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Thermal fluctuations of director orientation in nematic liquid crystals with inclusions

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We investigate thermal fluctuations of order parameters (director for mesomorphic subsystem and density for isomorphic liquid) in filled liquid crystal. We consider finite-size system with geometry of plane-parallel layer with zero boundary condition. We use a special model that takes into account the interaction of mesomorphic and isotropic subsystems and find general expressions for pair correlators. Based on these expressions we calculate the shift of critical temperature of isotropic liquid due to the interaction with the mesomorphic subsystem and space limitation.

Key words: *liquid crystal, impurity, pair correlation, critical temperature*

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1. Introduction

It is well known that in liquid-crystalline systems, thermal fluctuations of director orientation can be very strong especially in close vicinity to phase transition [1–3]. Since the susceptibility of the system is extremely high, any external perturbations can cause drastic changes in the behaviour of the system. We expect that if there are impurities in the system, they can affect its correlative behavior. To clarify this point we consider a mesomorphic system with isotropic inclusions. We propose an expression for the total energy of the system and based on this expression calculate (in general form) the pair correlators for fluctuations of order parameters (director for mesomorphic liquid and local density for isotropic liquid).

Plenty of different effects due to the presence of impurities can be observed in liquid crystals [4–8]. The most remarkable of them are the cooperative processes in ferronematics, i.e., liquid crystals with ferroparticles [8–16]. For these systems many fruitful results were obtained of both theoretical end experimental nature.

But this does not mean that if impurity particles have no magnetic moment then nothing interesting happens. For macroparticles one can mention very interesting effects dealing with topological defects in director distribution in filled liquid crystals [17–22]. From this point of view the size of the particles is the question of great importance. Here we consider microscopic impurities. Some useful results can be received in this case as well. Besides pair correlation we investigate the shift of critical temperature in the system due to the presence of mesomorphic component (i.e. liquid-crystalline subsystem).

2. Formalization of the problem

We consider the elastic energy of mesomorphic subsystem in the one-constant approximation, i.e. we take

$$F_{\rm el} = \frac{K}{2}\int\Big((\mathrm{div}\vec{n})^2 + (\mathrm{rot}\vec{n})^2\Big)\mathrm{d}V, \tag{1}$$

where K is elastic Frank constant. We also consider the isotropic subsystem of microscopic impurities. As an order parameter for this subsystem we take local density $\rho(\vec{r})$ of impurities. The energy related to the impurity subsystem is of the ordinary form

$$F_{\rm im} = \frac{1}{2}\int\Big(a\rho^2 + b(\nabla\rho)^2\Big)\mathrm{d}V, \tag{2}$$

and here a and b are phenomenological parameters of the model. We have to take into the account interactional part of energy between mesomorphic and isotropic subsystems. We do it at the stage of finding the fluctuation part of the total energy. This fluctuation part of the energy is caused by deviation of the director from its equilibrium direction and the density from its average value. We assume that the equilibrium director is oriented along z-axes and we define the average density of isotropic subsystem as ρ_0. Then we take $\vec{n} = \vec{n}_0 + \delta\vec{n}$ and $\rho = \rho_0 + \delta\rho$, where $\delta\vec{n} = (\delta n_x, \delta n_y, 0)$ is the fluctuation of the director as well as $\delta\rho$ is the fluctuation of density. Fluctuation parts of energies $F_{\rm el}$ and $F_{\rm im}$ then are as follows

$$\begin{aligned}\delta F_{\rm el} &= \frac{K}{2}\int\Bigg(\left(\frac{\partial\delta n_x}{\partial x} + \frac{\partial\delta n_y}{\partial y}\right)^2 + \left(\frac{\partial\delta n_x}{\partial y} - \frac{\partial\delta n_y}{\partial x}\right)^2 \\ &\quad + \left(\frac{\partial\delta n_x}{\partial z}\right)^2 + \left(\frac{\partial\delta n_y}{\partial z}\right)^2\Bigg)\mathrm{d}V, \qquad (3)\\ \delta F_{\rm im} &= \frac{1}{2}\int\Big(a(\delta\rho)^2 + b(\nabla\delta\rho)^2\Big)\mathrm{d}V. \qquad (4)\end{aligned}$$

