
INTERACTION BETWEEN DROPLETS IN NEMATIC EMULSION UNDER THE ACTION OF EXTERNAL FIELDS

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The results of investigations of the behavior of glycerol droplets in nematic emulsions under the action of external electric and magnetic fields are reported. The character of a pairwise interaction between two separate droplets on the liquid crystal (LC) surface and the mechanisms, through which the external fields affect this interaction, have been studied. The interaction intensity has been determined.

1. Introduction

The liquid crystal colloids have been studied very intensively recently, which is associated with the existence of long-range interactions between particles in those colloids owing to the orientational elasticity of the LC matrix [1–3]. A capability to easily change these interactions by applying certain external factors to the LC matrix opens new trends for both fundamental science and modern technologies destined at creating the new, highly ordered structures with controllable characteristics. In this case, it is very important to know the character and the magnitude of the interaction between particles in such complicated colloid systems.

The interaction between particles that are located at long distances from one another can be described in terms of the symmetry breaking in the distribution of the director around an individual particle, in the region close to its surface [4–6]. This symmetry is affected, in particular, by the boundary conditions and the anchoring of LC molecules at the surface of a separate particle. If the director field around a particle is characterized by three symmetry planes (i.e.

there is the quadrupole symmetry), the interaction is quadrupole by its character; if one of the symmetry planes is absent (there is the dipole symmetry of director deformations), the interaction is a dipole one; if two, it is a Coulomb one. It should be noted that any real electrostatic interactions are not meant here – we talk about the so-called “elastic” dipoles or quadrupoles; i.e. it is only an analogy, which stems from the similarity between the mathematical descriptions of electrostatic phenomena and the interaction of particles in a liquid crystal and enables the interactions that arise between particles in a liquid crystal to be well understood and described. In particular, the director distribution in the vicinity of particles with normal boundary conditions at their surfaces – which give rise to a “hyperbolic hedgehog” defect [1,2,7] – has a dipole configuration; this circumstance predetermines the dipole character of the interaction among several particles at large distances. In a nematic liquid crystal, such particles form one-dimensional linear chains, and the dipole character of the interaction is responsible for these chains. That is, we have a mere attraction in the case where elastic dipole moments are collinear and parallel to the line that connects the centers of droplets and a mere repulsion in the case where those moments are collinear to one another but perpendicular to the mentioned line.

As was demonstrated in works [8,9], the deformations of the director around a particle can be influenced by the cell’s walls as well. In particular, in the case of identical particles with normal boundary conditions at their surfaces, we can obtain either the quadrupole

symmetry, if the cell thickness is small, or the dipole one, if the cell thickness is large. An important role in the director distribution around the particle and, respectively, in the interaction between particles is also played by an external electric or a magnetic field. For instance, the transformation of an elastic dipole into a quadrupole under the action of an electric field was described in work [10]. In fact, the liquid crystal colloids are unique systems, in which matching the boundary conditions at the surface of a colloid particle and the director distribution in the LC bulk can be used to realize a certain multipole interaction, to determine the character of such an interaction, and to change this character by external fields.

Along with the systems, where particles are completely embedded into an LC, the case where particles are located on its surface is of very much interest. As was shown in work [11], the droplets with planar boundary conditions at their surface can form either one-dimensional linear chains or two-dimensional hexagonal structures in nematic emulsions of such a type; the specific configuration depends on the ratio between the thickness of the liquid crystal layer and the droplet dimensions. These structures are not characteristic of droplets in a bulk sample with planar boundary conditions and the quadrupole symmetry. But, since the particles are not embedded into the LC completely, one of the symmetry planes of the director distribution around droplets disappears, and the particles become elastic dipoles. In the present work, we consider the interaction which arises between particles in such a system. We examined the influence of an external electric or magnetic field on the distribution of the director near droplets and experimentally determined their interaction energy.

2. Experiment

In our experiments, the nematic emulsion was prepared in the same way as was described in works [11, 12]. A nematic LC film 20–200 μm in thickness was spread onto the glycerol surface. The director acquired the planar orientation at the LC–glycerol interface and the perpendicular orientation at the LC–air one. Such boundary conditions are referred to as hybrid ones. The whole system was subjected to heating, so that glycerol could diffuse freely into the LC; afterwards, the system was cooled down to room temperature. Several hours passed, glycerol droplets became formed at the LC–air interface. The size of droplets depended on the regime of cooling, so that it turned out possible to create a

system of many identical droplets with size from 1 to 20 μm . The droplets, which had no contact with air and were located near the LC–glycerol interface, formed ordinary chain structures of the quadrupole type, as it is required by planar conditions at the droplets' surfaces; while those droplets, which remained at the LC–air interface, could create – at a certain concentration – almost perfect two-dimensional hexagonal structures. Similar ordered structures were also observed in ordinary colloids [13–17], where the interaction is isotropic as well, but has another origin.

