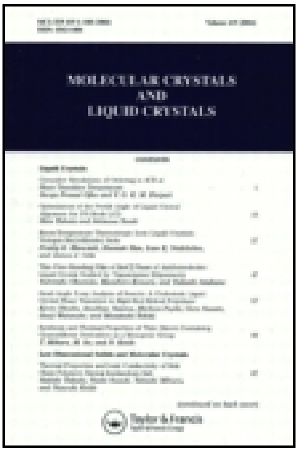

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# The Orientational Fluctuations in the Re-Orientation Process of a Nematic Liquid Crystal

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# The Orientational Fluctuations in the Re-Orientation Process of a Nematic Liquid Crystal

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*The field-induced molecular reorientation of liquid crystals is usually described by the Frank-Oseen equation with several simplifying assumptions. Among them the "classical" theory ignores thermal fluctuations in the liquid crystal structure. As a consequence, the static Frank-Oseen equation may give inconsistent results in some details of the reorientation process. This work is aimed to include formally the orientational fluctuations in the field-induced reorientation process in nematics. The simplified approach presented here is a "zero-order" approximation of the problem, nevertheless even in this form it allows for correct physical interpretation of the process for fields up to the threshold.*

**Keywords** Liquid crystals; molecular reorientation; orientational fluctuations

## 1. Introduction

The field-induced molecular re-orientation in liquid crystals (LC) (Frederiks transition) is well recognized and analyzed in details since a long time. The stationary distribution of the director in a liquid-crystalline structure subjected to the action of an electric (also optic or magnetic) field is calculated by solving the well-known Frank-Oseen (F/O) equation derived by the minimization of the Gibbs free energy of the system [1]. This static equation is obtained by several simplifying assumptions; one of them is that it ignores thermal fluctuations of the director orientation and considers only the thermodynamical averages of the respective parameters. Despite of that, the theory predicts fairly good experimental results and provides essential parameters of the reorientation process, like threshold field intensity and stationary solutions for structure deformation. However, as the consequence of this simplification, information about the reorientation process in the transient region is missing, where one of the possible solutions is stabilized. The formal problem concerns initial conditions which should be well-defined to solve the equation unambiguously, while the neglected fluctuations change them dynamically. The problem causes some intrinsic discordance of the results.

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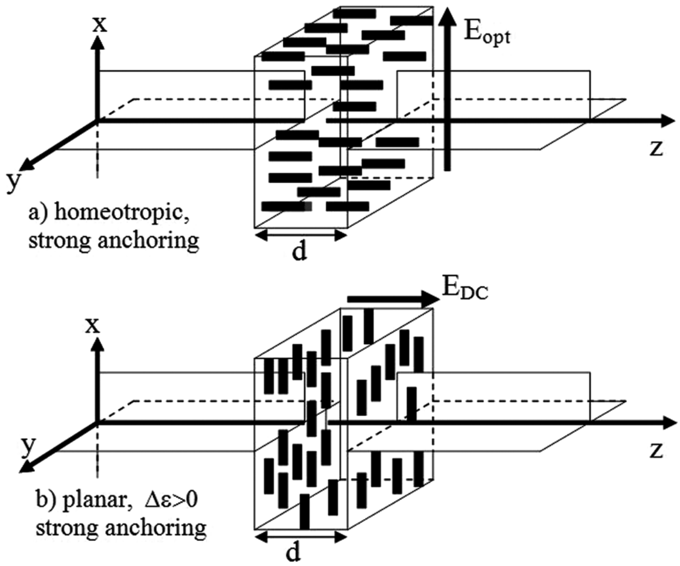


**Figure 1.** The system configuration discussed in the text.

In order to show the problem more clearly but not to complicate necessary calculations, let apply the F/O equation to discuss the simplest liquid-crystalline geometry presented in Figure 1, which is planar nematic structure in the DC or low-frequency electric field, or homeotropic nematics in the optical field (description of both are formally similar).

Additionally, on same regard, the strong anchoring at the boundaries and the perfect alignment is assumed. Introducing the angle $\theta(z)$ between the initial director orientation (x-axis) and the distorted molecular axis, as in Figure 2, the F/O equation in this case is reduced to the simple form:

$$K_1 \frac{d^2\theta}{dz^2} = \Delta\varepsilon\varepsilon_o E^2 \sin\theta\cos\theta \tag{1}$$

which approximate solutions can be easily found [1,2].

