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Lattice Textures in Cholesteric Liquid Crystals

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Abstract

Based on the Landau-De Gennes expansion of the free energy in powers of a symmetric traceless order parameter we discuss the energetics of various phases as a function of temperature and cholestericity.

1. Introduction

The blue phase, which appears in many liquid crystals within a narrow temperature interval between normal and cholesteric phase, has recently attracted increasing interest bot on the experimental and theoretical side.
An excellent survey is available [*1*] which describes the data accumulated over the years since the first observation by REINITZER in 1888. It also discusses the successes and failures of existing model calculations which all have difficulties in explaining the observed facts. At present, the most attractive candidate for the blue phase seems to be a body centered cubic texture which was recently sugested by HORNREICH and SHTRIKMAN [*2*] (H.S.) in a generalization of an observation by Brazovskii: This author noticed that, within the Landau-De Gennes free energy expansion, a superposition of plane waves with the momenta forming triangles enhances the cubic term. This leads to a phase transition before the ónset of the cholesteric phase. At lower temperatures, however, the order parameter increases and the cubic piece looses importance. Ultimately, the cholesteric phase does have the lowest energy because of its optimal ratio between quartic and quadratic terms.
Due to their precocious onset, such triangular textures could, in fact, be good candidates for the blue phase. The simplest Ansatz [*3*], however, in which only a single triangle of momenta is assumed, corresponding to a planar hexagonal texture, is not capable of explaining the experimentally observed optical isotropy [*1*]. Moreover, it is known from mean-field cosiderations of liquid solid transitions [*4*] that a body centered cubic (bcc) structure in space in which the momenta form a tetrahedron is favored energetically more than a single triangle. This led HS to propose the bbc texture for the blue phase of cholesteric liquid crystals. The optical isotropy would then be a direct consequence of the cubic symmetry as will be seen below in more detail.
The main defect of the work of HS is that the formalism employed is quite cumbersome. This is reflected in the complete change of most of their numbers in the free energy from

[1]) 1 Berlin (West) 33, Arnimallee 3

the first to the second edition of their preprint. Moreover, the existence of two blue phases was not manifest at the time of their calculation. We therefore found it worthwile to investigate systematically different possible non-uniform textures and to discuss their physical properties. Employing the Landau-De Gennes free energy in the same way as Refs. [3] we calculate a phase diagram for cholesteric, planar hexagonal, hexagonal close-packed, bcc, distorted bcc, and icosahedraltextures. The relevant physical parameters are two: The reduced temperature τ measured from the point of local instability and the parameter α with $\tau + 2\alpha$ determining the stability of the nematic component in the order parameter. The quantity α may be called cholesteric strength, or cholestericity, of the liquid crystal. Due to the analytic complexity we cannot give definite conclusions over the whole range of parameters τ and α. However, our analysis in some asymptotic regions, $\tau \to -\infty$ (low temperature) or $\alpha \to \infty$ (strongly cholesteric limit), makes distorted bcc and hexagonal close-packed textures quite unlikely. We do not find any range of α where two optically isotropic phases follow each other shortly before the onset of the cholesteric phase. Thus the recently observed second blue phase remains unexplained [1]. So does the experimental fact a Grandjean-Cano lines are found for the blue just as for the cholesteric phase between that convex lens and a plane plate [1]. If glass faces orient the helix orthogonal to it, it is hard to conceive how a bcc structure can exist between two faces only a few pitches apart. In addition, no Bragg reflexes have been seen [1] which would correspond to the 5 other momentum direction in the reciprocal lattice of the bcc structure.[2])

It should be noted that the treatment of the Landau-De Gennes free energy à la Ref. [3] does not have room for the temperature dependence of the wave length of the circularly polarized light nor for the volume change at the phase transition [1]. The first defect can be removed in principle by considering higher harmonics, i.e. by allowing for multiples of the momenta in the standing waves, the second by including an order parameter for the stress tensor of the liquid.

For the sake of completeness we give a translation of our methods based on Ref. [3] to those of HS. This should facilitate comparison of the results.

II. Theoretical Framework

The basis of our discussion will be the Landau-De Gennes expansion of the free energy. This consists of a quadratic piece

$$F_2 = \frac{1}{2} \int d^3x [aQ_{\alpha\beta}^2 + b(\partial Q_{\alpha\beta})^2 + c\, \partial_\alpha Q_{\alpha\gamma}\, \partial_\beta Q_{\beta\gamma} - 2d\varepsilon_{\alpha\beta\gamma} Q_{\alpha\delta}\, \partial_\gamma Q_{\beta\delta}] \tag{2.1}$$

with cubic and quartic interactions

$$F_3 = \frac{\lambda_4}{3!} I_4 \equiv \frac{\lambda_3}{3!} \int d^3x Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} \tag{2.2}$$

$$F_4 = \frac{\lambda_4}{4!} I_4 \equiv \frac{\lambda_4}{4!} \int d^3x (Q_{\alpha\beta}^2)^2 . \tag{2.3}$$

As usual, the coefficient a of $Q_{\alpha\beta}^2$ contains a factor $-(1 - T/T_c)$ causing a instability at a critical temperature T_c.

The last term in F_2 violates parity and is responsible for the formation of a helical ground state.

[2]) This situation has changed recently: See the note added in proof at the end of the paper.

The order parameter $Q_{\alpha\beta}$ is a traceless symmetric tensor field. For this reason (2.3) is the only quartic invariant. The other independent way of contracting the eight indices $\mathrm{tr}\,(Q^4)$, turns out to be proportional to (2.2):[3])

$$2\ \mathrm{tr}\ (Q^4) = (\mathrm{tr}\ Q^2)^2. \tag{2.4}$$

In order to see this one only has to diagonalize Q via a rotation and finds

$$\begin{aligned} -2\ \mathrm{tr}\ Q^4 + (\mathrm{tr}\ Q^2)^2 &= -2(Q_{11}^4 + Q_{22}^4 + Q_{33}^4) + (Q_{11}^2 + Q_{22}^2 + Q_{33}^2) \\ &= (Q_{11} + Q_{22} + Q_{33})\,(-Q_{11} + Q_{22} + Q_{33})\,(Q_{11} - Q_{22} + Q_{33}) \\ &\quad \times (Q_{11} + Q_{22} - Q_{33}) = 0. \end{aligned} \tag{2.5}$$

For small oscillations above the phase transition, correlation functions

$$\langle Q_{\alpha\beta}(x)\, Q_{\sigma\tau}(y)\rangle = \frac{1}{V} \sum_{\boldsymbol{q}} e^{i\boldsymbol{q}(\boldsymbol{x}-\boldsymbol{y})} G_{\alpha\beta}^{\sigma\tau}(\boldsymbol{q}) \tag{2.6}$$

are obtained by inverting the functional matrix in the quadratic form F_2: In momentum space

$$Q_{\alpha\beta}(x) = \frac{1}{\sqrt{V}} \sum_{\boldsymbol{q}} e^{i\boldsymbol{q}\boldsymbol{x}} Q_{\alpha\beta}(\boldsymbol{q}) \tag{2.7}$$

one may write

$$F_2 = \frac{1}{2} \sum_{\boldsymbol{q}} Q_{\alpha\beta}^*(q)\, t_\alpha{}^\gamma(q)\, \delta_\beta{}^\delta Q_{\gamma\delta}(q) \tag{2.8}$$

with

$$t_\alpha{}^\gamma(\boldsymbol{q}) = (a + bq^2)\, \delta_\alpha{}^\gamma + c q_\alpha q^\gamma + 2d \boldsymbol{S}_\alpha{}^\gamma \boldsymbol{q} \tag{2.9}$$

