Crystal Structure in Nematic Emulsion

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We describe the experimental observation of a crystal structure formed by glycerol droplets suspended in a nematic liquid crystal. The structure exhibits a high density hexagonal ordering. We have experimentally observed a noticeable interaction between droplets with tangential boundary conditions. Within the scope of known models we discuss the nature of appropriate mechanisms of the interaction.

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Dispersions of macromolecular foreign particles in a nematic liquid crystal (NLC), as a class of materials that exhibit collective behavior and some unusual structures, have attracted considerable interest in recent years [1,2]. The orientational elasticity of a nematic host gives rise to a specific anisotropic interaction between the particles. This interaction has both repulsive and attractive components. A combination of these interactions determines the disposition of suspended particles and thus the structure as a whole. Such types of structures, where the particles form long linear chains, were already observed in experiments with water droplets [3–5] or small hard polymer balls [6] suspended in NLC. The structure that consists of periodically aligned chains of droplets was observed in [7]. The experimental and theoretical studies of interactions of water droplets suspended in a liquid crystal have been generally performed for the strong normal anchoring of liquid crystal molecules at the droplet boundary [8–13]. In this case, distortion of the orientational order of a nematic induces a topological defect, in the form of a combination of the radial hedgehog and hyperbolic hedgehog, which accompanies each droplet [3,4]. Because of the dipolar nature of the defect and thus the dipole-dipole and quadrupole interaction, the droplets tend to form long linear chains [7]. As stated in [9,13], even this character of interaction can describe experimentally observed structures. The effective pair interaction between droplets has a different character depending on the boundary conditions between the droplet and liquid crystal molecules. A more complicated structure, and in particular a crystal one, was theoretically predicted in [14,15] for the case of weak anchoring. The character of interaction in the system of small particles suspended in a NLC was considered as an interaction via the elastic director field. In the present paper we for the first time report on experimental observation of a two dimensional high density hexagonal crystal structure formed by glycerol droplets suspended in a nematic liquid crystal.

A purified glycerol layer, with a thickness of about 5 mm, was covered with a thin layer of nematic liquid crystal 5CB, placed in a microscope heating stage (HS1-i, Instec, Inc.), and observed through a polarizing microscope. The temperature was changed with the accuracy of 0.03 K. The thickness of the LC film was set in the range of 60–80 μm. The orientation of the liquid crystal varied from a planar one at the glycerol interface to a homeotropic one at the air interface. As soon as thermodynamic equilibrium was achieved the sample was heated to the temperature of 50 °C. We assume that glycerol molecules diffuse into liquid crystal and the efficiency of the diffusion becomes higher for the higher temperature. Decreasing the temperature, one can observe effective condensation and a growth of glycerol droplets [16,17]. A majority of glycerol droplets moves down to the bottom interface, since the density of glycerol is higher than that of the liquid crystal. The exception is those droplets which, due to polarization forces, get trapped at the upper border of the liquid crystal layer. The energy of the van der Waals force is effective enough to balance the gravitation force and to keep droplets bounded at the surface. The van der Waals interaction between two identical spherical particles can be defined from [18–20] as

$$E = -\frac{A}{6}\left(\frac{2R^2}{d^2 - 4R^2} + \frac{2R^2}{d^2} + \ln\frac{d^2 - 4R^2}{d^2}\right), \quad (1)$$

where A is Hammaker's constant [18], that depends on a correlation between the dielectric permittivities of neighboring media. R is the droplet radius, d is the distance between droplet centers. In our case, when the interaction occurs between a droplet and a flat surface, $E \approx -\frac{A}{6}\left(\frac{R}{L} + \frac{R}{L+2R} + \ln\frac{L}{L+2R}\right)$, where L is the distance between the droplet surface and liquid-crystal–air interface. Since $L \ll R$, one can use the $E \approx -\frac{A}{6}\frac{R}{L}$. We can estimate L using the simple equation

