to predict the structures in achiral modulated nematics [22]. The obtained conditions for the stability of the TB and SB modulated phases agree with the ones derived from the continuum theoretical model [11], based on the elastic instability of a system formed by bent molecules, and Monte Carlo simulations [23]. In chiral systems biaxiality cannot be neglected [24]. A biaxial continuum model can explain destabilization of the chiral nematic phase with respect to the formation of the modulated nematic phase and the appearance of multiple nematic phases [8].

In this paper we show that the flexoelectric effect fails to explain a huge value of the compression modulus B measured both in chiral and achiral modulated nematics. As reported in [9], the value of B in the chiral N_{TB} phase is of the order of 10 MPa and is by an order of magnitude larger than in achiral N_{TB} phase. However, in the samples of achiral material, contrary to the chiral material, the homeotropic alignment was rather poor, therefore the actual values of B might be of the same order of magnitude. To verify the value of B we have recently performed additional measurements by AFM. Although the data are not very accurate, the compression modulus, calculated according to the DMT model [25] is approximately 10-30 MPa for both the chiral N_{TB} phase and for the smectic phase that appears in a one carbon longer homologue (the phase diagram was reported in [9]). Considering $B \sim K q^2$, where K is an elastic constant, $q = 2\pi/d$ and d is the heliconical pitch, the effective elastic constant in the chiral N_{TB} should be two to three orders of magnitude larger than in the achiral N_{TB}, because the pitch of the heliconical modulation is 10-times larger in the chiral N_{TB} phase. Inclusion of the flexoelectric terms in the model leads to the renormalization of elastic constants

in the modulated nematic phases. However, there is no physical reason why the renormalization should be orders of magnitude larger in the chiral N_{TB}. In ref. [9] we predicted that although the values of B obtained from the model are lower than the measured values, the relaxation of a one constant approximation may solve the problem. Here we show that it does not. In the achiral case the flexoelectric model predicts the reduction of the effective elastic constant, not an increase. For the chiral N_{TB} phase large enough effective elastic constant can be obtained only within a very narrow and unphysical window of chiral parameters. Therefore, it is an essential issue to give an alternative idea of the structure of modulated nematics to remove the discrepancy.

The paper is structured as follows. In the next section we first present calculation of the compression modulus of the achiral N_{TB} phase (Sect. II.A) using the uniaxial model and then the calculation of the compression modulus of the chiral N_{TB} phase (Sect. II.B), using the biaxial model and abandoning the one-constant approximation. Based on the huge descrepancy between the theoretically predicted and measured values of B, we propose a new structural model of the N_{TB} phase (Sect. III). In the final section (Sect. IV) we draw the conclusions.

II. COMPRESSION MODULUS OF THE N_{TB} PHASE

A. Achiral case

First we focus on the uniaxial model, which is used for achiral nematics. The TB nematic structure (Fig. 1) is characterized by the heliconical angle θ, local magnitude of polarization p_0 and the wavenumber of the helical modulation q. The free energy is expressed in terms of the local direction of the long molecular axes (director $\mathbf{n}$) and the local direction of polarization ($\mathbf{p}$), which is perpendicular to $\mathbf{n}$ [22]:

$$
\begin{aligned}
f = & \frac{1}{2}K_s(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}K_t\left[\mathbf{n} \cdot (\nabla \times \mathbf{n})\right]^2 \\
& + \frac{1}{2}K_b\left[\mathbf{n} \times (\nabla \times \mathbf{n})\right]^2 + \lambda p_0 \mathbf{p} \cdot (\mathbf{n} \times (\nabla \times \mathbf{n})) \\
& + \frac{1}{2}\mu p_0^2 + \frac{\kappa p_0^2}{2}\left[(\nabla \cdot \mathbf{p})^2 + (\nabla \times \mathbf{p})^2\right],
\end{aligned} \tag{1}
$$

where K_s, K_t and K_b are the splay, twist and bend elastic constants, respectively. λ and μ are parameters related to the flexoelectric coefficient and dielectric susceptibility, respectively. The last term in eq.(1) with the parameter κ is a gradient term in the order parameter $p_0\mathbf{p}$, characteristic for the modulated nematic phase, assuming that p_0 is constant. By using an ansatz for the TB phase:

