

QUASIAVERAGES IN MICROSCOPIC THEORY OF LIQUID CRYSTALS

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Currently, the theoretical substantiation of statistical physics of condensed media with spontaneously broken symmetry is a quasi-average concept by N.Bogoliubov [1]. Said concept extends Gibbs distribution to degenerate condensed media. Within liquid crystals, there occurs a spontaneous breaking of rotational and in some cases of translational invariance within a configuration space. Dynamic features of such media have been previously investigated mainly by phenomenology methods [2,3].

There in report is introduced an order-parameter operator for liquid crystals, which is expressed in terms of field operators. Thermodynamics and ideal hydrodynamics for uniaxial nematic was built. There is reviewed a connection between presently-proposed and phenomenological Hamiltonian approaches. A quasi-average of physical value is defined by relation

$$\langle a(\mathbf{x}) \rangle \equiv \lim_{\nu \rightarrow 0} \lim_{V \rightarrow \infty} \text{Sp} w_{\nu} \hat{a}(\mathbf{x}), \quad (1)$$

$$\hat{w}_{\nu} \equiv \exp(\Omega_{\nu} - Y_a \hat{\gamma}_a - \nu \hat{F}).$$

Here $\hat{\gamma}_a \equiv \int d^3x \hat{\gamma}_a(\mathbf{x})$ are operators of additive motion integrals ($\hat{H} = \int d^3x \hat{\varepsilon}(\mathbf{x})$ is Hamiltonian, $\hat{P}_k = \int d^3x \hat{\pi}_k(\mathbf{x})$ is a momentum operator, $\hat{N} = \int d^3x \hat{n}(\mathbf{x})$ is a particle number operator), ($Y_a \equiv Y_0, Y_k, Y_4$) are thermodynamic forces, (for simply we allow $Y_k = 0$). Thermodynamic potential Ω_{ν} should be defined from the normalization condition of $\text{Sp} w_{\nu} = 1$. Operator \hat{F} possesses the symmetry of the investigated phase and eliminates the degeneration of equilibrium state of statistical equilibrium. Let us define the liquid crystals order parameter by formula:

$$\hat{Q}_{uv} \equiv \nabla_u \hat{\psi}^+(\mathbf{x}) \nabla_v \hat{\psi}(\mathbf{x}) + \nabla_v \hat{\psi}^+(\mathbf{x}) \nabla_u \hat{\psi}(\mathbf{x}) - \frac{2}{3} \delta_{uv} \nabla_j \hat{\psi}^+(\mathbf{x}) \nabla_j \hat{\psi}(\mathbf{x}). \quad (2)$$

The source \hat{F} is a linear functional of the order parameter operator \hat{Q}_{uv} :

$$\hat{F} = \int d^3x f_{ik}(\mathbf{x}, t) \hat{Q}_{ik}(\mathbf{x}). \quad (3)$$

Here $f_{ik}(\mathbf{x}, t)$ are the c -number functions of coordinates and time respectively, which characterize equilibrium state values $Q_{ik}(\mathbf{x}) = \langle \hat{Q}_{ik}(\mathbf{x}) \rangle$. Structure of functions $f_{ik}(\mathbf{x}, t)$ is determined by the symmetry properties of the equilibrium phases. Taking into account definition (2) and form of additive integrals of motion one can obtain the following algebra:

$$\begin{aligned} [\hat{N}, \hat{Q}_{uv}(\mathbf{x})] &= 0, & i[\hat{P}_k, \hat{Q}_{uv}(\mathbf{x})] &= -\nabla_k \hat{Q}_{uv}(\mathbf{x}), \\ i[\hat{L}_i, \hat{Q}_{uv}(\mathbf{x})] &= -\varepsilon_{iuj} \hat{Q}_{jv}(\mathbf{x}) - \varepsilon_{ivj} \hat{Q}_{ju}(\mathbf{x}) - \varepsilon_{ikl} x_k \nabla_l \hat{Q}_{uv}(\mathbf{x}), \end{aligned} \quad (4)$$

