THERMAL EXPANSION AND BRAGG REFLEXES IN LATTICE TEXTURES OF CHOLESTERIC LIQUID CRYSTALS

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A simple general sum rule is derived predicting the thermal expansion of lattice textures at decreasing temperatures by relating it to the intensities of Bragg reflected light.

Recently, the investigation of Bragg reflexes in the blue phase of cholesteric liquid crystals [1] has beautifully confirmed the presence of a bcc lattice texture [2,3] between normal and cholesteric phases. In particular, the lattice planes with Miller indices $(n_1, n_2, n_3) = (110), (200), (220), (211)$ have well been stablished.

Apart from this, the data contain another important information: The wavelength of the reflected light increases strongly with decreasing temperature corresponding to an expansion of the textural lattice.

It is the purpose of this note to explain this phenomenon and to relate it quantitatively to the intensities and polarizations of the different Bragg lines. It is intuitively obvious that lower temperatures render increased spectral weight to the higher lines (200), (220), (211), etc.: As the order parameter increases, the nonlinear contributions to the free energy become more and more important and higher harmonics are needed in a Fourier decomposition of the order parameter. The texture "hardens". We shall see: At the same time, the geometry of the lattice must increase in order to satisfy a very general sum rule over the intensities. A second source of expansion derives from the fact that in a spatially complicated texture the order parameter may contain all five helicities, $m = \pm 2, \pm 1, 0$ not just $m = 2$ and 0 as in the purely cholesteric phase. The associated loss in bending energy may be compensated by gains in the nonlinear potential terms.

In order to see all this, let us recall the Landau expansion [‡1] of the free energy in terms of the traceless symmetric order parameter $Q_{\alpha\beta}$, $\alpha, \beta = 1, 2, 3$,

$$F = \int d^3x \{\tfrac{1}{2} [a Q_{\alpha\beta}^2 + b(\partial_\gamma Q_{\alpha\beta})^2 + c\,\partial_\alpha Q_{\alpha\gamma}\,\partial_\beta Q_{\beta\gamma}] - d\epsilon_{\alpha\beta\gamma} Q_{\alpha\delta}\,\partial_\gamma Q_{\beta\delta} + (\lambda_3/3!)\,Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\delta} + (\lambda_4/4!)\,(Q_{\alpha\beta}^2)^2\}. \tag{1}$$

The coefficient $a = -a_0(1 - T/T^*)$ contains the strong temperature dependence of the system with the coherence length $\xi(T) \equiv \sqrt{b/a} \equiv \xi_0/\sqrt{T/T^* - 1}$ diverging at T^*. The cholesteric phase arises from the parity violating d-term and is characterized by a helical solution of length scale $\xi_h = b/d = 1/k_h$ which can be measured via the wavelength of normally reflected circularly polarized light $\lambda_R = 4\pi\xi_h$.

It is useful to introduce a dimensionless order parameter

$$\varphi_{\alpha\beta} = \frac{\lambda_4}{\lambda_3}\frac{4}{\sqrt{6}} Q_{\alpha\beta} \tag{2}$$

and to work with a reduced free energy

‡1 See ref. [3] in ref. [3].

$$f \equiv (64\lambda_4^3/3\lambda_3^4)F = \int d^3x \{(\tau + 2\alpha)\varphi_{\alpha\beta}^2 + 2\alpha\xi_h^2[(\partial_\gamma\varphi_{\alpha\beta})^2 + (c/b)\,\partial_\alpha\varphi_{\alpha\gamma}\,\partial_\beta\varphi_{\beta\gamma}]$$

$$- 4\alpha\xi_h\epsilon_{\alpha\beta\gamma}\varphi_{\alpha\delta}\,\partial_\gamma\varphi_{\beta\delta} + \tfrac{1}{3}\sqrt{6}\varphi_{\alpha\beta}\varphi_{\beta\gamma}\varphi_{\gamma\alpha} + \tfrac{1}{8}(\varphi_{\alpha\beta}^2)^2\}\,, \tag{3}$$

where τ is a reduced temperature with $\tau + 2\alpha$ measuring the deviation from T^*:

$$\tau + 2\alpha \equiv \frac{4\lambda_4 b}{\lambda_3^2}\,\frac{a_0}{b}\left(\frac{T}{T^*} - 1\right) = \frac{4\lambda_4 b}{\lambda_3^2}\,\frac{1}{\xi^2(T)}\,. \tag{4}$$

The parameter α characterizes the cholesteric strength [3] of the system

$$2\alpha \equiv \frac{4\lambda_4 b}{\lambda_3^2}\,\frac{d^2}{b^2} = \frac{4\lambda_4 b}{\lambda_3^2}\,\frac{1}{\xi_h^2}\,. \tag{5}$$

The ratio of couplings $\lambda_4 b/\lambda_3^2$ can be deduced from the precocious onset of the nematic, $\alpha = 0$, phase transition which in the energy (3) occurs at [3] $\tau_c = 2/9$ such that

$$4\lambda_4 b/\lambda_3^2 = \tfrac{2}{9}\xi^2(T_c) = \tfrac{2}{9}\xi_0^2(1 - T_c/T^*)^{-1}\,. \tag{6}$$

Experimentally, $\xi(T_c) \approx 20\xi_0 \approx 600$ Å, $\xi_h \approx 2000/4\pi$ Å ≈ 159 Å and hence $\alpha \approx 1.6$.