The solutions, yielding the deformation distribution of the director $\theta(z)$ inside nematic structure, depend on the field intensity. For low fields $E < E_{th}$, the only solution is trivial, $\theta(z) = 0$, i.e., no reorientation occurs. For the field intensities

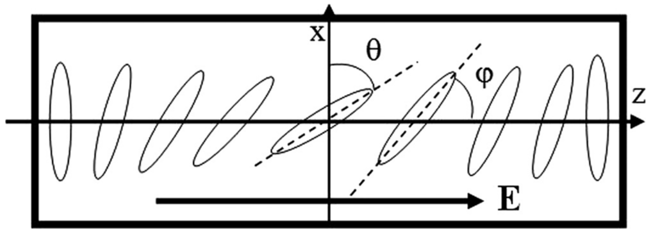


**Figure 2.** Definition of the deformation angle $\theta$ for the case shown in Figure 1b.

exceeding some threshold value $E_{th}$ the equation has three possible solutions: again $\theta(z) = 0$, and the additional two non-trivial, $\pm\theta(z)$ describing re-oriented structure, symmetrical with respect to the undistorted director orientation, because of the system symmetry. All the possible solutions, among which the one – $\theta(z) = 0$ – is unstable above threshold (for higher fields), whereas the others are stable, are illustrated in Figure 3.

In this case the theory leaves the question open, which one of the three possible solutions will realize, or how the system will stabilize. Clearly, it is not a formal (mathematical) but physical problem which can be solved neither by the static F/O-nor even by the related dynamic Ericson-Leslie equations. Both of them ignore thermally excited director fluctuations which are crucial in the initial sequence of the re-orientation process. If they are omitted, the re-orientation formally will never start by imposed boundary conditions, because the dielectric torque $\tau_{diel} \sim (\mathbf{n}_o \times \mathbf{E})(\mathbf{n}_o \cdot \mathbf{E})$ disappears for $\mathbf{E} \perp \mathbf{n}_o$. Then, in view of the F/O theory there is only one solution $\theta(z) = 0$ physically possible for the whole range of the field intensities, and no reorientation can occur.

To overcome the problem in this static approach, it is informally stated, that the assumed initial conditions are not realistic; in practice perfect alignment never exist, since there are always some small imperfections and thermal fluctuations of the director. In over-threshold region they break unstable equilibrium $\theta(z) = 0$ and establish one of the other two stable solutions $\theta(z) \neq 0$, so that finally the transition appears. This statement, true in fact, is valid not only for the fields exceeding the threshold, but for any other (also lower) field intensity as well. However, by taking the imperfections into account informally, only by introducing some initial tilt angle $\theta(z, E = 0) = \theta_t$ one changes the previously assumed geometry and the F/O equation (1) may be now re-written in the form:

$$\Delta\varepsilon\varepsilon_o E^2 \left(1 - \frac{2}{3}\theta_o^2\right)\theta_0 - K_1 \frac{\pi^2}{d^2}\theta_0 = K_1 \frac{\pi^2}{d^2}\theta_t \qquad (2)$$

where the searched deformation $\theta(z)$ is restricted to the first order of expansion,

$$\theta(z) = (\theta_o - \theta_t)\sin(\pi z/d) + \theta_t,$$

valid near the threshold for small $\theta$-angles.

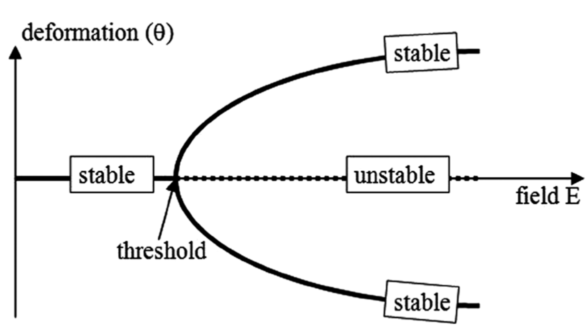


**Figure 3.** Graphical interpretation of the possible solutions of the F/O equation.

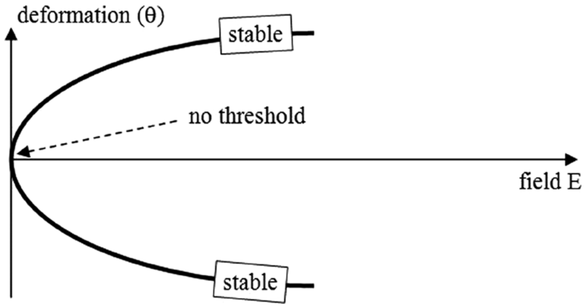


**Figure 4.** The possible solutions of the F/O-eq. in presence of an initial tilt $\theta_t$.



The equation (2) is no more obeyed by $\theta(z) = 0$ for any field intensity, but it has two another non-trivial solutions, describing structural re-orientation, starting at $E > 0$ without any threshold. They are plotted in Figure 4.