where \hat{L}_i orbital momentum. The quasi-average of order parameter $Q_{ik}(\mathbf{x}, \hat{\rho}) = \text{Sp} \hat{\rho} \hat{Q}_{ik}(\mathbf{x})$, where $\hat{\rho}$ is an arbitrary statistical operator, possesses the properties: $Q_{uv}(\mathbf{x}, \hat{\rho}) = Q_{vu}(\mathbf{x}, \hat{\rho})$, $Q_{uu}(\mathbf{x}, \hat{\rho}) = 0$, and, therefore, contains five independent values. Let us parametrize said values by relation

$$\begin{aligned} Q_{ik}(\mathbf{x}, \hat{\rho}) &= Q(\mathbf{x}, \hat{\rho}) \left(l_i(\mathbf{x}, \hat{\rho}) l_k(\mathbf{x}, \hat{\rho}) - \frac{1}{3} \delta_{ik} \right) + \\ &+ Q'(\mathbf{x}, \hat{\rho}) \left(m_i(\mathbf{x}, \hat{\rho}) m_k(\mathbf{x}, \hat{\rho}) - \frac{1}{3} \delta_{ik} \right). \end{aligned} \quad (5)$$

Here Q, Q' are modules of order parameter, \mathbf{l}, \mathbf{m} are vectors of spatial anisotropy and there are real and orthonormalized vectors (directors) $\mathbf{l}^2 = \mathbf{m}^2 = 1$, $\mathbf{l}\mathbf{m} = 0$. In general case the order parameter (5) describes biaxial liquid crystals. Individual cases with uniaxial liquid crystals are reproduced from this factor by limit transition $Q \rightarrow 0$, or $Q' \rightarrow 0$.

Symmetry of equilibrium state of uniaxial nematics with respect to rotation in real space has the form:

$$[\hat{w}, \hat{P}_k] = 0, \quad [\hat{w}, l_i \hat{L}_i] = 0, \quad (6)$$

where l_i — vector of spatial anisotropy. Taking into account formulae (6) and operator algebra (4) we come to the equations determining equilibrium structure of order parameter:

$$\begin{aligned} i\text{Sp}[\hat{w}, l_i \hat{L}_i] &= -l_i (\varepsilon_{iuj} Q_{jv}(\mathbf{x}, Y, \mathbf{l}) + \varepsilon_{ivj} Q_{ju}(\mathbf{x}, Y, \mathbf{l})) = 0, \\ i\text{Sp}[\hat{w}, \hat{P}_k] &= -\nabla_k Q_{ju}(\mathbf{x}, Y, \mathbf{l}) = 0, \end{aligned}$$

whereby the solution hereof is formed as

$$Q_{uv}(\mathbf{x}, Y, \mathbf{l}) \equiv Q_{uv}(Y, \mathbf{l}) = Q(Y) (l_u l_v - \frac{1}{3} \delta_{uv}), \quad Q(Y) = Q(Y_0, Y_4).$$

It is not a problem to find, in similar way, that function f_{uv} has the form $f_{uv} = l_u l_v - \frac{1}{3} \delta_{uv}$. Such liquid crystal is described by statistical operator $\hat{w} = \hat{w}(Y, \mathbf{l})$,

which depends on thermodynamic forces and director, whereby dependence of averages from last argument is kept the same after limits $V \rightarrow \infty$, $\nu \rightarrow 0$.