where

$$(S_\tau)_\alpha{}^\gamma = -2i\varepsilon_{\tau\alpha\gamma} \tag{2.10}$$

is the spin matrix for the tensor field $Q_{\alpha\beta}$. More symmetrically, $t_\alpha{}^\gamma \delta_\beta{}^\delta$ can be replaced by

$$\begin{aligned} T_{\alpha\beta}^{\gamma\delta} &= \frac{1}{4} (t_\alpha{}^\gamma \delta_\beta{}^\delta + t_\beta{}^\gamma \delta_\alpha{}^\delta + t_\alpha{}^\delta\, \delta_\beta{}^\gamma + t_\beta{}^\delta \delta_\alpha{}^\gamma) \\ &\quad - \frac{1}{6} (t_{\alpha\beta} + t_{\beta\alpha})\, \delta^{\gamma\delta} - \frac{1}{6} (t^{\gamma\delta} + t^{\delta\gamma})\, \delta_{\alpha\beta} + \frac{1}{9}\, t_\tau{}^\tau \delta_{\alpha\beta} \delta^{\gamma\delta}. \end{aligned} \tag{2.11}$$

The inversion problem therefore reduces to the solution of

$$\Gamma_{\alpha\beta}^{\gamma\delta}(\boldsymbol{q})\, G_{\gamma\delta}^{\sigma\tau}(\boldsymbol{q}) = I_{\alpha\beta}^{\sigma\tau} \tag{2.12}$$

where $I_{\alpha\beta}^{\sigma\tau}$ is the unit matrix in the space of symmetric traceless tensors:

$$I_{\alpha\beta}^{\sigma\tau} = \frac{1}{2} (\delta_\alpha{}^\sigma \delta_\beta{}^\tau + \delta_\alpha{}^\tau \delta_\beta{}^\sigma) - \frac{1}{3}\, \delta_{\alpha\beta} \delta^{\sigma\tau}. \tag{2.13}$$

It is most convenient to construct G from polarization tensors $\varepsilon_{\alpha\beta}^m(\hat{\boldsymbol{q}})$ which diagonalize

$$T_{\alpha\beta}^{\gamma\delta}(\boldsymbol{q})\, \varepsilon_{\gamma\delta}^{(m)}(\hat{\boldsymbol{q}}) = \tau^{(m)}(q)\, \varepsilon_{\alpha\beta}^{(m)}(\hat{\boldsymbol{q}}). \tag{2.14}$$

[3]) The same statement would be true for a purely antisymmetric $Q_{\alpha\beta}$.

The labels m may be chosen to measure the helicity of the spin-two excitations, i.e. the polarization along the momentum direction $\hat{\boldsymbol{q}} \equiv \boldsymbol{q}/q$:

$$(\boldsymbol{S}\hat{\boldsymbol{q}})\, \varepsilon_{\alpha\beta}^{(m)}(\hat{\boldsymbol{q}}) = m\varepsilon_{\alpha\beta}^{(m)}(\hat{\boldsymbol{q}}). \tag{2.15}$$

The solution of (2.15) is straight-forward in terms of a local orthonormal triplet of vectors oriented along $\hat{q}$:

$$\varphi^{(1)}(\hat{\boldsymbol{q}}),\ \varphi^{(2)}(\hat{\boldsymbol{q}}),\ \varphi^{(3)}(\hat{\boldsymbol{q}}) \equiv \hat{q}.$$

The spherical unit vectors

$$\begin{aligned} \varphi^{(+)}(\hat{\boldsymbol{q}}) &\equiv l(\hat{\boldsymbol{q}}) \equiv (\varphi^{(1)} + i\varphi^{(2)})/\sqrt{2} \\ \varphi^{(-)}(\hat{\boldsymbol{q}}) &\equiv l^*(\hat{\boldsymbol{q}}) \equiv (\varphi^{(1)} - i\varphi^{(2)})/\sqrt{2} \\ \varphi^{(0)}(\hat{\boldsymbol{q}}) &\equiv \varphi^{(3)}(\hat{\boldsymbol{q}}) \equiv \hat{\boldsymbol{q}} \end{aligned} \tag{2.16}$$

are a natural representation of helicity ± 1, 0, respectively. The coupling of two of these tensors (2.15) is then trivial:

$$\begin{aligned} \varepsilon_{\alpha\beta}^{(2)}(\hat{\boldsymbol{q}}) &= \varphi_\alpha{}^{(+)}\varphi_\beta{}^{(+)} = l_\alpha l_\beta \equiv \varepsilon_{\alpha\beta}^{(-2)}(\hat{\boldsymbol{q}})^* \\ \varepsilon_{\alpha\beta}^{(1)}(\hat{\boldsymbol{q}}) &= \frac{1}{\sqrt{2}}\,(\varphi_\alpha{}^{(+)}\varphi_\beta{}^{(0)} + \varphi_\alpha{}^{(0)}\varphi_\beta{}^{(+)}) = \frac{1}{\sqrt{2}}\,(l_\alpha\hat{q}_\beta + l_\beta\hat{q}_\alpha) = \varepsilon_{\alpha\beta}^{(-1)}(\hat{\boldsymbol{q}})^* \\ \varepsilon_{\alpha\beta}^{(0)}(\hat{\boldsymbol{q}}) &= \varphi_\alpha{}^{(0)}\varphi_\beta{}^{(0)} = \sqrt{\frac{3}{2}}\left(\hat{q}_\alpha\hat{q}_\beta - \frac{1}{3}\,\delta_{\alpha\beta}\right). \end{aligned} \tag{2.17}$$

By construction, these tensors are orthonormal

$$\operatorname{tr}\left(\varepsilon^{(m)}(\hat{q})\, \varepsilon^{(m')*}(\hat{q})\right) = \delta_{mn'} \tag{2.18}$$

and automatically diagonalize (2.14).
In fact, applying (2.9) we see

$$\begin{aligned} \tau^{(\pm 2)}(q) &= a + bq^2 \pm 2dq \\ \tau^{(\pm 1)}(q) &= a + (b + c/2)\, q^2 \pm 2dq \\ \tau^{(0)}(q) &= a + \left(b + \frac{2}{3}\,c\right) q^2. \end{aligned} \tag{2.19}$$

The correlation function $G(q)$ can now immediately be written down as

$$G_{\alpha\beta}^{\gamma\delta}(\boldsymbol{q}) = \sum_{m=-2}^{2} \frac{\varepsilon_{\alpha\beta}^{(m)}(\hat{\boldsymbol{q}})\, \varepsilon_{\gamma\delta}^{(m)}(\hat{\boldsymbol{q}})^*}{\tau^{(m)}(q)}. \tag{2.20}$$

The eigenvalues $\tau^{(m)}(q)$ are directly measurable by the angular dependence of light scattering: If a photon of momentum k and polarization ε_α absorbs an oscillation quantum of momentum q and reemerges with polarization ε_α', the cross section is given by

$$\frac{d\sigma}{d\Omega} = \frac{1}{32\pi^3}\, k^4 G_{\alpha\beta}^{\gamma\delta}(\boldsymbol{q})\, \varepsilon_\alpha\varepsilon_\beta\varepsilon_\gamma{}'^*\varepsilon_\delta{}'^*. \tag{2.21}$$