We consider the finite-size system of thickness L and assume that z-axis is perpendicular to the plane of the layer. Fluctuation part of the energy of the subsystem interaction in a general case can depend on fluctuations δn_x, δn_y, $\delta\rho$ and their derivatives as well. Here we will not consider the general situation and take the fluctuation part of interaction energy as follows:

$$\delta F_{\text{int}} = -W \int \frac{\partial \delta\rho}{\partial z}\Big(\frac{\partial \delta n_x}{\partial z} + \frac{\partial \delta n_y}{\partial z}\Big)\mathrm{d}V, \tag{5}$$

which means self-ordering of fluctuations along z-axis. Here W is the parameter that characterizes the energy of interaction of subsystems (it could be positive or negative). Let us consider the hard boundary conditions which mean the absence of fluctuations on the restricting surfaces. In this case we can take the next expansion for δn_x, δn_y and $\delta\rho$:

$$\delta n_\alpha = \sum_{m=1}^{\infty} \delta n_{\alpha,m} \sin\Big(\frac{\pi m z}{L}\Big), \tag{6}$$

$$\delta \rho = \sum_{m=1}^{\infty} \delta \rho_m \sin\Big(\frac{\pi m z}{L}\Big), \tag{7}$$

where $\alpha = x, y$. After inserting (6) and (7) in (3)–(5) and making Fourier transformation in xy-plane and integrating on z from 0 to L we can easily get

$$\delta F_{\text{el}} = \frac{KL^2}{2V} \sum_{m=1}^{\infty} \sum_{\vec q} \Big(q^2 + \frac{\pi^2 m^2}{L^2}\Big)\Big(|\delta n_{x,m}(q)|^2 + |\delta n_{y,m}(q)|^2\Big), \tag{8}$$

$$\delta F_{\text{im}} = \frac{L^2}{2V} \sum_{m=1}^{\infty} \sum_{\vec q} \Big(a + b(q^2 + \pi^2 m^2/L^2)\Big)|\delta\rho_m(q)|^2, \tag{9}$$

$$\delta F_{\text{int}} = -\frac{WL^2}{2V} \sum_{m=1}^{\infty} \sum_{\vec q} \frac{\pi^2 m^2}{L^2}\Big(\delta\rho_m^*(q)(\delta n_{x,m}(q) + \delta n_{y,m}(q)) + \delta\rho_m(q)(\delta n_{x,m}^*(q) + \delta n_{y,m}^*(q))\Big), \tag{10}$$

and here V is the volume of the system and the star means complex conjugation.

If we define symmetrical matrices $\hat{A}_m$ as follows

$$\hat{A}_m(q) = \begin{pmatrix} K\Big(q^2 + \frac{\pi^2 m^2}{L^2}\Big) & 0 & -\frac{W\pi^2 m^2}{L^2} \\ 0 & K\Big(q^2 + \frac{\pi^2 m^2}{L^2}\Big) & -\frac{W\pi^2 m^2}{L^2} \\ -\frac{W\pi^2 m^2}{L^2} & -\frac{W\pi^2 m^2}{L^2} & a + b\Big(q^2 + \frac{\pi^2 m^2}{L^2}\Big) \end{pmatrix} \tag{11}$$

then we can present the fluctuation part of total energy like this:

$$\delta F = \frac{L^2}{2V} \sum_{m=1}^{\infty} \sum_{\vec q} \delta\vec\eta_m^{+}(q) \hat{A}_m(q) \delta\vec\eta_m(q), \tag{12}$$

where

$$\delta\vec\eta_m(q) = \begin{pmatrix} \delta n_{x,m}(q) \\ \delta n_{y,m}(q) \\ \delta\rho_m(q) \end{pmatrix} \tag{13}$$

and "+" means transposition and complex conjugation.

