

Flexoelectricity induced spatially modulated phases in ferroics and liquid crystals
(Author review)

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Abstract

In the review we briefly analyze the state-of-art in the theory of flexoelectric phenomena and analyze how significantly the flexoelectric coupling can change the polar order parameter distribution in different ferroics and liquid crystals. The special attention is paid to the appearance of the spatially modulated phases induced by the flexocoupling in condensed and soft matter. Results of theoretical modeling performed in the framework of the Landau-Ginzburg-Devonshire formalism revealed that the general feature, inherent to both ferroics and liquid crystals, is the appearance of the spatially-modulated phases is taking place with increasing of the flexocoupling strength. We'd like to underline that theoretical and experimental study of flexoelectricity and related phenomena in nanosized and bulk ferroics, liquid crystals and related materials are very important for their advanced applications in nanoelectronics, memory devices and liquid crystals displays.

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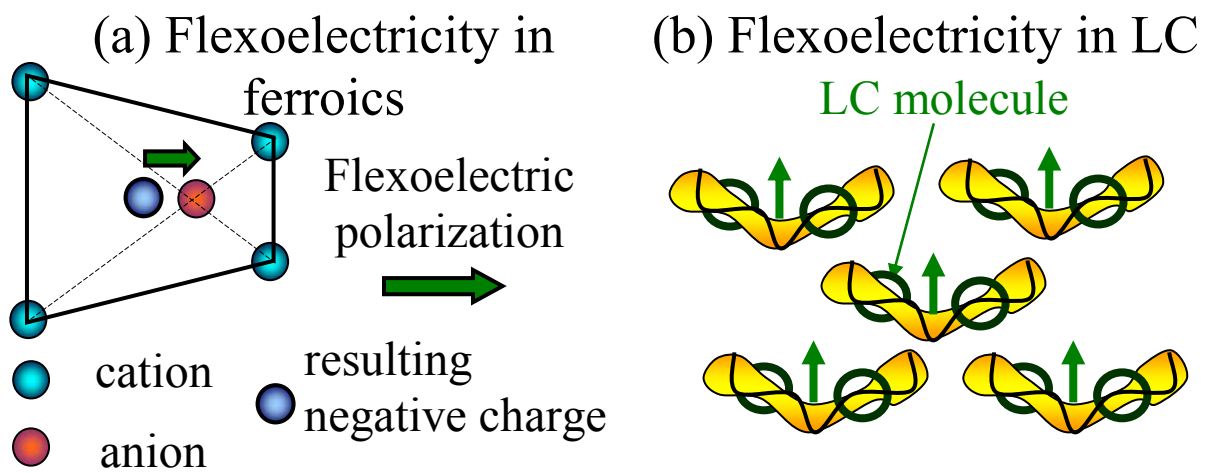
Highlights

- ▶ Analyzing the state-of-art in the theory of flexoelectric phenomena;
- ▶ Flexocoupling impact on the polar order in ferroics and liquid crystals;
- ▶ Appearance of the spatially modulated phases induced by flexocoupling.

Keywords

Ferroic; Flexoelectricity; Liquid crystal; Flexocoupling tensor; Flexoeffect; Bended molecule.

Graphical Abstract



1. Flexoelectric effect in ferroics

The flexoelectric effect, first predicted theoretically by Mashkevich and Tolpygo [1] in 1957, exists in any matter (condensed or soft one), making the effect universal [2, 3, 4, 5, 6]. The static *flexoelectric effect* is an electric polarization generated in solids by a strain gradient and vice versa, whereas broadly known piezoelectricity assume homogeneous strain conditions. The induced strain is linearly proportional to the polarization gradient and, and the proportionality coefficients f , which are the components of the flexocoupling tensor, are fundamentally quite small, $f \sim e/a$, where e and a are respectively electronic charge and lattice constant [7]. Rigorously, the direct and converse static flexoelectric coupling constants f_{ijkl} were described with a fourth-rank tensor, as [2-6]:

$$P_i^{flexo} = f_{ijkl} \frac{\partial u_{jk}}{\partial x_l} \quad u_{ij} = f_{ijkl} \frac{\partial P_k^{flexo}}{\partial x_l} . \quad (1)$$

in these expressions u_{jk} and P_i^{flexo} are the tensor strain and polarization vector components, respectively. The physical picture of the flexoelectric effect in solids is shown in **Figs. 1(a)-(c)**. When the geometric centers of positive and negative charges coincide, the net dipole moment of the unit cell is zero, and corresponding unstrained 2D structure of elementary charges is shown in **Fig.1(a)**. When each unit cell is uniformly tensiled and the tension gradually varies from one cell to another, the cations are displaced from the centre of the deformed unit cell and the strain gradient induces an uncompensated dipole moment via the flexocoupling mechanism [**Fig.1(b)**]. The inhomogeneous deformation of the unit cell also produces a net dipole moment via the flexocoupling effect [**Fig.1(c)**].

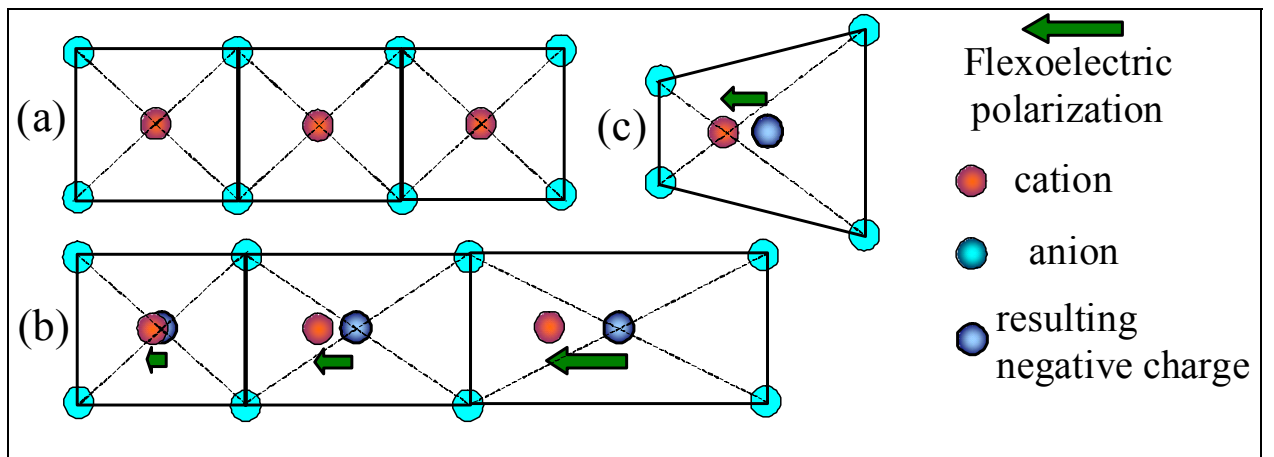


Figure 1. Origin of flexoelectric effect in solids. (a) Unstrained 2D structure of elementary charges with zero net dipole moment. **(b)** Each unit cell is uniformly tensiled, but the tension gradually varies from one cell to another. An uncompensated dipole moment appears via the flexocoupling mechanism. **(c)** An inhomogeneous deformation of the unit cell produces a net dipole moment via the flexocoupling effect. (Adapted from the papers [5, 11-13])

Unlike piezoelectricity, which exists only in noncentrosymmetric systems of 20 point groups, flexoelectricity occurs in all 32 crystalline point groups, because the strain gradients break inversion symmetry. Owing to the universal nature, flexoelectricity permanently attracts broad scientific interest, but its application potential in macro-materials is fundamentally limited due to the small strength f .

The flexoelectricity impact is of great importance in nanosized ferroics [8], for which the pronounced elastic strain and stress gradients are omnipresent near the surfaces, in thin films [9, 10, 11], at the topological defects, such as domain walls, and near the interfaces [10, 12, 13, 14]. Owing to the surface and interface effects, the flexoelectric effect appears spontaneously near the surface of thin films and nanoparticles [15]; everywhere, where the electric polarization distribution is inhomogeneous. Notably, that the influence of flexoelectricity is important not only in thin ferroic films and nanoparticles, but also in their micro- and nanograined ceramics [16, 17], where it should become competitive with surface piezoelectricity [18]. Despite the great importance of flexoelectricity, its tensorial components strength, estimated by Kogan [7] in early 1963, remained poorly known for most of ferroics [19], except for the experimental measurements [20, 21, 22] and *ab initio* calculations [23, 24] of some components for ferroelectric perovskites, and fundamental limits on the coefficients upper bonds [25].