Let the initial beam be polarized porthogonal to the scattering plane. If θ and φ denote angle and polarization direction of the scattered beam, respectively, the cross section becomes

$$\frac{d\sigma}{d\Omega} = \frac{1}{32\pi^3}\left[\frac{1}{6}\,\tau^{(0)^{-1}}\cos^2\varphi + \frac{1}{4}\,(\tau^{(2)^{-1}} + \tau^{(-2)^{-1}}\left(1 - \sin^2\varphi\,\sin^2\left(\frac{\theta}{2}\right)\right) + \frac{1}{4}\,(\tau^{(1)^{-1}} - \tau^{(-1)^{-1}})\sin^2\varphi\,\cos^2\left(\frac{\theta}{2}\right)\right]. \tag{2.22}$$

The dominant contribution to light scattering is given by the mode of largest fluctuations, i.e. of smallest $\tau^{(m)}(q)$. The minima of (2.19) are found by quadratic completion

$$\tau^{(\pm 2)}_{(q)} = a - \frac{d^2}{b} + \frac{d^2}{b}\left(\frac{q}{d/b} \pm 1\right)^2 \equiv a - \Delta^{(2)} + \Delta^{(2)}\left(\frac{q}{q^{(2)}} \pm 1\right)^2 \tag{2.23}$$

$$\tau^{(\pm 1)}_{(q)} = a - \frac{d^2}{b + c/2} + \frac{d^2}{b + c/2}\left(\frac{q}{d/(b + c/2)} \pm 1\right)^2 \equiv a - \Delta^{(1)} + \Delta^{(1)}\left(\frac{q}{q^{(1)}} \pm 1\right)^2$$

where

$$q^{(2)} = \frac{d}{b}, \qquad q^{(1)} = \frac{d}{b + c/2} \tag{2.24}$$

are the wave vectors at the minima and $\Delta^{(2)} = d^2/b$, $\Delta^{(1)} = d^2/(b + c/2)$ determine the size of fluctuations at these points, respectively.
From an analysis of the experiments [6] one may conclude that close to the critical region $\tau^{(\pm 2)}(q)$, $\tau^{(0)}(0)$ carry the dominant fluctuations. Thus, the field may be decomposed approximately as

$$Q_{\alpha\beta}(\boldsymbol{x}) \approx \sum_{n_j} \varepsilon^{(0)}(\boldsymbol{n}_j)\,\varphi_j{}^{(0)} + \sum_{\hat{\boldsymbol{q}}_i}\left(\varepsilon^{(2)}_{\alpha\beta}(\hat{\boldsymbol{q}}_i)\,\varphi_i{}^{(2)}e^{i\boldsymbol{q}_i\boldsymbol{x}} + \text{h.c.}\right). \tag{2.25}$$

Here $\boldsymbol{q}_i$ are several vectors of length q [2] and different directions while n_i are some unit vectors. Notice that we may always assume $\varphi^{(2)}$ to be real by choosing appropriate directions for $\varphi^{(1)}(\hat{\boldsymbol{q}})$, $\varphi^{(2)}(\hat{\boldsymbol{q}})$. The components $\varphi_i{}^{(0)}$ determine the optical unisotropy.
The components $\varphi_i{}^{(2)}$ are measurable via the Bragg reflection of circularly polarized light.

III. Free Energies of Most Important Phases

1. Cholesteric Phase

The cholesteric phase is characterized by the presence of one component $\varphi^{(0)}$ for optical unisotropy and another component $\varphi^{(2)}$ accounting for the selective reflection of circularly polarized light. The quadratic free energy is easily calculated:

$$F_2 = \frac{1}{2}\,[\tau^{(0)}(0)\,\varphi^{(0)^2} + \tau^{(2)}(q^{(2)})\,2\varphi^{(2)^2}] = \frac{a}{2}\,\varphi^{(0)^2} + \left(a - \frac{d^2}{b}\right)\varphi^{(2)^2}. \tag{3.1}$$

In the cubic invariant I_3 we have one contribution

$$I_3\colon \varphi^{(0)^3}\,\mathrm{tr}\,(\varepsilon^{(0)^3}) = \varphi^{(0)^3}\,\frac{1}{\sqrt{6}} \tag{3.2}$$

and six of the type

$$I_3 : \varphi^{(0)}\varphi^{(2)^2} \operatorname{tr}\left(\varepsilon^{(0)}(\boldsymbol{n})\, \varepsilon^{(2)}(\hat{\boldsymbol{q}})\, \varepsilon^{(-2)}(\hat{\boldsymbol{q}})\right) = \varphi^{(0)}\varphi^{(2)^2} \sqrt{\frac{3}{2}} \left(|\boldsymbol{ln}|^2 - \frac{1}{3}\right) \tag{3.3}$$

such that

$$F_3 = \frac{\lambda_3}{3!} \left[\varphi^{(0)^3} \frac{1}{\sqrt{6}} + \varphi^{(0)}\varphi^{(2)^2}\, 6 \sqrt{\frac{3}{2}} \left(|\boldsymbol{ln}|^2 - \frac{1}{3}\right)\right]. \tag{3.4}$$

The quartic invariant I_4 contains two parts: one in which each factor $\operatorname{tr} Q^2$ conserves momenta separately:

$$I_4 : \left[\varphi^{(0)^2} \operatorname{tr}\left(\varepsilon^{(0)}(\boldsymbol{n})\, \varepsilon^{(0)}(\boldsymbol{n})\right) + \varphi^{(2)^2} \operatorname{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}})\, \varepsilon^{(-2)}(\hat{\boldsymbol{q}}) + \text{h.c.}\right)\right]^2 = \left(\varphi^{(0)^2} + 2\varphi^{(2)^2}\right)^2 \tag{3.5}$$

which is, of course, just the square of the quadratic invariant $I_2 \equiv \int dx \operatorname{tr}(Q^2)$ accompanying the coefficient $a/2$ in (3.1). The other consists of pieces where only the sum over all four momenta vanishes with each Q^2 factor having non-zero momentum which are eight combinations of the type

$$I_4 : \varphi^{(0)^2}\varphi^{(2)^2} \operatorname{tr}\left(\varepsilon^{(0)}(n)\, \varepsilon^{(2)}(\hat{q})\right) \operatorname{tr}\left(\varepsilon^{(0)}(\boldsymbol{n})\, \varepsilon^{(-2)}(\hat{\boldsymbol{q}})\right) = \varphi^{(0)^2}\varphi^{(2)^2} \frac{3}{2} |\boldsymbol{ln}|^4. \tag{3.6}$$

Thus we have

$$F_4 = \frac{\lambda_4}{4!} \left[\left(\varphi^{(0)^2} + 2\varphi^{(2)^2}\right)^2 + \varphi^{(0)^2}\varphi^{(2)^2} 12 |\boldsymbol{ln}|^4\right]. \tag{3.7}$$

In order to simplify calculations it is convenient to introduce dimensionless quantities

$$\varphi^{(0)} \equiv \frac{6}{2\sqrt{6}} \frac{\lambda_3}{\lambda_4} x, \qquad \varphi^{(2)} \equiv \frac{3}{2\sqrt{6}} \frac{\lambda_3}{\lambda_4} \frac{y}{\sqrt{2}}$$
$$a \equiv a_0 \left(\frac{T}{T^*} - 1\right) \equiv \frac{\lambda_3^2}{4\lambda_4} (\tau + 2\alpha), \qquad a - \frac{d^2}{b} \equiv \frac{\lambda_3^2}{4\lambda_4} \tau. \tag{3.8}$$

Then, after dividing out a common factor, the free energy may be written as

$$f_{\text{chol}} = \frac{F_{\text{chol}}}{\frac{3}{64} \frac{\lambda_3^4}{\lambda_4^3}} = (\tau + 2\alpha)\, x^2 + \tau y^2 + \frac{1}{3} x^3 + x y^2 (3\, |\boldsymbol{ln}|^2 - 1)$$
$$+ \frac{1}{8} \left[(x^2 + y^2)^2 + 6 x^2 y^2\, |\boldsymbol{ln}|^2\right]. \tag{3.9}$$