If particles are located on the LC surface, then, owing to the incomplete immersion of glycerol droplets, there emerges an extra deformation of the director caused by a droplet [18]. The vertical component of this force attempts to move the droplet up or down, depending on the initial distribution of the director and the director distribution around the droplet, but, in any case, it tries to minimize the deformation energy in the LC. The vertical displacement of a droplet brings about a protrusion of the nematic–air interface. The capillary interaction, which arises in this case, has an attractive character, and its energy looks like [14, 19]

$$U_{\text{elc}}(r) = \frac{f_{\text{el}}^2}{2\pi\sigma_{\text{LCA}}} \ln\left(\frac{r}{\lambda}\right), \quad (1)$$

where σ_{LCA} is the surface tension at the LC–air interface, $\lambda = \sqrt{\sigma_{\text{LCA}}/(g\rho_{\text{LC}})}$ is the capillary length, ρ_{LC} the LC density, and g the free fall acceleration. At $f_{\text{el}} = 10^{-10}$ N, the interaction energy $U_{\text{elc}} \approx 3 \times 10^{-19}$ J ≈ 80 kT . At large distances between droplets, the capillary attraction comes into equilibrium with the dipole repulsion. Provided that the sample is hybrid, the immersion of droplets into the LC is incomplete, and the shape of a droplet is asymmetric, this elastic dipole–dipole interaction between particles can be written down in the form [11]

$$U_{\text{eldip}}(r, \theta) = K \frac{\alpha^2 R^4}{r^3} (1 - 3 \cos^2 \theta), \quad (2)$$

where the coefficient α makes correction for the incomplete immersion of a droplet into the LC, K is the averaged elastic constant of the LC, and θ is the angle between the droplet-to-droplet radius-vector and the director. If the thickness of the sample is small, being of the order of the droplet diameter, then $\theta \approx 0$, and there appears an attraction of the dipole type, which explains the formation of linear dipole chains. If the sample thickness is much larger than the droplet diameter, then $\theta \approx \pi/2$, and a repulsion of the same dipole type takes

place. In this work, we experimentally determined the character and the magnitude of the interaction between particles and compared the results obtained with those of theoretical calculations.

3. External Fields

In order to determine the magnitude and the character of the interaction between particles, it is necessary to have a tool which would enable one to affect the origin of this interaction. Then, by monitoring the variation in the behavior of individual droplets or their system, one could determine the parameters which would describe the corresponding behavior. In particular, it can be done experimentally, by applying an external field to the particles and observing their motions to the corresponding equilibrium positions after the field having been switched off. The particle motion invokes the counteraction of LC in the form of the Stokes friction force $6\pi\eta R \frac{dr}{dt}$ for a sphere with particle's size; here, R is the particle's radius, η the effective friction coefficient, and r the interparticle distance. The product of the particle's mass and the acceleration is neglected, because it is much smaller than the Stokes force magnitude. Therefore, knowing the velocities of particles, with which they move to their equilibrium positions, one can determine the character and the magnitude of the interaction between them. In experiments [7], the influence of the magnetic field on the chain structure of a number of ferroliquid droplets in the LC was studied. The application of a magnetic field gave rise to the repulsion of droplets from one another. On the contrary, switching the magnetic field off allowed elastic attractive interactions to bring particles together again. Making use of the technique described above enabled the authors of work [7] to determine – from experimental data – the force law $F \sim r^{-4}$ for droplets with normal boundary conditions, which are characterized by the dipole symmetry. This dependence corresponds to the interaction of two elastic dipoles along the direction which is parallel to the line connecting the centers of the droplets. In this work, a similar approach was applied to experimentally determine the character and the magnitude of the interaction between two individual droplets located at the nematic LC–air interface, by applying a magnetic or electric field along this interface. Such a geometry of the experiment allowed us to determine the interaction between elastic dipoles in the direction perpendicular to the line connecting the droplets' centers.