The direct and converse static flexoelectric effects, which lead to the appearance of polarization due to the strain gradient and vice versa [1], exist in a ferroic of arbitrary symmetry [8, 5, 6].

Corresponding tensorial Lifshitz invariant $\frac{f_{kl ij}}{2} \left(P_i \frac{\partial u_{kl}}{\partial x_j} - u_{kl} \frac{\partial P_i}{\partial x_j} \right)$ should be included to the free energy functional of all those ferroics, for which the polarization component(s) P_i is a primary order parameter. Using the way it was shown that the flexocoupling term in the form of Lifshitz invariant can induce thermodynamically stable incommensurate spatially modulated phase (**SMP**) in the temperature range between the disordered parent phase (**PP**) and long-range ordered homogeneous phase (**HP**) in many ferroics [26, 27, 28, 29]. Note that the static flexoelectric effect is omnipresent from the symmetry theory considerations, and the earliest [1] and recent [23, 24, 30] microscopic calculations give nonzero values of flexoelectric coefficients $f_{kl ij}$. Also it becomes possible to define the static flexoelectric coefficients from direct experiments [21, 22, 31], as well as from the fitting of soft phonon spectra in ferroelectrics (see e.g. [32] and refs. therein).

Notably, that chirality, being the property of an object to be incompatible with its mirror image, can be strongly affected by the flexoelectric coupling. In particular, bichiral structure of ferroelectric domain walls can be driven by flexoelectric coupling [33] and chiral-achiral phase transitions at the walls becomes possible [34].

From considerations of the symmetry theory stating that all terms and invariants, which existence does not violate the symmetry of the system, are allowed, Kvasov and Tagantsev et al [35] predicted the existence of a cross-term in the kinetic energy, $M_{ij} \frac{\partial P_i}{\partial t} \frac{\partial U_j}{\partial t}$, and named it dynamic flexoelectric effect (see reviews [3, 4] and refs therein). Here M_{ij} is the strength of dynamic flexoelectric coupling and U_i is elastic displacement. At present the situation with the magnitudes M_{ij} of dynamic flexoeffect is more complex and controversial than for the static one, because there are microscopic theories in which the effect is absent [36]. However, the Stengel result [36] contradicts to Kvasov and Tagantsev result [35], who evaluated the strength of the dynamic flexoelectric effect in SrTiO₃ from microscopic calculations and it appeared comparable to that of the static bulk flexoelectric effect. More discussion of the problem can be found in Refs.[32, 37].

2. Impact of the flexocoupling on phonon spectra and spatially modulated phases in ferroics

Investigation of dynamic characteristics of phase transitions in ferroics, such as their soft phonon spectra, attracts great attention, being the source of valuable information for fundamental physical research and advanced applications [38]. For ferroelectrics the frequency ω_{TO} of transverse optic (**TO**) soft mode depends on temperature T , at that $\omega_{TO}(T_C) = 0$ at transition temperature $T = T_C$ [39].

Basic experimental methods, which contain information about the soft modes and spatial modulation of the order parameter in ferroics (such as antiferroelectrics, proper and incipient ferroelectrics) are dielectric measurements [40], inelastic neutron scattering [39, 41, 42, 43, 44, 45], X-ray [46, 26, 47, 48], Raman [49] and Brillouin [46, 47, 50, 51, 52, 53] scatterings and ultrasonic pulse-echo method [50, 52] allowing hypersound spectroscopic measurements. Scattering experiments proved that not only the TO mode softens substantially with decreasing temperature to freeze out at T_C in ferroics (such as ferroelectric perovskites), but also finite wave vector anomalies appear in the transverse acoustic (**TA**) mode for structural phase transitions [54, 55, 56].

Using the Landau-Ginzburg-Devonshire (**LGD**) theory [57, 58, 59], Morozovska et al. derived analytical expressions for the soft phonon modes frequency $\omega(k)$ dependence on the wave vector k and examined the conditions of the soft acoustic TA-modes appearance in ferroelectrics depending on the magnitude of the flexoelectric coefficient f and temperature T . If the magnitude of the flexoelectric coefficient f is equal to the temperature-dependent critical value $f_{cr}(T)$ at the temperature $T = T_{IC}$, $|f| = f_{cr}(T_{IC})$, then the TA-mode frequency tends to zero at $k \rightarrow k_0^{cr}$ according to the linear law $\omega(k \rightarrow k_0^{cr}) \sim |k - k_0^{cr}|$ and, simultaneously, the ferroelectric polarization becomes spatially modulated.

When the magnitude of the flexocoefficient is more than the critical value $|f| > f_{cr}(T)$ in a temperature range $T_C < T < T_{IC}$ lower than Curie temperature T_C , corresponding to the incommensurate phase, the TA-mode becomes zero for two wave vectors $k = k_{1,2}^{cr}$ according to the square root law, $\omega(k \rightarrow k_{1,2}^{cr}) \sim \sqrt{|k_{1,2}^{cr} - k|}$, and does not exist in the range of wave vectors $k_1^{cr} < k < k_2^{cr}$, where the incommensurate modulation exists. At fixed flexocoefficient f the transition into the incommensurate phase can appear at the temperature T_{IC} that depends on f . In addition we predicted the appearance of the "rippled" flexocoupling-induced incommensurate phase in the ferroics with initially commensurate phases only. The available experimental data on hypersound velocity in the solid solutions $\text{Sn}_2\text{P}_2(\text{S,Se})_6$ [50] and neutron scattering in organic ferroelectric $(\text{CH}_3)_3\text{NCH}_2\text{COO}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ [44] are in a semi-quantitative agreement with the theoretical results [57-59]. For improvement and for quantification of the theory, it is necessary to measure the frequency dependence of the TA-modes in a uniaxial ferroelectric with a spatially modulated phase in the temperature interval near its appearance.

3. General formulation of Landau-Ginzburg-Devonshire formalism

LGD expansion of bulk (F_V) part of Helmholtz free energy F on the order parameter $\boldsymbol{\eta}$ and strain tensor components u_{ij} has the form:

$$F_V = \int_V d^3r \left(\begin{aligned} & \frac{a_{ij}(T)}{2} \eta_i \eta_j + \frac{a_{ijkl}}{4} \eta_i \eta_j \eta_k \eta_l + \frac{a_{ijklmn}}{6} \eta_i \eta_j \eta_k \eta_l \eta_m \eta_n - \eta_i E_i \\ & + \frac{g_{ijkl}}{2} \left(\frac{\partial \eta_i}{\partial x_j} \frac{\partial \eta_k}{\partial x_l} \right) + \frac{w_{ijkl}}{2} \left(\frac{\partial^2 \eta_i}{\partial x_j^2} \frac{\partial^2 \eta_k}{\partial x_l^2} \right) + \frac{h_{ijk}}{2} \eta_i^2 \left(\frac{\partial \eta_j}{\partial x_k} \right)^2 \\ & - \frac{f_{ijkl}}{2} \left(\eta_k \frac{\partial u_{ij}}{\partial x_l} - u_{ij} \frac{\partial \eta_k}{\partial x_l} \right) - q_{ijkl} u_{ij} \eta_k \eta_l + \frac{c_{ijkl}}{2} u_{ij} u_{kl} + \frac{v_{ijklmn}}{2} \left(\frac{\partial u_{ij}}{\partial x_m} \frac{\partial u_{kl}}{\partial x_n} \right) \end{aligned} \right) \quad (2a)$$

Coefficients $a_{ij}(T)$ explicitly depend on temperature T ; a_{ijkl} is regarded temperature independent, a_{ijklmn} is a temperature independent and positively defined. Constants g_{ijkl} and v_{ijklmn} determine magnitude of the gradient energy. Higher gradient tensors w_{ijkl} and h_{ijk} are positively defined, q_{ijkl} is the bulk striction coefficients; c_{ijkl} are components of elastic stiffness tensor [60]; f_{ijkl} are the components of flexocoupling tensor. In fact, only the Lifshitz invariant $\frac{f_{ijkl}}{2} \left(\eta_k \frac{\partial u_{ij}}{\partial x_l} - u_{ij} \frac{\partial \eta_k}{\partial x_l} \right)$ is relevant for the bulk contribution due to the surface energy presence in the spatially confined ferroics. The gradient terms like $v_{ijklmn} \left(\frac{\partial u_{ij}}{\partial x_k} \right) \left(\frac{\partial u_{lm}}{\partial x_n} \right)$ are responsible for the stable smooth distribution of

the order parameter at nonzero strain gradients, since the presence of Lifshitz invariant essentially changes the stability conditions [61]. E_i is the components of the field conjugated with order parameter component η_i . The field is a sum of external and internal one.