$$
\mathbf{n} = \{\cos\theta, \sin\theta\cos(qx), \sin\theta\sin(qx)\}, \tag{2}
$$
$$
\mathbf{p} = \{0, -\sin(qx), \cos(qx)\}, \tag{3}
$$

and minimizing the free energy $\int f dV$, where V is the sample volume, one finds that the TB structure is stable if $\mu = c\lambda^2/K_b$, with the temperature dependent dimensionless parameter $c < 1$. For the TB structure the splay term in the free energy is zero, and in the case of $K_b = K_t = K$ simple analytical expressions for θ, q and p_0 are obtained, so the free energy is expressed in terms of θ only. The compression energy is defined as $\frac{1}{2}B(\delta q/q)^2$ so the compression modulus is $B = q^2\partial^2 F/\partial\theta^2(\partial\theta/\partial q)^2$. One finds $\cos(2\theta) = \frac{1}{4}\left(c + \sqrt{8c + c^2}\right)$, $q = \frac{1}{2}\sqrt{-3c + \sqrt{8c + c^2}}\sqrt{\frac{\lambda^2}{K\kappa}}$ and

$$
B = Kq^2\frac{(c - \cos^3 2\theta)(\cos 2\theta - c)}{\cos^3 2\theta}. \tag{4}
$$

Taking $q = 2\pi/8\text{nm}$ (the value measured for CB7CB), $K \sim 1$ pN and the heliconical angle deep in the TB phase $\theta = 30$ deg [26] we find $c = 0.33$ and $B \sim 10^5$ Pa, which is by an order of magnitude lower than the measured value [9]. Larger values of K will give larger values of B, but to obtain the measured value of B (≈ 5 MPa) K should be by at least an order of magnitude larger. Relaxing the one constant approximation we do not obtain a qualitatively different result for B. We are not aware of measurements of the elastic constants in the N_{TB} phase, but the model itself gives renormalization of the elastic constants in the N_{TB} phase. In eq. (4) $K\left(c - \cos^3 2\theta\right)(\cos 2\theta - c)/\cos^3 2\theta$ can be considered as an effective elastic constant (K_{eff}) and at the parameters given above $K_{eff} = 0.3K$. In addition, we point out once again, that the compression modulus measurements were made using a not-perfectly aligned sample, so the actual value of B is expected to be even larger.

The expression for B for achiral modulated nematic has already been calculated in the case of small θ, where $B \sim K_tq^2\theta^4$ was found [27]. At $\theta = 16$ deg, $K_t \sim 1$ pN and $q = 2\pi/(10.5$ nm$)$ they find B of the order of kPa, which is the same result that we find, if we plug this cone angle and pitch into Eq. (4). While in [27] the authors find this value in good agreement with the value of B estimated from the rheological measurements, such a low value is several orders of magnitude lower than the value of B reported in [9]. The recent coarse-grained elastic model [28, 29] also predicts a rather low B.

Therefore, in the achiral system the problem with the magnitude of B predicted by the flexoelectric model already pops up. Next, we show that in the chiral system the problem becomes acute.

B. Chiral case

To describe structures of modulated nematics made of chiral molecules, biaxiality has to be considered [24]. In the biaxial model the free energy density is expressed in terms of three mutually perpendicular unit vectors $\mathbf{n}$, $\mathbf{l}$, and $\mathbf{m}$, with $\mathbf{n}$ pointing along the average local orientation of the long molecular axes, $\mathbf{l}$ along the molecular kink

(also the local polarization direction [24]) and $\mathbf{m} = \mathbf{n} \times \mathbf{l}$.

We use the expression for the free energy density for the nematic phase with the orthorhombic symmetry derived in [30]. The energy can be minimized by assuming the TB helix axis either in the same direction as the helix axis in the higher-temperature N* phase or in the direction perpendicular to it. Since the modulated nematic phase is found to be optically positive uniaxial at any temperature, while the chiral nematic phase is optically negative uniaxial, the helix axis in the TB phase has to be in the direction perpendicular to the helix axis in the N* phase. This consideration is further supported by two observations [8]: (1) The helical pitch tends to diverge when approaching the N_{TB} phase in the N* phase; (2) the helical axis is normal to cell surfaces as confirmed by the selective reflection in the N* state, whereas the modulated structure is formed along cell surfaces as evidenced by optically modulated structures in the N_{TB} phase.