The discussion of this expression can follow [3]. For τ large enough, the minimum at $x = 0$, $\varphi = 0$ is stable. As τ decreases, the asymmetric fluctuations in x due to xy^2 tend to destabilize this minimum. The lowest energy can be achieved by maximizing the coefficient of the cubic minimizing that of the quartic term. Both is true for[4])

$$\boldsymbol{n} \parallel \hat{\boldsymbol{q}}, \qquad \boldsymbol{l} \cdot \boldsymbol{n} = 0 \tag{3.10}$$

Non-trivial extrema are found at

$$x^2 - (1 - \alpha)\, x + \tau = 0 \tag{3.11}$$

[4]) The second statement follows form the first. Notice that for $\boldsymbol{l} \parallel \boldsymbol{n}$, $|\boldsymbol{ln}|^2 = 1/2$ such that the coefficient of xy^2 is only 1/2 as large, apart from the opposite sign.

i.e.

$$x_{1,2} = \frac{1-\alpha}{2} \pm \sqrt{\frac{(1-\alpha)^2}{4} - \tau} \tag{3.12}$$

and

$$y^2 = 3x^2 + 4\alpha x . \tag{3.13}$$

At the extremum, the energy is

$$f_{\text{ext}} = 2\left(x^2\tau - \frac{x^3}{3} + \alpha\tau x\right) \tag{3.14}$$

$$= 2\left[-\tau^2 + \frac{1}{3}\tau(1-\alpha) - \frac{4}{3}\left(\frac{(1-\alpha)^2}{4} - \tau\right)\left(\frac{1-\alpha}{2} \pm \sqrt{\frac{(1-\alpha)^2}{4} - \tau}\right)\right] \tag{3.15}$$

from which we conclude the + sign to have the lower energy. This energy may vanish before τ reaches zero with x and y jumping to non-zero values, such that the system undergoes a first order transition. Setting (3.14) equal to zero together with (3.11) one finds once (eliminating the lowest powers of x)

$$x = \frac{\tau + \alpha - \alpha^2}{\alpha + \frac{1}{3}} \tag{3.16}$$

and once (eliminating the highest powers)

$$x = -\frac{\left(\alpha + \frac{1}{3}\right)\tau}{\tau + \frac{1}{3}(\alpha - 1)} \tag{3.17}$$

from which one obtains the boundary for a first order transition between normal and cholesteric phase with $x \neq 0$, $y \neq 0$ as

$$9\tau^2 + 2(9\alpha - 1)\,\tau - 3\alpha(1-\alpha)^2 = 0 . \tag{3.18}$$

For $\alpha < 1$, this happens precociously at $\tau < 0$ while for $\alpha > 1$ the helical state is reached continously at the second order transition line $\tau = 0$.
In the limit of large cholestericity $\alpha \to \infty$, the field component x is frozen and the energy becomes simply

$$f_{\text{chol}} = \tau y^2 + \frac{1}{8} y^4 . \tag{3.19}$$

This is minimal at $y^2 = -4\tau$ with

$$f_{\min} = -2\tau^2 . \tag{3.20}$$

The same behaviour is observed in the low-temperature limit at any α as can be seen from (3.9): For $\tau \to -\infty$, the cubic term can be dropped and the energy is, to leading order in τ, symmetric in x and y

$$f \to \tau(x^2 + y^2) + \frac{1}{8}(x^2 + y^2)^2 . \tag{3.21}$$

Notice that if we had started out with several components $\varphi_j^{(0)}$, the energy (3.9) would have turned *each* $\boldsymbol{n}_j$ vector parallel to $\boldsymbol{q}$ such that, effectively, only a single field $\varphi^{(0)}$ survives.

It should be mentioned that the whole discussion based on truncating the free energy after the quartic term is consistent only for sufficiently small λ_3

$$\frac{\lambda_3^2}{\lambda_4} \ll a_0 \tag{3.22}$$

in which case the transition is almost of second order. For, consider some left-out terms of fifth and higher order in the free energy:

$$F_5 = \frac{\lambda_5}{5!} \int dx \operatorname{tr}(Q^5) + \cdots \frac{\lambda_n}{n!} \int dx \operatorname{tr}(Q^n) + \cdots. \tag{3.23}$$

They would contribute, in the dimensionless form,

$$f_5 \approx \frac{\lambda_5 \lambda_3}{\lambda_4^2} x^5 + \cdots + \frac{\lambda_n \lambda_3^{n-4}}{\lambda_4^{n-3}} x^5 + \cdots. \tag{3.24}$$

Since λ_n will, in general, be of the order of $a_0^{-(n-4)/2}\lambda_4$ such higher terms can be neglected only under the condition (3.22). Experimentally (3.22) does seem to be true since in the transitions are very weakly of first order with all observed latent heats being extremely small compared to the condensation energy away from the transition point. The lines

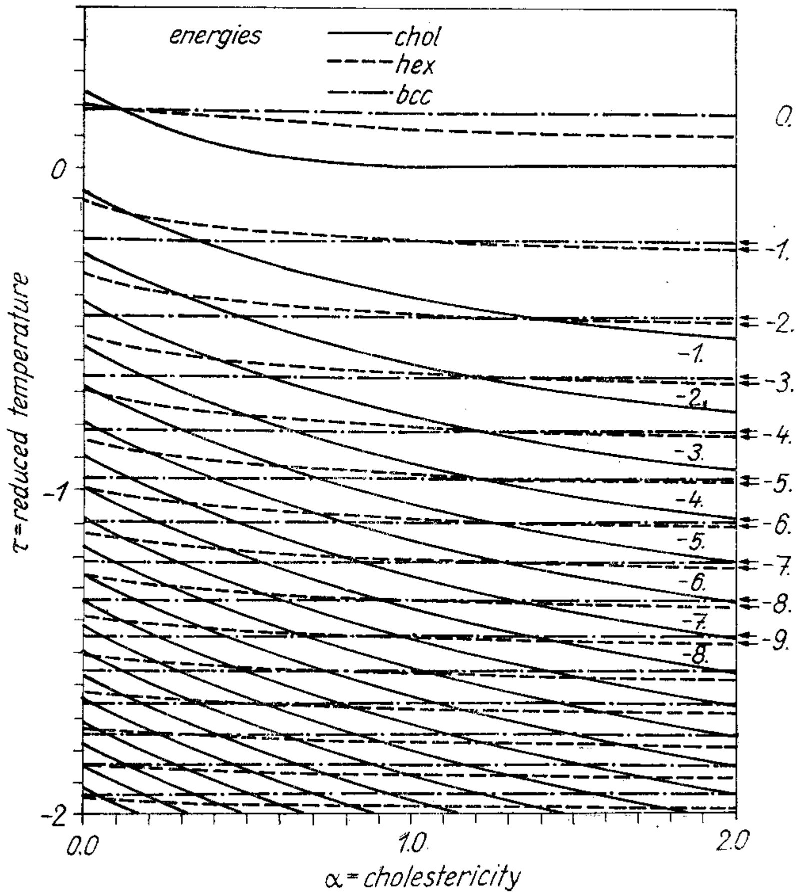


Fig. 1

of equal energy as a function of α, τ and are shown in Fig. 1. Since $\varphi^{(0)}$ and $\varphi^{(2)}$ determine optical anisotropy and reflection of circularly polarized light, respectively, we have also displayed the corresponding contour plots for x and y (see Figs. 2 and 3).