Lagrange function is $L = \int_t dt (F_V - K_V)$, where the free energy F_V is given by Eq.(2a), and

kinetic energy K_V is given by expression

$$K_V = \int_V d^3r \left(\frac{\mu}{2} \left(\frac{\partial \eta_i}{\partial t} \right)^2 + M_{ij} \frac{\partial \eta_i}{\partial t} \frac{\partial U_j}{\partial t} + \frac{\rho}{2} \left(\frac{\partial U_i}{\partial t} \right)^2 \right), \quad (2b)$$

The kinetic energy includes the dynamic flexocoupling term, $M_{ij} \frac{\partial \eta_i}{\partial t} \frac{\partial U_j}{\partial t}$, relating the order parameter η_i and elastic displacement U_i . Its tensorial strength is M_{ij} . ρ is the density of a ferroic.

The strain is $u_{ij} = \frac{1}{2} \left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right)$. Dynamic equations of state have the form of Euler-Lagrange equations for the order parameters:

$$\frac{\delta L}{\delta \eta_i} = 0, \quad \frac{\delta L}{\delta U_i} = 0. \quad (3)$$

4. Analytical solutions for ferroics with commensurate and incommensurate phases

Thermodynamic analyses of analytical solutions for commensurate and incommensurate ferroics basing on Eqs.(2) can be simplified keeping in mind that the contribution of the terms, which magnitude is proportional to the diagonal flexocoupling constants f_{iii} used to be much smaller than those proportional to the nondiagonal ones, f_{ijj} ($i \neq j$), due to the strong depolarization effect for diagonal modes [6, 57]. Keeping in mind that we are looking for large enough flexoeffect contribution ($|f| > f_{cr}(T)$), we are going to consider the nondiagonal terms ($\sim f_{ijj}$) only, and so the Lifshitz

invariant acquires the form $\frac{f_{ijj}}{2} \left(\eta_i \frac{\partial u_{ji}}{\partial x_j} - u_{ji} \frac{\partial \eta_i}{\partial x_j} \right)$. It what follows let us denote that $\eta_i = \eta$, $f_{ijj} \equiv f$

and $u_{ij} \equiv u$ [58, 59]. Thus Eq.(2a) can rewritten in the form [58, 59]:

$$F_V = \int_L dx \left(\frac{\alpha(T)}{2} \eta^2 + \frac{\beta}{4} \eta^4 + \frac{\gamma}{4} \eta^6 - \eta E + \frac{g}{2} \left(\frac{\partial \eta}{\partial x} \right)^2 + \frac{w}{2} \left(\frac{\partial^2 \eta}{\partial x^2} \right)^2 \right. \\ \left. + \frac{h}{2} \eta^2 \left(\frac{\partial \eta}{\partial x} \right)^2 - \frac{f}{2} \left(\eta \frac{\partial u}{\partial x} - u \frac{\partial \eta}{\partial x} \right) - qu \eta^2 + \frac{c}{2} u^2 + \frac{v}{2} \left(\frac{\partial u}{\partial x} \right)^2 \right) \quad (4)$$

For the sake of brevity we omitted all subscripts in the tensors in Eq.(4) (compare with Eq.(2a)). Coefficient $\alpha(T)$ explicitly depends on temperature T ; β is regarded temperature independent, $\gamma \geq 0$

is a temperature independent. Constants g and $v \geq 0$ determine magnitude of the gradient energy. Higher gradient tensors $w \geq 0$ and $h \geq 0$ are positively defined, q is the bulk striction constant, c is a component of elastic stiffness tensor

Note that the inclusion of nonlinear gradient term $\frac{h}{2} \eta^2 \left(\frac{\partial \eta}{\partial x} \right)^2$ in Eq.(4) is allowed by the symmetry. However the consideration of this term essentially complicates the analytical expressions we derived below and therefore we refer the question to further studies by putting $h=0$.

Thermodynamic equations of state obtained from the variation of the free energy (4) on order parameter η and strain u have the form [58]:

$$\alpha \eta + \beta \eta^3 + \gamma \eta^5 - g \frac{\partial^2 \eta}{\partial x^2} + w \frac{\partial^4 \eta}{\partial x^4} - \delta E - f \frac{\partial u}{\partial x} - 2q u \eta = 0, \quad (5a)$$

$$c u - v \frac{\partial^2 u}{\partial x^2} + f \frac{\partial \eta}{\partial x} - q \eta^2 = 0. \quad (5b)$$

The solution of these equations can be found after their linearization in the vicinity of spontaneous values η_s and u_s , namely $\eta = \eta_s + \delta \eta$ and $u = u_s + \delta u$. Then the Fourier expansion of the perturbations in k-domain yields to $\delta \eta = \int dk \exp(ikx) \tilde{\eta}$ and $\delta u = \int dk \exp(ikx) \tilde{u}$. Perturbation field has

a conventional form $\delta E = \int dk \exp(ikx) \tilde{E}$. In a high temperature parent phase $\alpha > 0$, $\eta_s = 0$, $u_s = 0$.

In a low temperature ordered phase, where $\alpha < 0$, $\eta_s \neq 0$, $u_s \neq 0$, the spontaneous strain and order parameter values can be determined from Eqs.(5) at zero gradients, namely

$$\alpha \eta_s + \beta \eta_s^3 + \gamma \eta_s^5 - 2q u_s \eta_s = 0 \quad \text{and} \quad c u_s - q \eta_s^2 = 0. \quad \text{In what follows } u_s = \frac{q}{c} \eta_s^2 \quad \text{and}$$

$$\alpha + \beta^* \eta_s^2 + \gamma \eta_s^4 = 0, \quad \text{where the coefficient } \beta^* = \left(\beta - 2 \frac{q^2}{c} \right). \quad \text{So that } \eta_s^2 = \frac{1}{2\gamma} \left(\sqrt{\beta^{*2} - 4\alpha\gamma} - \beta^* \right) \quad \text{for the}$$

first order phase transitions (where $\beta^* < 0, \gamma > 0$) and $\eta_s^2 = -\alpha/\beta^*$ for the second order phase

transitions (where $\beta^* > 0, \gamma = 0$). Note that the condition $c\beta > 2q^2$ should be valid for the second order

phase transitions. The solution of linearized equations (5) can be found after elementary transformations in the following form:

$$\tilde{\eta} = \tilde{\chi}(k) \tilde{E}, \quad \tilde{u} = -\frac{(ifk - 2q\eta_s)}{(c + vk^2)} \tilde{\chi}(k) \tilde{E} \quad (6)$$

The generalized susceptibility (Green function) is introduced here:

$$\tilde{\chi}(k) = \left(\alpha + 3\beta\eta_s^2 + 5\gamma\eta_s^4 - 2qu_s + gk^2 + wk^4 - \frac{4q^2\eta_s^2 + f^2k^2}{c + vk^2} \right)^{-1}. \quad (7)$$

The condition of the spatial modulation appearance with a period k is:

$$\alpha + 3\beta\eta_s^2 + 5\gamma\eta_s^4 - 2qu_s + gk^2 + wk^4 - \frac{4q^2\eta_s^2 + f^2k^2}{c + vk^2} = 0 \quad (8)$$

4.1. Flexocoupling induced SMPs in ferroics with commensurate phases

In a high temperature parent phase of **ferroics with commensurate phases**, for which $g > 0$ and $w = 0$, the values $\alpha > 0$, $\eta_s = 0$, $u_s = 0$. For the case the condition (8) transforms into the equivalent equation $(\alpha + gk^2)(c + vk^2) - f^2k^2 = 0$. Introducing the dimensionless wave vector k^* , flexoelectric coefficient f^* and gradient coefficient v^* as

$$k^* = \sqrt{\frac{2v}{c}}k, \quad f^* = \frac{f}{\sqrt{cg}}, \quad v^* = \frac{\alpha v}{cg}, \quad (9)$$

the solution of Eq.(8) is

$$k_{\pm}^* = \sqrt{f^{*2} - 1 - v^* \pm \sqrt{(f^{*2} - 1 - v^*)^2 - 4v^*}}. \quad (10)$$

Under the condition $f^{*2} \geq 1 + v^*$ the SMP with a minimal and maximal modulation periods, k_+^* and k_-^* , appears. Under the condition $f^{*2} < 1 + v^*$ the static homogeneous state is thermodynamically stable in the parent phase.