Using the polarization tensors $\epsilon^{(m)}(\hat{q})$ of helicity m [‡2],

$$\epsilon_{\alpha\beta}^{(2)}(\hat{q}) = l_\alpha l_\beta = \epsilon_{\alpha\beta}^{(-2)*}(\hat{q}),\quad \epsilon^{(1)}(\hat{q}) = \sqrt{1/2}\,[l_\alpha\hat{q}_\beta + (\alpha\beta)] = -\epsilon_{\alpha\beta}^{(-1)*}\,,\quad \epsilon_{\alpha\beta}^{(0)}(\hat{q}) = \sqrt{3/2}\,(\hat{q}_\alpha\hat{q}_\beta - \tfrac{1}{3}\delta_{\alpha\beta})\,,$$

where $l_\alpha = (l_\alpha^1 + i l_\alpha^2)/\sqrt{2}$ is a complex vector transverse to $\hat{q}$, with $l^1, l^2, \hat{q}$ being unit vectors forming a positively oriented triped, we may expand the order parameter in a periodic texture as

$$\varphi_{\alpha\beta} = \sum_{q} \epsilon_{\alpha\beta}^{(m)}(\hat{q})\,\varphi_q^{(m)}\exp(i\boldsymbol{q}\cdot\boldsymbol{x}) + \text{c.c.}\,, \tag{7}$$

where $\boldsymbol{q}$ are the momenta of the reciprocal lattice. In the bcc case under consideration,

$$\boldsymbol{q} = (q_0/\sqrt{2})(n_1, n_2, n_3) \equiv (q_0/\sqrt{2})\boldsymbol{n}\,,$$

where $n_{1,2,3}$ are integers with $\Sigma_{i=1}^3 n_i$ = even. Inserting (7) into the free energy, this may be written as

$$f = \sum_{\boldsymbol{n}} \{[\tau + 2\alpha + 2\alpha r_0\tfrac{1}{2}\boldsymbol{n}^2 q_0^2\xi_h^2]\,|\varphi_{\boldsymbol{n}}^{(0)}|^2 + [\tau + 2\alpha(1 - 1/4r_1) + 2\alpha r_1(\sqrt{1/2}|\boldsymbol{n}|q_0\xi_h \mp 1/2r_1)^2]\,|\varphi_{\boldsymbol{n}}^{(\pm1)}|^2$$

$$+ [\tau + 2\alpha(\sqrt{1/2}|\boldsymbol{n}|q_0\xi_h \mp 1)^2]\,|\varphi_{\boldsymbol{n}}^{(\pm2)}|^2\} + V(\varphi)\,, \tag{8}$$

where we have changed the subscripts $\boldsymbol{a}$ to $\boldsymbol{n}$ and collected all cubic and quartic terms in $V(\varphi)$. Here r_0, r_1 are given in terms of the ratio of the elastic constants b and c

$$r_0 \equiv 1 + \tfrac{2}{3}c/b = \tfrac{4}{3}(r_1 - 1)\,,\quad r_1 \equiv 1 + c/2b = (K_s + K_b)/2K_t = (K_{11} + K_{33})/2K_{22}\,. \tag{9}$$

On the right-hand side we have introduced the standard Frank constants since those can be found tabulated for many materials on the basis of data from Rayleigh scattering. For instance in MBBA or PAA near 25°C we have $K_{stb} \approx (6, 4, 7.5)$ or $(4.5, 2.9, 9.5) \times 10^{-7}$ dyne, such that $(r_0, r_1) = (1.92, 1.69)$ or $(2.88, 2.41)$, respectively.