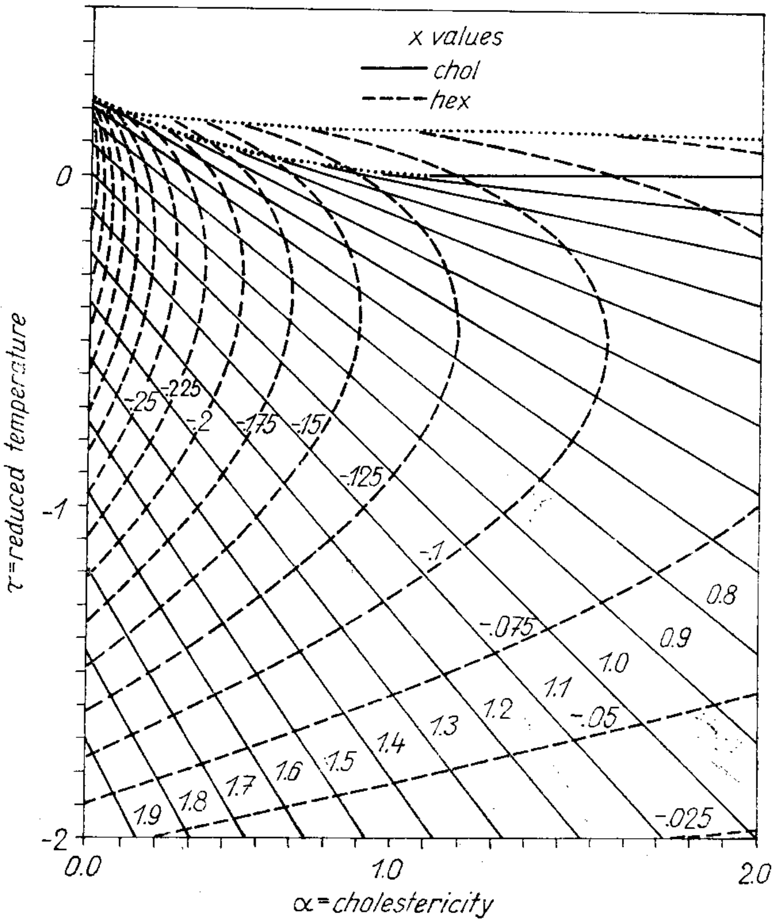


Fig. 2

2. Hexagonal Phase

This phase is characterized by the presence of one $\varphi^{(0)}(\boldsymbol{n})$ and three components $\varphi^{(2)}(\hat{\boldsymbol{q}}_i)$ with the momentum vectors $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$ forming a single triangle. In order to calculate the different contributions to the free energy we choose the directions

$$\hat{\boldsymbol{q}}_1 = \hat{\boldsymbol{x}}$$

$$\hat{\boldsymbol{q}}_2 = -\frac{\hat{\boldsymbol{x}}}{2} + \frac{\sqrt{3}}{2}\,\hat{\boldsymbol{y}} \tag{3.25}$$

$$\hat{\boldsymbol{q}}_3 = -\frac{\hat{\boldsymbol{x}}}{2} - \frac{\sqrt{3}}{2}\,\hat{\boldsymbol{y}}.$$

The polarization vectors $\boldsymbol{l}_i$ may then be taken as

$$\boldsymbol{l}_1 = \frac{1}{\sqrt{2}}\,(\hat{\boldsymbol{y}} + i\hat{\boldsymbol{z}})\; e^{i\gamma_1/2} \tag{3.26}$$

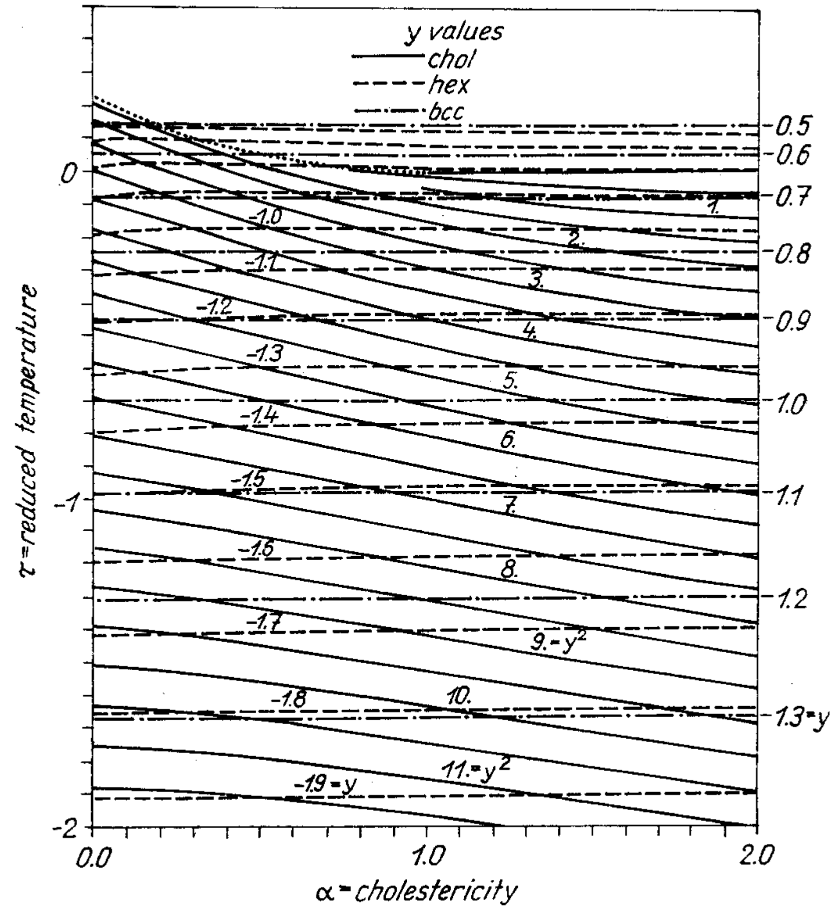


Fig. 3

$$\boldsymbol{l}_2 = \frac{1}{\sqrt{2}} \left(-\frac{\sqrt{3}}{2} \hat{\boldsymbol{x}} - \frac{1}{2} \hat{\boldsymbol{y}} + i\hat{\boldsymbol{z}} \right) e^{i\gamma_2/2}$$

$$\boldsymbol{l}_3 = \frac{1}{\sqrt{2}} \left(\frac{\sqrt{3}}{2} \hat{\boldsymbol{x}} - \frac{1}{2} \hat{\boldsymbol{y}} + i\hat{\boldsymbol{z}} \right) e^{i\gamma_3/2}.$$

Note that the chirality of all vectors has to be the same i.e. $\boldsymbol{l}^r = \operatorname{Re} \boldsymbol{l}$, $\boldsymbol{l}^i = \operatorname{Im} \boldsymbol{l}$, and $\hat{\boldsymbol{q}}$ have to form a positively oriented triped.
The quadratic energy now reads

$$F_2 = \frac{a}{2} \varphi^{(0)^2} + \left(a - \frac{d^2}{b} \right) \sum_{i=1}^{3} \varphi_i^{(2)^2}. \tag{3.27}$$

In the cubic invariant there is again the term (3.2) plus six terms (3.3), one for each momentum

$$I_3\colon \sqrt{\frac{3}{2}}\, \varphi^{(0)} \sum_i \varphi_i^{(2)^2} \left(|\boldsymbol{l}_i \boldsymbol{n}|^2 - \frac{1}{3} \right). \tag{3.28}$$

