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Interaction of foreign macrodroplets in a nematic liquid crystal and induced supermolecular structures

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The behavior of a system of macroscopic particles introduced in a nematic liquid crystal is studied theoretically. The energy of the pair interparticle interaction associated with the director elastic field deformation is found. The interaction intensity and character are studied as functions of the distance, the geometric parameters of foreign macroparticles, and the value of their anchoring to the mesophase. The interparticle interaction can cause nontrivial collective behavior that results in the formation of new spatially modulated structures in the macroparticle system. The periodic arrangement of chiral particles that induces a helical structure can give rise to two incommensurable periods in the average orientation distribution of macroparticles.
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I. INTRODUCTION

Colloid media formed by hard particles suspended in liquids are a widely abundant important state of matter and hence have attracted much interest in science, technology, and medicine [1–3]. Dispersed liquid crystals, i.e., the mesophase with macroscopic inclusions of a foreign substance [1,2], are a particular case of such systems. The physical properties of such media are thoroughly studied in Ref. [1], which also reveals the unsolved problems in this research field. The macroparticles introduced in a liquid crystal considerably influence the electro-optic properties of the latter, one of the reasons being the formation of new supermolecular structures induced by these particles [1,4,5]. We mean the induced optical gyrotropy [5,6] and production of threadlike structures consisting of colloid particles [1,7]. To describe the formation conditions and behavioral properties of the macroparticle-induced structures implies taking into account their interaction both associated with physical properties (charge, dipole moment, etc.) and caused by the director elastic field deformation. An interaction produced by the director deformation was considered by many authors [1,8,9]. The physical mechanism of this interaction is that the foreign macroparticle distorts the director distribution that can occupy a region much greater than its dimensions and thus provides an effective interaction with another similar microparticle via mediation of the elastic field deformation. The physical criterion of this description follows from the observation that for the director field deformation treatment to be adequate, the macroparticle size must be greater than the mesophase molecule dimensions but much smaller than the distance between the macroparticles. The macroparticle may also be regarded as a microparticle surrounded by a ‘‘solvate shell’’ provided the interaction between such a particle and the mesophase molecules is much more intense than the intermolecular interaction responsible for the mesophase formation. The solvate formation may be regarded as a macrocluster; thus its interaction with another similar formation may be described in terms of the director field deformation. The validity of this treatment depends on whether we can impose the boundary conditions on the director for such a formation. In this sense, the interaction of liquid colloid droplets (neglecting of probable shape deformation) also is associated with the director elastic field deformation in the mesophase in which these droplets are dissolved. Neglecting other possible mechanisms of interdroplet interaction, we shall consider the macroparticle interaction via the director field deformation. This is the main subject of this study.

The purpose of this paper is to calculate the interaction energy of macroparticles introduced in the nematic liquid crystal that is associated with the director field deformation to describe the dependence of the interaction intensity and character on the distance and geometrical and physical parameters of foreign macroparticles. The physical factors are assumed to be the macroparticle shape and the director anchoring to the macroparticle surface; the latter is determined by the nature of the interaction with mesophase molecules. Which of the two limiting cases occurs, i.e., either (i) the director distribution on the given macroparticle surface is determined by the total self-consistent effect of all other macroparticles or (ii) the director distribution in the region circumjacent to the macroparticle is determined by this very macroparticle, depends on the value of the director anchoring to the macroparticle surface and the concentration of the latter. In case (ii), the director anchoring to the macroparticle is regarded as the boundary condition that governs the director deformation field to be found. The problem concerning the interaction of spherical macroparticles via the director field deformation, formulated in this manner, was solved in [8]. Case (i), when the director distribution on each cluster surface is determined by the self-consistent interaction of all macroparticles, was considered in [9]. In particular, Lopatnikov and Namiot [9] have calculated the interaction energy for cylindrically symmetric particles. However, the general problem of how to calculate the macroparticle interaction energy as a function of cluster geometric parameters and anchoring has not been either formulated or solved. In the present paper we have managed to find the self-consistent

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pair interaction energy for macroparticles of arbitrary shapes, for any dependence of anchoring on the macroparticle surface coordinate and for different Frank elastic constants, from the general premises. Our approximation infers the self-consistence of the director field on an individual macroparticle surface and the director produced by all other macroparticles. The self-consistent molecular field approximation for macroparticles implies that the field distribution on the surface of an individual particle is determined by the joint effect of all other clusters (and is equal to the distribution on the cluster boundary in the case when their would be no particle). Then the interaction of the individual particle with the director field deformation produced by the other macroparticles is determined by the anchoring on the surface of this particle. It is analogous to the molecular field approximation and is correct for deriving the pair interaction energy produced by the collective behavior of foreign macroparticles. In the opposite case we would have to consider strong deformations of the director field and it would be impossible to employ the continuum theory of the elastic director field deformation that involves expansion in small gradients.

The self-consistent approach provides a possibility to avoid the above difficulties, so we have managed to find the energy of the pair interaction of macroparticles introduced in the nematic liquid crystal. The problem is formally split into two separate problems: to find the director field distribution and to find the interation energy with regard to physical and geometrical properties of macroparticles.

The director distribution in the vicinity of a macrodroplet introduced in a nematic liquid crystal was considered in many papers (e.g., see [4,5,11,10], which followed the pioneering paper by Brochar and de Gennes [11]. In [11], in particular, the director distribution was obtained in the one-constant approximation in terms of the multipole expansion. However, the expansion coefficients were not associated with the physical and geometrical parameters of macroparticles.

In the present paper the director distribution is derived for the general case of different elastic Frank constants and, moreover, the multipole expansion parameters are found in terms of geometric and physical characteristics of macroparticles. Thus both the behavior and the value of the pair interaction energy are described with no additional restrictions.

Having found the interparticle interaction energy, we can study the thermodynamic behavior of an aggregate of such macroparticles and describe the conditions for the creation of new supermolecular structures. The character and intensity of the interparticle interaction in the system of foreign macroparticles in a nematic liquid crystal can be such that a temperature and concentration phase transition can occur in the system and produce a spatially inhomogeneous distribution. In this paper the conditions are found under which the macroparticles arrange in a spatially periodic manner and the effect of such an arrangement on the resultant orientational supermolecular structure is studied. If macroparticles possess chiral properties, then their aggregate may be regarded as a kind of lyotropic cholesteric liquid crystal with induced gyrotropy. The spatially modulated arrangement of macroparticles with helical orientation structure gives rise to a new period of the particle average orientation distribution that is incommensurate with the spiral lead.

In Sec. II we formulate the problem of how to find the interaction energy for the macroparticles introduced in the nematic liquid crystal and describe the approximations employed. The general expression for the interaction energy is derived for different Frank constants and arbitrary particle shapes. In the Sec. III the expression obtained is analyzed for specific geometrical shapes of particles and used to calculate the pair interaction energy for spherical, cylindrical, etc., macroparticles with regard to the anchoring dependence on the surface coordinate of the foreign macroparticle. The expressions are compared to the previous results of other authors. Section IV describes the thermodynamical behavior of an aggregate of macroparticles introduced in the nematic liquid crystal, taking into account their interaction via the director deformation field. The conditions are found for a temperature and concentration phase transition accompanied by the formation of a spatially inhomogeneous macroparticle distribution in the mesophase. In Sec. V we describe a supermolecular structure that can appear in a system of chiral macroparticles introduced in the nematic liquid crystal. The spatially periodic distribution of these particles, along with inducing the gyrotropy, can cause a new period that is incommensurate with the spiral lead in the average orientation distribution of macroparticles. In Sec. VI, we analyze the conditions of the above-mentioned structure formation and the possibilities to observe them experimentally.

II. FORMULATION OF THE PROBLEM

The phenomenological free energy of a deformed nematic liquid crystal is determined by the Frank energy

$$E_f=\frac{1}{2}\int d\vec{r}\{K_{22}(\operatorname{div}\vec{n})^2 +K_{22}(\vec{n}\operatorname{rot}\vec{n})^2+K_{33}(\vec{n}\times\operatorname{rot}\vec{n})^2\}, \tag{1}$$

where K_{ii} are the elastic Frank constants and $\vec{n}$ is the director. The integration extends over the whole crystal volume.

Being introduced in the nematic liquid crystal, the macrodroplets produce relevant deformation of the director elastic field. A droplet is treated as a macroscopic one in the sense that the energy of its interaction with the nematic liquid crystal can be obtained from the known director distribution on the macroparticle surface. For the sake of brevity, in what follows such macroparticles will be referred to as clusters.