The reason of this change in the solution-sets of the F/O-eq., caused by the initial tilt angle, can be clearly illustrated graphically. Figure 5 explains how the introduction of $\theta_t$ cancels the threshold effect.

The F/O-eq. expresses the balance between elastic torque $\tau_{el}$ (left side of Eq. (1), assumed to be linear) and the dielectric torque $\tau_{diel}$ (right side). Intersection of the corresponding curves in Figure 4 gives the resulting deformation $\theta(z)$ at a certain field E. As it follows from Eq. (1), the slope $(d\tau_{diel}/dE)$ depends on the field intensity [3]. For small intensities ($E_1$) the slope is small and both the curves $\tau_{diel}(\theta,E_1)$, $\tau_{el}(\theta)$ intersect only at $\theta=0$, then no deformation occurs. For higher intensities ($E_2$) the slop rises so, that $\tau_{diel}(\theta,E_2)$, $\tau_{el}(\theta)$ may intersect also for >0, then a certain deformation is possible (Fig. 1a). Thus, there is a certain threshold intensity, where $E_1 < E_{th}$, and $E_2 > E_{th}$.

If some initial tilt $\theta_t$ is introduced (Fig. 1b), the plots intersect exclusively at $\theta > 0$ for any field intensity ($E_1$, $E_2$) and for any slope of the dielectric curve; it means, that some deformation ($\theta_1$, $\theta_2$) always occurs. In this case (i.e., $\theta_t \neq 0$) the threshold effect then vanishes.

As a result, the F/O equation provides following, formally possible solutions:

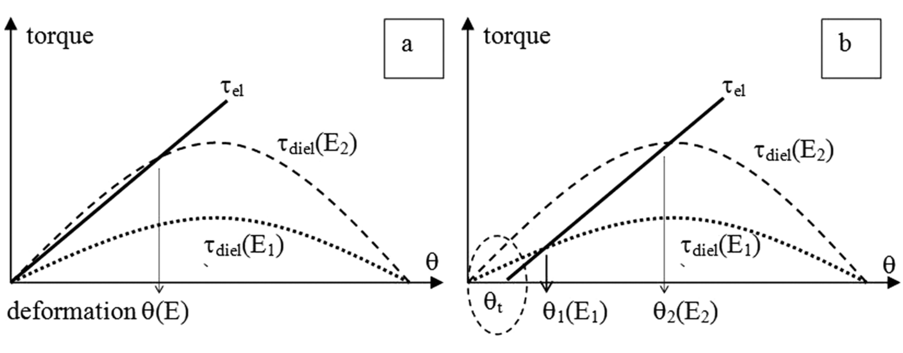


**Figure 5.** The balance between the dielectric and elastic torques $\tau_{diel}$ (dotted curves), $\tau_{el}$ (solid line) below ($E_1$) and above ($E_2$) the threshold intensity; a) without and b) with initial tilt $\theta_t$.

*either* **no re-orientation can occur** at any field intensity (perfect alignment) although **the theory predicts the threshold only in this case**, *or* **the re-orientation appears at each field without threshold** (imperfections present).

In contrast to that, in real conditions, i.e., by presence of orientational fluctuations, the re-orientation threshold effect is observed. Obviously, to avoid the above inconsistence, the fluctuations should be formally included in the description of the field-induced reorientation process. The discrepancy can be avoided by supplementing the stationary solutions of Eq. (2) with a contribution of fluctuations, and showing that the threshold effect is still preserved. The approximate approach proposed here, describing the contribution of fluctuations in the Frederiks transition, is based on some experimental observations presented in the next section.



## 2. Experiment and Discussion

The orientational fluctuations were observed by means of the depolarized homodyne speckle interference in the simple set-up shown in Figure 6.