In a **low temperature long-range ordered phase of ferroics with commensurate phases**, where $\alpha < 0$, $\eta_s \neq 0$, $u_s \neq 0$, introducing the renormalized positive parameter $\alpha_s = \alpha + \left(3\beta - 2\frac{q^2}{c}\right)\eta_s^2 + 5\gamma\eta_s^4$ in Eq.(8), it reads as $(\alpha_s + gk^2)(c + vk^2) - f^2k^2 - 4q^2\eta_s^2 = 0$. Using the dimensionless wave vector k^* , flexoelectric coefficient f^* , gradient coefficient v^* and electrostriction constant Q_s^2 (introduced similarly to those in Eq.(9))

$$k^* = \sqrt{\frac{2v}{c}}k, \quad f^* = \frac{f}{\sqrt{cg}}, \quad v_s^* = \frac{\alpha_s v}{cg}, \quad Q_s^2 = 4\frac{q^2\eta_s^2}{\alpha_s c}, \quad (11)$$

we get:

$$k_{\pm}^* = \sqrt{f^{*2} - 1 - v_s^* \pm \sqrt{(f^{*2} - 1 - v_s^*)^2 - 4v_s^*(1 - Q_s^2)}}. \quad (12)$$

Under the condition $f^{*2} < 1 + v_s^*$ the static homogeneous state is thermodynamically stable in the parent phase. Under the condition $f^{*2} \geq 1 + v_s^*$ the SMP with a minimal and maximal modulation periods given by expression (12) appears.

4.2. Flexocoupling impact on SMPs periods in ferroics with incommensurate phases

In a high temperature parent phase of **ferroics with incommensurate phases, for which $g < 0$ and $w > 0$** , the values $\alpha > 0$, $\eta_s = 0$, $u_s = 0$, the condition (8) transforms into the equivalent equation is $(\alpha + gk^2 + wk^4)(c + vk^2) - f^2 k^2 = 0$. Introducing the dimensionless wave vector k^* , flexoelectric coefficient f^* , gradient coefficient v^* and electrostriction constant Q_s^2 as:

$$k^* = \sqrt{\frac{2(gv + cw)}{-cg}}k, \quad f^* = \frac{f}{\sqrt{-cg}}, \quad v^* = -\frac{\alpha v}{cg}, \quad w^* = -\frac{cw}{vg} \quad (13)$$

we get the solution:

$$k_{\pm}^* = \sqrt{1 + f^{*2} - v^* \pm \sqrt{(1 + f^{*2} - v^*)^2 - 4v^*(w^* - 1)}}. \quad (14)$$

Assuming that $(gv + cw) > 0$, the static homogeneous state is thermodynamically stable in the parent phase under the condition $f^{*2} < v^* - 1$. Under the condition $f^{*2} \geq v^* - 1$ the SMP phase with a minimal and maximal modulation periods, k_+^* and k_-^* , given by Eq.(14) appears.

In a **low temperature long-range ordered phase of ferroics with incommensurate phases**, where $\alpha < 0$, $\eta_s \neq 0$, $u_s \neq 0$, Eqs.(8) reads $(\alpha_s + gk^2 + wk^4)(c + vk^2) - f^2 k^2 - 4q^2 \eta_s^2 = 0$. Introducing positive dimensionless wave vector k^* , flexoelectric coefficient f^* , gradient coefficients v_s^* and w^* , and electrostriction constant Q_s^2 as

$$k^* = \sqrt{\frac{2(gv + cw)}{-cg}}k, \quad f^* = \frac{f}{\sqrt{-cg}}, \quad v_s^* = -\frac{\alpha_s v}{cg}, \quad w^* = -\frac{cw}{vg}, \quad Q_s^2 = 4 \frac{q^2 \eta_s^2}{\alpha_s c}, \quad (15)$$

we get the expression

$$k_{\pm}^* = \sqrt{1 + f^{*2} - v_s^* \pm \sqrt{(1 + f^{*2} - v_s^*)^2 - 4v_s^*(w^* - 1)(1 - Q_s^2)}}. \quad (16)$$

Under the condition $f^{*2} < v_s^* - 1$ the static homogeneous state is thermodynamically stable in the parent phase. Under the condition $f^{*2} \geq v_s^* - 1$ the SMP phase appears.

Reference values of LDG-expansion coefficients and other parameters introduced in Eqs.(9), (11), (13) have been estimated for ferroics with incommensurate and commensurate phases in Ref.[58]. Namely the parameters $\alpha_s = (0 - 2) \times 10^3 \text{ C}^{-2} \cdot \text{mJ}$, β changes from $-5 \times 10^8 \text{ J C}^{-4} \cdot \text{m}^5$ for the ferroics with the first order phase transitions to $+1 \times 10^8 \text{ J C}^{-4} \cdot \text{m}^5$ for the ferroics with the second order phase transitions, γ changes from $10^9 \text{ J C}^{-6} \cdot \text{m}^9$ to $10^{11} \text{ J C}^{-6} \cdot \text{m}^9$, η_s changes from 0 to 0.7 C/m^2 in dependence on temperature, q is about 10^9 Vm/C , c is about $(1 - 10) \times 10^{10} \text{ Pa}$. The gradient coefficient g changes from $-6 \times 10^{-10} \text{ C}^{-2} \cdot \text{m}^3 \text{J}$ for ferroics with incommensurate phase like $\text{Sn}_2\text{P}_2\text{Se}_6$ to $+5 \times 10^{-10} \text{ C}^{-2} \cdot \text{m}^3 \text{J}$ for ferroics like $\text{Sn}_2\text{P}_2\text{S}_6$ with commensurate phases only. The higher gradient $w=0$ for ferroics

with commensurate phases and is about $(1 - 3) \times 10^{-27} \text{ J} \cdot \text{m}^5 / \text{C}^2$ for ferroics with incommensurate phase. Flexocoefficient f changes from -5 V to $+5 \text{ V}$, v is within the range $(10^{-7} - 10^{-6}) \text{ V s}^2 / \text{m}^2$. Using the reference values we estimated that dimensionless parameters changes in the range $Q^* = (0.02 - 0.8)$, $w^* = 0$ for ferroics with commensurate phase and $w^* = -(2 - 20)$ for ferroics with incommensurate phase, $f^* = (-5 - +5)$, $v^* = (-5 - +5)$ and $k^* = (0 - 10)$. Thus for a reasonable range of striction, nonlinearity and elastic stiffness coefficients the inequality $0 \leq Q^* < 1$ is likely to be valid.