$$\frac{A}{6}\frac{R}{L^2} = \frac{4\pi}{3}R^3(\rho_{\mathrm{G}} - \rho_{\mathrm{LC}})g\,, \quad (2)$$

where ρ_{G} and ρ_{LC} are the densities of glycerol and liquid crystal, respectively. g is the free fall acceleration. Taking $A \approx 10^{-20}$ J [21], it gives $L \approx 0.5$ μm for the average droplet size of 7 μm. Taking into account that the surface tensions of glycerol (G), liquid crystal (LC), and air (Ar) are related as [22] $\sigma_{\mathrm{GAr}} > \sigma_{\mathrm{LCAr}} > \sigma_{\mathrm{GLC}}$, one can state that glycerol droplets are fully surrounded by the liquid crystal, and interaction via the elastic director field becomes appropriate for consideration.

The crystal structure made of glycerol droplets becomes well distinguished approximately 4 h after the room temperature was achieved; see the microscopic picture in Fig. 1a. The time required to build the structure is in agreement with that obtained in [13] for two droplets as 120 s. Since too many droplets are involved in the structuring process, much more time is required to tune the droplets into the stable position. The two-dimensional structure exhibits high density hexagonal packing with well-defined distances and angles, Fig. 1b. For each droplet radius, the distance between droplets is different while the hexagonal positioning is maintained. Heating of the system to the temperature that corresponds to the nematic-isotropic transition makes droplets randomly distributed; see Fig. 1c. A part of the droplets moves down where droplets merge with the glycerol layer. Some droplets merge with each other. It is an important fact, since both attractive and repulsive forces are necessary for the existence of a thermodynamically stable structure. Furthermore, attractive forces must be of a longer range comparable to the repulsive ones. Experimental observation of crystal structure was reported in [23–25] for charge stabilized colloids as a result of the van der Waals attraction and Coulomb repulsion. In our system the repulsive force naturally arises from interaction via the elastic deformation of liquid crystal [9,15] and has the quadrupolar character:

$$U_q = \frac{\gamma_{3113}^2}{\pi K}\,\frac{1}{d^5}(8 - 40\cos^2\theta + 35\cos^4\theta), \tag{3}$$

where γ_{3113} is the component of tensor that characterizes the geometrical form of the particles and depends on the anchoring at the particle surface, K is the elastic constant of liquid crystal, θ is the angle between the director and normal $\vec{\nu}$ to the liquid-crystal–air interface taken at the distance that corresponds to the bottom boojum level. This interaction is anisotropic; however, it remains repulsive for the geometry we consider in our experiment [12,13]. This interaction is attractive when the line joining the particle centers makes an angle between 31° and 70° to the z axis [4].

Now we proceed to discussion of the attractive force. Neither van der Waals [19,20] nor Casimir [20,26] forces can be large enough to create crystal ordering within the system of glycerol droplets suspended in a nematic liquid crystal. One can estimate the energy of van der Waals attraction from Eq. (1) for the distance between two neighboring droplets $d \approx 15\ \mu\mathrm{m}$. It gives $\sim 10^{-20}$ J. This is a couple of orders of magnitude lower than the repulsion that comes from the elastic interaction via director field [9]. According to [27,28], the Casimir force, the force originated from fluctuations of the order parameter of a liquid crystal, has the same order of magnitude as the van der Waals force. There are two possible interactions that could give rise to large enough attractive forces to build the experimentally observed structure. The first one is related to distortion of the liquid-crystal–air interface. Since glycerol droplets have a weight, the interface is bent around the point where the droplet is trapped, which costs some energy. The force that arises from the deformation of the interface is attractive and tends to make all small bends join together [29]. This force must exist also at the temperature above the clearing point of the liquid crystal, which contradicts the experimental results. The second source of interaction can be attributed to the dipole-dipole interaction [9,13,15]:

$$U_d = \frac{\beta_{313}^2}{\pi K}\,\frac{1}{d^3}(2 - 3\cos^2\theta), \tag{4}$$

where β_{313} is the component of tensor that characterizes the geometrical form of the particles and depends on the anchoring at the particle surface. This interaction is also anisotropic but can be attractive for small θ.