In addition, there may be the six triangular contributions

$$\begin{aligned} I_3\colon & \varphi_1^{(2)} \varphi_2^{(2)} \varphi_3^{(3)} \operatorname{tr} \left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_1)\, \varepsilon^{(2)}(\hat{\boldsymbol{q}}_2)\, \varepsilon^{(2)}(\hat{\boldsymbol{q}}_3) + \text{c.c.} \right) \\ &= \varphi_1^{(2)} \varphi_2^{(2)} \varphi_3^{(2)} [(\boldsymbol{l}_1 \boldsymbol{l}_2)(\boldsymbol{l}_2 \boldsymbol{l}_3)(\boldsymbol{l}_3 \boldsymbol{l}_1) + \text{c.c.}] \end{aligned} \tag{3.29}$$

coming from 3! permutations and a total reversal of all momentum lines. Let $\boldsymbol{n}$ have the components

$$\boldsymbol{n} = (n_x, n_y, n_z) = \sin\theta\,(\cos\varphi\hat{\boldsymbol{x}} + \sin\varphi\hat{\boldsymbol{y}}) + \cos\theta\hat{\boldsymbol{z}}. \tag{3.30}$$

For symmetry reasons we shall assume all $\varphi_i^{(2)}$ to be the same. Then the sum over i in (3.28) can be performed

$$\sum_i \left(|\boldsymbol{l}_i\boldsymbol{n}|^2 - \frac{1}{3}\right) = \frac{3}{4}(n_x^2 + n_y^2 + 2n_z^2) - 1 = \frac{1}{2} - \frac{3}{4}\sin^2\theta. \tag{3.31}$$

For the evaluation of (3.29) we notice that

$$(\boldsymbol{l}_i\boldsymbol{l}_j) = -\frac{3}{4}e^{i(\gamma_i+\gamma_j)/2} \tag{3.32}$$

such that (3.29) becomes

$$-\varphi^{(2)^3}\,6\left(\frac{3}{4}\right)^3 2\cdot\cos(\gamma_1 + \gamma_2 + \gamma_3). \tag{3.33}$$

Consider now the quartic invariant I_4. There is again the square of I_2:

$$I_2^2 = \left(\varphi^{(0)^2} + 2\sum_i \varphi_i^{(2)^2}\right) \to \left(\varphi^{(0)^2} + 6\varphi^{(2)^2}\right). \tag{3.34}$$

The eight combinations (3.6) have to be taken now for each momentum $\hat{\boldsymbol{q}}_i$ resulting in

$$I_4\colon\ \varphi^{(0)^2}\sum_i \varphi_i^{(2)^2}\frac{3}{2}(\boldsymbol{l}_i\boldsymbol{n})^4. \tag{3.35}$$

Inserting the $\boldsymbol{l}_i$ vectors we find

$$\begin{aligned}\sum_i |\boldsymbol{l}_i\boldsymbol{n}|^4 &= \frac{3}{4} + \frac{1}{4}(n_x^2n_y^2 + n_y^2n_z^2 + n_z^2n_x^2)\\ &= \frac{3}{4} + \frac{1}{4}\sin^2\theta\left(\frac{1}{2}\sin^2 2\varphi\,\sin^2\theta + \cos^2\theta\right).\end{aligned} \tag{3.36}$$

Contrary to the cholesteric phase there may now be contributions linear in $\varphi^{(0)}$ and cubic in $\varphi^{(2)}$ with the three momenta forming a triangle. They are of the form

$$I_4\colon\ \varphi^{(0)}\varphi_1^{(2)}\varphi_2^{(2)}\varphi_3^{(2)}\left[\mathrm{tr}\left(\varepsilon^{(0)}(\boldsymbol{n})\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_1)\right)\mathrm{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_2)\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_3)\right) + \text{c.c.} + 2\text{ cyclic permutations}\right]. \tag{3.37}$$

There are eight of them corresponding to the $24 = 4!$ permutation of the four polarization tensors, apart from the complex conjugate. Inserting the explicit forms we see that

$$\mathrm{tr}\left(\varepsilon^{(0)}(\boldsymbol{n})\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_i)\right) = \sqrt{\frac{3}{2}}(\boldsymbol{l}_i\boldsymbol{n})^2 e^{i\gamma_i}$$

$$\mathrm{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_j)\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_k)\right) = (\boldsymbol{l}_j\boldsymbol{l}_k)^2 e^{i(\gamma_j+\gamma_k)}.$$

With the symmetric Ansatz of all $\varphi_i^{(2)}$ being equal, (3.37) leads to

$$I_4\colon\ \varphi^{(0)}\varphi^{(2)^3}\sqrt{\frac{3}{2}}\left(\frac{3}{4}\right)^2\frac{3}{4}(n_x^2 + n_y^2 - 2n_z^2)\cdot 2\cos(\gamma_1 + \gamma_2 + \gamma_3) \tag{3.38}$$

The last contribution to I_4 comes from two different momenta appearing twice, i.e.

$$I_4\colon \varphi_i^{(2)^2}\varphi_j^{(2)^2}\left[\operatorname{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_i)\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_j)\right)\operatorname{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_i)\,\varepsilon^{(-2)}(\hat{\boldsymbol{q}}_j)\right)\right.$$
$$\left.+\operatorname{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_i)\,\varepsilon^{(-2)}(\hat{\boldsymbol{q}}_j)\right)\operatorname{tr}\left(\varepsilon^{(-2)}(\hat{\boldsymbol{q}}_i)\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_j)\right)\right]$$
$$= \varphi_i^{(2)^2}\varphi_j^{(2)^2}(|\boldsymbol{l}_i\boldsymbol{l}_j|^4 + |\boldsymbol{l}_i\boldsymbol{l}_j^*|^4)\,. \tag{3.39}$$

With the symmetric ansatz $\varphi_i^{(2)} \equiv \varphi^{(2)}$ the sum can be found as

$$\varphi^{(2)^4}\cdot 3\left[\left(\frac{3}{4}\right)^4 + \left(\frac{1}{4}\right)^4\right]. \tag{3.40}$$

Collecting all terms gives

$$F_{\text{hex}} = \frac{a}{2}\,\varphi^{(0)^2} + \left(a - \frac{d^2}{b}\right)3\varphi^{(2)^2} + \frac{\lambda_3}{3!}\left[\varphi^{(0)^3}\frac{1}{\sqrt{6}} + \varphi^{(0)}\varphi^{(2)^2}3\sqrt{6}\left(\frac{1}{2} - \frac{3}{4}\sin^2\theta\right)\right.$$
$$\left. - \varphi^{(2)^3}12\left(\frac{3}{4}\right)^3\cos\left(\gamma_1+\gamma_2+\gamma_3\right)\right]$$
$$+ \frac{\lambda_4}{4!}\left[\left(\varphi^{(0)^2} + 6\varphi^{(2)^2}\right)^2 + \varphi^{(0)}\varphi^{(2)^3}\frac{27}{8}\sqrt{6}\,(1 - 3\sin^2\theta)\right.$$
$$\left. + \varphi^{(0)^2}\varphi^{(2)^2}\left(\frac{3}{4} + \frac{1}{4}\sin^2\theta\left(\frac{1}{2}\sin^2 2\varphi\sin^2\theta + \cos^2\theta\right)\right) + \frac{3\cdot 41}{16}\,\varphi^{(2)^4}\right]. \tag{3.41}$$

In terms of reduced variables this reads

$$f_{\text{hex}} = (\tau + 2\alpha)\,x^2 + 3\tau y^2$$
$$+ \frac{1}{3}\,x^3 + \frac{3}{2}\,xy^2\left(1 - \frac{3}{2}\sin^2\theta\right) - \frac{27}{32}\sqrt{3}\,y^3\cos\left(\gamma_1+\gamma_2+\gamma_3\right)$$
$$+ \frac{1}{8}\,x^4 + \frac{21}{16}\,x^2y^2\left(1 + \frac{1}{3}\sin^2\theta\left(\frac{1}{2}\sin^2 2\varphi\sin^2\theta + \cos^2\theta\right)\right)$$
$$+ \frac{699}{8^3}\,y^4 - \frac{27}{8^2}\sqrt{3}\,xy^3\left(1 - \frac{3}{2}\sin^2\theta\right)\cos\left(\gamma_1+\gamma_2+\gamma_3\right). \tag{3.42}$$

The xy^2 term is maximized by choosing $\theta = 0$, i.e. $\boldsymbol{n}$ vertical to the triangle formed by $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$. This drives x to negative values. Similarly, the y^3 term becomes strongest by choosing $\cos(\gamma_1+\gamma_2+\gamma_3) = +1$. Then y takes positive values. Since for the same choices the quartic pieces xy^3 and x^2y^2 also become smallest we can be sure to have minimized the energy with respect to the direction of $\boldsymbol{n}$.