The energy of the cluster–nematic-liquid crystal interaction may be written as

$$E_s=\sum_{\hat{\imath}}\oint ds\,W_s[\vec{\nu}(s)\times\vec{n}(s)]^2, \tag{2}$$

where $\vec{n}(\vec{s})$ is the director value at the point s of the cluster surface, $\vec{\nu}(s)$ is the normal to the surface at this point, which determines the easy direction, and W_s is the director anchoring to the surface which depends on the surface point in the general case. The integral in Eq. (2) extends over the closed surface S_j of each cluster. All the clusters (labeled with the subscript j) are assumed to be identical; their number in the volume under consideration is N.

Due to the surface energy (2), the director field is deformed near each cluster. The mutual influence of deformation fields produced by various clusters causes an elastic deformation interaction of the latter in the liquid crystal. Our first task is to find the intensity and character of this interaction.

For various values of anchoring W_s and cluster concentration, two physical situations can occur: (a) For relatively low values of W_s and large cluster concentrations, the director distribution on the given cluster surface is determined mainly by the sum of contributions of all other clusters, while the contribution of the given cluster in $\vec{n}(s)$ is negligible; (b) for relatively high values of W_s, the director distribution on the cluster surface is mainly determined just by this cluster. In case (a) we can employ the approach analogous to the molecular field approximation. Formally, the director distribution may be regarded as given in the whole space including the volume occupied by the clusters. Within the given cluster volume, the director distribution is assumed to be similar to that in the absence of the cluster. Then we can employ the Fourier representation for the director in the whole space and thus the problem is considerably simplified. Henceforth we shall consider case (a).

The director distribution can be found from the minimum condition for the sum of energies (1) and (2). We assume that the director change due to the clusters is small, i.e.,

$$\vec{n}(\vec{r})=\vec{n}_0+\delta\vec{n}(\vec{r}), \qquad |\delta\vec{n}|\ll 1. \tag{3}$$

Here $\vec{n}_0$ is the director value in the absence of droplets. The initial nematic state (without clusters) is assumed to be homogeneous.

In the Fourier representation we have

$$\delta\vec{n}(\vec{r})=\frac{1}{(2\pi)^3}\int d^3\vec{q}\,\exp(-i\vec{q}\cdot\vec{r})\,\delta\vec{n}(\vec{q}). \tag{4}$$

The normalization condition for the director is $\vec{n}^2=1$. Then, to within $(\delta\vec{n})^2$ we have

$$\delta\vec{n}\cdot\vec{n}_0=0. \tag{5}$$

We substitute the Fourier expansion (4) in the Frank energy (1) to obtain

$$E_f=\frac{1}{2}\,\frac{1}{(2\pi)^3}\int d^3q\{K_{11}|\vec{q}\cdot\delta\vec{n}(\vec{q})|^2 + K_{22}|[\vec{n}\times\vec{q}]\cdot\delta\vec{n}(\vec{q})|^2+K_{33}|(\vec{n}_0\cdot\vec{q})\,\delta\vec{n}(\vec{q})|^2\}. \tag{6}$$

To simplify the expression (6), we choose the special basis

$$\vec{e}_1=\frac{(\vec{q}_\perp\times\vec{n}_0)}{q_\perp}, \quad \vec{e}_2=\frac{\vec{q}_\perp}{q_\perp}, \quad \vec{e}_3=\vec{n}_0, \quad \vec{q}_\perp=\vec{n}_0\times\vec{q}. \tag{7}$$

For this basis we have $\vec{q}=(q_\perp,0,q_\|)$ and $\delta\vec{n}=(\delta n_1,\delta n_2,0)$ and Eq. (6) reduces to

$$E_f=\frac{1}{2}\,\frac{1}{(2\pi)^3}\sum_i\int d^3q\{K_{ii}q_\perp^2+K_{33}q_\|^2\}|\delta n_i(\vec{q})|^2. \tag{8}$$

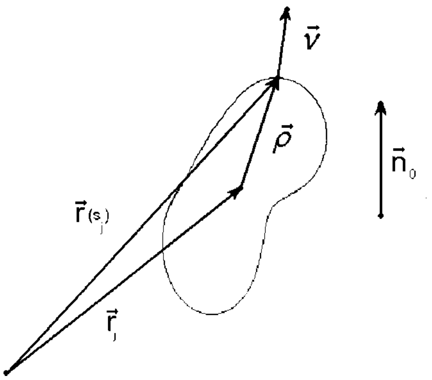

FIG. 1. Vectors which describe the space allocation of the jth cluster and its surface.

In order to derive an equation for $\delta n_i(\vec{q})$ from the minimum condition for the sum of energies (1) and (2), we first have to transform the expression (2) with regard to Eq. (4). To do this we choose some arbitrary point for the coordinate origin and take the radius vector $\vec{r}(s_j)$ from this point to the given point on the jth cluster surface (see Fig. 1). Moreover, we take the radius vector $\vec{r}_j$ from the same point to the jth cluster center (the latter may be assumed to be, say, the cluster center of mass). Then we have

$$\vec{r}(s_j)=\vec{r}_j+\vec{\rho}. \tag{9}$$

Here $\vec{\rho}=\vec{\rho}(s_j)$ is the radius vector from the cluster center to the given point on the surface s_j.

Now let us expand $\vec{n}(s_j)\equiv\vec{n}(\vec{r}_j+\vec{\rho})$ in a Taylor series in $\vec{\rho}$. Having done this, we obtain an expression for the director value on the jth cluster surface in terms of the director value in the jth cluster center and its derivatives. We remind the reader that, according to the molecular field idea, the director value within the volume occupied by the jth cluster is taken to be equal to the value with no cluster.

With an accuracy of second derivatives, we then have

$$\vec{n}(s_j)=\vec{n}(\vec{r}_j+\vec{\rho})\approx\vec{n}_0+\delta\vec{n}(\vec{r}_j)+(\vec{\rho}\cdot\vec{\nabla})\,\delta\vec{n}(\vec{r}_j) +\frac{1}{2}(\vec{\rho}\cdot\vec{\nabla})^2\delta\vec{n}(\vec{r}_j). \tag{10}$$

We restrict ourselves to the linear approximation with respect to $\delta\vec{n}$ in the quantity $[\vec{\nu}(s_j)\times\vec{n}(s_j)]^2$ contained in Eq. (2). Then we obtain

$$\begin{aligned}[\vec{\nu}(s_j)\times\vec{n}(s_j)]^2&=1-[\vec{\nu}(s_j)\cdot\vec{n}(s_j)]^2\approx 1-[\vec{\nu}(s_j)\cdot\vec{n}_0]^2\\ &\quad-2[\vec{\nu}(s_j)\cdot\vec{n}_0][\vec{\nu}(s_j)\cdot\delta\vec{n}(\vec{r}_j)]\\ &\quad+2[\vec{\nu}(s_j)\cdot\vec{n}_0](\vec{\rho}\cdot\vec{\nabla})[\vec{\nu}(s_j)\cdot\delta\vec{n}(\vec{r}_j)]\\ &\quad-[\vec{\nu}(s_j)\cdot\vec{n}_0](\vec{\rho}\cdot\vec{\nabla})^2[\vec{\nu}(s_j)\cdot\delta\vec{n}(\vec{r}_j)].\end{aligned} \tag{11}$$

The next step is to substitute the expansion (11) in Eq. (2) taking into account Eq. (4). When doing this we write all the scalar products in the local bases $(\vec{\kappa}_1^j, \vec{\kappa}_2^j, \vec{\kappa}_3^j)$ associated with each cluster. For example,

$$\vec{\nu}(s_j)\cdot\delta\vec{n}(\vec{r}_j)=\sum_{l=1,2,3}[\vec{\nu}(s_j)\cdot\vec{\kappa}_l][\delta\vec{n}(\vec{r}_j)\cdot\vec{\kappa}_l]$$

$$=\sum_{l=1,2,3}\nu_l(\delta\vec{n}\cdot\vec{\kappa}_l).$$

As a result we have

$$E_s=\sum_j\oint ds\,W_s\{1-(\vec{\nu}(s)\cdot\vec{n}_0)^2\}$$
$$+\frac{1}{(2\pi)^3}\sum_j\int d^3q\,\exp(-i\vec{q}\cdot\vec{r}_j)$$
$$\times\Bigg\{-\sum_{k,l}\alpha_{kl}(\vec{n}_0\cdot\vec{\kappa}_k)[\delta\vec{n}(\vec{q})\cdot\vec{\kappa}_l]$$
$$+i\sum_{k,l,m}\beta_{klm}(\vec{n}_0\cdot\vec{\kappa}_k)[\delta\vec{n}(\vec{q})\cdot\vec{\kappa}_l](\vec{q}\cdot\vec{\kappa}_m)$$
$$+\sum_{k,l,m,n}\gamma_{klmn}(\vec{n}_0\cdot\vec{\kappa}_k)[\delta\vec{n}(\vec{q})\cdot\vec{\kappa}_l](\vec{q}\cdot\vec{\kappa}_m)(\vec{q}\cdot\vec{\kappa}_n)\Bigg\}. \tag{12}$$

The expression (12) contains cluster characteristics given in the local coordinate system, i.e.,

$$\alpha_{kl}=2\oint ds\,W_s\nu_k(s)\nu_l(s),$$

$$\beta_{klm}=2\oint ds\,W_s\nu_k(s)\nu_l(s)\rho_m(s),$$

$$\gamma_{klmn}=\oint ds\,W_s\nu_k(s)\nu_l(s)\rho_m(s)\rho_n(s). \tag{13}$$

These quantities depend on the cluster shape and density of the anchoring energy W_s; they are similar for all clusters (inasmuch as the clusters are assumed to be identical).

