Variational Approach in the Theory of Liquid-Crystal State

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Abstract. The variational calculus by Leonhard Euler is the basis for modern mathematics and theoretical physics. The efficiency of variational approach in statistical theory of liquid-crystal state and in general case in condensed state theory is shown. The developed approach in particular allows us to introduce correctly effective pair interactions and optimize the simple models of liquid crystals with help of realistic intermolecular potentials.

1. Introduction
The calculus of variations [1-3], first appeared in the work of Euler in 1744 [1] and described in detail in “The Elements of the Calculus of Variations” [3] in 1766, was the foundation not only of mathematics but also of theoretical physics.

Variational methods are characterized by the effectiveness, generality and universality of the approach and give a complete look to the theory.

In the molecular-statistical and thermodynamic theory these are variational approaches based on the variational principles of Gibbs W, Boltzmann L, Bogolyubov N N, Onsager L, Prigogine I and others.

Liquid crystals are characterized by the structural diversity of the mesophase and the complex structure and the interaction of structural elements (in particular, mesogenic molecules).

They are condensed molecular systems with orientational long-range order and incomplete translational order. In accordance with this "structural" definition, their distinctive feature is the strong relationship of translational and internal, orientational molecular variables. Thus, the "dimensionality" of the statistical problem is at least twice as high as that of simple systems [4,5].

2. Theory
Let \( H(1, ..., N) \) be Hamiltonian of original realistic model of liquid crystal with internal degrees of freedom (where \( m= (r_m, \Omega_m, \zeta_m) \)) and \( H_0 \) be Hamiltonian of simplified exactly solvable "approximating" model (for example, with multiple or discrete variables, etc.).

The Bogolyubov variational principle follows from the convexity of the continuous functional

\[
F[H_0 + A] = -kT \ln \text{tr} \exp \left( -\frac{(H_0 + A)}{kT} \right),
\]

where, \( k \) – Boltsmann constant, \( T \) – temperature, \( A=H-H_0 \)

\[
\delta^2 F[H_0 + A] = -k^{-1} T^{-1} \langle \delta A | \delta A \rangle_{H_0 + A} \leq 0
\]
Where $\langle B \rangle$ is average value and $\langle B|C \rangle = \langle BC \rangle - \langle B \rangle \langle C \rangle$ is the second semiinvariant (cumulant) over Gibbs canonical distribution.

It follows

$$F[H_0] + \langle H-H_0 \rangle_H \leq F[H] \leq F[H_0] + \langle H-H_0 \rangle_0 = F_M,$$

(3)

The universal approach to a molecular theory of liquid-crystal state is developed on the basis of this double inequality (general variational principle by Bogolubov N N) that can also be used for qualitative estimate of approximations accuracy.

Functional $F_M$ on the right side of this inequality is the model Helmholtz free energy. Its minimum condition over approximating Hamiltonian parameters $H_0$ is

$$\langle H-H_0 | \delta H_0 \rangle_0 = 0$$

(4)

After that $F_M$ gives the best approximation $F[H]$, and thus determines the approximate expression for the Helmholtz energy of initial molecular model of a liquid crystal.

In a classic case we substitute Hamilton operators $H, H_0$ for potential energies $U_N, V_0$. At that $F_M$ is the configuration part of the Helmholtz free energy.

The initial model can include translation, orientation, conformation variables and three-, four-partial interactions. In the framework of a unified variational approach it is possible to approximate this complex realistic model by much simpler "solvable" models, for example, with a spatial lattice structure, with a discrete set of possible orientations, with separation of spatial $r$, conformation $\zeta$ and orientation $\Omega$ variables, with the effective pair interactions and others. Moreover, in each case we get best-in-class approximation model of Helmholtz function and thermodynamic properties of a liquid crystal. In particular, additive models

$$V_i(1,\ldots,N) = V_i(r_1,\ldots,r_N) + V_o(\Omega_1,\ldots,\Omega_N) + V_\zeta(\zeta_1,\ldots,\zeta_N)$$

(5)

or

$$V_i(1,\ldots,N) = \sum_{i\in\Omega} V_i(i)$$

(6)

(a self-consistent field) correspond to the statistical independence (or "uncoupling") of relevant variables. But in this case, unlike the similar approximation of distribution functions multiplicativity, the received results will be thermodynamically consistent.