Let us now study the behaviour of this final expression in the limit of large cholestericity. Then x is again frozen and we remain with

$$f \xrightarrow[\alpha\to\infty]{} 3\tau y^2 - \frac{27}{32}\sqrt{3}\,y^3 + \frac{233\cdot 3}{8^3}\,y^4. \tag{3.43}$$

This is of the generic form

$$f = a\tau y^2 + by^3 + cy^4 \tag{3.44}$$

which is minimal at

$$y = -\frac{3b}{8c}\left(1 + \sqrt{1 - \frac{32ac}{9b^2}\,\tau}\right) \tag{3.45}$$

with

$$f_{\min} = -y^3 \left(\frac{b}{2} + cy\right). \tag{3.46}$$

The onset of the first order phase transition is at

$$y_0 = -\frac{b}{2c} \tag{3.47}$$

or

$$\tau_0 = \frac{b^2}{4ca}. \tag{3.48}$$

In the hexagonal case these values are

$$y_0^{\text{hex}} = \frac{72}{233}\sqrt{3} \approx 535 \tag{3.49}$$

$$\tau_0^{\text{hex}} = \frac{1}{8}\,\frac{3^5}{233} \approx .130. \tag{3.50}$$

Thus for large α, the phase transition takes place into the hexagonal configuration before reaching the cholesteric phase at $\tau_0 \approx .130$. For low temperatures, however, the hexagonal energy decreases slower than the cholesteric. The energies become equal at

$$\tau_{\text{hex}\leftrightarrow\text{chol}} \underset{\alpha \to -\infty}{\approx} -28.5.$$

The reason, why ultimately the cholesteric phase falls lower is the following: Asymptotically, by^3 can be neglected and

$$f \to -\frac{a^2}{4c}\tau^2 \tag{3.51}$$

such that in the hexagonal phase

$$f_{\text{hex}} \to -\frac{3 \cdot 8^3}{233 \cdot 4}\tau^2 \approx -1.648\tau^2.$$

The quartic coefficient always contains the square of the quadratic contribution plus additional possible combinations from (3.38). With the normalization (3.8) this amounts to

$$c \geqq \frac{a^2}{8} \tag{3.52}$$

with the equality sign only for a single momentum q such that all other quartic contribution vanish. The full contour plots of f_{hex} are shown in Fig. 1. For their calculation we have taken the extremal conditions

$$\frac{\partial f}{\partial x} = 0, \quad \frac{\partial f}{\partial y} = 0,$$

brought them to the forms

$$y = -\frac{27}{233}\sqrt{3}\,(2+x)\left[1+\sqrt{1-\frac{16\cdot 8\cdot 233}{27^2\cdot 3}\,\frac{(2\tau+x+x^2)}{(2+x)^2}}\right]$$

$$x = -\frac{1}{\left(1-\frac{9}{16}\sqrt{3}\,y\right)}\left\{\left(\tau+\frac{14}{3}\alpha-\frac{9}{16}\sqrt{3}\,y+\frac{355}{3\cdot 4^3}y^2\right)\right.$$
$$\left.-\sqrt{\left(\tau+\frac{14}{3}\alpha-\frac{9}{16}\sqrt{3}\,y+\frac{355}{3\cdot 4^3}y^2\right)^2-\frac{7}{2}y^2\left(1+\frac{9}{32}\sqrt{3}\,y\right)\left(1-\frac{9}{16}\sqrt{3}\,y\right)}\right\} \tag{3.53}$$

and iterated from $(x, y) = (-.281, -.376)$ a few times. The result can be inserted into (3.42) at $\theta = 0$ and yields the minimal free energy (see Figs. 1—3).

3. The Body Centered Cubic Phase

Here we assume

$$\varphi(x) = \varphi^{(2)}\sum_{i=1}^{6}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_i)\,e^{i\boldsymbol{q}_i\boldsymbol{x}}+\text{c.c.}\right) \tag{3.54}$$

where q_i are the six vectors in the reciprocal lattice of a body centered cubic crystal. Due to the absence of $\varphi^{(0)}$, this phase is optically isotropic. The reason why $\varphi^{(0)}$ may be dropped is the decoupling from $\varphi^{(2)}$ in the pieces linear in $\varphi^{(0)}$, i.e. $\varphi^{(0)}\varphi^{(2)2}$, $\varphi^{(0)}\varphi^{(2)3}$ are all absent in the free energy. This will be seen in detail in the next section. The momenta

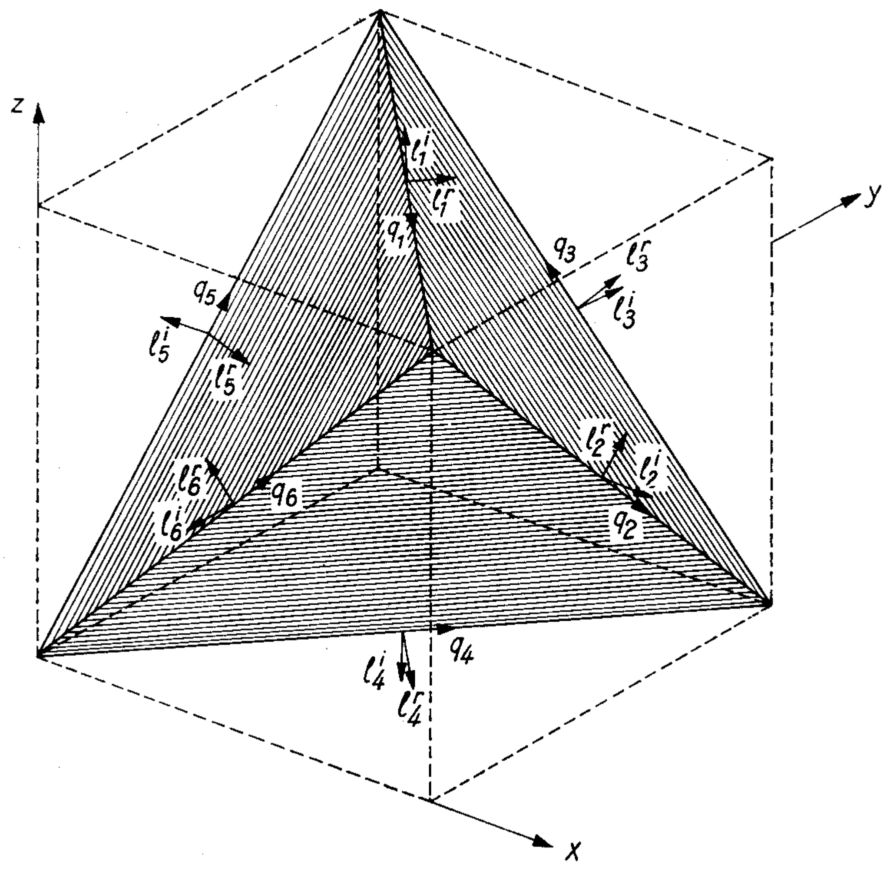


Fig. 4

may be chosen along the face diagonals of a cubus. The polarisation vectors are assigned according to the following list (see Fig. 4).