Coherent light beam was focused on a nematic sample to have the waist of about $10 \div 20\,\mu m$. After passing the LC-cell it formed twinkling speckle field, where a detector was placed. Both configurations shown in Figure 1. were investigated, but detailed measurements were made for the planar cells in a low frequency (300 – 1000 Hz) E-field. The samples in the set-up were oriented with initial director position making 45 degree in respect to light polarization plane, whereas the detector measured speckle intensity in the perpendicular plane (the measurement in crossed polarizers).

The speckle size and intensity depend on the number of phasors in the object area–here the set-up aperture, which is the beam waist – and its correlation [4]. Many chaotic phasors inside the aperture give small speckles of low intensity. Contrary, the speckle size and intensity increase if the phasors become spatially correlated, so that they cover large area. The orientational fluctuations as the phasors are stochastic events. Therefore, as distinct from the speckles generating by static phasors, the speckle image forming by the fluctuations changes dynamically, since the magnitude and the correlation area of the fluctuations change permanently in time. The signal, known as a speckle noise, collected by the detector placed in the interference field, varies then also in time. The noise intensity is small when many spatially uncorrelated fluctuations give compensating contributions at the detector input, and rises with increasing correlation area of the fluctuations.

Any particular fluctuation $\delta\mathbf{n}$ of the director in the considered configuration (Fig. 1b) can be decomposed onto the "in-plane" component $\delta n_y$ and "off-plane" component $\delta n_z$. The latter component, $\delta n_z$, which in term of angular tilt $\theta$ introduced

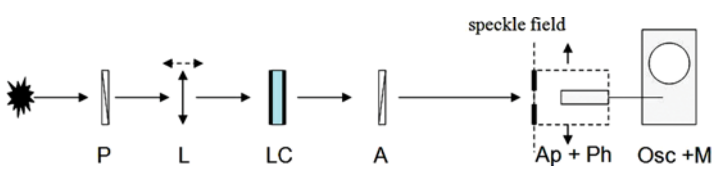


**Figure 6.** The experimental lay-out in the depolarized speckle-interference measurements: P, A – polarizers, L–movable lens, LC–liquid-crystalline cell, Ap + Ph–photomultiplier with diaphragm, Osc + M – oscilloscope/meter. (Figure appears in color online.)

above can be denoted as $\delta\theta$, corresponds to splay, twist, and bend deformations, respectively

$$\frac{\partial\theta}{\partial z}, \frac{\partial\theta}{\partial y}, \frac{\partial\theta}{\partial x}$$

It can be shown by simple geometrical analysis [5], that this component, $\delta\theta$, provides major contribution to the speckle noise in the arrangement shown in Fig. 5. Also, only this component can essentially affect the field-induced reorientation process.

Generally, the interaction between the field and a fluctuation is possible by given field intensity, when the fluctuation is sufficiently large. Necessary size of the fluctuation is determined by the relation of its dielectric and thermal energies. Approximate calculation for PCB, the LC-material used in the experiment, gives the corresponding energies per single, individual LC-molecule of the order:

$$(\varepsilon_o \varepsilon \Delta E^2/n) \approx 10^{-27}\text{J, and } (kT_{300K}) \approx 10^{-21}\text{J},$$

where $n$ is here the molecular concentration and $E = 1\,V/\mu m$ is assumed.

Since the destructive thermal component overcomes six orders of magnitude the electric field action on a single molecule, then the collective motion of more then $10^6$ molecules is needed for the field to compete with uncorrelated thermal excitation. Otherwise the electric field "doesn't see" (smaller) fluctuations. The formation of a fluctuation is the probabilistic process, then one can expect that such large fluctuations may happen; it can be only the question how often. In the experiment, the increase of the detected signal was incidentally observed, like in Figure 7, that may indicate a fluctuation spatially correlated over the area comparable with the set-up aperture.

