

DEFORMATION ENERGETIC EFFECTS FOR CHOLESTRIC LIQUID CRYSTALS

V.B.NEMTSOV AND V.S.VIKHRENKO

Belarussian State Technological University, Minsk,
220 630, Belarus

Abstract New energetic effects for cholesteric liquid crystals subjected to orientational deformation such as the heat production or absorption at isothermal deformation, the chemical potential changing of multicomponent cholesterics and the temperature variation at adiabatic deformation, the noticeable difference between the isothermal and adiabatic moduli of torsion are predicted. The theory of these effects is developed on the basis of the previously obtained thermodynamic relations for a deformed liquid crystal.

It is well known¹ that crystals and liquids generate or absorb the entropy and the heat if they are subjected to the usual isothermal mechanical deformation connected with the volume and form variation. The entropy increment in this processes is defined by

$$\Delta S = \alpha_{ij} \Delta \tau_{ij}, \quad \alpha_{ij} = (\partial \varepsilon_{ij} / \partial T)_{\tau_{ij}}. \quad (1)$$

Here τ_{ij} , ε_{ij} , α_{ij} are the tensors of force stresses, deformations and thermal coefficients, respectively, T is the temperature. We adopt summation convention over repeated indices.

For an isotropic case and for liquid crystals without the positional ordering we have

$$\varepsilon_{ij} = 3^{-1} \delta_{ij} (\delta V / V_0), \quad \alpha_{ij} = 3^{-1} \delta_{ij} V_0^{-1} (\partial V / \partial T)_P, \quad \tau_{ij} = -P \delta_{ij}, \quad (2)$$

where P is the pressure, V_0 is the volume of a system before the deformation, δV is the variation of volume V , δ_{ij} is the Kroneker's symbol.

In the following we show that the isothermal orientational deformation of the nonsymmetrical liquid crystals, especially the cholesterics, can cause the new energetic effects.

We rederive the previously obtained results^{2,3} and extend them on the case of multicomponent cholesteric liquid crystals.

The orientational deformation pseudotensor is defined by the expression⁴

$$\gamma_{ij} = e_{imn} n_m (\partial n_n / \partial x_j), \quad (3)$$

where n_m is the director, e_{imn} is the Levi-Civita tensor.

In equilibrium state of a cholesteric liquid crystal the tensor γ_{ik} do not equal to zero due to the absence of the symmetry centre. In the coordinate system with x_3 -axis directed along the helical symmetry axis the director is represented by $n_3 = 0$, $n_1 = \cos \theta$, $n_2 = \sin \theta$, $\theta = x_3 p_0^{-1} + const$, where p_0 is the helical pitch in the nondeformed state of the cholesteric. According to (3) the only nonzero component of γ_{ij} is $\gamma_{33}^0 \equiv \gamma_0 = 2\pi / p_0$.

In analogy with the tensor α_{ij} we introduce the tensor β_{ij} of the temperature orientational deformation coefficients by the relation

$$\beta_{ij} = (\partial \gamma_{ij} / \partial T)_{p,\pi}. \quad (4)$$

Here π_{ij} is the moment stress tensor (couple stress tensor)

The only nonzero component of the tensor β_{ij} ,

$$\beta_{33} = \beta = -(2\pi / p_0^2) (\partial p_0 / \partial T)_{p,\pi} \quad (5)$$

exists in the above mentioned coordinate system.

The presence of a new energetic effect is proved using the thermodynamic expressions which generalize known ones for media with orientational ordering. The generalization accounts for the orientational deformation.

For the volume densities of the free energy F and the Gibbs thermodynamic potential $\Phi = F - \tau_{ij}\varepsilon_{ij} - \pi_{ij}\gamma_{ij}$ the next relations

$$dF = \tau_{ij}d\varepsilon_{ij} + \pi_{ij}d\gamma_{ij} - SdT, \quad d\Phi = -\varepsilon_{ij}d\tau_{ij} - \gamma_{ij}d\pi_{ij} - SdT. \quad (6)$$

are true. The last relation leads to the expressions

$$\varepsilon_{ij} = -(\partial\Phi / \partial\tau_{ij})_{T,\pi}, \quad \gamma_{ij} = -(\partial\Phi / \partial\pi_{ij})_{T,\tau}, \quad S = -(\partial\Phi / \partial T)_{\tau,\pi}, \quad (7)$$

Therefore the tensors of temperature deformation coefficients are determined in terms of the volume density of entropy

$$\alpha_{ij} = (\partial S / \partial\tau_{ij})_{T,\pi}, \quad \beta_{ij} = (\partial S / \partial\pi_{ij})_{T,\tau}. \quad (8)$$

Let us consider S as a function of τ_{ij} , π_{ij} and T . Then

$$dS = \alpha_{ij}d\tau_{ij} + \beta_{ij}d\pi_{ij} + C_{\tau,\pi}dT / T_0, \quad (9)$$

where $C_{\tau,\pi} = T_0(\partial S / \partial T)_{\tau,\pi}$ is the heat capacity and T_0 is the temperature of the nondeformed state. The quantities α_{ij} , β_{ij} and $C_{\tau,\pi}$ are referred to the initial equilibrium state, so $C_{\tau,\pi} = C_P$. One can see on the basis of equation (2) that the term $\alpha_{ij}d\tau_{ij}$ takes the usual form $V_0^{-1}(\partial V / \partial T)_P dP$.