We use the same ansatz for the TB structure as before (eqs.(2) and (3)) and in addition $\mathbf{p} = \mathbf{l}$. Out of 12 elastic deformations only 5 are different from zero and the expression for the free energy density derived in [30] becomes:

$$
\begin{aligned}
f = {} & k_1 \mathbf{l} \cdot (\nabla \times \mathbf{l}) + k_2 \mathbf{m} \cdot (\nabla \times \mathbf{m}) + k_3 \mathbf{n} \cdot (\nabla \times \mathbf{n}) \\
& + \frac{1}{2} K_4 [\mathbf{l} \cdot (\nabla \times \mathbf{l})]^2 + \frac{1}{2} K_5 [\mathbf{m} \cdot (\nabla \times \mathbf{m})]^2 \\
& + \frac{1}{2} K_6 [\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 + \frac{1}{2} K_7 [\mathbf{n} \cdot (\nabla \times \mathbf{m})]^2 \\
& + \frac{1}{2} K_{10} [\mathbf{m} \cdot (\nabla \times \mathbf{n})]^2 - \lambda p_0 \mathbf{l} \cdot [\mathbf{n} \times (\nabla \times \mathbf{n})] + \frac{1}{2} \mu p_0^2 ,
\end{aligned}
\tag{5}
$$

where k_i, $i = 1, 2, 3$ are chiral parameters and K_i, $i = 4, 5, 6, 7, 10$, are elastic constants (the same numbering is used as in [30]). We further simplify the free energy density expression by using a two-constant approximation (we checked a general solution as well, but the result is qualitatively the same). The elastic constants in front of the gradient terms in $\mathbf{l}$ and $\mathbf{m}$ scale with the biaxial order parameter and are expected to be much lower than the elastic constants in front of the gradient term of the director $\mathbf{n}$. So we set $K_6 = K_{10} = K$ and $K_4 = K_5 = K_7 = \beta K$, where $\beta << 1$ and obtain the following expression for the free energy density:

$$
\begin{aligned}
f = {} & \frac{q}{2} \left[(2k_1 + k_2 + k_3) + (k_2 - k_3) \cos 2\theta \right] + \frac{K}{4} q^2 (1 + 3\beta) \\
& + \frac{K}{4} q^2 (\beta - 1) \cos 2\theta + \frac{1}{2} \mu p_0^2 - \frac{1}{2} \lambda p_0 q \sin 2\theta .
\end{aligned}
\tag{6}
$$

Minimization of the free energy gives that the TB phase is stable if μ is lower that the critical value μ_0

$$
\mu_0 = \frac{k_{13} + k_{23}}{k_{13}(1 - \beta) + k_{23}(1 + 3\beta) - 4\beta} \frac{\lambda^2}{K} ,
\tag{7}
$$

where $k_{13} = k_1/k_3$ and $k_{23} = k_2/k_3$. Expressing again μ with the temperature dependent parameter c as $\mu = c\mu_0$ the equilibrium values of θ, p_0, q and B can be expressed

in terms of c, the chiral parameters and elastic constants:

$$
\cos(2\theta) = \mathcal{C} (k_{13}, k_{23}, \beta, c) ,
\tag{8}
$$

$$
q = \frac{k_3}{K} \mathcal{Q} (k_{13}, k_{23}, \beta, c) ,
\tag{9}
$$

$$
p_0 = \frac{\lambda q \sin 2\theta}{2c\mu_0} ,
\tag{10}
$$

$$
B = Kq^2 \mathcal{B} (k_{13}, k_{23}, \beta, c) ,
\tag{11}
$$

where $\mathcal{C}$, $\mathcal{Q}$, $\mathcal{B}$ are analytical, but very complex expressions depending on k_{13}, k_{23}, β and c. Here we give only graphs of θ, q and $K_{eff} = K\mathcal{B}$ as a function of c at a chosen (unphysical) set of parameters k_{13}, k_{23} and β, which give the same orders of magnitude of θ, q and B as experimentally measured (see Fig. 2).