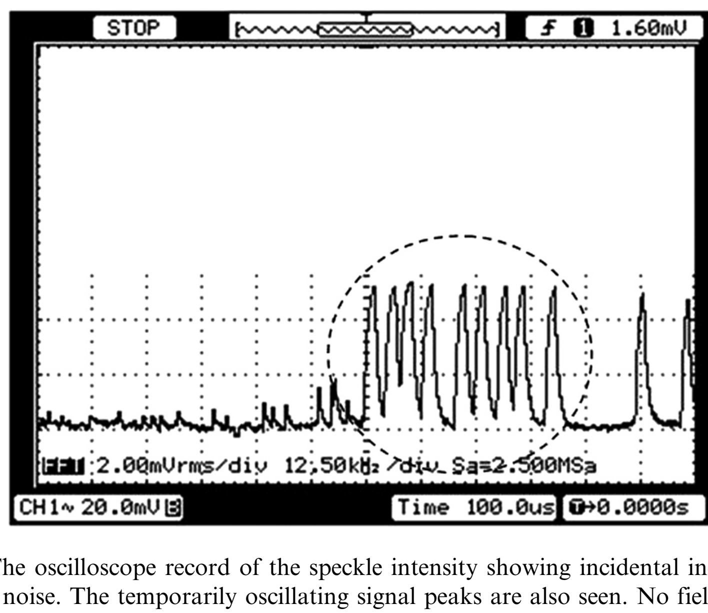


**Figure 7.** The oscilloscope record of the speckle intensity showing incidental increase of the fluctuation noise. The temporarily oscillating signal peaks are also seen. No field is applied.

A fluctuation, large enough to react with the applied field, can be either enhanced or quenched by induced dipolar torque, depending on configuration. The quenching effect ("fluctuations freezing") in high intensity field is known since long time and described in the literature [6]. The amplification, in contrast, can occur in the Frederiks transition geometry by the field intensity lower than the reorientation threshold. In this experiment the effect was observed for both the LF-electric- and optical fields. Figure 8 presents the measurements of the average amplitude of the speckle noise in the sub-threshold field range. The results indicate, that the fluctuations increase with the field before the re-orientation begins. Similar effect, although not discussed, can be noticed in measurements made by different technique also in other reports [7].

The induced fluctuations of the director prevailingly relax exponentially, loosing their energy by molecular friction, according to Ericksen-Leslie (E/L) equation [1,8]:

$$J\frac{\partial^2\theta}{\partial t^2} + \gamma_1\frac{\partial\theta}{\partial t} = K_1\frac{\partial^2\theta}{\partial z^2} \tag{3}$$

with rotational viscosity coefficient $\gamma_1$.

Usually the inertial term in the equation (3) can be omitted as small in comparison to the frictional term, and the equation yields the exponential decay expression for $\theta$(t):

$$\theta_i(q) \approx \theta_{i0}\exp\left(-\frac{q^2K_1}{\gamma_1}t\right)\cdot\exp(iqx) \tag{3a}$$

The exponential decay of the noise peaks was detected in the experiment. However, several cycles of oscillations of the measured signal was irregularly also observed, with and without applied field, as shown in Figure 7.

It seems to be likely, that some director fluctuations may oscillate a while before they relax, if the frictional energy loss can be compensated in some way. The fluctuations are fed with energy by thermal excitation. Let then complete E/L eq. by a

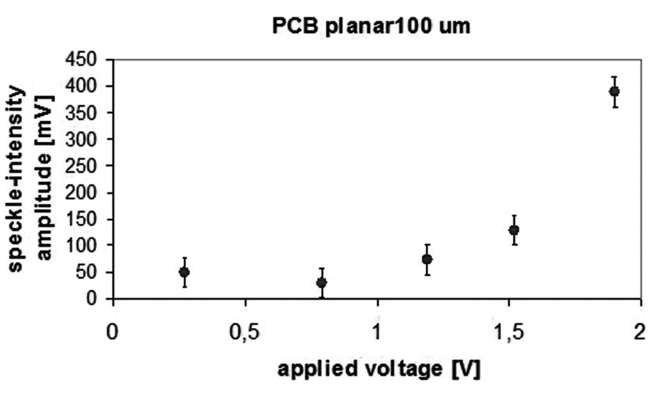


**Figure 8.** The average amplitude of the speckle intensity versus applied field below the re-orientation threshold, that was in this case 1,8 V.

thermal stimulus $F_\tau(kT)$ (as yet we don't need to define it strictly):

$$J\frac{\partial^2\theta}{\partial t^2} = K_1\frac{\partial^2\theta}{\partial z^2} - \gamma_1\frac{\partial\theta}{\partial t} + F_\tau(kT) \tag{4}$$

and assume, that temporarily the thermal and frictional terms (the second and the third term in the right side) are approximately equal and they compensate mutually. In this case the inertial term can't be neglected as previously. If the considered fluctuation is sufficiently large and an electric field is applied, the oscillation is fed also by the field. The effect is illustrated in Figure 9.