It is convenient for the analysis that follows to take the local basis to be the one in which the tensor α_{kl} takes the diagonal form, i.e.,

$$\alpha_{kl}=a_k\delta_{kl}. \tag{14}$$

The anchoring (12) is written in the local basis, whereas the volume energy (8) is written in the special basis (7). In order to carry out variations in $\delta n_i(\vec{q})$ we write the scalar product $(\delta\vec{n}(\vec{q})\vec{\kappa}_l^j)$ that enters Eq. (12) in terms of the basis (7) to obtain

$$\delta\vec{n}(\vec{q})\cdot\vec{\kappa}_l=\sum_i[\vec{e}_i\cdot\delta\vec{n}(\vec{q})](\vec{e}_i\cdot\vec{\kappa}_l)$$

$$=\frac{1}{q_\perp}\{\delta n_1(\vec{q})[(\vec{q}_\perp\times\vec{n}_0)\cdot\vec{\kappa}_l]+\delta n_2(\vec{q})(\vec{q}_\perp\cdot\vec{\kappa}_l)\}. \tag{15}$$

Thus we can write the minimum condition for the total energy, i.e.,

$$\frac{\delta}{\delta n_i(\vec{q})}\{E_f+E_S\}=0. \tag{16}$$

This condition yields

$$\frac{1}{2}\frac{1}{(2\pi)^3}\{K_{ii}q_\perp^2+K_{33}q_\parallel^2\}\delta n_i^*(\vec{q})=-\frac{\delta}{\delta n_i(\vec{q})}E_s, \tag{17}$$

whence we find

$$\delta n_i(\vec{q})=-\frac{2(2\pi)^3}{K_{ii}q_\perp^2+K_{33}q_\parallel^2}\left(\frac{\delta}{\delta n_i}E_s\right)^*. \tag{18}$$

An expression for $[\delta/\delta n_i(\vec{q})]E_s$ can be easily found from Eq. (12) within the context of Eq. (15). Substituting this expression in Eq. (18) yields an explicit expression for $\delta n_i(\vec{q})$. Then we substitute this expression for $\delta n_i(\vec{q})$ again in Eq. (12) and thus obtain

$$E_s=\sum_j\oint ds\,W_s[1-[\vec{\nu}(s)\cdot\vec{n}_0]^2]$$
$$+\frac{2}{(2\pi)^3}\sum_{j,j'}\sum_{l,l'}A_lA_{l'}\int d^3q\,\exp[-i\vec{q}\cdot(\vec{r}_j-\vec{r}_{j'})]$$
$$\times\Bigg\{\frac{[\vec{\kappa}_l^j\cdot(\vec{q}_\perp\times\vec{n}_0)][\vec{\kappa}_l^{j'}\cdot(\vec{q}_\perp\times\vec{n}_0]}{q_\perp^2(K_{11}q_\perp^2+K_{33}q_\parallel^2)}$$
$$+\frac{(\vec{\kappa}_l^j\cdot\vec{q}_\perp)(\vec{\kappa}_l^{j'}\cdot\vec{q}_\perp)}{q_\perp^2(K_{22}q_\perp^2+K_{33}q_\parallel^2)}\Bigg\}. \tag{19}$$

To simplify the notation in Eq. (19), we introduce the operators

$$A_l^j=\sum_k\alpha_{kl}(\vec{n}_0\cdot\vec{\kappa}_k^j)+\sum_{k,m}\beta_{klm}(\vec{n}_0\cdot\vec{\kappa}_k^j)\left(\vec{\kappa}_m^j\cdot\frac{\partial}{\partial\vec{r}_j}\right)$$
$$+\sum_{k,m,n}\gamma_{klmn}(\vec{n}_0\cdot\vec{\kappa}_k^j)\left(\vec{\kappa}_m^j\cdot\frac{\partial}{\partial\vec{r}_j}\right)\left(\vec{\kappa}_n^j\cdot\frac{\partial}{\partial\vec{r}_j}\right). \tag{20}$$

When deriving Eq. (20), use was made of the obvious identity

$$(\vec{\kappa}_l^j\cdot\vec{q})\exp[-i\vec{q}(\vec{r}_j-\vec{r}_{j'})]$$
$$=-i\left[\left(\vec{\kappa}_l^j\cdot\frac{\partial}{\partial\vec{r}_j}\right)\right]\exp[-i\vec{q}(\vec{r}_j-\vec{r}_{j'})]$$

Integrating over q in Eq. (19) is an easy task in the coordinate system with the basis

$$\vec{r}_1=\frac{\vec{R}_\perp\times\vec{n}_0}{R_\perp},\quad \vec{r}_2=\frac{\vec{R}_\perp}{R_\perp},\quad \vec{r}_3=\vec{n}_0, \tag{21}$$

$$\vec{R}=\vec{r}_j-\vec{r}_{j'},\quad \vec{R}_\perp=\vec{n}_0\times\vec{R}. \tag{22}$$

The basis (21) is turned with respect to the one (7) at some angle φ about the axis $\vec{n}_0=\vec{e}_3=\vec{r}_3$. The quantities $q_\perp$ and $q_\parallel$ are similar in both bases (7) and (21).

Since in the new basis

$$\exp[-i\vec{q}(\vec{r}_j-\vec{r}_{j'}]\equiv\exp(-i\vec{q}\vec{R})$$
$$=\exp\{-i[q_\perp R_\perp\cos\varphi+q_\parallel R_\parallel]\}$$

and the denominators of the fractions in Eq. (19) do not depend on the angle φ, it is not difficult to carry out integration over φ. For example,

$$\int d^3q\frac{\exp[-i\vec{q}(\vec{r}_j-\vec{r}_{j'})](\vec{\kappa}_l^j\cdot\vec{q}_\perp)(\vec{\kappa}_{l'}^{j'}\cdot\vec{q}_\perp)}{q_\perp^2(K_{22}q_\perp^2+K_{33}q_\parallel^2)}$$
$$=\int_0^\infty dq_\perp q_\perp\int_{-\infty}^\infty dq_\parallel\frac{\exp(-i\vec{q}\vec{R})}{(K_{22}q_\perp^2+K_{33}q_\parallel^2)}$$
$$\times\int_0^{2\pi}d\varphi\frac{\exp(-iq_\perp R_\perp\cos\varphi)(\vec{\kappa}_l^j\cdot\vec{q}_\perp)(\vec{\kappa}_{l'}^{j'}\cdot\vec{q}_\perp)}{q_\perp^2}$$
$$=\pi\int_0^\infty dq_\perp q_\perp\{Q_{l,l'}^+J_0(q_\perp R_\perp)+Q_{l,l'}^-J_2(q_\perp R_\perp)\}$$
$$\times\int_{-\infty}^\infty dq_\parallel\frac{\exp(-iq_\parallel R_\parallel)}{K_{22}q_\perp^2+K_{33}q_\parallel^2}, \tag{23}$$

where $J_n(q_\perp R_\perp)$ is the Bessel function of the relevant order. Besides that we have introduced the notation

$$Q_{l,l'}^{(\pm)}=(\vec{r}_1\cdot\vec{\kappa}_l^j)(\vec{r}_1\cdot\vec{\kappa}_{l'}^{j'})\pm(\vec{r}_2\cdot\vec{\kappa}_l^j)(\vec{r}_2\cdot\vec{\kappa}_{l'}^{j'}).$$