4.3. Discussion of analytical results

Diagram of the stable phases, which exist in ferroics with commensurate and incommensurate SMP phase is shown in **Figure 2**, and the phase boundary separating SMP and HP phases is shown by solid curve for commensurate ferroics (with $g > 0$ and $w = 0$) and dashed curve for incommensurate ones (with $g < 0$ and $w > 0$). As one can see, the minimal absolute value of the flexoconstant $|f_{cr}^*| = 1$ is required for SMP appearance in ferroics with commensurate phases. That say the HP is absolutely stable in the ferroics at $|f^*| < 1$ and $v^* = 0$, at that the value $|f_{cr}^*|$ monotonically increases with v^* increasing (see Ref.[58] and red solid curve in **Fig.2** described by the function $|f^*| = \sqrt{v^* + 1}$). In contrast to the ferroics with commensurate phases, the SMP appears at $f^* = 0$ and $v^* \geq 1$ in the ferroics with incommensurate phases. Then the maximal absolute value $f_{cr}^*(v^*)$ appears and increases quasi-linearly with v^* increasing (see Ref.[58] and blue dashed curve in **Fig.2** described by the function $|f^*| = \sqrt{v^* - 1}$).

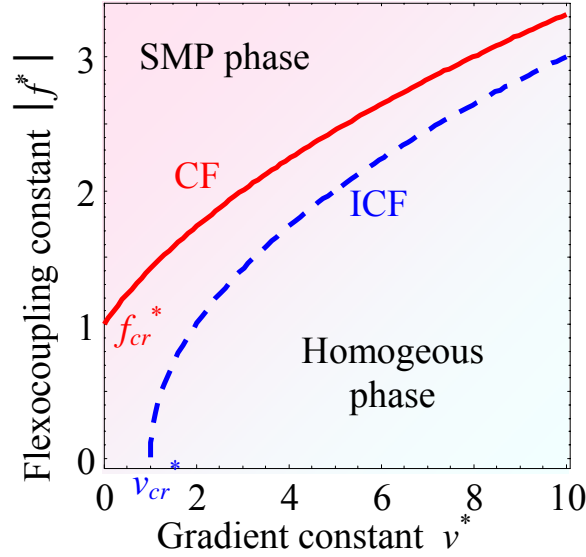


Figure 2. Diagram of the SMP phase stability in ferroics with commensurate (solid curve with legend CF) and incommensurate (dashed curve with legend ICF) phases plotted in coordinates f^* and v^* .

Dependences of the wave vectors k_+^* and k_-^* on the dimensionless flexoconstant f^* and gradient constant v^* calculated for ferroics with commensurate phases are shown in **Figs. 3**. The curves behavior is very similar in the parent ($\alpha > 0$) and long-range ordered ($\alpha < 0$) phases [e.g. compare plots (a) and (b), or (c) and (d), correspondingly]. A "gap" (i.e. the absence of k_{\pm}^* at $f^* < f_{cr}^*$) exists for all curves corresponding to different v^* -values [see **Figs.3(a)** and **3(b)**]. The gap width d is conditioned by the value $f_{cr}^*(v^*)$ and it increases with v^* increasing [compare different curves in **Figs.3(a)** and **3(b)**]. At $f^* > f_{cr}^*$ the wave vector k_-^* decreases and k_+^* increases with f^* increasing [compare dashed and solid curves in **Figs.3(a)** and **3(b)**]. There is the maximal positive value $v_{cr}^*(f^*)$ of SMP appearance at fixed f^* value [see **Figs.3(c)** and **3(d)**]. At $v^* < v_{cr}^*$ wave vector k_-^* increases and k_+^* decreases with v^* increasing [compare dashed and solid curves in **Figs.3(c)** and **3(d)**].

Dependences of the wave vectors k_+^* and k_-^* on the dimensionless flexoconstant f^* and gradient constant v^* calculated for ferroics with incommensurate phases are shown in **Figs.4**. A gap d exists only for the two curves corresponding to the highest v^* -values [see in **Figs 4(a)** and **4(b)**], as it follows from the dependence $f_{cr}^*(v^*)$ analyzed in Refs.[58-59]. The wave vector k_-^* decreases with $|f^*|$ increasing, while k_+^* increases with $|f^*|$ increasing [compare dashed and solid curves in **Figs 4(a)** and **3(b)**]. **Figs.4(c)** and **4(d)** plotted for ferroics with incommensurate phases show the same behavior as the **Figs.3(c)** and **3(d)** for ferroics with commensurate phases. Actually, there is the

maximal positive value $v_{cr}^*(f^*)$ of SMP appearance at fixed f^* value [see **Figs.4(c)** and **4(d)**]. At $v^* < v_{cr}^*$ wave vector k_-^* increases and k_+^* decreases with v^* increasing [compare dashed and solid curves in **Figs.4(c)** and **4(d)**].

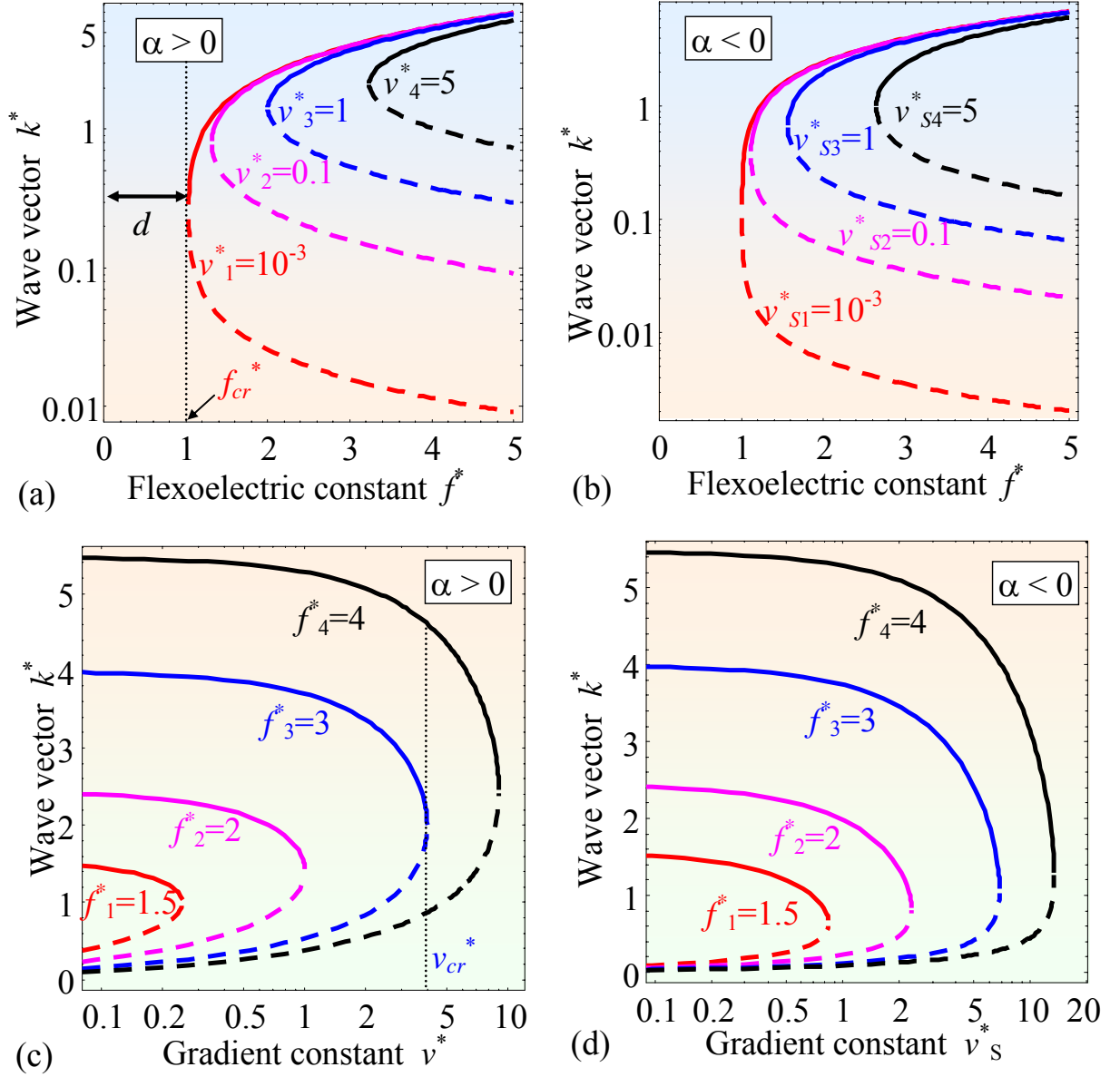


Figure 3. Ferroics with commensurate phases. Dependences of the wave vectors k_+^* (solid curves) and k_-^* (dashed curves) on the flexoelectric constant f^* (**a,b**) and elastic strain gradient constant v^* (**c**) and v_s^* (**d**). Different plots are calculated for $\alpha > 0$ (**a,c**) and $\alpha < 0$ (**b,d**). Different curves in each of the plots are calculated for several values of f_i^* , v_i^* and v_{si}^* listed in the legends at the plots. Parameter $Q_S^2 = 0.95$ for the plots (**b**) and (**d**).

