

Condensed state physics in biology: liquid crystal - semiconductor system

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Abstract. The possibility of application of condensed state physics methods for the study of biological objects is considered. The object of use is a cell with a liquid crystal as a model of a biological system living cell. The system of liquid crystal- semiconductor was experimentally investigated by methods of modulation spectroscopy. By determining the value of electric reflection, it is possible to judge about the state of surface polarization of liquid crystal. Exposure to an electric field changes the energy of the semiconductor's zone structure, which leads to changes in the optical properties of both crystals. To investigate the optical modulation changes in our case, we used the method with the use of electric field which allowed us to measure the modulation of the spatial charge. The study of thin layers (up to 120nm) of various nematic liquid crystals has shown that at values of electric fields comparable to Fredericks transition threshold, the orientation angle of liquid crystal molecules changes due to the interaction of surface polarization with the external field, and an odd electrooptic effect is observed. If the value of the electric field is much larger than the threshold of the Fredericks transition, the electric moment, which depends nonlinearly on the field, predominates and leads to an even electrooptic effect. The results of the study are proposed to be used for the development of new drugs and materials with specified parameters for medicine.

1 Introduction

The twentieth century is called the century of industrialization, rapid development of physics, engineering and technology. The twenty-first century can be confidently called the century of biology, chemistry and medicine, as well as information technology which penetrated into all spheres of human life. Nowadays, there are more and more opportunities to solve tasks at the intersection of scientific and technological fields. Thanks to the use of artificial intelligence and neural networks, new drugs are created, the development of which is ten times faster; new materials with specified properties suitable for use in medicine are modeled.

In [1] the possibility of using nanomaterials such as nanoparticles, nanofibers, metal organic frameworks for clinical treatment of tissue regeneration were studied. The study showed that due to the complex topography formed around the inflamed tissue, the

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application of nanomaterial based therapy is difficult. Precious metal nanozymes can emit enzyme activity, allowing them to target drug delivery to tissues and cells, which could be used to treat, for example, cancer. They can also serve as a contrast agents for tissue visualization in diagnostics [2].

Regeneration initiated by stem cells has been considered in [3, 4]. The case in point is the treatment of periodontitis and repair of tissue defects. It was found that in order to increase the efficiency of tissue regeneration, it is necessary to strictly control stem cell apoptosis. In [5], alginate based hydrogels with nanomaterials are studied and used as dressings for bone regeneration and wound healing, polymer scaffolds can be implanted in complex fractures, which have high mechanical strength and at the same time flexibility.

A review [6] collected information on the use of different types of liquid crystals (LC) in pharmacy which are used for point drug delivery, such as lyotropic liquid crystals (LLC) which have less toxicity and higher penetration ability. The LLC molecule has a hydrophilic head and a hydrophobic tail, so it is possible to form "compartments" to hold water soluble and water insoluble drugs. Antitumor drugs captured by lyotropic liquid crystal provide 10 times faster release, three times more effective in destroying cancer cells.

Lipid liquid crystals have been used to successfully treat schizophrenia and bipolar disorder [7]. The prolonged acting drug has a release time of one month. The obtained LC have a hexagonal structure, which accounts for the slow and controlled release of the drug. It was proved that the proposed formulation is safe, it does not cause skin damage at the injection site, it is also harmless to vital organs. Consequently, the drug can be used as an option when developing a long acting dosage form of aripiprazole LLC.

Scientists are looking for new shapes and arrangements of various materials for their further utilization to create new technologies, hardware and engineering solutions. Thus, in [8] a three component system of liquid crystal-polymer-nanoparticles is considered. Each component of this structure has its advantages and disadvantages, but their joint consideration will eliminate a number of problems, which will significantly expand the range of application of multicomponent systems. The analysis reveals possibilities of perspective implementation of multicomponent systems not only in traditional technologies of information display systems, but also in the field of creation of universal devices for photonics and nonlinear optics.

The operation of biosensors is based on certain reactions that detect changes in optical, thermal, chemical and electrical properties. They are used to diagnose a specific disease, to study DNA hybridization, protein binding and enzyme detection. The conditions under which the desired particle attaches to a surface are considered, whereby the optical properties of this biological system change when exposed to it, consequently changing the refractive index of the substance. The resulting optical signal can be measured. The peculiarity of biosensors on liquid crystals is that they have low power consumption, fast response, high sensitivity and they are easy to operate.