The free energy has to be minimized at every fixed temperature T and cholestericity α with respect to variations in $\varphi_{\boldsymbol{n}}^{(m)}$ and in the basic wave number q_0 determining the wavelength of the lowest Bragg reflex (1, 1, 0). The

[‡2] In terms of the spin matrix $\boldsymbol{S}$, the $\epsilon_{\alpha\beta}^{(m)}$ satisfy

$$(\boldsymbol{S}\hat{\boldsymbol{q}})_{\alpha\beta}\epsilon_{\beta\gamma}^{(m)}(\hat{q}) \equiv -i\epsilon_{\alpha\beta\delta}\hat{q}_\delta\epsilon_{\beta\gamma}^{(m)}(\hat{q}) + (\alpha \leftrightarrow \gamma) = m\epsilon_{\alpha\gamma}^{(m)}(\hat{q})\,.$$

important point is now that q_0 only appears in the terms written down explicitly in (8). Thus we can directly minimize f with respect to q_0 and obtain

$$\frac{k_\mathrm{h}}{q_0}=\frac{\Sigma_n n^2 [(|\varphi_n^{(2)}|^2+|\varphi_n^{(-2)}|^2)+r_1(|\varphi_n^{(1)}|^2+|\varphi_n^{(-1)}|^2)+r_0|\varphi_n^{(0)}|^2]}{\Sigma_n\sqrt{2}|n|\,[(|\varphi_n^{(2)}|^2-|\varphi_n^{(-2)}|^2)+\frac{1}{2}(|\varphi_n^{(1)}|^2-(\varphi_n^{(-1)}|^2)]}\equiv\frac{\Sigma_n n^2 A_n}{\Sigma_n\sqrt{2}|n|B_n}. \tag{10}$$

In the purely cholesteric phase there is only a single wave with $q_0 \neq 0$, namely $\varphi^{(2)} \neq 0$, and we obtain the usual result $k_\mathrm{h}/q_0 = 1$, i.e. the wavelength of the reflected light is given by the pitch of the helix. In general, however, the wavelength is larger than that since $n^2 \geqslant \sqrt{2}|n|$ and experimentally $r_0, r_1 > 1$.

We may bring the expression to a more useful form by observing that, from symmetry arguments, $\varphi_n^{(m)}$ must be the same for equal $|n_1|$, $|n_2|$, $|n_3|$ and their 6 permutations. Altogether there are, for $n_1 \geqslant n_2 \geqslant n_3 \geqslant 0$,

$$\eta_n = 48/2^{N_0} N_\mathrm{equ}! \tag{11}$$

combinations where N_0 is the number of vanishing and N_equ that of equal values of $|n_i|$: $\eta_{110} = 12$, $\eta_{200} = 6$, $\eta_{220} = 12$, $\eta_{211} = 24$, ... Thus we may write

$$\frac{k_\mathrm{h}}{q_0}=\frac{\Sigma_{n_1\geqslant n_2\geqslant n_3}\frac{1}{24}n^2\eta_n A_n}{\Sigma_{n_1\geqslant n_2\geqslant n_3}\frac{1}{24}\sqrt{2}|n|\eta_n B_n}=\frac{A_{110}+A_{200}+4A_{220}+6A_{211}+\ldots}{B_{110}+\sqrt{1/2}B_{200}+2B_{220}+2\sqrt{3}B_{211}+\ldots}. \tag{12}$$

The amplitudes $\varphi_n^{(m)}$ are mostly measurable in light scattering at Bragg angles. In single reflexes, three amplitudes are directly accessible via the intensities

$$\int \mathrm{d}\omega\, I_\mathrm{VV} = \tfrac{1}{2}\pi\,\omega_0^2\Omega\,|\tfrac{1}{2}\varphi^{(2)} - \sqrt{1/6}\,\varphi^{(0)}|^2 ,$$

$$\int \mathrm{d}\omega\, I_\mathrm{HV} = \tfrac{1}{2}\pi\,\omega_0^2\Omega\,[\tfrac{1}{4}\sin^2\tfrac{1}{2}\theta\,|\varphi^{(2)}|^2 + \tfrac{1}{4}\cos^2\tfrac{1}{2}\theta\,|\varphi^{(1)}|^2] , \tag{13}$$

$$\int \mathrm{d}\omega\, I_\mathrm{HH} = \tfrac{1}{2}\pi\,\omega_0^2\Omega\,|\tfrac{1}{2}\sin^2\tfrac{1}{2}\theta\,\varphi^{(2)} + \sqrt{1/6}(1+\cos^2\tfrac{1}{2}\theta)\,\varphi^{(0)}|^2 ,$$

if $\varphi^{(2)}$ and $\varphi^{(0)}$ are relatively real or imaginary. Here θ is the scattering angle with $\sin\frac{1}{2}\theta = (4\pi/q_0)|n|/\sqrt{2}$, the subscripts V, H denote the polarizations of initial and final photons with respect to the scattering plane (V = vertical, H = horizontal), and Ω is the sample volume. In these formulas we have neglected $\varphi^{(-1)}$, $\varphi^{(-2)}$ since their contributions should be suppressed due to their higher quadratic coefficients in (8). At the same level of approximation we may include only the (1, 1, 0), (2, 0, 0), and (2, 2, 0) intensities, in the sum (12).

A resolution of other amplitudes $\varphi^{(m)}$ requires the measurement of line intensities in double Bragg scattering which will hopefully be performed in the near future.

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