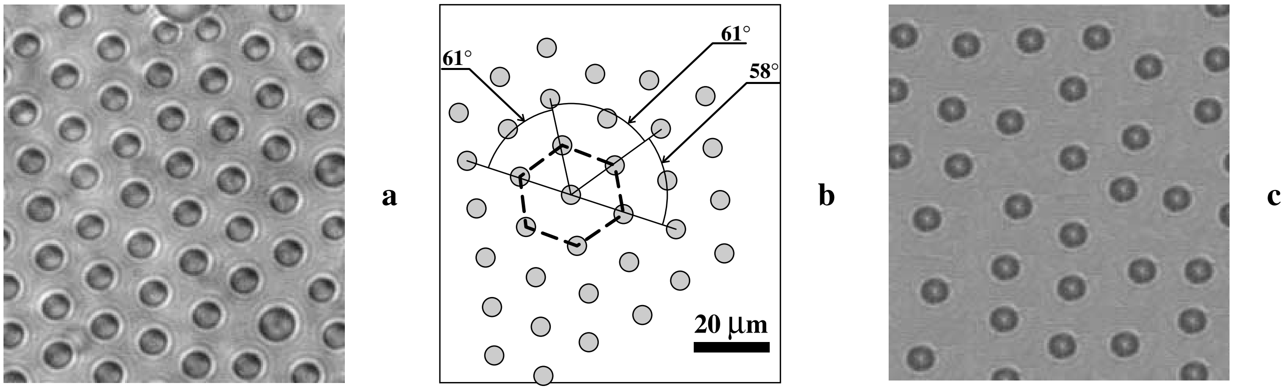

FIG. 1. Microscopic picture of glycerol droplets with the planar boundary conditions suspended in a nematic liquid crystal. The droplets exhibit high density hexagonal packing for all temperature range of the nematic phase (a), and become randomly distributed for the temperature above the nematic-isotropic transition (c). (b) is a schematic representation of the observed structure.

There is another important feature of the experiment. Since glycerol produces tangential alignment whereas air tends to align LC normally, liquid crystal molecules have a different orientation at the top and bottom interfaces [30,31]. In this case the director distribution uniformly varies from homeotropic to planar. It means that there is either an angle between the global director distribution and axis between boojums (in this case the droplet axis coincides with the axis between boojums) or the bottom boojum is shifted from the droplet axis (we believe that the top boojum location coincides with the point of contact between droplet and interface). Irrespective of these scenarios, each of which requires an additional detailed investigation, one can state that the orientation of the symmetry axis of the distorted region does not coincide with the orientation of the director in the layer. Thus, the cylindrical symmetry applicable for the spindlelike distorted region is also broken. Broken spherical and cylindrical symmetries lead to effective interaction energy through the deformation of the elastic director field that includes both the dipolar and quadrupolar components [9,13,15]. It means that both repulsion as well as attraction influence droplet distribution. Physically, the attraction arises because the joining of separate deformations of the director around the droplets will decrease the deformation energy of the liquid crystal. Figure 2 represents a visual example of when convexities in the director distribution enclose into hollows that may decrease the elastic energy. Since the proposed approach does not depend on the character of the boundary conditions, we can determine effective interaction energy using the geometrical parameters of the droplets and sample from Eqs. (3) and (4):

$$U = \frac{\beta_{313}^2}{\pi K}\frac{1}{d^3}(2 - 3\cos^2\theta) + \frac{\gamma_{3113}^2}{\pi K}\frac{1}{d^5}(8 - 40\cos^2\theta + 35\cos^4\theta). \qquad (5)$$