In [9], the authors propose a novel highly sensitive liquid crystal sensor for detection of herpes simplex virus infection. A textile mesh was used to construct a switchable detector optical device. The proposed biosensor has good prospects for early diagnosis and preventive measures for transmissible herpes infections. The same approach can also be implemented to fabricate biosensors for the detection of other viruses.

The filamentous protein structures within each cell form the cytoskeleton, which is located between the nucleus and the cell membrane and plays an important role in maintaining the shape of the cell as well as in its response to external stimuli. The cellular cytoskeleton consists of actin filaments, which are microtubules made of tubulin protein and intermediate filaments. When these elongated filaments are combined within the cell, different structural shapes emerge [10]. In addition, various forms of liquid crystals (nematic, smectic, chiral) are contained in the structures of the cytoskeleton and subcellular filaments.

Liquid crystals (cytoplasm and karyoplasm) have the ability to release quanta of electromagnetic energy under mechanical impact on them. When mechanical impact decreases, liquid crystal is able to absorb a quantum of electromagnetic energy, accumulating its energy in itself. Such properties of liquid crystals allow signaling to all parts of the brain of a living organism about the situation created in all parts of the organism, including the brain.

It is known from condensed state physics that liquid crystals are very sensitive to the influence of external fields (mechanical, thermal, electric, magnetic) [11, 12]. Consequently, any cell of a living organism is also affected by these forces. Disturbance of cellular orderliness leads to disruption of tissue functions. As a result, we can observe and study the formation of various topological defects, structural transitions, and molecular self-organization. These effects occur almost instantaneously in a fraction of a second. In this case, we can use a cell containing a liquid crystal and methods used in liquid crystal physics to study a biological cell [13-17]. That is, the liquid crystal cell is a prototype of a living cell. Here a wide range of possibilities opens up depending on the type of liquid crystal used and its physical characteristics, the orientation of molecules; the surface properties of the plates between which the LC is placed; the design of the cell; the method of influence on the cell; the type of external field and its parameters. As a result of such studies, we will have a comprehensive view of cell biology through which genetic and molecular features are studied simultaneously with the physical and mechanical properties of cells.

Thus, it is currently relevant to conduct research at the interface of sciences, in particular, physics and biology, and further utilization of their results, for example, in medicine and pharmacy. It is possible to use the physics of liquid crystals in the development of modern optical biosensors, as well as biomaterials to improve, for example, tissue regeneration.

2 Materials and methods

Let us consider the method of electric reflection in the liquid crystal-semiconductor system. The most promising methods of studying the state of liquid crystals near the surface of a solid body are methods of modulation spectroscopy. It should be noted that the method of electrical reflection gives direct information about the surface polarization of LC. The essence of the effect is that when a crystalline sample is placed in an electric field, there is a change in the energy zone structure, which manifests itself in a change in its optical properties, such as transmission or reflection coefficient.

Such a change, for example, of the reflection coefficient of a semiconductor placed in an electric field is determined by the increment of the imaginary and real ϵ_r parts of the dielectric permittivity. Moreover, in a field of intensity E , the changes of these quantities are equal, respectively [18]:

$$\Delta\epsilon_i(\omega, E) = \frac{B\theta^{1/2}}{\omega^2} F\left(\frac{\omega_d - \omega}{\theta}\right), \quad \Delta\epsilon_r(\omega, E) = \frac{B\theta}{\omega^2} G\left(\frac{\omega_d - \omega}{\theta}\right), \quad (1)$$

the reflection coefficient will be determined by the following expression:

$$\Delta R/R = \alpha(\omega)\Delta\epsilon_i + \beta(\omega)\Delta\epsilon_r, \quad (2)$$

where ω is the frequency of light $\theta = E^2/2\mu^*$; μ^* is the effective mass of the electron $\hbar = 2|P_{cv}n|^2(2\mu^*)^{3/2}$; P_{cv} is the momentum matrix element between the Bloch functions of the conduction band and valence band for vector \mathbf{d} is a unit vector along the field $\mathbf{d}(\omega) = \partial \ln R / \partial \epsilon_i$; $\beta(\omega) = \partial \ln R / \partial \epsilon_r$.