For the uniaxial N* with the helix in the direction perpendicular to the long molecular axis it is straightforward to find: $B^* = Kq^{*2}$ and $q^* = k_3/K$. We thus see, that $\mathcal{Q}$ presents a factor by which the helical pitch is changed and $\mathcal{B}$ gives renormalization of the elastic constant K. From Fig. 2 we see, that one can find such values of k_{13}, k_{23} and β that the pitch in the N_{TB} phase is approximately 10-times lower than in the N* phase and the effective elastic constant in N_{TB} is two orders of magnitude larger than in the N* phase. Such values can be obtained only by a fine tuning of k_1 and k_2 which should both be comparable to k_3, but, in fact, they both scale with β. Since the modulated structure is quite universal, it is highly unlikely that it would be a result of some very special values of chiral parameters and restricted to a small region of rather unphysical values.

We thus propose that one should search for a structural model beyond the heliconical structure described by the flexoelectric elastic model and in the next section we give one possibility which is consistent with the current experimental evidence.

III. STRUCTURAL MODEL OF THE N_{TB} PHASE

The flexoelectric model ignores short range positional order of the nematic phase. The NMR studies [31, 32] suggested that short range smectic clusters exist in the N_{TB} phase. It is also known that for many bent-core materials such smectic fluctuations (cybotactic groups) persist in the nematic phase through a wide temperature range, and thus might influence the elastic energy of the nematic phase profoundly [33]. It should also be noticed that in the homologue series of dimers molecules with a longer spacer have strong tendency to form antiphase (modulated smectic) structures [9]. Doping the N_{TB} phase with chiral compounds seems to have a non-monotonic influence on the chiral pitch [9].

Taking into account all these facts, we have to search for a short helical structure that is driven by steric interactions rather than elastic constant anomaly or flexoelectricity. For the modulated nematic structure with high

B we propose a structure built of smectic layer fragments with an anticlinic tilt at the layer boundaries along the layer normal (Fig. 3a). The neighboring layer fragments are shifted by half molecular length and mutually rotated by 90 degrees about the layer normal. Such arrangement minimizes the excluded volume between the neighboring clusters. The proposed local structure is additionally stabilized if molecules adopt a conformation in which two mesogenic units are not co-planar but form bent-propeller and each unit by itself forms a bent-propeller (Fig. 3b) [33]. A slight imbalance of chiral conformations over planar conformations was proven for some dimer mosogens [34, 35] also forming the N_{TB} phase [36]. Since it is experimentally observed that the position of the x-ray signals does not change at the N* - N_{TB} transition, only the width of the signals slightly narrows, we suggests that the transition occurs by hindering the rotation of molecules in the clusters. Lowering the temperature within the N_{TB} phase lowers the birefringence of the phase [26], which indicates the increase of the tilt of molecules with respect to the local layer normal. The arrangement of the intercalated fragments in the N_{TB} phase produces the C4 symmetry and therefore the helical pitch with two molecular distances. For a chiral additive or for a system made of enantiopure dimers the additional interactions will modify the short range pitch resulting in two periodicities: the one coming from steric interactions is incommensurate with the one resulting from chiral interactions thus larger pitches can be obtained in such systems, similarly as for the SmC phases with a 3 and 4 layer "basic" crystallographic unit structures and much longer 'optical' helix. For such structures a huge value of B is a manifestation of the internal short helical structure.

IV. CONCLUSIONS

To conclude, we have shown that the flexoelectric model cannot describe the large compression mudulus of achiral and chiral TB nematics, even if biaxial order parameter is included and a one-constant approximation is abandoned. In the chiral case the experimentally observed order of magnitude of the compression modulus is obtained theoretically only at a very specific range of the biaxial chiral parameters. This result, together with some further experimental evidence from the NMR and X-ray studies, lead us to conclude that internal structure of nematic TB is driven mainly by steric interactions. We suggest that this short-range modulated smectic structure is the driving force for the formation of the short-pitch helix also in the TB nematic phase. Qualitatively such weakly temperature dependent smectic fluctuations may significantly affect the elastic properties. Flexoelectric interactions seem to be only a consequence of the local polarization due to the short helical packing of molecules and drive the reduction of the helical pitch in the chiral TB nematic phase compared to the chiral

FIG. 1. *(Color online)* The twist-bend nematic structure is characterized by the heliconical angle θ and the wavenumber of the helical modulation q, which is related to the helical pitch as $2\pi/q$. The local direction of the long molecular axis is given by the director $\mathbf{n}$ (blue arrow) and the local direction of polarization by the unit vector $\mathbf{p}$ (red arrows), which is perpendicular to $\mathbf{n}$. The direction of the twist-bend modulation is along the x-direction.