To integrate over $q_\perp$ and $q_\parallel$, we make use of the relations

$$\int_{-\infty}^\infty dq_\parallel\frac{\exp(-iq_\parallel R_\parallel)}{K_{22}q_\perp^2+K_{33}q_\parallel^2}=\frac{\pi}{q_\perp\sqrt{K_{22}K_{33}}}\exp\left\{-\left(\frac{K_{22}}{K_{33}}\right)^{1/2}R_\parallel q_\perp\right\}$$

and

$$\int_0^\infty dq_\perp q_\perp\exp\left\{-\left(\frac{K_{22}}{K_{33}}\right)^{1/2}R_\parallel q_\perp\right\}J_n(q_\perp R_\perp)$$
$$=\frac{\{\sqrt{1+\gamma^2}-\gamma\}^n}{R_\perp\sqrt{1+\gamma^2}},\quad \gamma=\left(\frac{K_{22}}{K_{33}}\right)^{1/2}\frac{R_\parallel}{R_\perp}.$$

We skip the details and write the final expression for E_s. It is given by

$$E_s=\sum_j\oint ds\,W_s\{1-[\vec{\nu}(s)\cdot\vec{n}_0]^2\}$$
$$+\frac{1}{4\pi}\sum_{j,j'}\sum_{l,l'}A_lA_{l'}\sum_\mu\frac{1}{\sqrt{K_{\mu\mu}}}$$
$$\times\left\{\frac{Q_{l,l'}^+}{\sqrt{K_{33}R_\perp^2+K_{\mu\mu}R_\parallel^2}}+(-1)^\mu\right.$$
$$\left.\times\frac{Q_{l,l'}^-}{R_\perp^2}\frac{(\sqrt{K_{33}R_\perp^2+K_{\mu\mu}R_\parallel^2}-\sqrt{K_{\mu\mu}R_\parallel^2})^2}{\sqrt{K_{33}R_\perp^2+K_{\mu\mu}R_\parallel^2}}\right\}. \tag{24}$$

Once more, we recall that $\vec{\kappa}_l^j$ are the unit vectors of the local basis associated with the jth cluster and $\vec{R}=\vec{r}_j-\vec{r}_{j'}, R_\parallel=(\vec{n}_0\vec{R})$, and $\vec{R}_\perp=\vec{n}_0\times\vec{R}$.

It is not difficult to show by substituting Eq. (18) in Eq. (8) that expressions for E_s and E_f in Eq. (24) are similar except for the first term. The first term in Eq. (24) corresponds to the total energy of individual clusters (with no account of their elastic interaction).

III. ENERGY OF THE PAIR DEFORMATION INTERACTION OF CLUSTERS

The terms with fixed subscripts j and j' entering the sum of energies E_f+E_s describe the energy of elastic interaction of clusters j and j'. We denote this energy by $U_{jj'}$. Then we have

$$U_{jj'}=\frac{1}{2\pi}\sum_{l,l'}A_l^jA_{l'}^{j'}\sum_\mu\frac{1}{\sqrt{K_{\mu\mu}}}\left\{\frac{Q_{l,l'}^+}{\sqrt{K_{33}R_\perp^2+K_{\mu\mu}R_\parallel^2}}\right.$$
$$\left.+(-1)^\mu\frac{Q_{l,l'}^-}{R_\perp^2}\frac{\sqrt{K_{33}R_\perp^2+K_{\mu\mu}^2R_\parallel^2}+\sqrt{K_{\mu\mu}^2R_\parallel^2}}{\sqrt{K_{33}R_\perp^2+K_{\mu\mu}^2R_\parallel^2}}\right\}. \tag{25}$$

The elastic energy of the cluster pair interaction is obtained for arbitrary (but fixed) cluster orientations both with respect to each other and with respect to the director.

If one or a few clusters occur in the system, then the angles that determine cluster orientations with respect to the director and each cluster orientation with respect to the other can be found from the minimum condition for the energy E_f+E_s. This is the usual way of considering such situations (e.g., see [9,5]).

If, however, many clusters occur in the system, which is the case under consideration in this paper, one has to introduce the cluster velocity and center-of-mass distributions and employ the averaged quantities. We shall discuss this aspect in detail later.

Now let us analyze the structure of the formula that describes the cluster elastic interaction energy (25). As follows from Eqs. (25) and (20), the expression for the cluster elastic interaction energy is actually the series expansion in terms of the reciprocal intercluster distance. The first term in Eq. (20), associated with $\{\alpha_{kl}\}$, determines the term of Eq. (25) whose decrease is the slowest when the distance between the clusters under consideration is increased. This term decreases as $1/R$. In addtion, the term whose decrease with increasing R is the fastest is determined by the last term in Eq. (20).

It is not difficult to verify that the contribution of the term with $\{\alpha_{kl}\}$ in the energy (25) vanishes when the director is oriented along any vector of the local basis given by the condition (14). Moreover, the torque produced by the liquid crystal with respect to the cluster is equal to zero too. If none of the cluster basis vectors are oriented along the director, then the contribution of the term with $\{\alpha_{kl}\}$ is dominant in the energy (25). That is why in what follows we assume that the orientational transition has already occurred and the contribution of $\{\alpha_{kl}\}$ in the elastic energy is no longer significant.

If some vector of the local basis is parallel to the director $\vec{n}_0$, then two other basis vectors lie in the plane perpendicular to $\vec{n}_0$. The unit vectors $\vec{r}_1$ and $\vec{r}_2$ lie in the same plane, so we denote $\vec{r}_1\cdot\vec{\kappa}^j_l$ and then find from Eq. (24) that

$$Q^{\pm}_{l,l'}=\cos(\Psi^j_l+\Psi^{j'}_{l'}). \tag{26}$$

Though the contribution of $\{\alpha_{kl}\}$ in the energy (25) is insignificant for some cluster orientations, there remains the contribution determined by the terms that contain $\{\beta_{klm}\}$ and $\{\gamma_{klmn}\}$.

Now we specify the cluster shape and calculate the energy of cluster pair interaction.

(a) Spherical clusters: $W_s=W=\text{const}$. According to Eq. (13) we have

$$\alpha_{ik}=\alpha_{ii}\delta_{ik}, \quad \alpha_{11}=\alpha_{22}=\alpha_{33}=\frac{8\pi}{3}Wr_0^2, \quad \beta_{klm}=0,$$

$$\gamma_{klmn}=\frac{4\pi}{15}Wr_0^4(\delta_{kl}\delta_{mn}+\delta_{km}\delta_{\ln}+\delta_{kn}\delta_{lm}), \tag{27}$$

where r_0 is the radius of the spherical cluster. Assuming for the sake of simplicity that $K_{11}=K_{22}=K_{33}=K$, we find from Eq. (25), taking into account Eq. (27), that

$$U_{jj'}=\frac{6}{\pi K}\left(\frac{4\pi}{15}Wr_0^4\right)^2(3-30\cos^2\theta+35\cos^4\theta),$$

$$\cos\theta=\frac{R_\parallel}{R}. \tag{28}$$

In the case of spherical clusters and $W_s=\text{const}$, the interaction energy is determined by the last term of the expansion (20).

Let us discuss the choice of the local basis $(\vec{\kappa}^j_1,\vec{\kappa}^j_2,\vec{\kappa}^j_3)$. If the clusters are spherical and $W_s=\text{const}$, then the choice of the local basis $(\vec{\kappa}^j_1,\vec{\kappa}^j_2,\vec{\kappa}^j_3)$ is unimportant. If, however, $W_s\neq\text{const}$ or the clusters are asymmetric, then the set of parameters $\{\alpha_{kl}\},\{\beta_{klm}\},\{\gamma_{klmn}\}$ depends on the specified local basis. In order to provide an unambiguous of the parameter choice we take the set of unit vectors $(\vec{\kappa}^j_1,\vec{\kappa}^j_2,\vec{\kappa}^j_3)$ in a way to ensure that the tensor α_{kl} should take the diagonal form in this basis, i.e., it must satisfy the condition (14). Moreover, we require that the basis should be such that

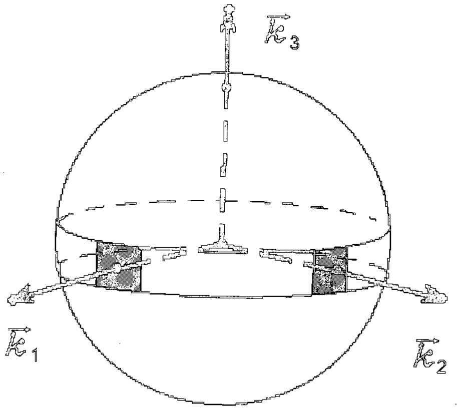

FIG. 2. Example of how the coordinate dependence of the anchoring W_s influences the structure of the energy of the cluster pair deformation interaction.

$$a_1\geqslant a_2\geqslant a_3. \tag{29}$$

These requirements provide an unambiguous choice of the local basis. At the same time, the parameters $\{\alpha_{kl}\},\{\beta_{klm}\}$, and $\{\gamma_{klmn}\}$ do not depend on the subscript &&84 (the cluster number) and are unambiguous characteristics of the clusters. They are determined by the cluster geometry and the density of anchoring W_s.