In order to find the threshold effect let assume that the field vector is perpendicular to the initial director orientation (x-axis) and $\Delta\varepsilon > 0$. In this case, the stationary solution provides unstable equilibrium, as discussed before. Yet, oscillating fluctuations are excited stochastically in certain time intervals. In an oscillating LC molecular group the electric field induces an alternating dipole moment. The angle between induced dipole and the field vector is always less then $\pi/2$, so that generated dielectric torque pulls the dipoles in opposite phase to the restoring elastic torque. In that way the oscillation amplitude is amplified by the field and the frequency is lowered. This interaction between the induced dipole moment and the field enhances oscillation until the average position of the dipole remains intact ($\mathbf{n} \perp \mathbf{E}$), so that the director macroscopically does not re-orient. The enhancement however is broken in the already deformed structure, where the field can only re-orient the central position (shift the equilibrium) of the thermal fluctuations. The same mechanism quenches them in the fully re-oriented structure, ($\mathbf{n} \parallel \mathbf{E}$). For convenience, the oscillating fluctuation, correlated large enough to react with the field will be further called "the fluctuon".

By the presence of the electric field the E/L-eq. of motion (4) comprises then also the dielectric torque term and now reads:

$$J\frac{\partial^2\theta}{\partial t^2} = K_1\frac{\partial^2\theta}{\partial z^2} + \varepsilon_o\Delta\varepsilon E^2\sin\theta\cos\theta \tag{5}$$

In the first approximation, the expression of a fluctuon $\delta\theta = \theta_f(z,t)$ having the wave vector q which is not too large, can be limited to the zero-term of the Fourier expansion:

$$\theta_f(z,t) \approx \theta(t)\sin\left(\frac{\pi}{d}z\right)$$

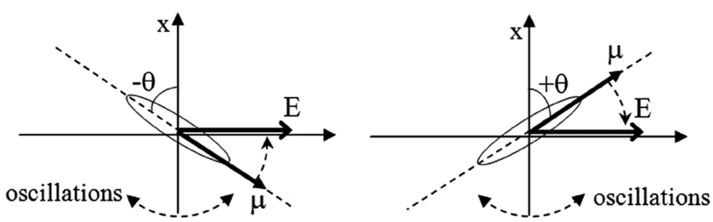


**Figure 9.** The oscillation enhancement of the induced dipole moment $\mu$ in the electric field E.

so, that (5) becomes:

$$J\frac{\partial^2\theta}{\partial t^2}+\frac{\pi^2 K_1}{d^2}\theta\sin\left(\frac{\pi}{d}z\right)-\varepsilon_o\Delta\varepsilon E^2\sin\theta\cos\theta=0$$

By considering the oscillating director with small amplitude ($\theta$«1 rd) and short wave vector q = 1/d, in fixed location, where the amplitude reaches maximum, i.e., in the center of the fluctuon: z = $\frac{1}{2}$d, the equation of motion can be now written in the canonic form:

$$\frac{\partial^2\theta}{\partial t^2}+\omega^2\theta=0$$

with frequency

$$\omega^2=\frac{1}{J}\left(\frac{\pi^2 K_1}{d^2}-\varepsilon_o\Delta\varepsilon E^2\right). \tag{6}$$

The oscillating energy of such a fluctuon per unit volume is:

$$W_{osc}=\frac{1}{2}J\omega^2\theta_m^2. \tag{7}$$

Substituting (6) in (7) gives:

$$W_{osc}=\frac{1}{2}\left(\frac{\pi^2 K_1}{d^2}-\varepsilon_o\Delta\varepsilon E^2\right)\theta_m^2. \tag{8}$$

The dielectric torque exerted by the field on periodically rotating dipoles counteracts with the elastic torque, so the dipoles periodically gain and loose the dielectric energy

$$W_{diel}=-\vec{\mu}\vec{E}=\varepsilon_o\Delta\varepsilon E^2\sin^2\theta\approx\varepsilon_o\Delta\varepsilon E^2\theta^2$$

at the expense- or in favor- of the energy of LC elastic reaction. Therefore in Eq. (8), providing the total energy of oscillations, these two terms have opposite signs.

The director average orientation of the fluctuon can be hold at $\theta=0$, if the oscillating dipoles pass the central position, where the angle changes sign. It is possible until the total oscillating energy doesn't vanish,

$$W_{osc}>0$$

However, if the field rises and becomes strong enough, that

$$W_{osc}=0, \tag{9}$$

the field-enhanced oscillations over the position $\theta=0$ stop. There are still possible thermal fluctuations, but the average value $<\theta(t)>\neq 0$. By this field intensity then the re-orientation occurs.