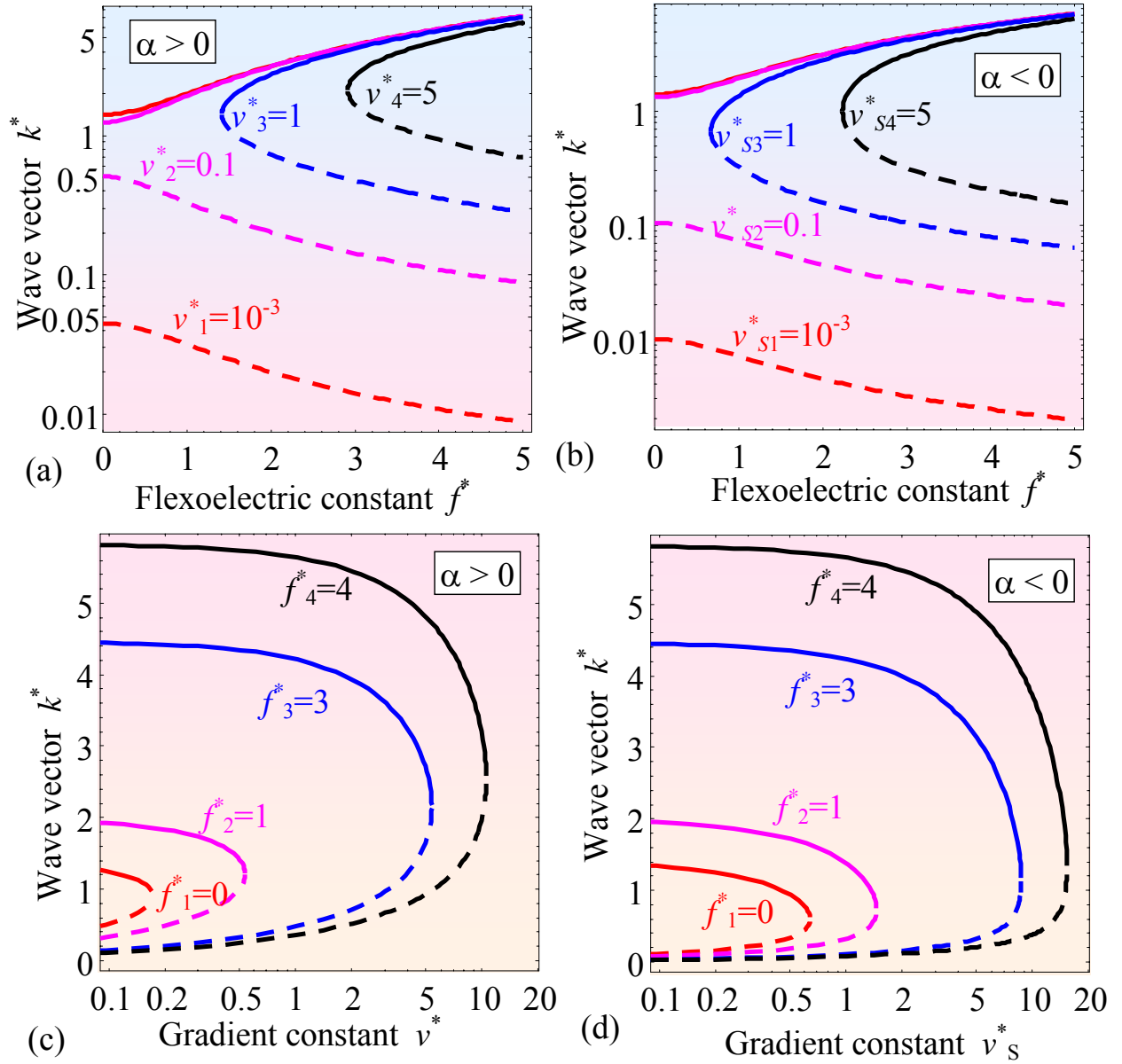


Figure 4. Ferroics with incommensurate phases. Dependences of the wave vectors k_+ (solid curves) and k_- (dashed curves) on the flexoelectric constant f^* (a,b) and elastic strain gradient constant v^* (c) and v_s^* (d). Different plots are calculated for $\alpha > 0$ (a,c) and $\alpha < 0$ (b,d). Different curves in each of the plots are calculated for several values of f_i^* , v_i^* and v_{Si}^* listed in the legends at the plots. Parameters $w^* = 2$ and $Q_s^2 = 0.95$ for the plots (b) and (d).

5. Flexoelectricity in liquid crystals

Both theoretical and experimental study of the flexoelectricity in liquid crystals (LC) is a challenge [62, 63, 64], at that corresponding research approaches should be adapted for three main types of liquid crystals: nematic, smectic and cholesteric [65]. Among them the flexoeffect impact is relatively well-studied in nematics [66, 67].

In a nematic liquid crystal (NLC) molecular long axes are oriented approximately parallel to each other, but the centers of mass of the molecules are located randomly, as in the liquid. The direction of dominant orientation is characterized by the order parameter - director vector \mathbf{n} , which bistable states, \mathbf{n} and $-\mathbf{n}$, are energetically equivalent in the absence of external electric field. NLC, even if they consist of polar molecules, are non-polar substances, which can be polarized by an electric field \mathbf{E} [68]. The interaction with the field is analogous to the piezoelectric effect in solids, which consists in the appearance of polarization in the creation of elastic stresses.

On the other hand, electric polarization is induced by deformations of the longitudinal and transverse bends. The effect was firstly predicted theoretically by Meyer in 1969 [69] and then revealed experimentally. This direct coupling is a direct flexoelectric effect in LC. Similarly to solids, there is also a converse static flexoeffect in soft matter, when the applied external field polarizing the NLC, creates distortions in the director distribution. That say the static flexoelectric effect in the NLC is the coupling of the electric field with the spatial gradient of the director field, $\vec{P}^{flexo} \sim f \cdot \vec{n}(\nabla \vec{n})$, where f is the flexoelectric coefficient that couples the polarization vector with the longitudinal or transverse bending. Corresponding contribution of flexoelectricity to the thermodynamic potential is proportional to the strength of the applied electric field (similar to the piezoelectric effect in solids). The information about dynamic flexoeffect in LC is absent.

In contrast to the well-studied Fredericks effect, caused by the anisotropy of the dielectric constant and being quadratic to the applied electric field, the flexoelectric effect linear in the electric field caused in NLC was revealed in 1969 [68]. It is conditioned by the by the distortion of the director field in NLC. Similarly to the omnipresence of flexoelectric effect in solids, it turned out that the flexoelectric polarization is a universal property of NLC [62]. The physical picture of the flexoelectric effect in NLC is shown in **Figs. 5(a)** and **(b)**, respectively. Polar molecules change their orientation in external electric field or due to elastic stimuli and their net dipole moments appears.