To illustrate how the coordinate dependence of the anchoring W_s influences the structure of the energy of cluster pair deformation interaction, we consider an example. We consider a spherical cluster with the anchoring density $W_1=\text{const}$ whose surface contains two ‘‘spots’’ with the anchoring energy $W_2=\text{const}$ (but $W_1\neq W_2$). We assume that the location of the spots with energy W_2 is determined by the angles $(-\varphi_0\leqslant\varphi\leqslant\varphi_0;\pi/2-\theta_0\leqslant\theta\leqslant\pi/2+\theta_0)$ and $(\pi/2-\varphi_0\leqslant\varphi_0\leqslant\pi/2+\varphi_0;\pi/2-\theta_0\leqslant\theta\leqslant\pi/2-\theta_0)$. The angle φ is relative to the unit vector $\vec{\kappa}_1$ and the angle θ is relative to the unit vector $\vec{\kappa}_1$ (see Fig. 2).

With the spot positions being as given above, we find from Eq. (13) that

$$\alpha_{lk}=\frac{8\pi}{3}W_1r_0^2\delta_{kl}+\Delta\alpha_{kl}, \tag{30}$$

$$\Delta\alpha_{11}=\Delta\alpha_{22}=8(W_2-W_1)r_0^2\varphi_0\left\{\sin\theta_0-\frac{1}{3}\sin^3\theta_0\right\},$$

$$\alpha_{33}=\frac{16}{3}(W_2-W_1)r_0^2\varphi_0\sin^3\theta_0. \tag{31}$$

All other elements $\Delta\alpha_{lk}$ vanish.

We see that, for the above spot positions and basis, the tensor α_{lk} is diagonal and the requirement (29) is satisfied provided $W_2\geqslant W_1$. For the basis being chosen in such a manner, the nonvanishing components of β_{klm} are given by

$$\beta_{313}=\beta_{323}=(W_2-W_1)r_0^3\sin\varphi_0\left\{\sin\theta_0-\frac{1}{4}\sin 4\theta_0\right\}. \tag{32}$$

According to Eq. (25), in the case of spherical clusters with spots and for $\vec{\kappa}_3^j \| \vec{\kappa}_3^{j'} \| \vec{n}_0$, the elastic interaction energy is described by the expression

$$U_{jj'}=\frac{\beta_{313}^2}{\pi}\sum_{\mu}\frac{K_{\mu\mu}}{\{K_{33}R_\perp^2+K_{\mu\mu}R_\|^2\}^{3/2}}\left\{\frac{3K_{\mu\mu}R_\|^2}{K_{33}R_\perp^2+K_{\mu\mu}R_\|^2}-1\right\}. \tag{33}$$

We note that in the case of clusters shaped as ellipsoids of revolution with the axes along $\vec{\kappa}_3^j$ and with the spots positioned in the same range of angles as given above, the pair interaction energy is also described by an expression similar to Eq. (33). The only difference is the expression for the parameter β_{313}. In this case the formula (33) reproduces the result obtained in Ref. [9].

(b) Cylindrical clusters: $W_s=W=\text{const}$. Suppose $\vec{\kappa}_3$ is directed along the cylinder axis. If the cylinder radius is very small (a needle-shaped cluster), so that endface contributions in the anchoring may be disregarded, then we have

$$\alpha_{11}=\alpha_{22}=2\pi W\rho_0 L. \tag{34}$$

Here ρ_0 is the cylinder diameter and L is its length. All elements α_{kl} other than those given by Eq. (34) vanish. The nonzero elements of $\{\beta_{klm}\}$ are given by

$$\beta_{113}=\beta_{223}=\pi W\rho_0 L^2. \tag{35}$$

If the cylinder is assumed to be asymmetric and to possess a not very small radius (a finger-shaped cluster), then other elements of β_{klm} are not equal to zero along with Eq. (35). For example, for a cylinder whose endfaces are a hemisphere of radius r_0 and a plane, the other two nonzero elements are

$$\beta_{311}=\beta_{322}=\frac{2\pi}{3}Wr_0^3. \tag{36}$$

In the case when the above-mentioned asymmetric cylinders are parallel to each other and to the director $\vec{n}_0$, the energy of the pair interaction of such clusters is described by the expression

$$U_{jj'}=\frac{\beta_{313}^2}{\pi}\sum_{\mu}\frac{K_{\mu\mu}}{\{K_{33}R_\perp^2+K_{\mu\mu}R_\|^2\}^{3/2}}\left\{\frac{3K_{\mu\mu}R_\perp^2}{K_{33}R_\perp^2+K_{\mu\mu}R_\|^2}-1\right\}. \tag{37}$$

In the previous sections we considered some examples of clusters of given shapes. Now we do not specify the cluster shape and discuss one more example that is of interest because the pair interaction energy can be obtained in the form described by Goossens [12]. We assume first that $K_{11}=K_{22}=K_{33}=K$ and second that only the skew symmetric elements β_{321} and β_{312} do not vanish. If the clusters are oriented in a way that $\vec{\kappa}_3^j \| \vec{\kappa}_3^{j'} \| \vec{n}_0$, then their interaction energy reduces to

$$U_{jj'}=\frac{1}{2\pi K}\sum_{l,l'}\sum_{m,m'}\beta_{3lm}\beta_{3l'm'}(\vec{\kappa}_l^j\cdot\vec{\kappa}_{l'}^{j'})\times\frac{3(\vec{\kappa}_m^j\cdot\vec{R})(\vec{\kappa}_{m'}^{j'}\cdot\vec{R})-(\vec{\kappa}_l^j\cdot\vec{\kappa}_{l'}^{j'})R^2}{R^5}. \tag{38}$$

If φ is the angle between $\vec{\kappa}_1^j$ and $\vec{\kappa}_1^{j'}$, then we have $\vec{\kappa}_1^j\cdot\vec{\kappa}_1^{j'}=\vec{\kappa}_2^j\cdot\vec{\kappa}_2^{j'}=\cos\varphi$, $\vec{\kappa}_1^j\cdot\vec{\kappa}_2^{j'}=\cos(\varphi+\pi/2)=-\sin\varphi$, etc.

Within the context of the equation $\vec{\kappa}_m^{j'}\cdot\vec{R}=(\vec{\kappa}_m^{j'}\cdot\vec{\kappa}_1^j)(\vec{\kappa}_1{}^j\cdot\vec{R})+(\vec{\kappa}_m^{j'}\cdot\vec{\kappa}_2^j)(\vec{\kappa}_m^{j'}\cdot\vec{R}_2)$ (for $m=1,2$), the formula (38) can be easily reduced to

$$U_{jj'}=A(\vec{R})\cos 2\varphi+B(\vec{R})\sin 2\varphi. \tag{39}$$

Thus, in the case under consideration the energy of intercluster elastic interaction is given by the expression derived by Goossens [12] to describe the interaction of cholesteric molecules.

We remind the reader that our term ‘‘cluster’’ implies macrodroplets for which the droplet–nematic-liquid crystal anchoring is given by Eq. (2). We have already mentioned in the Introduction that an interaction of foreign molecules with those of the nematic liquid crystal is much stronger than the energy of intermolecular interaction in the nematic liquid crystal. In this case a kind of solvate shell is formed around each foreign droplet. The microscopic droplet surrounded by a solvate shell may be regarded as a cluster in our sense.

IV. SYSTEM OF MACRODROPLETS IN A LIQUID CRYSTAL

To describe the peculiarities of the macrodroplet system behavior in the mesophase implies taking into account their interaction via the director elastic field. We have already shown that a foreign macrodroplet produces liquid crystal distortion in a region much greater than the droplet dimensions and thus leads to an effective interaction with another similar macrodroplet via the director field deformation. The interdroplet interaction via the director elastic field is of the type given by Eq. (25); it is physically obvious that for reasons analogous to those in [13], the macrodroplet distribution within a limited liquid crystal sample can be inhomogeneous. The purpose of this section is to show that a spinodal decay can occur in a system of macrodroplets introduced in a liquid crystal, which results in a spatial modulation of droplet distribution. It should be emphasized that this distribution is associated with the type of interdroplet interaction and physically reflects the instability of the ‘‘gaseous’’ phase of macrodroplets introduced in the crystal. It is clear that the macrodroplet arrangement in the mesophase depends on both the spatial positions and relative orientations of individual macrodroplets. In order to demonstrate the mechanism and character of the phase transition accompanied by the formation of modulated macrodroplets distribution we consider a system of spherical foreign macrodroplets in the nematic mesophase. In this case, the interdroplet interaction energy is described by Eq. (28) and we need not consider their relative orientation. Thus we can regard the system of foreign macrodroplets in the mesophase as the Ising model lattice gas without fixing the basis of the initial arbitrary lattice. This treatment is completely analogous to the model of substitution or interstitial solid solution [14] and we shall employ the approach proposed in this paper.