3. Finding pair correlators

To diagonalize the expression (12) we take new order parameters $\vec{\xi}_m(q)$ according to relation

$$\vec{\eta}_m(q) = \hat{U}_m(q)\vec{\xi}_m(q), \tag{14}$$

and in this case from (12) we can get

$$\delta F = \frac{L^2}{2V}\sum_{m=1}^{\infty}\sum_{\vec{q}} \delta\vec{\xi}_m^{+}(q)\hat{B}_m(q)\delta\vec{\xi}_m(q), \tag{15}$$

where matrix

$$\hat{B}_m(q) = \hat{U}_m^{+}(q)\hat{A}_m(q)\hat{U}_m(q) \tag{16}$$

should be of diagonal form. Matrix $\hat{U}_m(q)$ can be presented as a direct sum of unit eigenvectors $\vec{e}_{i,m}(q)$ $(i = 1, 2, 3)$ of matrix $\hat{A}_m(q)$. Diagonal elements of matrix $\hat{B}_m(q)$ then coincide with eigenvalues of matrix $\hat{A}_m(q)$.

Eigenvalues of matrix $\hat{A}_m(q)$ are

$$\lambda_1^{(m)}(q) = K\Big(q^2 + \frac{\pi^2 m^2}{L^2}\Big), \tag{17}$$

$$\lambda_{2,3}^{(m)}(q) = \frac{1}{2}\Big(F_{+}^{(m)}(q) \pm \sqrt{[F_{-}^{(m)}(q)]^2 + 8w_m^2}\Big), \tag{18}$$

where we have defined

$$F_{\pm}^{(m)}(q) \equiv K\Big(q^2 + \frac{\pi^2 m^2}{L^2}\Big) \pm \Big(a + b\Big(q^2 + \frac{\pi^2 m^2}{L^2}\Big)\Big), \tag{19}$$

$$w_m \equiv \frac{W\pi^2 m^2}{L^2}\,. \tag{20}$$

The corresponding eigenvectors are

$$\vec{e}_{1,m}(q) = \frac{1}{\sqrt{2}}\begin{pmatrix}-1\\ 1\\ 0\end{pmatrix}, \tag{21}$$

$$\vec{e}_{k,m}(q) = \sqrt{\frac{1}{2} \mp \frac{F_{-}^{(m)}(q)}{2\sqrt{[F_{-}^{(m)}(q)]^2 + 8w_m^2}}}\begin{pmatrix} 2w_m\Big(F_{-}^{(m)}(q) \mp \sqrt{[F_{-}^{(m)}(q)]^2 + 8w_m^2}\Big)^{-1}\\ 2w_m\Big(F_{-}^{(m)}(q) \mp \sqrt{[F_{-}^{(m)}(q)]^2 + 8w_m^2}\Big)^{-1}\\ 1\end{pmatrix}, \tag{22}$$

and here $k = 2, 3$. Then we get for the fluctuation part of the total energy

$$\delta F = \frac{L^2}{2V}\sum_{m=1}^{\infty}\sum_{\vec{q}}\sum_{k=1}^{3}\lambda_k(q)|\delta\xi_m^k(q)|^2, \tag{23}$$

where $\delta\xi_m^k(q)$ is k-th element of vector $\delta\vec{\xi}_m(q)$. After statistical averaging we can find that

$$\langle|\delta\xi_m^k(q)|^2\rangle = \frac{k_\mathrm{B}TV}{L^2}\,\frac{1}{\lambda_k^{(m)}(q)}\,. \tag{24}$$

But as usual we need to know the correlators $\langle\delta\eta_m^i(q)[\delta\eta_m^j(q)]^*\rangle$. Namely we can get

$$\begin{aligned}\langle\delta\eta_m^i(q)[\delta\eta_m^j(q)]^*\rangle &= \sum_{k=1}^{3} U_m^{ik}(q)[U_m^{kj}]^+(q)\langle|\delta\xi_m^k(q)|^2\rangle \\ &= \sum_{k=1}^{3} e_{k,m}^i(q)[e_{k,m}^j(q)]^*\langle|\delta\xi_m^k(q)|^2\rangle,\end{aligned} \tag{25}$$

here we have defined elements of eigenvectors $\vec{e}_{k,m}(q)$ as $e_{k,m}^i$ $(i,k=1,2,3)$.