The functions $F[(\omega_d - \omega)/\theta]$ and $G[(\omega_d - \omega)/\theta]$ are expressed through the Airy functions $\text{Ai}(x)$ and $\text{Bi}(x)$ and the unit inclusion function $\mathbf{h}(x)$ [18]:

$$F\left(\frac{\omega_d - \omega}{\theta}\right) = \pi \left[\text{Ai}^2\left(\frac{\omega_d - \omega}{\theta}\right) - \left(\frac{\omega_d - \omega}{\theta}\right) \text{Ai}^2\left(\frac{\omega_d - \omega}{\theta}\right) - \left(\frac{\omega_d - \omega}{\theta}\right)^2 \text{H}\left(\frac{\omega_d - \omega}{\theta}\right) \right], \quad (3)$$

$$G\left(\frac{\omega_d - \omega}{\theta}\right) = \pi \left[Ai'\left(\frac{\omega_d - \omega}{\theta}\right) Bi\left(\frac{\omega_d - \omega}{\theta}\right) - \left(\frac{\omega_d - \omega}{\theta}\right) \cdot Ai\left(\frac{\omega_d - \omega}{\theta}\right) Bi'\left(\frac{\omega_d - \omega}{\theta}\right) - \left(\frac{\omega_d - \omega}{\theta}\right)^{1/2} H\left(\frac{\omega_d - \omega}{\theta}\right) \right].$$

It should be noted that, due to experimental difficulties, fields of 10^6 V/cm are usually required to record the electrical reflection spectra. All existing methods of electrical reflection differ in the way of applying the electric field to the sample and achieving the required intensity. The method using electrolyte realizes the possibility of modulating the spatial charge field at the semiconductor-electrolyte interface. Such field changes can be used for the purposes of optical modulation measurements.

The electrochemical properties of the boundary plane between a semiconductor and an electrolyte are discussed in great detail in [19, 20]. In the state of equilibrium, the electrochemical potentials of electrons in the solid and in the electrolyte should be the same, so when the semiconductor is placed in the electrolyte, electrons from one material pass from one to the other, until the electrochemical potentials are equalized, while the space charge near the surface of the semiconductor changes or, if it is not there, is established. Moreover, a layer of space charge will also be present on the electrolyte side (Huy layer). The field of such a layer is described by the expression [19]:

$$\frac{d\phi}{dx} = \frac{kT}{eL} F(Y, U_B), \tag{4}$$

where L is the length of the Debye shielding for the intrinsic material:

$$L = \left(\frac{\epsilon_0 kT}{8\pi e^2 n} \right)^{1/2}, \tag{5}$$

Here k is Boltzmann constant, T is temperature, e is electron charge, n is electron concentration, ϵ_0 is dielectric constant of vacuum;

$$F(Y, U_B) = [e^{-U_B}(e^{-Y} - 1) + e^{U_B}(e^Y - 1) + (e^{-U_B} - e^{U_B})Y]^{1/2}, \tag{6}$$

where $Y = e\phi/kT$; $U_B = Y - U_x$; U_x is the difference between the Fermi energies of the investigated material and the own material.

The electrolyte ions cannot approach the semiconductor surface closer than the value of their radius, hence, there will be a thin layer near the surface, which will not obey the electrostatic equations for continuous media. This is the so-called Helmholtz layer, and the potential distribution in it is difficult to calculate. The thickness of the space charge layer in the electrolyte (Debye shielding length) can reach $\sim 5 \text{ \AA}$ for electrodes with high conductivity. From the point of view of optical modulation experiments, this is convenient because the capacitance of such a layer creates a shunt circuit for an AC voltage in the same way as the capacitance of the space charge in a semiconductor. The impedance of the Helmholtz layer in the case of aqueous electrolytes can always be made negligibly small. The influence of field inhomogeneity can be made small by modulation by an alternating field in the presence of a constant electric bias [19].

To investigate the ordering of nematics in such layers, and to study more specifically the surface states of nematic single crystals, electrical reflection is the most sensitive tool. This is because a solid crystal and a nematic liquid crystal (NLC) in direct contact change their surface states depending on each other. This process proceeds until the electrochemical potentials of the semiconductor and the NLC are equalized. In the semiconductor, the process is accompanied by redistribution of charges in the surface region and possibly injection of the latter into the liquid crystal. In nematics, due to the fact that they have low conductivity and a large length of molecules possessing a dipole moment, this leads to a corresponding orientation of the dipole moments of the molecules. When the state of the liquid crystal is changed by some external influence, such as an electric or magnetic field, there should be a change in the surface states of the semiconductor. This can be registered by means of methods of highly sensitive modulation spectroscopy under the condition of sufficiently large changes in the optical properties of the semiconductor in the region between

Let us consider the methods of registration of electrical reflection spectra. Here, the small value of the variable signal of electric reflection $\Delta R/R$ against the background of a large level of constant reflection R (the ratio $\Delta R/R$ on average takes the value 10^{-5}) creates additional difficulties in registration. This issue is simplified if we take into account that $\Delta R/R$ is a value changing periodically in time. The latter circumstance is caused by the regularity of the external influence on the semiconductor. In this regard, to isolate $\Delta R/R$ from the noise, we can apply the principle of synchronous detection, which consists in the following.