FIG. 2. The effective elastic constant (K_{eff}) in the chiral N_{TB} as a function of the temperature dependent parameter c. The insets: The ratio between the helix wavevector in the chiral N_{TB} (q) and N* phase (q^*) and the helix cone angle (θ) as a function of c. Parameter values: $k_{13} = 0.82$, $k_{23} = 0.87$ and $\beta = 0.1$.

pitch in the higher-temperature N* phase.

FIG. 3. *(Color online)* a) A smectic layer fragment (a cybotactic group) as a basic unit of the modulated nematic phase. b) Excluded volume is additionally reduced if mesogenic units have a shape of a bent-propeller.

[1] G. Pelzl, A. Eremin, S. Diele, H. Kresse, and W. Weisflog, *J. Mater. Chem.* **12**, 2591 (2002).

[2] M. Cestari, S. Diez-Berart, D. A. Dunmur, A. Ferrarini, M. R. de la Fuente, D. J. B. Jackson, D. O. Lopez, G. R. Luckhurst, M. A. Perez-Jubindo, R. M. Richardson, J. Salud, B. A. Timimi, and H. Zimmermann, *Phys. Rev. E* **84**, 031704 (2011).

[3] C. Meyer, G. R. Luckhurst, and I. Dozov, *Phys. Rev. Lett.* **111**, 067801 (2013).

[4] V. Borshch, Y.-Ki Kim, J. Xiang, M. Gao, A. Jakli, V. Panov, J. Vij, C. Imrie, M.-G. Tamba, G. Mehl, O. D Lavrentovich, *Nat. Commun.* **4**, 2635 (2013).

[5] D. Chen, J. H. Porada, J. B. Hooper, A. Klittnick, Y. Shen, M. R. Tuchband, E. Korblova, D. Bedrov, D. M. Walba, M. A. Glaser, J. E. Maclennan, and N. A. Clark, *Proc. Natl. Acad. Sci. USA* **110**, 15931 (2013).

[6] E. Gorecka, M. Salamonczyk, A. Zep, D. Pociecha, C. Welch, Z. Ahmed, and G. H. Mehl, *Liq. Cryst.* **42**, 1 (2015).

[7] D. Chen, M.Nakata, R. Shao, M. R. Tuchband, M. Shuai, U. Baumeister, W. Weissflog, D. M. Walba, M. A. Glaser, J. E. Maclennan, and N. A. Clark, *Phys. Rev. E* **89**, 022506 (2014).

[8] A. Zep, S. Aya, K. Aihara, K. Ema, D. Pociecha, K. Madrak, P. Bernatowicz, H. Takezoe, and E. Gorecka, *J. Mater. Chem. C* **1**, 46 (2013).

[9] E. Gorecka, N. Vaupotič, A. Zep, D. Pociecha, J. Yoshioka, J. Yamamoto and H. Takezoe, *Angew. Chem. Int. Ed.* **54**, 10155 (2015).

[10] R. B. Meyer, in *Structural Problems in Liquid Crystal Physics*, edited by R. Balian and G. Weil, Les Houches Summer School in Theoretical Physics, 1973. Molecular Fluids (Gordon and Breach, New York, 1976), pp. 273373.

[11] I. Dozov, *Europhys. Lett.* **56**, 274 (2001).

[12] M. R. Dodge, C. Rosenblatt, R. G. Petschek, M. E. Neubert, and M. E. Walsh, *Phys. Rev. E* **62**, 5056 (2000).

[13] B. Kundu, R. Pratibha, and N. V. Madhusudana, *Phys. Rev. Lett.* **99**, 247802 (2007).

[14] P. Sathyanarayana, M. Mathew, Q. Li, V. S. S. Sastry, B. Kundu, K. V. Le, H. Takezoe, and S. Dhara, *Phys. Rev. E* **81**, 010702 (2010).

[15] P. Sathyanarayana, P. Tadapatri, U. S. Hiremath, C. V. Yelamaggad, and K. S. Krishnamurthy, *J. Phys. Chem.* **114**, 1745 (2010).

[16] P. Sathyanarayana, B. K. Sadashiva, and S. Dhara, *Soft Matter* **7**, 8556 (2011).

[17] V. S. R. Jampani, M. Škarabot, I. Muševič, K. V. Le, H. Takezoe, and S. Dhara, *Phys. Rev. E* **85**, 011702 (2012).