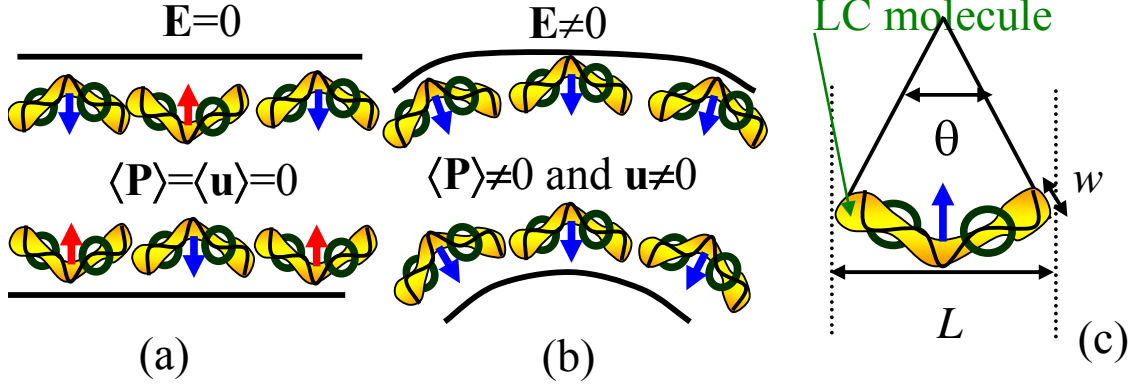


Figure 5. Illustration of the nature of the flexoelectric effect for the bend-shaped LC molecules. Red and blue arrows indicate the dipole moments of the bended polar LC molecules. **(a)** External electric field or strain are absent ($E=0$ and $\mathbf{u}=0$). **(b)** External electric field (or strain) is present ($E \neq 0$ and $\mathbf{u} \neq 0$).

If the dielectric anisotropy of NLC, $\epsilon_a K$ is small enough (satisfying the conditions listed in Ref.[62]) then e.g. the external electric field \mathbf{E}_z changes the orientation of director \mathbf{n}_x in the cell for the fields higher than the threshold value, $E > E_t$, where E_t is the threshold value of the field. E_t is inversely proportional to the flexoelectric coefficient f and given by expression (see Ref.[62]):

$$E_t = \frac{2\pi K}{|f|d} \left(1 - \frac{\epsilon_a K}{4\pi f^2} \right)^{-1} \quad (17)$$

The size of LC cell is d , ϵ_a is a relative dielectric permittivity. From the formula (17) the threshold value of the field is the smaller the larger is the flexoelectric constant $|f|$. Furthermore a planar oriented LC with rigid boundary conditions at $z = \pm d/2$ in an external field, which exceeds the threshold value $E > E_t$, forms a periodic structure due to the flexoelectric effect. If the dielectric anisotropy is not small, then instead of the periodic structure, the usual Fredericks transition takes place [62]. Note that relatively small changes in molecular shapes can lead to strong changes in their polar properties. For instance the first observations found ferroelectric polarization switching [70, 71] in bend-shaped LC molecules, but later it appeared that the switching reveals antiferroelectric behavior [72, 73, 74, 75, 76, 77, 78, 79, 80].

5.1. Estimates of flexoelectric polarization and coefficients in LCs

Flexoelectricity as defined by Meyer [69] for NLC with bend-shaped e molecules is a special case of the general definition Eq.(1), where the gradient of the strain is replaced by the gradient of the director \mathbf{n} . It was assumed that the constituent molecules of the NLCs are rotate freely around their axes; and so their average dipole moments is zero in the absence of electric fields, and the net polarization of the material is also zero [62]. When LC consists of polar bend-shaped molecules they

can become macroscopically polar. It follows from symmetry considerations that the strain-induced flexoelectric polarization \vec{P}^{flexo} can be expressed via the director vector \vec{n} and its gradient $\nabla\vec{n}$ as [69, 62]:

$$\vec{P}^{flexo} = f_1\vec{n}(\nabla\vec{n}) + f_3\vec{n}(\nabla\times\vec{n})\times\vec{n} \quad (18)$$

The value of polarizaion \vec{P}^{flexo} is characterized by two flexoelectric coefficients, f_1 and f_3 , for splay and bend, respectively. The microscopic origin of these phenomenological flexocoelectric cefficients contains at least two different mechanisms, dipolar and quadrupolar, exist (see details in Refs.[62] and [81]).

The estimates below are based on the results of Ref.[62].The dipolar mechanism is sensitive to the molecular shape. By dimensional considerations one can estimate the flexocoefficients due to dipolar mechanism as $|f_{1,3}| \leq \mu_e/a^2$, where $\mu_e \sim (3-15)\times 10^{-30}$ C·m is the molecular dipole moment and the distance $a \sim (2-4)$ nm. This means that f_1 and f_3 are expected to be of the order of pC/m. Hence these estimates show that the dipolar flexoelectric coefficients [being of the order of (1-10) pC/m] are too small for practical applications. However the estimates give essentially underestimated values, as discussed below.

Assuming a random 3D-distribution of the centre of masses of the bent-core NLC molecules, Helfrich [82, 83], Derzhanski and Petrov [84] derived another (more rigorous) expression for the observable bending flexoelectric coefficient [62], $f_3 = \frac{\mu_{\perp}K_3}{2k_B T} \theta^3 \sqrt{N\left(\frac{w}{L}\right)^2}$. Here μ_{\perp} is the dipole moment perpendicular to the long axis, K_3 is the bend elastic constant, θ is the bending angle (see **Fig. 5(c)** and Ref.[62]), N is the concentration number, L is the length, w is the width of the molecules, $k_B T$ is the thermal energy. The measurements of f_3 in calamitic NLCs revealed essentially higher values than expected from the estimate, indicating that not only the dipolar mechanism contributes to flexoelectricity, and it is also caused by the interaction between the electric field gradient and the molecular quadrupole moments [85, 86]. Molecules of band-core NLCs are characterized by an angle $\theta_0 \approx 60$ degree, which is much larger than θ_0 of calamitic NLCs [62]. Therefore in these compounds the dipolar contribution to f_3 can be higher at least in an order of magnitude, while f_1 may be of the same order as estimated. Moreover, band-core nematics exhibit a giant flexoelectric effect with f_1 much larger than expected from the above estimates [62].

5.2. Free energy functional with flexoelectric coupling in liquid crystals and SMPs

Using the definition of the flexoelectric coupling, Eq.(18), introduced in the subsection 5.1, the bulk part of the total free energy could be decomposed in several parts, namely bulk part $g_{bulk}(T, S, \vec{n})$, determining symmetry of ordered phase and its dependence on temperature T ; distortion elastic energy $g_{elastic}(S, \vec{n}, \vec{\nabla} \otimes \vec{n})$ and electrostatic/flexoelectric $g_{flexoelect}(S, \vec{n}, \vec{\nabla} \otimes \vec{n})$ contributions:

$$G_V = \int d^3 r \left[g_{bulk}(T, S, \vec{n}) + g_{elastic}(S, \vec{n}, \vec{\nabla} \otimes \vec{n}) + g_{flexoelect}(S, \vec{n}, \vec{\nabla} \otimes \vec{n}) \right] \quad (19)$$

Here we introduced scalar degree of ordering S and unit vector \vec{n} determining local direction of symmetry axis (vector field of director). Distortion energy contribution (“elastic” energy) could be expressed via director vector \vec{n} and its spatial derivatives as follows [68]:

$$g_{elastic} = \frac{K_1}{2} (\text{div}(\vec{n}))^2 + \frac{K_2}{2} (\vec{n} \cdot \text{rot}(\vec{n}))^2 + \frac{K_3}{2} (\vec{n} \times \text{rot}(\vec{n}))^2 \quad (20)$$

Here K_1 , K_2 and K_3 are elastic coefficients corresponding to transversal bending, twist deformation of director field and longitudinal bending respectively, these parameters are proportional to the square of ordering degree S . Electrostatic field \vec{E} contribution to the free energy at the fixed potentials of electrodes is (see e.g. [68]):

$$\begin{aligned} g_{flexoelect} &= -f_1 (\vec{E} \cdot \vec{n}) \text{div}(\vec{n}) - f_3 (\vec{E} \cdot (\vec{n} \times \text{rot}(\vec{n}))) - \frac{\varepsilon_0 \varepsilon}{2} (\vec{E})^2 \\ &\equiv -f_1 (\vec{E} \cdot \vec{n}) \text{div}(\vec{n}) + f_3 (\vec{E} \cdot (\vec{n} \cdot \vec{\nabla}) \cdot \vec{n}) - \frac{\varepsilon_0 \varepsilon}{2} (\vec{E})^2 \end{aligned} \quad (21)$$

Here we introduced f_1 and f_3 are flexoelectric coefficients corresponding to longitudinal and transversal bending, ε_0 is a universal dielectric constant, ε is a relative dielectric permittivity that is regarded isotropic. In the latter transformation we take into account that $\vec{n} \cdot \vec{n} \equiv 1$.