From this point forth, the calculations are formally equivalent to those of the E/L-theory, but here they don't concern the static re-orientation, but the fluctuating director;by using expression (8), the condition (9) yields:

$$\frac{1}{2}\left(\frac{\pi^2 K_1}{d^2} - \varepsilon_o \Delta\varepsilon E_{th}^2\right)\theta_m^2 = 0 \tag{10}$$

Thus the threshold field intensity is:

$$E_{th} = \frac{\pi}{d}\sqrt{\frac{K_1}{\varepsilon_o \Delta\varepsilon}} \tag{11}$$

in accordance with the static E/L-theory.

The last part of the above discussion can be referred also to the fluctuations relaxing exponentially, without oscillation. In frame of used procedure this process can be considered as a motion with supercritical damping. In this case the expression (10) is also applicable, since by satisfying condition (9) the rotational friction disappears.

Equivalently, one can re-consider Eqs. (4) and (5); if the molecular friction instantaneously dominates over the negligible thermal and inertial terms, the viscous movement of the director is governed by the reduced equation:

$$\gamma_1 \frac{d\theta_m}{dt} + \left(\frac{\pi^2 K_1}{d^2} - \varepsilon_o \Delta\varepsilon E^2\right)\theta_m = 0$$

The solution $\theta_m(t)$ takes the form of the expression (3a) with the field-dependent relaxation-time constant $t_d$:

$$\frac{1}{t_d} = \left(\frac{\pi^2 K_1}{\gamma_1 d^2} - \frac{\varepsilon_o \Delta\varepsilon}{\gamma_1} E^2\right).$$

The relaxation process is stopped when the field reaches the value causing $t_d \to \infty$, than if:

$$\left(\frac{q^2 K_3}{\gamma_1 d^2} - \frac{\varepsilon_o \Delta\varepsilon}{\gamma_1} E_{th}^2\right) = 0.$$

This gives the threshold field of the reorientation initiated by the fluctuation with wave vector q:

$$E_{th}^2(q) = \frac{q^2 K_1}{\varepsilon_o \Delta\varepsilon}. \tag{11a}$$

The threshold field intensity (11a) takes the minimal value for $q = \pi/d$ (the spatially largest fluctuation possible by the imposed boundary conditions), equal to the value derived from the expression (11). The expression (11) complies with the relation given by E/L-theory, however here it is derived by considering thermal fluctuations instead of ignoring them.

From the above presented picture of the re-orientation process one another remark is to notice. In the view of the proposed approach, the molecular transition doesn't occur in the whole LC-structure at once (homogeneously), but it is initiated in many particular spots, where the stochastically distributed fluctuons appear. Thereafter it extends over the structure via LC-elastic coupling. It would be interesting to check experimentally this supposition. This would be an additional verification of this approach. Suggested way to prove the effect is the investigation of the dynamics of the reorientation process.

## 3. Conclusions

The approximate description of the director fluctuations in the field-induced re-orientation of a nematic structure was presented. It points out formally, that the threshold effect is behaved also in the presence of the thermally induced orientational fluctuations of the director. This approach consistently completes the static Frank-Oseen theory and related Ericson-Leslie equation in the initial sequence of the reorientation process. Although simplifications, obtained expression for the re-orientation threshold intensity gives correct value, in accordance with the Frank-Oseen theory.

## Acknowledgment

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## References

[1] de Gennes, P. G. (1973). *The physics of Liquid Crystals*, Clarendon, Oxford.
[2] Oswald, P., & Pieranski, P. (2005). *Nematic and Cholesteric Liquid Crystals*, Taylor and Francis: London, New York, Singapore.
[3] Sierakowski, M. (2009). *Phot. Lett. Poland*, *1* (X).
[4] Goodman, J. W. (2007). Speckle Phenomena in Optics, Roberts & Company.
[5] Sierakowski, M. (2010). *Phot. Lett. Poland*, *2*(3).
[6] Chandrasekhar, S. (1992). *Liquid Crystals*, Cambridge University Press: New York.
[7] Galatola, P. (1992). *J. Phys. II France*, *2*, 1995.
[8] Khoo, I. C., & Woo, S. T. (1993). *Optics and nonlinear optics of liquid crystals.* Series in nonlinear optics–volume 1, World Scientific Publishing.