The increment of the entropy is expressed as

$$\Delta S = \alpha_{ij}\Delta\tau_{ij} + \beta_{ij}\pi_{ij} + C_P\Delta T / T_0, \quad \Delta T = T - T_0. \quad (10)$$

The additional variation of the entropy due to orientational deformation is determined by the second term in expression (10)

$$\Delta S_n = \beta_{ij}\pi_{ij}. \quad (11)$$

This quantity will be considered further in some details.

The moment stress tensor is expressed through the orientational deformation tensor and the isothermal Frank's moduli K_{ijkl}^0

$$\pi_{ij} = K_{ijkl}^0 (\gamma_{kl} - \gamma_{kl}^0). \quad (12)$$

For nematics and other centrosymmetric liquid crystals $\gamma_{ik}^0 = 0$. In this case the elastic moment stresses obey the conventional expression.

The nonvanishing component of π_{ij} is

$$\pi_{33} = K_2^0 (\gamma - \gamma_0), \quad \gamma = \partial\theta / \partial z = 2\pi / p, \quad (13)$$

where K_2^0 is the isothermal modulus of torsion, p is the spiral pitch for deformed state of the cholesteric.

Taking into account equations (11), (13) and (5) one finds the entropy increment and the heat production

$$\Delta S_\pi = -(2\pi / p_0^2) (\partial p_0 / \partial T)_{p,\pi} K_2^0 (\gamma - \gamma_0), \quad \Delta Q_\pi = -T_0 \Delta S_\pi. \quad (14)$$

The temperature increment caused by the adiabatic orientational deformation is equal to

$$\Delta T = -C_{v,\gamma} T_0 \beta K_2^0 (\gamma - \gamma_0), \quad (15)$$

where $C_{v,\gamma}$ is the volume density of heat capacity at constant volume

The difference between the adiabatic K_2 and isothermal K_2^0 Frank's moduli is determined by the expression^{2,3}

$$K_2 - K_2^0 = C_{v,\gamma}^{-1} T \beta^2 (K_2^0)^2. \quad (16)$$

We now turn to the discussion of the caloric effect. According to equation (14) the heat is absorbed ($\Delta Q_\pi > 0$) if $\gamma > \gamma_0$ and $(\partial p_0 / \partial T) < 0$ or $\gamma < \gamma_0$ and $(\partial p_0 / \partial T) > 0$; otherwise the heat is liberated ($\Delta Q_\pi < 0$).

For the most part of cholesterics the helical pitch decreases as the temperature increases ($\partial p_0 / \partial T < 0$) and the magnitude of $p_0 (\partial p_0 / \partial T)$ varies within the wide limits⁵ and ranges up to about 100K^{-1} . For the unwinding

of the cholesteric structure when $\gamma \rightarrow 0$ ($p \rightarrow \infty$) equations (14) reduce to $\Delta S_\pi = (4\pi^2 / p_0^3) K_2^0 (dp_0 / dT), \Delta Q_\pi = T_0 \Delta S_\pi$.

Typically for $K_2^0 = 10^{-11} \text{N}, T_0 = 300 \text{K}, p_0 = 6 \cdot 10^{-7} \text{m}, p_0^{-1} (\partial p_0 / \partial T) = -10 \text{K}^{-1}$ we find $\Delta S_\pi = 10^4 \text{J} / \text{mK}, \Delta Q_\pi = 3 \cdot 10^6 \text{J} / \text{m}^3$. For fully untwisted spiral the entropy increment ΔS_π is of the order of cholesteric-isotropic transition entropy difference.

For the multicomponent cholesterics instead of the relation (6) for the volume density of Gibbs thermodynamic potential one would write

$$d\Phi = -\varepsilon_{ij} d\tau_{ij} - \gamma_{ij} d\pi_{ij} - SdT + \sum_{\alpha} \mu_{\alpha} dc_{\alpha}, \tag{17}$$

where μ_{α} and c_{α} are the chemical potential and the volumetric molar concentration $c_{\alpha} = n_{\alpha} / V, n_{\alpha}$ is the quantity of moles in the system.