The surface energy contribution has the form:

$$G_S = \int_S d^2 r \left(\frac{K_1}{2h_1} n_1^2 + \frac{K_2}{2h_2} n_2^2 + \frac{K_3}{2h_3} n_3^2 \right), \quad (22)$$

where the analog of the extrapolation lengths, h_i , are introduced ($i=1, 2, 3$).

Euler-Lagrange equation for the director vector is:

$$\frac{\partial (g_{bulk} + g_{elastic} + g_{flexoelect})}{\partial n_i} - \frac{\partial}{\partial x_j} \left(\frac{\partial (g_{elastic} + g_{flexoelect})}{\partial n_{i,j}} \right) = \lambda n_i \quad (23)$$

Here we introduced Lagrange multiplier λ to take into account the condition $\vec{n} \cdot \vec{n} \equiv 1$ and used short hand designation for tensor of gradient of director field, $n_{i,j} \equiv \partial n_i / \partial x_j$. Evident form of (S1.4) is rather cumbersome (see e.g. [68]). Only for the case $K_1=K_2=K_3$ one could get simple expression:

$$\frac{\partial(g_{elastic})}{\partial \vec{n}} - \frac{\partial}{\partial x_j} \left(\frac{\partial(g_{elastic})}{\partial \vec{n}_j} \right) = -K \Delta \vec{n} \quad (24)$$

For instance, flexoelectric term contribution is

$$\frac{\partial g_{flexoelect}}{\partial \vec{n}} - \frac{\partial}{\partial x_j} \left(\frac{\partial g_{flexoelect}}{\partial \vec{n}_j} \right) = -f_1 [\vec{E} \operatorname{div}(\vec{n}) - \vec{\nabla}(\vec{n} \cdot \vec{E})] + f_3 [(\vec{E} \cdot (\vec{\nabla} \otimes \vec{n})) - \vec{E} \operatorname{div}(\vec{n}) - (\vec{E} \cdot \vec{\nabla})\vec{n}] \quad (25)$$

Using the formalism Eqs.(19)-(25) with the natural boundary conditions for polarization and director, at the LC film boundaries $z = \pm d/2$, namely

$$\left. \frac{\partial \theta}{\partial z} - \frac{1}{h_3} \sin \theta \cos \theta = 0 \right|_{z=-d/2}, \quad \left. \frac{\partial \theta}{\partial z} + \frac{1}{h_3} \sin \theta \cos \theta = 0 \right|_{z=+d/2}, \quad (26)$$

we calculated and analyzed the influence of the flexoelectric coupling on the director orientation and induced polarization in a NLC film. Note that $n_1 = \cos \theta \cos \varphi$, $n_2 = \cos \theta \sin \varphi$ and $n_3 = \sin \theta$ in a spherical coordinate frame. Polarization is given by Eq.(18), namely, $\vec{P}^{flexo} = f_1 \vec{n}(\nabla \vec{n}) + f_3 \vec{n}(\nabla \times \vec{n}) \times \vec{n}$.

Profiles of the director angle θ and polarization calculated for a 20-nm film are shown in **Fig.6(a)** and **6(b)**, respectively. It is seen from the figures that without flexoelectric coupling ($f=0$) any oscillations or maxima, or any other features are absent at the director and polarization distributions [see black curves in **Figs.6**]. Relatively small flexoelectric coupling with the strength ($0.3V < f < 0.5V$) leads to the small maximums on the director angle θ profiles near the LC boundaries [see blue and magenta curves in **Figs.6(a)**]. At the same time the features (increase or maxima) on the profiles of flexo-polarization are noticeable [see blue and magenta curves in **Figs.5(b)**]. Flexoelectric coefficient $f \geq 0.7V$ induces the LC film transition into a spatially modulated phase with quasi-harmonic modulation of the director angle $\theta \cong \theta_0 \cos(qz)$ and polarization $P \cong P_0 \cos(qz)$ [see red curves in **Figs.6**].

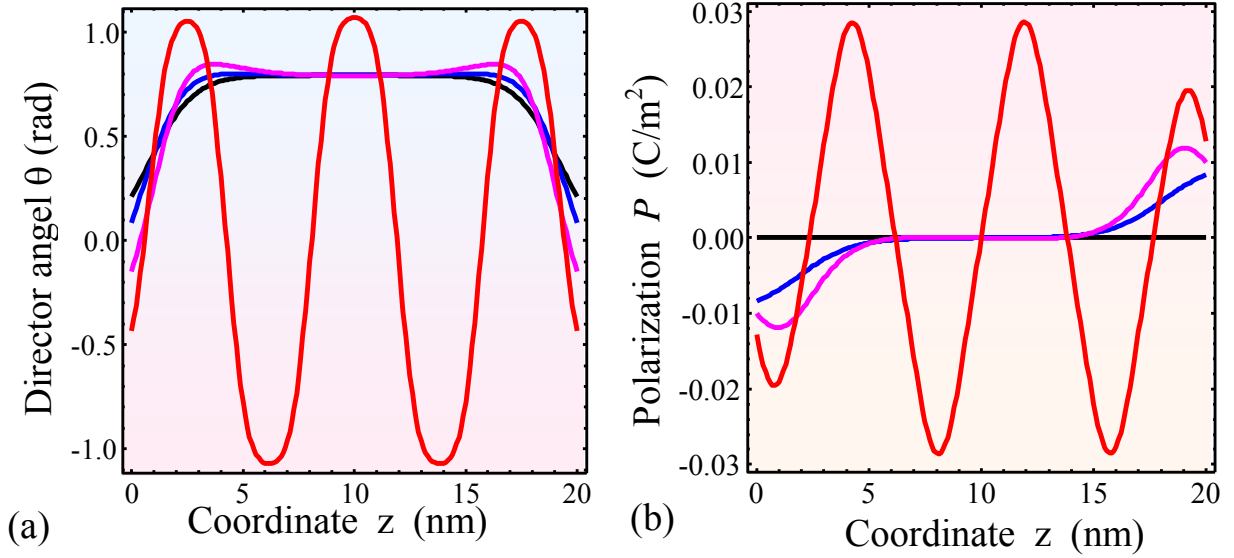


Figure 6. Influence of the flexoelectric coupling on the director orientation and polarization in a NLC. Order parameter – director angle θ (a) and polarization (b) distribution across the LC film of thickness 20 nm calculated for different values of flexoelectric coefficient $f = 0, 0.3, 0.50, 0.7$ V (black, blue, magenta, red curves respectively).

Therefore an oriented LC film with the boundary conditions (25) imposed at the cell boundaries forms a spatially-modulated periodic structure due to the flexoelectric effect without any external field. If the flexocoupling strength is relatively small in comparison dielectric anisotropy energy, the usual Fredericks transition takes place in external electric field instead of the spatially-modulated structure.

Note that the spatially modulated polarization phases have been firstly revealed in a smectic liquid crystal [62, 87]. As discussed by Bailey and J'akli, [88] a steric or electrostatic inclusion in the core of NLC molecules leads to layer modulation [62], in which the broken smectic ribbons are separated by melted fluid nematic regions (see Ref.[62] and refs [89, 90, 91] therein on the small-angle X-ray scattering (SAXS) measurements). These smectic clusters are at least partially ferroelectric and they can exhibit the soft mode-type low-frequency dielectric relaxations [92] and the giant flexoelectric effects [93, 94].

6. Conclusions

In the review we briefly analyze the state-of-art in the theory of flexoelectric phenomena and analyze how significantly the flexoelectric coupling can change the polar order parameter distribution in ferroics and liquid crystals. The special attention is paid to the appearance of the spatially modulated phases induced by the flexocoupling in solids and soft matter. Results of theoretical modeling performed in the framework of the Landau-Ginzburg-Devonshire formalism revealed that the general feature is the appearance of the spatially modulated phases in ferroics and liquid crystals taking place with increasing of the flexocoupling strength. We'd like to underline that theoretical and experimental

study of flexoelectricity and related phenomena in nanosized and bulk ferroics, liquid crystals are very important for their advanced applications in nanoelectronics, memory devices and LC displays.

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