In a horizontal magnetic field, glycerol droplets, which make up a hexagonal lattice, become rearranged into a structure composed of a plenty of short chains. They are oriented along the field, and their lengths increase with the field strength H [20]. Such a behavior stems from the fact that the director changes its orientation towards to the magnetic field direction owing to the anisotropy of the magnetic susceptibility $\Delta\chi$. The magnetic field governs the director distribution up to a distance $\xi(H) = H^{-1}\sqrt{K/\Delta\chi}$ from the surface. The director deviation at a depth of the order of the droplet diameter can be determined from the relation $\theta = d/\xi_H$. The variation of the director orientation gives rise to the variation of the character of the interaction as well, because the angle between the droplet-to-droplet radius-vector and the director changes, and the interaction transforms from dipole repulsion to dipole attraction. The modification of the character of the interaction takes place if the relation $\cos^2(d/\xi_H) \leq \frac{1}{3}$ for the director deviation angle from the droplet-to-droplet radius-vector holds true. In our experiment, this condition was already satisfied at $H \approx 200$ Gs; in this case, the dipole repulsion transforms into the dipole attraction, which causes the formation of chains.

We carried out a special experiment destined at studying the behavior of only two droplets $5 \mu\text{m}$ in radius. After the magnetic field with the strength $H \approx 2$ kGs had been switched on, the droplets attracted each other, and the line connecting their centers remained parallel to the field direction. Further, the magnetic field was switched off, and the droplets started to repulse each other. The pair interaction energy at the particle repulsion after the field having been switched off was determined from the variations of droplets' velocities. The latter were calculated making use of the results of measurements of exact droplets' positions carried out by the videorecording at a rate of 10 frames per second and following the technique described in work [21]. Having determined the positions of droplets in every frame, we found the distance between them at every time moment (Fig. 2,*a*) and calculated the corresponding repulsion force after the magnetic field having been switched off. Further, by integrating the dependence of the force acting between the droplets on the interdroplet distance over the latter, we obtained the pair interaction energy between two droplets. Using the least squares method, we found that the interaction energy has the dipole character: it is proportional to r^{-3} (Fig. 2,*b*), and the corresponding fitting dependence $y = a + b/x^3$ demonstrated the best agreement with experimental data if $a = -68.47$ and $b = 3.12 \times 10^4$.

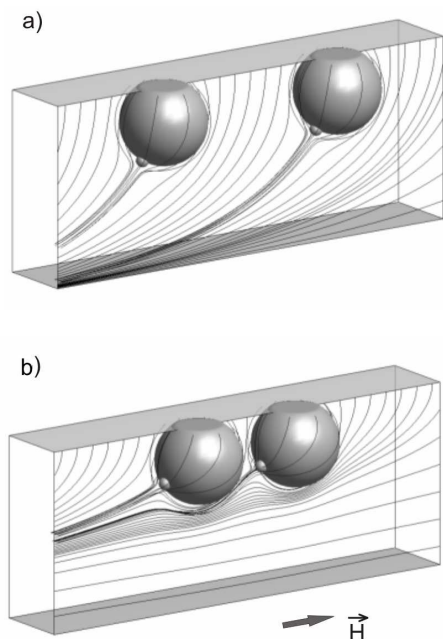


Fig. 1. Director distribution around two droplets, which are located at the LC–air interface, in the absence of a magnetic field (a) and if a horizontal magnetic field is applied (b). After the magnetic field has been switched on, the LC molecules attempt to become oriented in parallel to the field direction, which causes the boojums on the droplets to shift and thus gives rise to the appearance of the horizontal component of the elastic dipole moment, i.e. to the emergence of the attraction between droplets

It follows from the experimental results that the interaction energy of the dipole repulsion between droplets $U(r) \approx 140 kT$, which is two orders of magnitude higher than the thermal energy kT . As was already said, the equilibrium distance between droplets in such systems is determined by a balance between the capillary attraction and the repulsion occurring owing to director field deformations. It is evident that those interaction energies correlate well with each other, the capillary attraction energy being of the same order as the dipole repulsion energy between two droplets. In a magnetic field, no extra interactions arise, except those resulted from a change of the director distribution. Therefore, the presented results can be regarded as a straightforward experimental determination of the magnitude of the elastic interaction. The influence of an external electric field has a more complicated character.