Equation (17) yields

$$\varepsilon_{ij} = -\left(\frac{\partial \Phi}{\partial \tau_{ij}}\right)_{\pi, \tau, c_{\alpha}}, \quad \gamma_{ij} = -\left(\frac{\partial \Phi}{\partial \pi_{ij}}\right)_{\tau, T, c_{\alpha}}$$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{\tau, \pi, c_{\alpha}}, \quad \mu_{\alpha} = \left(\frac{\partial \Phi}{\partial c_{\alpha}}\right)_{T, \tau, \pi}. \tag{18}$$

If the chemical potential is considered as a function of τ_{ij}, π_{ij}, T and c_{β} , its variation is

$$d\mu_{\alpha} = \left(\frac{\partial \mu_{\alpha}}{\partial \tau_{ij}}\right) d\tau_{ij} + \left(\frac{\partial \mu_{\alpha}}{\partial \pi_{ij}}\right) d\pi_{ij} + \left(\frac{\partial \mu_{\alpha}}{\partial T}\right) dT + \sum \left(\frac{\partial \mu_{\alpha}}{\partial c_{\beta}}\right) dc_{\beta}. \tag{19}$$

For the simplification of notations here and below the indices which define the character of the partial derivatives are omitted.

Taking into account the relations

$$\frac{\partial \mu_{\alpha}}{\partial \tau_{ij}} = -\frac{\partial \varepsilon_{ij}}{\partial c_{\alpha}}, \quad \frac{\partial \mu_{\alpha}}{\partial \pi_{ij}} = -\frac{\partial \gamma_{ij}}{\partial c_{\alpha}}, \tag{20}$$

which results from equations (18) the equation (19) can be written in the form

$$d\mu_{\alpha} = -\left(\frac{\partial \varepsilon_{ij}}{\partial c_{\alpha}}\right) d\tau_{ij} - \left(\frac{\partial \gamma_{ij}}{\partial c_{\alpha}}\right) d\pi_{ij} +$$

$$(\partial\mu_\alpha / \partial T)dT + \sum_{\beta} (\partial\mu_\alpha / \partial c_\beta)dc_\beta, \quad (21)$$

where all the derivatives are referred to the initial nondeformed state.

Then the increment of μ_α is equal to

$$\begin{aligned} \Delta\mu_\alpha &= -(\partial\varepsilon_{ij} / \partial c_\alpha)\Delta\tau_{ij} - (\partial\gamma_{ij} / \partial c_\alpha)\Delta T_{ij} + \\ &(\partial\mu_\alpha / \partial T)\Delta T + \sum_{\beta} (\partial\mu_\alpha / \partial c_\beta)\Delta c_\beta. \end{aligned} \quad (22)$$

By the use of equation (2) the term $-(\partial\varepsilon_{ij} / \partial c_\alpha)d\tau_{ij}$ can be written in the traditional form: $V_\alpha dP_\alpha$, where $V_\alpha = \partial V / \partial n_\alpha$ is the partial molar volume. Due to moment stresses the additional term in the chemical potential variation appears and it is defined by $\Delta\mu_\alpha^\pi = -(\partial\gamma_{ij} / \partial c_\alpha)\pi_{ij}$.

In the introduced coordinate system

$$\gamma_{33}^0 = 2\pi / p_0, (\partial\gamma_{33}^0 / \partial c_\alpha) = -(2\pi / p_0^2)(\partial p_0 / \partial c_\alpha)$$

and the increment $\Delta\mu_\alpha^\pi$ can be expressed as

$$\Delta\mu_\alpha^\pi = (2\pi / p_0^2)(\partial p_0 / \partial c_\alpha)K_2^0(\gamma - \gamma_0). \quad (23)$$

For the unwinding of the cholesteric structure

$$\Delta\mu_\alpha^\pi = -(4\pi^2 / p_0^3)(\partial p_0 / \partial c_\alpha)K_2^0. \quad (24)$$

For the small concentration of the component α one finds $p_0 = A / c_\alpha$ and $(\partial p_0 / \partial c_\alpha) = -p_0 / c_\alpha$. This gives the possibility to estimate the magnitude of $\Delta\mu_\alpha^\pi$.

It is interesting to note that for $P = \text{const}, T = \text{const}$ and $\mu_\alpha = \text{const}$ from equation (22) we get immediately

$$(\partial\gamma_{ij} / \partial c_\alpha)\pi_{ij} = \sum_{\beta} (\partial\mu_\alpha / \partial c_\beta)\Delta c_\beta \quad (25)$$

or in the coordinate system

$$-(2\pi / p_0^2)(\partial p_0 / \partial c_\alpha)K_2^0(\gamma - \gamma_0) = \sum_{\beta} (\partial\mu_\alpha / \partial c_\beta)\Delta c_\beta. \quad (26)$$

The last relations mean that the orientational deformation can result in changing the component concentration.

REFERENCES

1. J.F.Nye, Physical Properties of Crystals. (Clarendon Press, Oxford, 1964).
2. V.B.Nemtsov, Teor. i Mat. Fiz., (Moscow), 14, 262 (1973).
3. V.B.Nemtsov, Ukrain. Fiz. Zh., (Kiev), 37, 378 (1992).
4. V.B.Nemtsov, Physica, 86A, 513 (1977).
5. P.G de Gennes, The Physics of Liquid Crystals (Clarendon Press, Oxford, 1974).