Let the signal, which contains useful information at the input of the synchronous detector, has the form [21]:

$$U_B = U(t) \cos(\omega t + \phi_1), \quad (7)$$

where $U(t)$ is the amplitude of the modulating signal, and the conductance of the detector circuit varies periodically according to a linear law:

$$g(t) = g_o [1 + \alpha \cos(\omega t + \phi_2)], \quad (8)$$

where ϕ_1 is the phase of the signal, ϕ_2 is the phase of the conversion.

As a result of the transformation at the output of the device, the signal will be of the form:

$$I = U_B g(t) = U(t) g_o \left\{ \cos(\omega t + \phi_2) + \frac{\alpha}{2} [\cos(\phi_1 - \phi_2) + \cos(2\omega t + \phi_1 + \phi_2)] \right\}. \quad (9)$$

From here we can see that a component responsible for the low-frequency component appears in the equation, it is proportional to the amplitude of the modulating signal, which can be isolated with a low-pass filter:

$$I_{lf} = \frac{1}{2} \alpha U(t) g_o \cos(\phi_2 - \phi_1). \quad (9)$$

At such a conversion, the signal-to-noise ratio $\frac{S}{N}$:

$$\frac{S}{N} = \left(\frac{U_o^2}{N_o} \right) 2\tau_{RC}, \quad (T_o \gg \tau_{RC}), \quad (10)$$

where N_o is the spectral density of white noise, T_o is the observation time, U_o is the amplitude of the harmonic signal $I_c(t) = U_o \sin \omega_o t$.

3 Results and discussion

Let us consider studies of the orientation of molecules of various nematics on the semiconductor surface in the absence and under the action of external electric fields by the method of reflection conoscopy [22]. As a result of the experimental studies it was found that LC molecules can form different boundary conditions. Examples of data regarding the orientation of molecules in external fields are summarized in Table 1. It should be noted that SnO₂ tin dioxide substrates give strong binding to many nematic molecules. This allows them to be used as the top substrate in studies of the orientation of molecules at the boundary with a second substrate.

It should be noted that at strong boundary conditions and negative dielectric anisotropy the Fredericks threshold fields in alternating and constant fields coincide. And at weak boundary conditions, the magnitude of threshold fields at constant voltage cell is much smaller than the threshold for alternating fields. In this case, the threshold is determined not by dielectric anisotropy, but by surface polarization and the flexoelectric effect. However, in alternating electric fields, the orientation of dipoles at the boundaries stabilizes, leading to seemingly strong boundary conditions.

In the absence of external fields, the molecules of LC on the semiconductor surface are oriented by the microrelief of the faces and the surface charge field arising from the distortion of the semiconductor's zone structure. The magnitude and sign of the charge affect the distribution of the director of NLC on the substrate surface. Since the magnitudes of the orientation angles of molecules depend on the field and its distribution, it is possible to

estimate the magnitudes of surface charges and their locations on the semiconductor surface using LC. The corresponding calculations of surface charges and zone structure are usually performed using the method of Garrett and Bragger [18, 22]. The electrostatic potential ϕ is equal to the potential energy of an electron in the space charge layer and characterizes the curvature of the crystal energy zones in this region. The sign of the electrostatic potential will be negative if the zones near the surface are curved upward and positive if the Fermi level is in the upper half of the forbidden zone. The calculation of the field distribution in a semi infinite semiconductor is done by solving the Poisson equation. The field outside the semiconductor decreases according to the law $E \sim E_{01} \exp(-az)$.

Table 1. Boundary conditions of the NLC in different situations.