Using a glycerol we have realized tangential boundary conditions around each droplet. In this case two boojums accompany the glycerol droplet. Such director distribution destroys the spherical symmetry of a droplet freely suspended in a liquid crystal. The distorted region becomes spindlelike. Actually, a correct approach implies calculation of the exact director distribution as well as the distorted region from minimization of the liquid crystal free energy. To avoid such a complicated task, one can consider the all distorted region as a particle. Now we have spindlelike particles with a planar boundary condition. In this case β_{313} and γ_{3113} can be defined from the geometrical form and anchoring energy [15] as $\beta_{313} = \frac{1}{3}\pi W R^3$ and $\gamma_{3113} = \frac{4}{15}\sqrt{6}\pi W R^4$. The minimum of the energy is realized at the distance between droplets d_0, given by

$$d_0 = \sqrt{\frac{5}{3}\,\frac{8 - 40\cos^2\theta + 35\cos^4\theta}{3\cos^2\theta - 2}\,\frac{\gamma_{3113}}{\beta_{313}}}. \qquad (6)$$

The experimental dependence of the average distance between droplets on the droplet radius is shown in Fig. 3. The dependence was measured for the thickness of a liquid crystal layer of 70 μm. Considering a uniform change in director distribution from the bottom to the top surface, one can extract θ for all droplet sizes. To perform theoretical calculations we fixed the average value of θ, $\theta = 11°$. The dependence obtained from (6), represented by a solid line in Fig. 3, is in a quantitative and qualitative agreement with the experimental data.

Summarizing, we experimentally observed a two-dimensional crystal structure formed by glycerol droplets suspended in a nematic liquid crystal. The structure exhibits a high density hexagonal ordering with the well-defined distance between droplets and angles. Within the scope of known models we discussed the origin of the

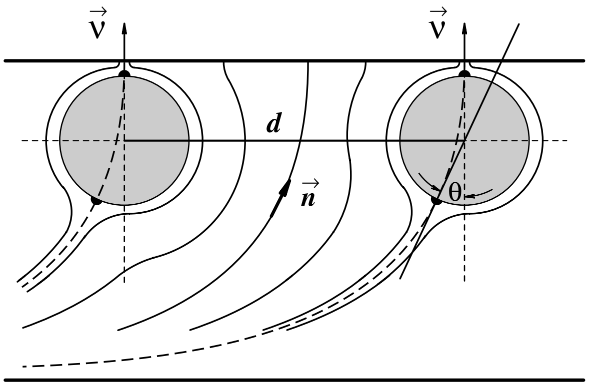

FIG. 2. Schematic representation of the director distribution around glycerol droplets.

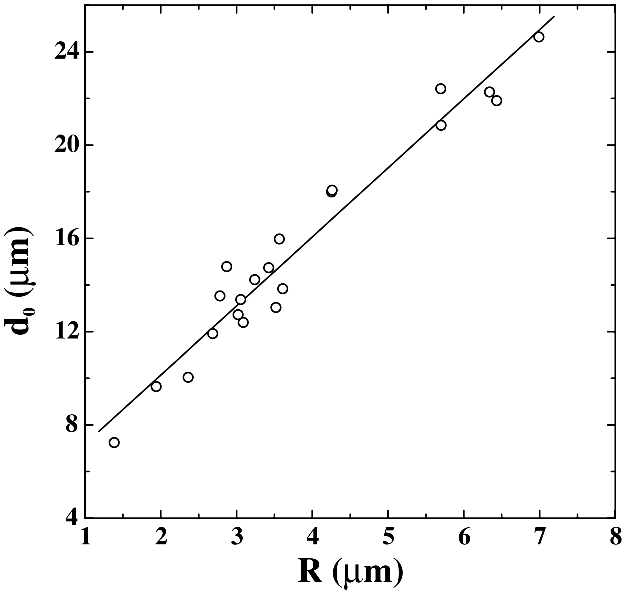

FIG. 3. Distance between droplets as a function of the droplet radius. Open circles represent experimental measurements; the solid line represents the dependence obtained from Eq. (6).

repulsive and attractive interaction. The elastic interaction seems to be especially appropriate for the creation of the crystal structure.

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