In an ac electric field with a frequency of 10 kHz and applied along the LC–air interface, the behavior of those droplets is somewhat different. Although two separate droplets also attract each other under the action of the

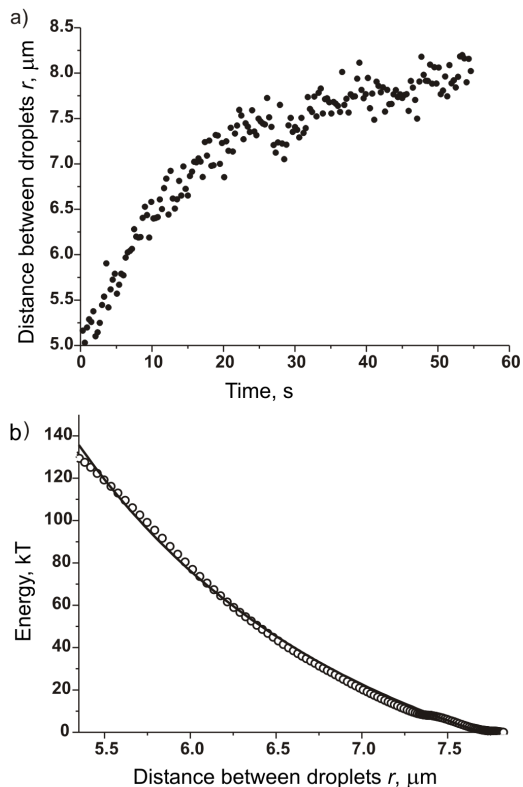


Fig. 2. (a) Dependence of the center-to-center distance between two glycerol droplets on the time after the magnetic field has been switched off; the elastic interaction repulses the droplets away from each other. (b) The interaction energy between two droplets just after the magnetic field has been switched off (points correspond to the experimentally restored interaction potential, solid curve depicts the approximation function $y = a + b/x^3$ with the fitted values $a = -68.47$ and $b = 3.12 \times 10^4$)

electric field, now we have a more powerful tool to affect the properties of the system than a magnetic field proposes. In the case of electric field, droplets come closer to each other much faster; so that, by applying weak fields with a strength of the order of about $0.1 V/\mu m$, one can overcome the elastic repulsion between the droplets and make them to merge together in the field direction, which has not been observed even in strong magnetic fields. The application of an electric field also changes the director distribution around the droplets, but the origin of why the droplets behave in such a manner is different. Owing to the difference between dielectric permittivities of the LC and glycerol, the electric field induces a real dipole moment in each droplet, so that the electrostatic dipole–dipole interaction emerges, and

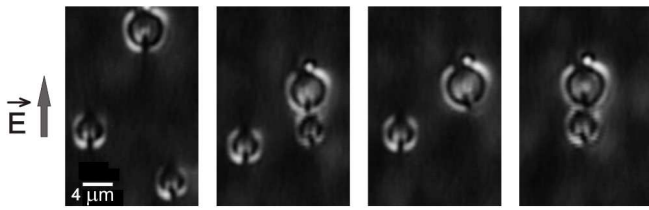


Fig. 3. Three glycerol droplets, which moves on the surface of a nematic LC under the action of an electric field (photos were made in crossed polarizers)

its energy looks like [10]

$$U_{dd}(r, \vartheta) = 12\pi\epsilon_0\epsilon_{LC} \left(\frac{\epsilon - \epsilon_{LC}}{\epsilon + 2\epsilon_{LC}} \right)^2 \frac{R^6 E^2}{r^3} (1 - 3\cos^2 \vartheta), \quad (3)$$

where ϵ is the dielectric permittivity of glycerol, ϵ_{LC} the averaged dielectric permittivity of the LC, and E the electric field strength. For instance, at $\vartheta = 0$, Eq. (3) gives the interaction energy of about $850 kT$ for two droplets, each with the radius $R = 2.3 \mu\text{m}$, that are located at the distance $r = 10 \mu\text{m}$ from each other in an electric field $E = 0.1 \text{ V/cm}$ ($\epsilon_{LC} = 8.7$ and $\epsilon = 40$). It is the electrostatic nature of the interaction that is the dominant reason of why the droplets come closer to each other in the applied electric field and why this interaction depends on the orientational angles ϑ of individual dipoles with respect to the radius-vector between them.

The latter phenomenon is easy to be observed experimentally, while examining the behavior of three droplets in the electric field (Fig. 3), which neatly reveals the angular dependence of the interaction. Two droplets located on a straight line oriented along the field direction attract each other stronger, move towards each other faster, and eventually merge together, in spite of the fact that the distance between them was first longer than the distance to the third droplet, whose position deviates from the direction of the applied field. The third droplet also interacts with the other two ones, but the character of its motion is more complicated. First, it vibrates owing to its thermal motion and under the action of two other droplets, until it finds itself in the sector of attraction; then, it forms a chain, which is directed along the applied field, with a droplet that was formed as a result of the merging of two other droplets. Ultimately, all the three droplets can merge together. Such a behavior testifies that electrostatic interaction