Let's introduce into consideration densities and flux densities of additive integral of motion. According to [4]

$$\dot{\hat{n}}(\mathbf{x}) = -\nabla_k \hat{g}_k(\mathbf{x}), \quad \hat{g}_k(\mathbf{x}) = i \int d^3 x' x'_k \int_0^1 d\lambda [\hat{\varepsilon}(\mathbf{x} - (1-\lambda)\mathbf{x}'), \hat{n}(\mathbf{x} + \lambda\mathbf{x}')] \quad (7)$$

is flux density operator of particle number,

$$\begin{aligned} \dot{\hat{\pi}}_i(\mathbf{x}) &= -\nabla_k \hat{t}_{ik}(\mathbf{x}), \\ \hat{t}_{ik}(\mathbf{x}) &= -\hat{\varepsilon}(\mathbf{x})\delta_{ik} + i \int d^3 x' x'_k \int_0^1 d\lambda [\hat{\varepsilon}(\mathbf{x} - (1-\lambda)\mathbf{x}'), \hat{\pi}_i(\mathbf{x} + \lambda\mathbf{x}')] \end{aligned} \quad (8)$$

is flux density operator of momentum,

$$\dot{\hat{\varepsilon}}(\mathbf{x}) = -\nabla_k \hat{q}_k(\mathbf{x}), \quad \hat{q}_k(\mathbf{x}) = \frac{i}{2} \int d^3 x' x'_k \int_0^1 d\lambda [\hat{\varepsilon}(\mathbf{x} - (1-\lambda)\mathbf{x}'), \hat{\varepsilon}(\mathbf{x} + \lambda\mathbf{x}')] \quad (9)$$

is flux density operator of energy. According to (5), relation

$$Q_{ik}(\mathbf{x}, \hat{\rho}) \equiv \frac{3}{2} l_j(\mathbf{x}, \hat{\rho}) Q_{jp}(\mathbf{x}, \hat{\rho}) l_p(\mathbf{x}, \hat{\rho}) (l_i(\mathbf{x}, \hat{\rho}) l_k(\mathbf{x}, \hat{\rho}) - \frac{1}{3} \delta_{ik}) \quad (10)$$

can be defined indirectly a unit anisotropy vector (director) in terms of order parameter for uniaxial liquid crystal. Let's introduce spatial anisotropy vector operator in accordance with approach [5]

$$\delta l_k(\mathbf{x}, \hat{\rho}) \equiv \text{Sp} \delta \rho \hat{l}_k(\mathbf{x}, \hat{\rho}). \quad (11)$$

We have to find explicit form of operator $\hat{l}_k(\mathbf{x}, \hat{\rho})$ in terms of order parameter operator $\hat{Q}_{ik}(\mathbf{x})$. This will allow us to obtain dynamical equations for set of parameters of abridge description and to establish connection between proposed microscopic approach and Hamilton approach. Varying of (10) and taking into account identity $l_i(\mathbf{x}, \hat{\rho}) \hat{l}_i(\mathbf{x}, \hat{\rho})$, one can obtain

$$\hat{l}_j(\mathbf{x}, \hat{\rho}) = \frac{\hat{Q}_{uv}(\mathbf{x}) l_v(\mathbf{x}, \hat{\rho})}{Q(\mathbf{x})} \delta_{uj}^\perp(\mathbf{I}(\mathbf{x}, \hat{\rho})). \quad (12)$$

In accordance with (10),(12) we obtain the following expression:

$$i \text{Sp} \hat{\rho} [\hat{\pi}_i(\mathbf{x}), \hat{l}_\lambda(\mathbf{x}, \hat{\rho})] = -l_i(\mathbf{x}', \hat{\rho}) \delta_{u\lambda}^\perp(\mathbf{I}(\mathbf{x}, \hat{\rho})) \nabla'_u \delta(\mathbf{x} - \mathbf{x}') - \delta(\mathbf{x} - \mathbf{x}') \nabla_i l_\lambda(\mathbf{x}, \hat{\rho}). \quad (13)$$