Name of NLC	Sign ϵ_{it}	P ₁				P ₂				Flint glass	Fused Quartz	U _c , V
		SnQ	Ge	FeS	CdS	SnQ	Ge	FeS	CdS			
n-(4-methoxybenzylidene)-n-butylaniline (MBBA) C ₁₁ H ₂₁ NO	-	⊥	∕	∕	∕	⊥	⊥	⊥	⊥	∕	∕	-1,6
		⊥	⊥	⊥	⊥	∕	∕	∕	∕	∕	∕	+0,8
		⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	∕	∕	-3,2
n-(4'-ethoxybenzylidene)-n-butylaniline (EBBA) C ₁₁ H ₂₃ NO	-	⊥	∕	∕	∕	⊥	⊥	⊥	⊥	∕	∕	-1,4
		⊥	⊥	⊥	⊥	∕	∕	∕	∕	∕	∕	+0,6
Two ring ether C ₄ H ₉ C ₆ H ₄ COOC ₂ H ₄ OC ₆ H ₁₉	-0	⊥	⊥	⊥	⊥	∕	∕	∕	∕	⊥	⊥	-60
		∕	∕	∕	∕	⊥	⊥	⊥	⊥	⊥	⊥	+32
A mixture of n-n-butyl-n'-heptanoyloxybenzene and MBBA	-	⊥	∕	∕	∕	⊥	⊥	⊥	⊥	⊥	⊥	-4,2
		∕	∕	∕	∕	∕	∕	∕	∕	∕	∕	+4,2
n-butoxybenzene and 4(β-methylbutyl) aniline	-	∕	∕	∕	∕	∕	∕	∕	∕	∕	∕	-3,8
		⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	∕	∕	+3,8
		⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	⊥	-5,6	

P₁ - lower and P₂ - upper bounding surfaces of the NLC; ⊥ - homeotropic orientation; ∕ - oblique orientation of the NLC molecules.

In studies of the orientation of NLCs with different dielectric anisotropy on a number of semiconductors with different types of conductivity, degree of doping and stoichiometry: Si, PbS, FeS, EuS Table 1 it was found that in the absence of external fields in the layer of NLC on the semiconductor surface there is a deformation type transverse bend (Fig. 1).

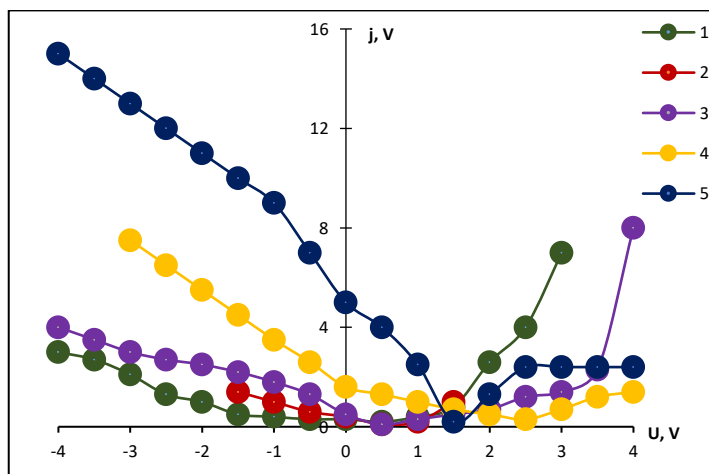


Fig. 3. Dependence of the magnitude of the potential on the bias voltage: 1 $\pm x = 1.9$; 2 $\pm x = 1.8$; 3 $\pm x = 1.73$; 4 $\pm x = 1.4$; 5 $\pm x = 1.65$.

In the presence of an external potential, a homeotropic orientation can be achieved on the semiconductor. This potential value corresponds to the potential of the semiconductor surface, the sign corresponds to that predicted by the theory of Garrett and Bragger [18, 22],

as illustrated in Fig. 3. The magnitude of the potential depends on the degree of doping of the substrate stoichiometry for the type iron disulfide semiconductor.

With increasing temperature, the averaged orientation angle of molecules in the NLC layer between isotropic substrates, as a rule, decreases [23]. This statement is true in the case of metallic, ionic and semiconductor crystals. The corresponding dependence shown in Fig. 4 apparently cannot be explained only by the action of surface electric fields, since in the Fredericks effect the orientation angle of molecules increases with increasing temperature. The real reason for the unusual relationship between temperature and the orientation of NLC molecules may be the disproportionate change in the elastic moduli and dielectric

anisotropy ϵ_a : $E_c \sim \sqrt{S \frac{k_{ii}}{\epsilon_a}}$, S is the degree of ordering NLC molecules [24, 25]. The surface potential of the semiconductor changes insignificantly when the temperature changes up to 40°C. It is also necessary to take into account the peculiarities of nematic ordering near the substrate surface, for example, the appearance of surface polarization.