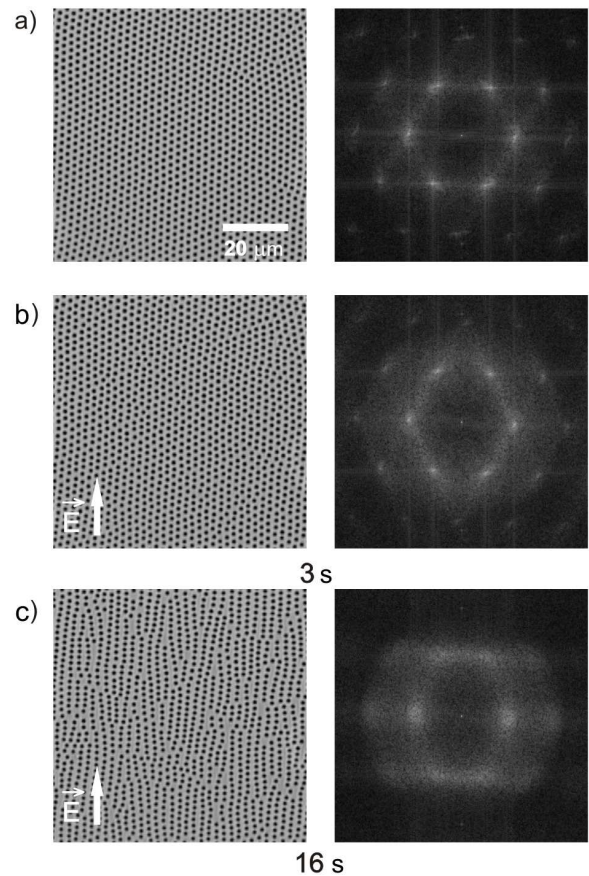


Fig. 4. Microphotos of the aggregates of glycerol droplets and the corresponding simulated diffraction patterns (Fourier transforms): (a) in the absence of the field (a hexagonal structure), (b) in 3 s after the electric field directed along the structure has been switched on (the lattice becomes squeezed along the field direction, and (c) in 16 s after the electric field has been switched on (the transformation into a system of long chains)

between droplets is much stronger than their interaction through the deformations of the director field, because the former turns out capable to overcome the elastic repulsion between droplets which always exists between them. Following the same scheme, which was described above while discussing the application of a magnetic field, we determined that the interaction energy for droplets $4.5 \mu\text{m}$ in diameter amounts to about $500 kT$.

We also studied the influence of an electric field on the system of many droplets which form a hexagonal structure (Fig. 4, a). If the electric field with a strength of $0.1 \text{ V}/\mu\text{m}$ is applied along the interface, the hexagonal structure becomes first squeezed along the direction of the applied field (Fig. 4, b), i.e. it becomes anisotropic in this direction; further, its period along

the field direction becomes shorter, and chains are formed at last (Fig. 4,c). These transformations are well observable, if one simulates the diffraction patterns of the corresponding structures, taking advantage of the Fourier transformations of relevant optical images. In particular, the diffraction pattern given by the hexagonal structure in the absence of the field is a regular hexagonal array composed of six separate light spots. In 3 s after the field has been applied, the lattice anisotropy becomes noticeable; and, in 16 s, the lattice is transformed under the action of the electric field into a system of chains, so that the light smeared lines, which are almost parallel to one another but perpendicular to the direction of the applied field and, hence, to the direction of chains, appear in the diffraction pattern. The squeezing of the structure is explained by the variation of the dipole interaction between real dipole moments. If the electric field is switched off, the hexagonal arrangement becomes restored, and the droplets return back into their initial equilibrium positions. This occurs, because the induced dipole moments disappear, so that the previous mechanism of formation of the hexagonal structure becomes recovered.

To summarize, the results reported in this work experimentally confirmed the dipole character of the interaction between glycerol droplets in a nematic emulsion, provided that the droplets are located at the LC surface, and allowed us to estimate the magnitude of this interaction. The results obtained agree well with the theoretical estimations of the interaction through a deformation of the elastic field of the director. This provides a rather powerful tool for the further research of the collective nature of the interaction in many-particle liquid crystal systems.

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ВЗАЄМОДІЯ КРАПЕЛЬ У НЕМАТИЧНІЙ ЕМУЛЬСІЇ ПІД ВПЛИВОМ ЗОВНІШНІХ ПОЛІВ

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Резюме

Представлено результати досліджень поведінки крапель гліцерину в нематичних емульсіях під впливом зовнішніх (електричного та магнітного) полів. Досліджено характер парної взаємодії двох окремих крапель на поверхні рідкого кристала (РК) і механізми впливу на нього зовнішніх полів, визначено величину цієї взаємодії.