Many-particle interactions play an important role in condensed matter. Potential energy is

$$U_N = \sum_{p=2}^{N} \frac{1}{p!} \sum_{i_1 \neq \ldots \neq i_p} \Phi_p(i_1,\ldots,i_p)$$

(7)

Let us find the equations defining effective potentials of pair intermolecular interactions $\Phi_{2\text{eff}}(...)$ that best take into account ($n=4$) the true many-particle interaction $\Phi_3(...)$ and $\Phi_4(...)$.

Equation (4) gives

$$\left\langle \sum_{i<j} \Phi_{2\text{eff}}^{\text{eff}}(i,j) \right\rangle_{\text{eff}} = 0$$

(8)

$$\Phi_{2\text{eff}}^{\text{eff}}(i,j) = \Phi_{2}(i,j) + \frac{1}{\rho_{2}(i,j)} \left( \sum_{i_1 \neq j \neq i_2} \Phi_3(i,j,i_1) \rho_3(i,j,i_1) \right) +$$

$$+ \frac{1}{2} \sum_{i_1 \neq j \neq i_2} \Phi_4(i,j,i_1,i_2) \rho_4(i,j,i_1,i_2) \rho_4(i,j,i_1,i_2) di_1 di_2.$$

(9)

However, effective potentials of pair intermolecular interactions (9), unlike the true ones, depend on the thermodynamic state parameters and the short-range order. This makes their "calibration" complicated, especially when used in the description of phase transitions.
For simplest models with traditional expansion of potentials in a series of spherical and Fourier harmonics in self-consistent field approximation the variational approach allows us to simplify significantly a system of equations obtained. The self-consistent potential involves the contributions of high order harmonics in average form [5].

To describe a liquid-crystal state it is fundamentally important to take into account the pairwise repulsion of solid anisometric cores. The attempts to use only the anisotropic van-der-Waals attraction of molecules on a lattice (the simplest classic model of the molecular field by Mayer – Saupe) to obtain the agreement with an experiment require interaction constant to be more than two orders of magnitude greater than the real values. Variational theory allows to take into account the repulsion of solid cores by taking a system with such interaction as a base.

\[ V_{i,j}(1, \ldots, N) = \sum_{i \neq j} V_{i,j}^{\infty} + \sum_{i} V(i), \]  

where the hard core of approximating potential \( V_{i,j}^{hc} \) must match or include the core source of real interaction. Hence,

\[ (V(1) - \Phi(1))\rho^{\infty}(1) = \frac{1}{(p-1)!} \sum_{i \neq j} \int \Phi_{i,j}^{\infty}(1, i_2, \ldots, i_p)\rho^{\infty}(1, i_2, \ldots, i_p)d\vec{i}_2 \ldots d\vec{i}_p, \]

where \( \Phi_{i,j}^{\infty}(\ldots) \) is the "soft" part of the intermolecular potentials without hard core. This way we can improve Onsager and van-der-Waals type formulas.

3. Conclusion

Thus, the developed approach makes it possible to optimize the simple models of liquid crystals using realistic intermolecular potentials.

The considered approach allows to take into account many-particle interactions and introduce effective pairwise intermolecular interactions.

The consistent description of liquid crystals structure involves hierarchy of spatial scales [6]. The approach may be useful for the solution of this problem.

On the whole, the variational approach can be successfully applied to the development of liquid crystals theory on the unified basis due to its universality and effectiveness.

References
[1] Euler L. Methodus inveniendi lineas curvas proprietate maximi minimive gaudentes. Lausanne-Geneva, 1744.
[2] Lagrange J L. Essai d’une nouvelle methode pour determiner les maxima et les minima des formules integrales indefinies // Torino, Miscellanea Taurinensia, 1762. 2. P. 335-362.
[3] Euler L. Elementa calculi variationum // St. Petersburg, Novi Commentarii academiae scientiarum imperiales Petropolitanae, 1766. 10. P. 51-93.
[4] The Molecular Physics of Liquid Crystals (Ed G R Luckhurst, G W Gray) Academic Press, 1979. 494 P.
[5] Bazarov I P, Gevorkyan E V. The Statistical Physics of Liquid Crystals. Moscow University Press. 1992. 496 P. (in Russian).
[6] Gevorkyan E V. Hierarchy of spatial scales and relaxation times in liquid-crystal systems. Bulletin of Moscow Region State University. Phys.Math. 2016. no. 4. P.24-31. DOI: 10.18384/2310-7251-2016-4-24-31.