[18] S. Kaur, J. Addis, C. Greco, A. Ferrarini, V. Görtz, J. W. Goodby, and H. F. Gleeson, *Phys. Rev. E* **86**, 041703 (2012).

[19] N. Avci, V. Borshch, D. D. Sarkar, R. Deb, G. Venkatesh, T. Turiv, S. V. Shiyanovskii, N. V. S. Rao, and O. D. Lavrentovich, *Soft Matter* **9**, 1066 (2013).

[20] M. Majumdar, P. Salamon, A. Jákli, J. T. Gleeson, and S. Sprunt, *Phys. Rev. E* **83**, 031701 (2011).

[21] K. Adlem, M. Čopič, G. R. Luckhurst, A. Mertelj, O. Parri, R. M. Richardson, B. D. Snow, B. A. Timimi, R. P. Tuffin, and D. Wilkes, *Phys. Rev. E* **88**, 022503 (2013).

[22] S. M. Shamid, S. Dhakal, and J. V. Selinger, *Phys. Rev. E* **87**, 052503 (2013).

[23] R. Memmer, *Liq. Cryst.* **29**, 483 (2002).

[24] N. Vaupotič, Mojca Čepič, M. A. Osipov, and E. Gorecka, *Phys. Rev. E* **89**, 030501(R) (2014).

[25] B. V. Derjaguin, V. M. Muller, and Y. P. Toporov, *J. Colloid Interface Sci.* **53**, 314 (1975).

[26] C. Meyer, G. R. Luckhurst, and I. Dozov, *J. Mater. Chem. C* **3**, 318 (2015).

[27] S. M. Salili, C. Kim, S. Sprunt, J. T. Gleeson, O. Parri, and A. Jákli, *RSC Adv.* **4**, 57419 (2014).

[28] C. Meyer and I. Dozov, *Soft Matter* **12**, 574 (2015).

[29] Z. Parsouzi et al, arXiv:1512.03102v1 [cond-mat.soft] 9 Dec 2015

[30] S. Stallinga and G. Vertogen, *Phys. Rev. E* **49**, 1483 (1994).

[31] A. Hoffman, A. G. Vanakaras, A. Kohlmeier, G. H. Mehl, D. J. Photinos, *Soft Matter* **11**, 850 (2015).

[32] T. Ivšič, M. Vinkovič, U. Baumeister, A. Mikleuševiča, and A. Lesac, *Soft Matter* **10**, 9334 (2015).

[33] S. Aya, S. Ogino, Y. Hayashi, K. Okano, D. Pociecha, K. V. Le, F. Araoka, S. Kawauchi, E. Gorecka, N. Vaupotič, H. Takezoe, and K. Ishikawa, *Phys. Rev. E* **90**, 042506 (2014).

[34] H. Kurosu, M. Kawasaki, M. Hirose, M. Yamada, S. Kang, J. Thisayukta, M. Sone, H. Takezoe, and J. Watanabe, *J. Phys. Chem. A* **108**, 4674 (2004).

[35] M. Zennyoji, Y. Takanishi, K. Ishikawa, J. Thisayukta, J. Watanabe, and H. Takezoe, *Mol. Cryst. Liq. Cryst.* **366**, 693 (2001).

[36] J. W. Emsley, M. Lelli, A. Lesage, G. R. Luckhurst, *J. Phys. Chem. B* **117**, 6547 (2013).
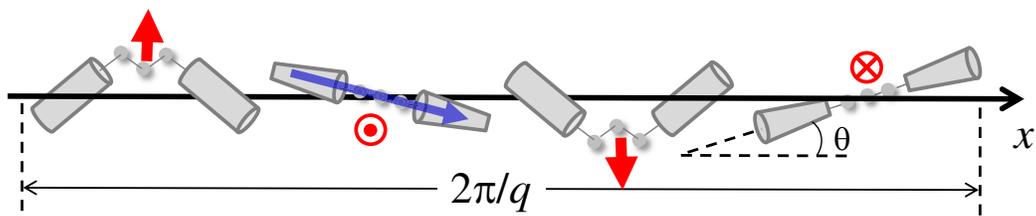
Figure 1   25Jan2016

Figure 2   25Jan2016

(a)

(b)

Figure 3ab   25Jan2016