The free energy of a solution of macrodroplets in a liquid crystal in the self-consistent field and the binary interaction approximation may be written in the form

$$F=\frac{1}{2}\sum_{R,R'}U(\vec{R}-\vec{R}')f(\vec{R})f(\vec{R}')+kT\sum_{R}\{f(\vec{R})\ln f(\vec{R})-[1-f(\vec{R})]\ln[1-f(\vec{R})]\}-\mu\sum_{R}f(\vec{R}), \qquad (40)$$

where $U(\vec{R}-\vec{R}')$ is the interaction potential, $f(\vec{R})$ is the probability that the droplets fill in the initial arbitrary lattice, μ is the chemical potential, and T is the absolute temperature. The minimum of Eq. (40) corresponds to the self-consistent field solution for $f(\vec{R})$ i.e.,

$$f(\vec{R})=\left\{1+\exp\left[-\frac{\mu}{kT}+\sum_{R}\frac{U(\vec{R}-\vec{R}')}{kT}f(\vec{R}')\right]\right\}^{-1}. \qquad (41)$$

Each set of thermodynamic functions of state corresponds to a solution that describes some phase of droplet arrangement. If their distribution can be inhomogeneous, then the solution (41) serves to find the stable phase associated with the interaction temperature and character. An efficient way to obtain such a distribution was proposed in [14]. If the droplets solution is disordered, then by definition the mean value $\langle f(r)\rangle=C_0$, where C_0 is the relative macrodroplet concentration. The concentration inhomogeneity gives rise to an additional term $f(r)=C_0+\delta C(r)$, where $\delta C(r)$ is the change of the probability that an arbitrary site of the initial Ising lattice is occupied. If the concentration inhomogeneities are smooth and their scale is much longer than the intermolecular distance, the quantity $\delta C(r)$ may be interpreted as the change of macrodroplet composition in the relevant physically small volume that contains many elementary cells of the initial lattice. When passing from a lattice to a continuum description, we can write the free energy increment $\Delta F=F-F(C_0)$ associated with the inhomogeneous macrodroplet distribution in terms of the power series expansion in $\delta C(r)$, i.e.,

$$\Delta F=\frac{1}{2}\int d\vec{r}\{b\,\delta c^2(r)+a_{\parallel}(\nabla_z\delta c)^2+a_{\perp}(\nabla_{\perp}\delta c)^2\}, \qquad (42)$$

where

$$b=\int d\vec{R}U(\vec{R})+\frac{kT}{c_0(1-c_0)},\quad a_{\parallel}=-\frac{1}{2}\int d\vec{R}R_{\parallel}^2U(\vec{R}),$$

$$a_{\perp}=-\frac{1}{2}\int d\vec{R}R_{\perp}^2U(\vec{R}),\quad \vec{R}=r-r', \qquad (43)$$

and $R_{\parallel}^2$ and $R_{\perp}^2$ are the components of the interdroplet distance vector along and perpendicular to the director. Thus we see that the minimum of the functional (42) realizes a spatially inhomogeneous macrodroplet distribution only provided the signs satisfy some relations and the values of coefficients determined by the interdroplet interaction potential are given by Eq. (43). In order to reveal the conditions under which the homogeneous macrodroplet distribution becomes unstable, we have to calculate all the coefficients. This can always be done; however, for the sake of simplicity and clearness we consider a cylindrical sample with the base radius L and height d, the boundary condition being that the director is normal to the cylinder base. Then, for the interaction energy given by Eq. (28), we find that in the cylindrical coordinate system

$$b=\int R_{\perp}dR_{\perp}\int dR_{\parallel}\int d\phi\frac{A}{(R_{\perp}^2+R_{\parallel}^2)^{5/2}}\times\left\{3-30\frac{R_{\parallel}^2}{R_{\perp}^2+R_{\parallel}^2}+35\left(\frac{R_{\parallel}^2}{R_{\perp}^2+R_{\parallel}^2}\right)^2\right\},$$

$$a_{\parallel}=-\frac{1}{2}\int R_{\perp}dR_{\perp}\int R_{\parallel}^2dR_{\parallel}\int d\phi\frac{A}{(R_{\perp}^2+R_{\parallel}^2)^{5/2}}\times\left\{3-30\frac{R_{\parallel}^2}{R_{\perp}^2+R_{\parallel}^2}+35\left(\frac{R_{\parallel}^2}{R_{\perp}^2+R_{\parallel}^2}\right)^2\right\},$$

$$a_{\perp}=-\frac{1}{2}\int R_{\perp}^3dR_{\perp}\int dR_{\parallel}\int d\phi\frac{A}{(R_{\perp}^2+R_{\parallel}^2)^{5/2}}\times\left\{3-30\frac{R_{\parallel}^2}{R_{\perp}^2+R_{\parallel}^2}+35\left(\frac{R_{\parallel}^2}{R_{\perp}^2+R_{\parallel}^2}\right)^2\right\}, \qquad (44)$$

where $A\equiv(6/\pi\sqrt{K})[(4\pi/15)WR_0^4]^2$ is the coefficient in the energy of interaction between foreign spherical macrodroplets in the nematic liquid crystal and R_0 is the macrodroplet radius. After integration is carried out, we have

$$b=\frac{kT}{c_0(1-c_0)}-\frac{2\pi AdL^2}{L^2(L^2+d^2)^{1/2}}\left(1-\frac{d^2}{L^2}\right)^2, \qquad (45)$$

while the coefficients $a_{\parallel}$ and $a_{\perp}$ are given by

$$a_{\parallel}=\frac{\pi Ad^3L^2}{3(L^2+d^2)^{5/2}}\left(1-2\frac{d^2}{L^2}\right) \qquad (46)$$

and

$$a_{\perp}=\frac{3\pi AdL^4}{(L^2+d^2)^{5/2}}\left[1+\frac{4}{9}\frac{d^2}{L^2}\left(\frac{5}{2}+\frac{d^2}{L^2}\right)\right]. \qquad (47)$$

The critical temperature of the loss of stability of a homogeneous macrodroplet distribution is determined by the condition $b=0$ and in the case under consideration is described by the expression

$$\frac{kT_c}{c_0(1-c_0)}=\frac{2\pi AdL^2}{L^4(L^2+d^2)^{1/2}}\left(1-\frac{d^2}{L^2}\right)^2. \qquad (48)$$

Thus, for a given macrodroplet concentration C_0 in a cylindrical liquid crystal sample, the homogeneous macrodroplet distribution is unstable for $T<T_0$. The wavelength of the induced modulated macrodroplet distribution may be estimated. As follows from Eq. (47), the macrodroplet distribution is periodic along the director only for $2d^2 \ll L^2$. The modulation period of the macrodroplet concentration along the director $\lambda_\parallel = \sqrt{a_\parallel / b}$ is in our case equal to

$$\lambda_\parallel \simeq \sqrt{\frac{d^2}{6\left(1-\dfrac{T}{T_c}\right)}} \simeq \sqrt{\frac{T_c}{6(T_c-T)}}\, d. \tag{49}$$

The instability of the homogeneous distribution along the cylindrical sample radius occurs for any proportion of dimensions. For $d<R$ we have

$$\lambda_\perp \simeq \sqrt{\frac{3T_c}{2(T_c-T)}}\, L.$$

Thus we draw a conclusion that the homogeneous distribution of macrodroplets introduced in a nematic liquid crystal is unstable in a limited sample of mesophase and a spatially modulated distribution can be formed. The instability criterion $b=0$, given by the relation (48), may be interpreted as the condition for the formation of a spatially inhomogeneous macrodroplet distribution for a given temperature that depends on the foreign macrodroplet concentration in the liquid crystal. For temperatures for which the mesophase exists, both the temperature and concentration phase transition can occur, which results in the formation and rearrangement of a supermolecular structure.

V. MACRODROPLET-INDUCED SUPERMOLECULAR STRUCTURES

In the preceding section we considered spatially inhomogeneous structures in the gaseous phase of macrodroplets (clusters). As the cluster concentration becomes greater or the cluster surface energy increases, a new quasicrystalline phase can be formed. This phase includes not only the orientational ordering of clusters but also the spatial ordering of the cluster center-of-mass arrangement. The spatial ordering of the cluster system can again be caused by the deformation repulsion of clusters.