4. Shift of critical parameters

Knowing the expressions for eigenvectors $\vec{e}_{k,m}(q)$ and eigenvalues $\lambda_k^{(m)}(q)$ one can find the pair correlators $\langle\delta\eta_m^i(q)[\delta\eta_m^j(q)]^*\rangle$. For example, the correlator of density fluctuations is

$$\begin{aligned}\langle|\delta\rho_m(q)|^2\rangle &\equiv \langle|\delta\eta_m^3(q)|^2\rangle = \sum_{k=1}^{3}|e_{k,m}^3(q)|^2\langle|\delta\xi_m^k(q)|^2\rangle \\ &= \frac{k_\mathrm{B}TV}{L^2}\Big(a + b(q^2+\pi^2m^2/L^2) - \frac{2w_m^2}{K(q^2+\pi^2m^2/L^2)}\Big)^{-1}.\end{aligned} \tag{26}$$

We see that in comparison with the pure isotropic system, the structure of pair correlator in the case of mixed system is more complex. There is an extension caused by interaction with mesomorphic subsystem in the expression (26).

We also know that for infinite system

$$\langle|\delta\rho(q)|^2\rangle \sim \frac{1}{a+bq^2} \tag{27}$$

and the condition for critical point is $a=0$. As usual one takes

$$a = a_0(T-T_\mathrm{c}), \tag{28}$$

where T_c is critical temperature. Obviously the interaction with mesomorphic subsystem causes a shift of critical parameters and namely, critical temperature. For the mixed system we have the following equation for new critical temperature $T_\mathrm{c}^\mathrm{mix}$:

$$a + \frac{b\pi^2}{L^2} - \frac{2w_1^2L^2}{K\pi^2} = a + \frac{b\pi^2}{L^2} - \frac{2W^2\pi^2}{KL^2} = 0. \tag{29}$$

Taking into account (28) we get

$$T_\mathrm{c}^\mathrm{mix} = T_\mathrm{c} + \frac{\pi^2}{a_0L^2}\Big(\frac{2W^2}{K} - b\Big). \tag{30}$$

The shift of critical temperature (in comparison with spatially infinite system) takes place for two reasons (in our case). First of all critical temperature changes as a result of space limitation (addition $b\pi^2/L^2$ in equation (29)). This lowers critical temperature. The presence of mesomorphic subsystem rises the critical temperature (addition $2W^2\pi^2/(KL^2)$ in equation (29)). Thus, the total change of critical temperature can be both positive and negative.

5. Conclusion

We have shown that the interaction of isotropic and mesomorphic subsystems causes significant changes in the structure of order parameter fluctuations. Nevertheless from the point of view of possible experiment we should note that it is hard enough to clarify the effect of impurities on correlative behavior of the system. As a matter of fact, in the experiment we normally measure the intensity of light scattering [1–3,22]. This intensity is determined mainly by the most singular correlator. This means that the above mentioned peculiarities of pair correlation cannot be seen from direct measurements.

It is much easier to find the shifts of critical parameters (for example critical temperature). Similar results (using different model) concerning the dependence of critical temperature on the concentration of impurities were received previously [4,23]. Here we have considered one of the possible mechanisms of interaction between mesomorphic and isotropic subsystems. Using the above proposed scheme we can consider a more general model of interaction. But in any case we get expressions for critical parameter shifts and then compare experimental data with theoretical predictions. Moreover, to compare the predictions of the model with experimental data we can interpret the above considered system (probably with minor modifications) as the isotropic liquid with mesomorphic inclusions. From this point of view our results are in good agreement with experimental data not only in the part of critical temperature shift but regarding the structure of pair correlation functions as well (see for example [23–25]).

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Теплові флуктуації орієнтації директора в нематичному рідкому кристалі з домішками

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Досліджуються теплові флуктуації параметрів порядку (директор для рідкокристалічної підсистеми та густина для ізотропної рідини) в рідкому кристалі з домішками. Розглядається просторово обмежена система з геометрією плоского паралельного прошарку з нульовими граничними умовами. Запропоновано модель, що враховує взаємодію рідкокристалічної та ізотропної підсистем та знаходяться загальні вирази для парних кореляторів. На основі цих виразів розраховується зсув критичної температури ізотропної підсистеми, що виникає внаслідок взаємодії з рідким кристалом та через просторове обмеження.

Ключові слова: *рідкий кристал, домішка, парні кореляції, критична температура*

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