At the investigation of condensed matter with spontaneously broken symmetry within microscopic approach, an important role is paid of local transformations

with the generator of broken symmetry. For liquid crystals it's necessary to consider local spatial deformations, defined by the following unitary operator

$$U_f = \exp(-i) \int d^3x f_i(\mathbf{x}) \hat{\pi}_i(\mathbf{x}), \quad (14)$$

where $f_i(\mathbf{x})$ is some arbitrary function of spatial coordinates, that determines a unitary transformation of deformations U_f . The field operators are transformed thereby as

$$U_f^+ \hat{\psi}(\mathbf{x}) U_f = \left| \frac{\partial x'}{\partial x} \right|^{1/2} \hat{\psi}(\mathbf{x}), \quad U_f^+ \hat{\psi}^+(\mathbf{x}) U_f = \left| \frac{\partial x'}{\partial x} \right|^{1/2} \hat{\psi}^+(\mathbf{x}), \quad (15)$$

where $x'_i = x_i - u_i(\mathbf{x})$, $\left| \frac{\partial x'}{\partial x} \right| = \det \frac{\partial x'_i}{\partial x_j} = \det b_{ij} = J(\mathbf{x})$, where $u_i(\mathbf{x})$ — vector of displacement, being a transformation parameter functional $f_i(\mathbf{x})$ and point x_i : $u_i(\mathbf{x}) = u_i(f_i(\mathbf{x}')\mathbf{x})$, whereby $u_i(0, \mathbf{x}) = 0$. At transformations arbitrary deformations (15) $\hat{\rho}_f = U_f \hat{\rho} U_f^+$ director $l_i(\mathbf{x}, \hat{\rho})$ changes as follows:

$$l_i(\mathbf{x}, U_f^+ \hat{\rho} U_f) = l_i(\mathbf{x}'(f_i(\mathbf{x}')\mathbf{x}), \hat{\rho}).$$

In case of infinitesimal transformations $\delta \hat{\rho}_f = i \int d^3x' \delta f_j(\mathbf{x}') [\hat{\pi}_j(\mathbf{x}', \hat{\rho})]$, taking into account (13), (15), one can obtain:

$$\delta l_i(\mathbf{x}) = \delta f_j(\mathbf{x}) \nabla_j l_i(\mathbf{x}) + l_j(\mathbf{x}) \delta_{ik}^+ (\mathbf{l}(\mathbf{x})) \nabla_k \delta f_j(\mathbf{x}). \quad (16)$$

Let's consider local-equilibrium states of liquid crystals. Statistical operator for such states according to (1), (6) has the form:

$$\hat{w}_\nu(Y, \mathbf{l}) \equiv \exp\{\Omega_\nu(Y, \mathbf{l}) - \int d^3x Y_a(\mathbf{x}) \hat{\zeta}_a(\mathbf{x}) - \nu \int d^3x l_i l_k U_f^+ \hat{Q}_{ik}(\mathbf{x}) U_f\}. \quad (17)$$

Here thermodynamic forces $Y_a(\mathbf{x})$ and director $l_k(\mathbf{x}') \equiv \underline{l}_j b_{kj}(\mathbf{x}') / |\underline{l}_\lambda b_{p\lambda}(\mathbf{x}')|$, (\underline{l}_j - const) are arbitrary functions of the coordinates. Varying the thermodynamic potential

$$\Omega = \Omega(Y(\mathbf{x}'), \mathbf{l}(\mathbf{x}')) = \int d^3x \omega(\mathbf{x}, Y(\mathbf{x}'), \mathbf{l}(\mathbf{x}')) \quad (18)$$