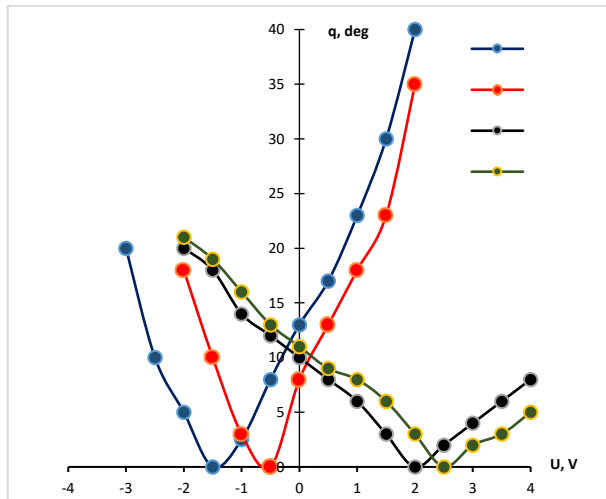


Fig. 4. Dependences of the inclination angle of molecules at the boundary with the germanium type substrate 1 ($T = 20^\circ\text{K}$), 2 ($T = 40^\circ\text{K}$); n-type- 3 ($T = 20^\circ\text{K}$), 4 ($T = 40^\circ\text{K}$) on the bias voltage.

To elucidate the mechanism of orientation of LC molecules, it is essential to clarify the boundary conditions. For this purpose, the effect of meander electric pulses with a polarity change time of ~ 10 ns on a homeotropically oriented LC layer was investigated. The results of these studies are shown in Figs. 3 and 4, from which it follows that at fields slightly different from the Fredericks field $E \sim E_c$, apparently, a "weak" adhesion of LC molecules with the substrate is manifested. The main mechanism of reorientation of the LC layer in this case is the change of boundary conditions due to the interaction of surface polarization with the external field and leading to the odd electrooptic effect. At $E \gg E_c$, the electric moment quadratic in the field dominates (Fig. 3 and 4), leading to an even electrooptic effect. The above allows us to assert that there is a "weak" coupling at the semiconductor interface and, at $E = 0$, an oblique orientation of molecules on the semiconductor surface. Then the value of the external potential $\varphi = \varphi_0$, compensating the charge of the semiconductor surface, corresponds to the homeotropic orientation of molecules on the surface.

Let us consider the estimation of the orientation of LC molecules on the semiconductor surface. The corresponding equation of state of LC will have the form (11):

$$\frac{d^2\theta}{dz^2} = 0. \tag{11}$$

Boundary conditions:

$$k \left(\frac{d\theta}{dz} \right) \Big|_{z=\pm\sigma} - PE \Big|_{z=\pm\sigma} = 0, \quad E = E_0 + E_1. \quad (12)$$

Since $E_1 \sim \exp(-\lambda z)$, the solution of (11) is sought as a function $\theta = (E_0 + E_1) p_0 \lambda z$. This means that the difference in the path of ordinary and extraordinary rays of light passing through a layer of NLC is zero when $E_1 = -E_0$. It is also significant that if the Fredericks effect is manifested, then in pure form the effect of the field of surface charges of the substrate on the polarized layer of NLC appears to be determinant in the vicinity of the point of phase transition nematic liquid crystal \rightarrow isotropic liquid. Away from it, the superposition of various factors complicates the physical picture and the isolation of each factor separately is impossible without the use of special methods. One of such methods is the method of reflection in the system NLC-semiconductor.

4 Conclusions

Liquid crystals play an important role in medicine, biology and pharmacy, providing new opportunities for diagnostics, research and treatment. Their unique properties and wide range of applications make them a key component of modern scientific and technological innovations, offering new approaches to biosensing and modeling of living systems. This article presents the applicability of approaches from condensed state physics to biological objects. A liquid crystal cell is used as a model of a biological system. The system of liquid crystal and semiconductor is analyzed using modulation spectroscopy. Measurement of the electrical reflection allows to evaluate the state of surface polarization of the liquid crystal. The influence of the electric field changes the energy structure of the semiconductor, leading to changes in the optical properties of both crystals. A method using electrolyte was used to analyze the optical modulation changes, which allowed the measurement of spatial charge modulations. The study of thin layers of various nematic liquid crystals showed that when the values of electric fields comparable to the Fredericks transition threshold, the orientation angle of liquid crystal molecules changes due to the interaction of surface polarization with the external field, an odd electrooptic effect is observed. If the value of the electric field significantly exceeds the threshold of the Fredericks transition, the electric moment that depends nonlinearly on the field predominates, which leads to an even electrooptic effect. The results of the study are expected to be used to create new drugs and materials with specified parameters for medical purposes.

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