It is a very difficult problem to develop a consistent theory of phase transitions from the gaseous to quasicrystalline phase in terms of the cluster interaction energy (25). We shall not do it now. It should be just noted that the temperature of the transition to the quasicrystalline state in a cluster system may be estimated in terms of the Ising model in the self-consistent field approximation [15]. According to this model, the phase transition temperature T_c can be found from the equation

$$k_B T_c = g_0 J, \tag{50}$$

where g_0 is the number of nearest neighbors and J is the interaction constant.

The estimates for cluster concentrations that satisfy Eq. (51) for T_c, say, equal to the room temperature (see in what follows), show that the quasicrystalline phase formation is quite realistic. That is why now we assume that the quasicrystalline phase of a cluster system is already formed and consider the probable consequences of this phase transition.

In the previous analysis, when considering the energy (25) of binary deformation interaction between clusters, we mentioned the addends associated with the quantity $\{\beta_{klm}\}$. These terms are responsible for inducing the cholesteric phase in the nematic liquid crystals. If the cluster system in the nematic liquid crystal is regarded as a certain analog of the lyotropic liquid crystal, then the terms of the type (39) contained in the interaction energy can give rise to the cholesteric twisting. In the general case, the asymmetric cluster orientation is described by three basis unit vectors $\{\vec{\kappa}_i\}$. If, however, the clusters are sufficiently elongated along some axis, then the preferable orientation of the unit vector associated with this axis can be taken for the new director $\{\vec{m}\}$ in the ''lyotropic'' liquid crystal under consideration. The presence of other basis unit vectors can be approximately taken into account by introducing pseudoscalar terms in the cluster interaction energy of the type (39). Actually, this procedure is employed in the treatment of traditional cholesterics [12]. Once the energy of binary cluster interaction including the pseudoscalar terms of the type (39) is known, we can employ the molecular statistics approach to obtain the Frank energy and to calculate the Frank constants K_{ii} and the cholesteric twisting period q (see, e.g., [4,6]).

Now we can formulate the main purpose of this section. It is to reveal what happens if the cholesteric twisting in the cluster system occurs simultaneously with the spatial ordering of the cluster center-of-mass distribution. We shall show that the incommensurability effect can lead to the formation of a new spatially periodic structure in the director $\vec{m}$ distribution. First of all, we remind the reader that this situation is similar to the incommensurability effect in a spin system considered in Refs. [16,17]. Along with this analogy, we consider the mathematical substantiation of incommensurability in our case. To give such a substantiation means to understand the anchoring mechanism of the short-range order associated with the periodic cluster arrangement and the long-range order described by the field distribution of the director $\vec{m}$. Before doing this, we remind the reader of some points. In the molecular statistics approach, the free energy can be obtained from the Gibbs distribution in the self-consistent field approximation (see, e.g., [18,4]). The expression for the Gibbs distribution contains the total energy of interacting particles, i.e., clusters in our case. In the self-consistent field approximation, it can be written as

$$H = \sum_{\vec{r}\vec{r}\,'\Omega,\Omega'} V(\vec{r},\vec{r}\,',\Omega,\Omega')f(\vec{r},\Omega)f(\vec{r}\,',\Omega'). \tag{51}$$

Here $\vec{r}$ and $\vec{r}\,'$ give the positions of cluster centers while Ω and Ω' determine the angular orientation of the unit vectors $\vec{\kappa}$ and $\vec{\kappa}\,'$, which are parallel to the cluster long axes. In view of the above reasoning we have

$$\vec{m} = \vec{m}(r) = \langle \vec{\kappa} \rangle. \tag{52}$$

The angular brackets denote averaging over a physically small volume that nevertheless contains many clusters. The function $f(\vec{r},\Omega)$ contained in Eq. (52) determines the probability that a site of the periodic structure of the cluster system is occupied. It may be written as

$$f(\vec{r},\Omega)=\delta(x-n_1a_1)\,\delta(y-n_2a_2)\,\delta(z-n_3a_3)\,f_0(\vec{m}\vec{\kappa}). \tag{53}$$

Here $\delta(x-n_1a_1)$ does not vanish and it is equal to one only for $n_1=0,\pm1,\pm2,\ldots$; the quantities a_1, a_2, and a_3 determine the structure periods along *x*, *y*, and *z*, respectively. The function $f_0(\vec{m},\vec{\kappa})$ determines the angular arrangement of cluster long axes. Within the context of Eq. (54), expression (52) is periodic in x,y,z. In order to pass from summation to integration in Eq. (52), we make use of the Poisson formula. In the one-dimensional case, the Poisson formula for a periodic function $\Phi(x)$ is given by

$$\sum_n \Phi(x_n)=\int dx\,\Phi(x)+\sum_k \int dx\,\Phi(x)\cos\left(\frac{2\pi}{a}kx\right), \tag{54}$$

where *a* is the period of the function $\Phi(x)$.

We apply the transformation of Eq. (55) to Eq. (52). The terms originating from the first term on the right-hand side of Eq. (55) provide no information about the periodic structure and hence are associated with the spatially homogeneous distribution of cluster centers. Just this case was considered in Ref. [19] in terms of molecular statistics. Information on the periodic structure is contained in the second term on the right-hand side of the transformation (55).

Before discussing the role of periodic terms in our problem, we remind the reader that an analogous procedure of passage from the discrete spectrum to the continuum in terms of the Poisson formula has been successfully employed in the study of de Haas–van Alfven effect (see, e.g., [19]). In this problem, the second term on the right-hand side of Eq. (55) provides information on the discrete spectrum and gives rise to magnetic moment oscillations with growing magnetic field the (de Haas–van Alfven effect). In a similar way, in our problem the second term on the right-hand side of Eq. (55), when applied to Eq. (52), provides information on the discrete periodic distribution of cluster centers.

Thus, having transformed Eq. (52) with the use of Eq. (55), we find that

$$H=\int d\vec{r}\,d\vec{r}\,'\,d\Omega d\Omega'\,V(\vec{r},\vec{r}\,',\Omega,\Omega')\,f_0(\vec{m}\vec{\kappa})\,f_0(\vec{m}\,'\vec{\kappa}\,')$$
$$\times\left\{1+\sum_i \cos(k_ix_i)+\sum_i \cos(k_ix_i')+\cdots\right\}. \tag{55}$$

Here

$$k_i=\frac{2\pi}{a_i},\quad x_1=x,\quad x_2=y,\quad x_3=z. \tag{56}$$

The formula (56) contains only the terms whose oscillations are the slowest. We restrict the consideration to these terms. In order to obtain the Frank energy from Eq. (56), we pass to the new variables (58) and expand the integrand of Eq. (56) in a power series of $\vec{r}_1$ up to the second-order terms (see, e.g., [18,20]).

In the initial spatially homogeneous system,

$$V(\vec{r},\vec{r}\,',\Omega,\Omega')=V(\vec{r}-\vec{r}\,',\Omega,\Omega')=V(\vec{r}_1;\Omega,\Omega').$$

Since

$$\cos(k_ix_i)+\cos(k_ix_i')=2\cos k_i\left(\frac{x_i+x_i'}{2}\right)\cos k_i\left(\frac{x_i-x_i'}{2}\right), \tag{57}$$

it is clear that of all the terms contained in Eq. (56), only $\vec{m}(\vec{r})=\vec{m}(\vec{r}_0+\frac{1}{2}\vec{r}_1)$ and $\vec{m}\,'\equiv\vec{m}(\vec{r}\,')=\vec{m}(\vec{r}_0-\frac{1}{2}\vec{r}_1)$ must be expanded in an $\vec{r}_1$ series. In this sense, the procedure of deriving the Frank energy with regard to the cluster centers lattice does not differ from that of Refs. [18,20]. That is why we shall omit here the details of the calculation which are given in [18,20].

If the periodic terms are neglected while the pseudoinvariants associated with $\{\beta_{klm}\}$ are taken into account, one obtains the standard expression for the Frank energy of a cholesteric, i.e.,

$$\mathfrak{I}=\frac{1}{2}\int d\vec{r}_0\{K_{11}(\operatorname{div}\vec{m})^2+K_{22}(\vec{m}\times\operatorname{rot}\vec{m})^2$$
$$+K_{33}[\vec{m}\times\operatorname{rot}\vec{m}]^2+K_2(\vec{m}\cdot\operatorname{rot}\vec{m})\}. \tag{58}$$

Taking into account the terms of the type (59) in Eq. (56), one obtains, instead of Eq. (60), a similar expression with an obvious substitution of K_{ii}' for K_{ii}, where K_{ii}' is given by

$$K_{ii}'=K_{ii}+\sum_j \Delta K_{ii}^j\cos k_jx_j^{(0)}. \tag{59}$$

Moreover, with the periodic terms being taken into account, K_2 is replaced by

$$K_2'=K_2+\sum_j \Delta K_2^j\cos k_jx_j^{(0)}. \tag{60}$$

The explicit expressions for the amplitudes ΔK_{ii}^j and ΔK_2^j in terms of the cluster binary interaction energy $V(\vec{r}_1;\Omega,\Omega')$ can be obtained from the relevant integral expressions ΔK_{ii} for and ΔK_2 by means of the formal substitution of $V(\vec{r}_1;\Omega,\Omega')\cos(k_jx_j^{(1)}/2)$ for $V(\vec{r}_1;\Omega,\Omega')$. In this formula, $x_j^{(1)}$ are the components of the vector $\vec{z}_1$.