(18) with respect to the thermodynamics forces and to director, we obtain the form of the second law of thermodynamics for the local equilibrium state:

$$\delta \omega = \frac{\partial \omega}{\partial Y_a} \delta Y_a + \left(\frac{\partial \omega}{\partial l_i} - \nabla_k \frac{\partial \omega}{\partial \nabla_k l_i} \right) \delta l_i, \quad (19)$$

where ω is a density of thermodynamic potential. Now, let us find the expression for flux densities of additive integral of motion in local-equilibrium state. We find flux density of energy from relations [6]:

$$\underline{Y}_a (Y_k \zeta_a + Y_0 \zeta_{ak}) = 0, \quad (20)$$

which is adequate also in the given case. According to (7)–(9), (15), (16) flux densities of additive integral of motion have the form

$$\zeta_{ak} = -\frac{\partial}{\partial Y_a} \frac{\omega Y_k}{Y_0} + \left[\frac{\partial \omega}{\partial \nabla_k l_j} \nabla_i l_j + \frac{\partial \omega}{\partial l_k} l_i - l_i \nabla_j \frac{\partial \omega}{\partial \nabla_k l_j} \right] \frac{\partial}{\partial Y_a} \frac{Y_i}{Y_0}. \quad (21)$$

Let us establish connection between given microscopic approach and Hamilton approach. For this reason we define Poisson bracket by equality

$$\{a(\mathbf{x}), b(\mathbf{x}')\} \equiv -i \text{Sp} \hat{\rho} [\hat{a}(\mathbf{x}, \hat{\rho}) \hat{b}(\mathbf{x}', \hat{\rho})].$$

Here in the right-hand side of this relation $\hat{a}(\mathbf{x}, \hat{\rho}) \hat{b}(\mathbf{x}', \hat{\rho})$ are a variation of physical values operators. Since these are explicit form of additive integrals of motion and order parameter in terms of field operators, we obtain Poisson brackets

$$\begin{aligned} \{n(\mathbf{x}), n(\mathbf{x}')\} &= 0, \quad \{\pi_i(\mathbf{x}), n(\mathbf{x}')\} = n(\mathbf{x}) \nabla'_i \delta(\mathbf{x} - \mathbf{x}'), \\ \{\pi_i(\mathbf{x}), \pi_k(\mathbf{x}')\} &= -\pi_i(\mathbf{x}) \nabla_k \delta(\mathbf{x} - \mathbf{x}') + \pi_k(\mathbf{x}) \nabla'_i \delta(\mathbf{x} - \mathbf{x}'), \\ \{\pi_i(\mathbf{x}), l_\lambda(\mathbf{x}')\} &= \delta(\mathbf{x} - \mathbf{x}') \nabla_i l_\lambda(\mathbf{x}) + l_i(\mathbf{x}') \delta_{\lambda u}^\perp(\mathbf{1x}') \nabla'_u \delta(\mathbf{x} - \mathbf{x}') + \\ &e^{-W(\mathbf{x}')} \frac{1}{2} \delta_{\lambda \nu}^\perp(\mathbf{1x}') l_u(\mathbf{x}') \nabla_i [\nabla_u (\delta(\mathbf{x} - \mathbf{x}') \nabla_\nu h(\mathbf{x})) + \nabla_\nu (\delta(\mathbf{x} - \mathbf{x}') \nabla_u h(\mathbf{x}))], \\ \{n(\mathbf{x}), l_\lambda(\mathbf{x}')\} &= 2\pi_\nu(\mathbf{x}') e^{-W(\mathbf{x}')} \nabla'_u \delta(\mathbf{x} - \mathbf{x}') [l_\nu(\mathbf{x}') \delta_{\lambda u}^\perp(\mathbf{1x}') + l_u(\mathbf{x}') \delta_{\lambda \nu}^\perp(\mathbf{1x}')], \\ \{n(\mathbf{x}), W(\mathbf{x}')\} &= 4\pi_j(\mathbf{x}') e^{-W(\mathbf{x}')} \nabla'_j \delta(\mathbf{x} - \mathbf{x}'), \\ \{\pi_i(\mathbf{x}), W(\mathbf{x}')\} &= 2l_i(\mathbf{x}') l_j(\mathbf{x}') \nabla_j \delta(\mathbf{x} - \mathbf{x}') + \nabla'_i \delta(\mathbf{x} - \mathbf{x}') + \\ &\nabla_i W(\mathbf{x}) \delta(\mathbf{x} - \mathbf{x}') + e^{-W(\mathbf{x}')} \nabla_i \nabla_j [\delta(\mathbf{x} - \mathbf{x}') \nabla_j n(\mathbf{x})], \end{aligned}$$