Now we employ the general expression for the Frank energy with respect to the periodic terms to consider a special case when the cholesteric twisting of the director $\vec{m}$ occurs along the z_0 axis and $\vec{m}$ depends only on the coordinate z_0. We take $\vec{m}$ to be given by

$$\vec{m}=\{\sin\theta\cos\varphi,\sin\theta\sin\varphi,\cos\theta\}. \tag{61}$$

Then the expression for the Frank energy reduces to

$$\begin{aligned}\Im=\frac{1}{2}\int & dz_0 K_{11}\left(1+\frac{\Delta K_{11}^{(3)}}{K_{11}}\cos k_3 z_0\right)\sin^2\theta\left(\frac{d\theta}{dz_0}\right)^2\\ & +K_{22}\left(1+\frac{\Delta K_{22}^{(3)}}{K_{22}}\cos k_3 z_0\right)\left(\frac{d\varphi}{dz_0}\right)^2\sin^4\theta\\ & +K_{33}\left(1+\frac{\Delta K_{33}^{(3)}}{K_{33}}\cos k_3 z_0\right)\cos^2\theta\\ & \times\left[\left(\frac{d\theta}{dz_0}\right)^2+\left(\frac{d\varphi}{dz_0}\right)^2\sin^2\theta\right]\\ & -K_2\left(1+\frac{\Delta K_2^{(3)}}{K_2}\cos k_3 z_0\right)\frac{d\varphi}{dz_0}\sin^2\theta. \end{aligned}\tag{62}$$

A usual step in the theory of cholesterics is to take

$$K_2=qK_{22},\quad \varphi=qz_0.\tag{63}$$

Moreover, to illustrate the appearance of the incommensurability effect in our case we restrict the consideration to the one-constant approximation, i.e., we assume that

$$\begin{gathered}K_{11}=K_{22}=K_{33}=K,\\ \Delta K_{11}^{(3)}=\Delta K_{22}^{(3)}=\Delta K_{33}^{(3)}=\Delta K.\end{gathered}\tag{64}$$

Taking into account these restrictions, we find from Eq. (64) that

$$\begin{aligned}\Im=\frac{K}{2}\int dz_0\Bigg\{&\left(1+\frac{\Delta K}{K}\cos k_3 z_0\right)\left(\frac{d\theta}{dz_0}\right)^2\\ &+q^2\left(\frac{\Delta K}{K}-\frac{\Delta K_2^{(3)}}{K_2}\right)\cos k_3 z_0\sin^2\theta\Bigg\}.\end{aligned}\tag{65}$$

We transform the factor in the second term to obtain

$$\begin{aligned}\cos k_3 z_0\sin^2\theta&=\frac{1}{2}\cos k_3 z_0(1-\cos\theta)\\ &=\frac{1}{2}\cos k_3 z_0-\frac{1}{4}\cos(2\theta+k_3 z_0)\\ &\quad-\frac{1}{4}\cos(2\theta-k_3 z_0).\end{aligned}\tag{66}$$

The last term on the right-hand side of Eq. (68) is the one with the slowest oscillations. Inasmuch as we are interested in studying the formation of long-wavelength structures in Eq. (67), we retain in Eq. (67) only the last term contained on the right-hand side of Eq. (68).

We introduce a new ‘‘slow’’ variable given by

$$\psi=k_3 z_0-2\theta\tag{67}$$

and thus obtain from Eq. (67)

$$\Im=\frac{K}{8}\int dz_0\left\{\left(\frac{d\psi}{dz_0}-k_3\right)^2-q^2\left(\frac{\Delta K}{K}-\frac{\Delta K_2}{K_2}\right)\cos\psi\right\}.\tag{68}$$

When deriving Eq. (70) we neglected the fast oscillating term $(\Delta K/K)\cos k_3 z_0$ in the factor $[1+(\Delta K/K)\cos k_3 z_0]$ before the first term since this term is small and, moreover, it is multiplied by the slowly varying quantity $(d\psi/dz_0-k_3)^2$ and hence is nearly zero due to averaging.

The functional (70), to within a constant, reduces to the standard form

$$\Im=\frac{K}{8}\int dz\left\{\left(\frac{d\psi}{dz}-k_3\right)^2-2\zeta(\cos\psi-1)\right\},\tag{69}$$

where $2\zeta=q^2(\Delta K/K-\Delta K_2/K_2)$.

The functional (71) is widely employed in the studies of incommensurability effects (see, e.g., [21,22]). The extremum of the functional (71) is realized in the solutions of the Euler-Lagrange equation

$$\frac{d^2\psi}{dz^2}-\zeta\sin\psi=0,\tag{70}$$

which may be written as [21,22]

$$z=\int_0^{\psi}\frac{d\psi'}{\sqrt{c-2\zeta\cos\psi'}},\tag{71}$$

where C is the first integral of motion of Eq. (72). This solution describes the periodic arrangement of solitons in the director distribution through the z dependence of θ, which is related to ψ in terms of Eq. (69). We have

$$l=\frac{4\tau}{\sqrt{\zeta}}K(\tau),\tag{72}$$

where $K(\tau)$ is the elliptic function of the argument

$$\tau=\sqrt{\frac{4\zeta}{c+2\zeta}}.\tag{73}$$

Since $K(\tau)\to\ln[4/(1-\tau^2)]$ as $\tau\to1$, we see from Eq. (74) that long-period structures can appear in the system. This is a manifestation of the incommensurability effect. The details of this phenomenon are considered in Refs. [16,17,21] in terms of the functional (71). Thus, in the presence of the Lifshitz pseudoinvariant, the periodic arrangement of centers of clusters (foreign droplets) induces gyrotropy and, moreover, produces one more incommensurable period in the distribution of the mean macrodroplet orientations.

VI. CONCLUSIONS

In this paper the Frank energy and the surface energy of macroclusters introduced in a nematic are used to derive a general expression for the energy of the cluster deformation interaction. The cluster shape and the coordinate dependence of the cluster anchoring are arbitrary. The energy of binary elastic interaction of clusters depends on cluster orientations and intercluster distances. Explicit expressions for the constants entering the energy of the pair cluster interaction are obtained for some cases of specified cluster shapes and anchoring distributions. It is shown that for certain cluster shapes and surface energies, the interaction energy can contain a pseudoscalar that is responsible for the cholesteric twisting effect.

The system of deformation-interacting clusters is considered in both gaseous and crystalline approximations. In the gaseous approximation, which corresponds to relatively small cluster concentrations, instability criteria are found for a spatially homogeneous cluster distribution in a nematic liquid crystal.

The crystalline approximation is associated with higher cluster concentrations. In this state, a preferable orientation of cluster long axes occurs; cluster centers are spatially ordered and form a lattice. It is shown that if a Lifshitz pseudoinvariant responsible for the gyrotropy occurs in the system, then, in the crystalline phase, one more incommensurable long-period structure appears in the distribution of mean orientations of cluster long axes. A mechanism of supermolecular structure formation is proposed.

The above considered behavior of a system of macrodroplets introduced in the mesophase should be observed experimentally. Let us estimate the conditions under which these effects can occur.

Having assumed that a spatially homogeneous arrangement of macrodroplets occurs for temperatures of mesophase existence, i.e., $T\sim 300$ K, we find from Eq. (48), for anchoring $W\sim 10^{-2}$dyn/s m^2 and macrodroplet dimensions $R_0 \sim 300$ Å, that such structures can occur in a usual sample of size 10 μm for relative concentrations $C_0\sim 10^{-3}$. For concentrations an order of magnitude greater and for chiral droplet interaction energies such that $J=(\beta_{311}/\pi K)(1/\langle R\rangle^3)$, the formula (51) yields the value of critical temperature that is equal to the mesophase existence temperature. The formation of a distorted supermolecular structure with two incommensurable periods in the distribution of macrodroplet mean orientations is a finer effect since it depends as well on the mesophase characteristics. It can be observed, however, by optical methods [23].

Thus we have solid grounds to state that a system of macrodroplets introduced in a liquid crystal can produce, due to the interaction via the deformation of the director elastic field, new supermolecular structures that possess necessary electric and optical properties of an effective medium.

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