where $W(\mathbf{x}) \equiv \ln Q(\mathbf{x})$. It is obvious from represented formulas, that for harmonization of Poisson brackets algebra it's necessary to supplement the total set of hydrodynamic parameters by an additional value $W(\mathbf{x})$, being physically the smectic variable parameter. When $W \gg 1$, Poisson brackets can be simplified, eventually becoming [2,3].

$$\begin{aligned} \{n(\mathbf{x}), W(\mathbf{x}')\} &= 0, \quad \{n(\mathbf{x}), l_i(\mathbf{x}')\} = 0, \quad \{\pi_i(\mathbf{x}), W(\mathbf{x}')\} = \nabla_i W(\mathbf{x}) \delta(\mathbf{x} - \mathbf{x}'), \\ \{\pi_i(\mathbf{x}), l_\lambda(\mathbf{x}')\} &= \nabla_i l_\lambda(\mathbf{x}) \delta(\mathbf{x} - \mathbf{x}') + l_i(\mathbf{x}') \delta_{\lambda u}^\perp(\mathbf{1x}') \nabla'_u \delta(\mathbf{x} - \mathbf{x}'). \end{aligned} \quad (22)$$

Hypothesis of abridged description in latter case for nematic liquid crystals is expressed like

$$\hat{\rho}(t) \xrightarrow[t \gg \tau]{} \hat{\rho}(\zeta(x, t), \mathbf{1}(x, t)), \quad (23)$$

where τ is relaxation time, and smectic properties are not considered here. Equations of motion for parameters of abridge description using equations (11), (13), (22), (23) have the form

$$\dot{\zeta}_a(\mathbf{x}) = -\nabla_k \text{Sp} \hat{\rho}(\zeta, \mathbf{1}) \hat{\zeta}_{ak}(\mathbf{x}), \quad \dot{l}_i(\mathbf{x}) = i \text{Sp} \hat{\rho}(\zeta, \mathbf{1}) [\hat{H}, \hat{l}_i(\mathbf{x})]. \quad (24)$$

In the leading approximation with respect to the gradients of thermodynamic forces and to director, we obtain hydrodynamic equation of nematics

$$\dot{\zeta}_a(\mathbf{x}) = -\nabla_k \zeta_{ak}(\mathbf{x}), \quad \dot{l}_i(\mathbf{x}) = -(Y_k(\mathbf{x})/Y_0(\mathbf{x}))\nabla_k l_i(\mathbf{x}) - l_k(\mathbf{x})\delta_{ik}^{\perp}(\mathbf{1x})\nabla_j(Y_k(\mathbf{x})/Y_0(\mathbf{x})). \quad (25)$$

Following from equations (25) and definition of entropy density $\sigma = -\omega + Y_a \zeta_a$, there appears an adiabaticity of motion of considering condensed matter $\dot{\sigma} = \nabla_i(\sigma Y_i/Y_0)$.

REFERENCES

1. **Bogoliubov N.N.** — JINR Preprint D-781, Dubna, 1960.
2. **Lebedev V.V., Kats E.M.** — Dynamics of Liquid Crystals, M.: Nauka, 1983, p.144.
3. **Volovik G.E.** — Lett. JETP, 1980, v.31, No.5, p.297-300.
4. **Akhiezer A.I., Peletminsky S.V.** — Methods of Statistical Physics. Pergamon Press, New York, 1971, p.368.
5. **Kovalevsky M.Y., Rozhkov A.A.** — TMP, 1997, v.113, No.2, p.313-330.
6. **Kovalevsky M.Y., Krasnikov V.A., Peletminsky S.V.** — DAN USSR, 1988, v.303, No.2, p.337-340.