$$\begin{aligned}
\hat{\boldsymbol{q}}_1 &= \frac{1}{\sqrt{2}}(\hat{\boldsymbol{x}} - \hat{\boldsymbol{y}}) & l_1 &= \frac{1}{2}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}) + \frac{i}{\sqrt{2}}\hat{\boldsymbol{z}} \\
\hat{\boldsymbol{q}}_2 &= \frac{1}{\sqrt{2}}(\hat{\boldsymbol{y}} - \hat{\boldsymbol{z}}) & l_2 &= \frac{1}{2}(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}) + \frac{i}{\sqrt{2}}\hat{\boldsymbol{x}} \\
\hat{\boldsymbol{q}}_3 &= \frac{1}{\sqrt{2}}(\hat{\boldsymbol{z}} - \hat{\boldsymbol{x}}) & l_3 &= \frac{1}{2}(\hat{\boldsymbol{z}} + \hat{\boldsymbol{x}}) + \frac{i}{\sqrt{2}}\hat{\boldsymbol{y}} \\
\boldsymbol{q}_4 &= \frac{1}{\sqrt{2}}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}}) & l_4 &= \frac{1}{2}(\hat{\boldsymbol{x}} - \hat{\boldsymbol{y}}) - \frac{i}{\sqrt{2}}\hat{\boldsymbol{z}} \\
\boldsymbol{q}_5 &= \frac{1}{\sqrt{2}}(\hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}) & l_5 &= \frac{1}{2}(\hat{\boldsymbol{y}} - \hat{\boldsymbol{z}}) - \frac{i}{\sqrt{2}}\hat{\boldsymbol{x}} \\
\boldsymbol{q}_6 &= \frac{1}{\sqrt{2}}(\hat{\boldsymbol{z}} + \hat{\boldsymbol{x}}) & l_6 &= \frac{1}{2}(\hat{\boldsymbol{z}} - \hat{\boldsymbol{x}}) - \frac{i}{\sqrt{2}}\hat{\boldsymbol{y}}
\end{aligned} \tag{3.55}$$

where we have dropped the phase factors $e^{i\gamma_i/2}$ of l_i, for brevity. The resulting scalar products are given in Table 1.

Notice that the scalar products (3.29) in each of the four triangles

$$123, \quad 1\bar{6}5, \quad \bar{2}\bar{6}4, \quad 3\bar{5}4 \tag{3.56}$$

have the maximal norm 3/4. This is important for the precocious onset of this phase. The bars on top of the numbers account for the fact that for these momenta the complex conjugate piece in the expansion (3.54) is required to close the triangle.

Consider now the different contributions to the free energy. Since there are six lines, the quadratic energy is

$$F_2 = \frac{a}{2}\varphi^{(0)^2} + \left(a - \frac{d^2}{b}\right) 6\varphi^{(2)^2} \tag{3.57}$$

where we have assumed all $\varphi_i^{(2)}$ to be equal, for symmetry reasons. For the cubic invariant (3.29) we form the scalar products $(\boldsymbol{l}_1\boldsymbol{l}_2)(\boldsymbol{l}_2\boldsymbol{l}_3)(\boldsymbol{l}_3\boldsymbol{l}_1)$ for each of the triangles (3.56)

$$\begin{aligned}
&123: && (\boldsymbol{l}_1\boldsymbol{l}_2)(\boldsymbol{l}_2\boldsymbol{l}_3)(\boldsymbol{l}_3\boldsymbol{l}_1) = \left(\frac{3}{4}\right)^3 e^{3i\alpha} \\
&1\bar{6}5: && (\boldsymbol{l}_1\boldsymbol{l}_6{}^*)(\boldsymbol{l}_6{}^*\boldsymbol{l}_5)(\boldsymbol{l}_5\boldsymbol{l}_1) = \left(-\frac{3}{4}\right)\left(-\frac{3}{4}\right)\left(\frac{3}{4}\right) c^{-3i\alpha} \\
&\bar{2}\bar{6}4: && (\boldsymbol{l}_2{}^*\boldsymbol{l}_6{}^*)(\boldsymbol{l}_6{}^*\boldsymbol{l}_4)(\boldsymbol{l}_4\boldsymbol{l}_2{}^*) = \frac{3}{4}\left(-\frac{3}{4}\right)\left(-\frac{3}{4}\right) e^{3i\alpha} \\
&3\bar{5}4: && (\boldsymbol{l}_3\boldsymbol{l}_5{}^*)(\boldsymbol{l}_5{}^*\boldsymbol{l}_4)(\boldsymbol{l}_4\boldsymbol{l}_3) = \left(-\frac{3}{4}\right)\left(-\frac{3}{4}\right)\frac{3}{4} e^{-3i\alpha}.
\end{aligned} \tag{3.58}$$

Table 1

The scalar products $((\boldsymbol{l}_i \boldsymbol{l}_j)$. The lower numbers stand for $(\boldsymbol{l}_i \boldsymbol{l}_i^*)$. The matrix is symmetric for the upper and hermitian for the lower elements. The angle α is given by $\alpha = \text{arc cos}\,(1/3)$.

$(\boldsymbol{l}_i\boldsymbol{l}_j)$ $(\boldsymbol{l}_i\boldsymbol{l}_j^*)$	1	2	3	4	5	6
1	1 0	$\frac{3}{4}e^{i\alpha}$ $\frac{1}{4}$	$\frac{3}{4}e^{i\alpha}$ $\frac{1}{4}$	$\frac{1}{2}$ $-\frac{1}{2}$	$\frac{3}{4}e^{-i\alpha}$ $\frac{1}{4}$	$-\frac{1}{4}$ $-\frac{3}{4}e^{-i\alpha}$
2		0 1	$\frac{3}{4}e^{i\alpha}$ $\frac{1}{4}$	$-\frac{1}{4}$ $-\frac{3}{4}e^{-i\alpha}$	$\frac{1}{2}$ $-\frac{1}{2}$	$\frac{3}{4}e^{-i\alpha}$ $\frac{1}{4}$
3			0 1	$\frac{3}{4}e^{-i\alpha}$ $\frac{1}{4}$	$-\frac{1}{4}$ $-\frac{3}{4}e^{-i\alpha}$	$\frac{1}{2}$ $-\frac{1}{2}$
4				0 1	$-\frac{1}{4}$ $-\frac{3}{4}e^{-i\alpha}$	$-\frac{1}{4}$ $-\frac{3}{4}e^{i\alpha}$
5					0 1	$-\frac{1}{4}$ $-\frac{3}{4}e^{-i\alpha}$
6						0 1

Hence (3.33) becomes

$$\varphi^{(2)^3}\, 6 \left(\frac{3}{4}\right)^3 2[\cos(3\alpha + \gamma_1 + \gamma_2 + \gamma_3) + \cos(-3\alpha + \gamma_1 + \gamma_5 - \gamma_6) + \cos(3\alpha - \gamma_2 + \gamma_4 - \gamma_6) + \cos(-3\alpha + \gamma_3 + \gamma_4 - \gamma_5)]. \tag{3.59}$$

The angle α is given by

$$\alpha = \arctan 2\sqrt{2} = \text{arc cos}\,\frac{1}{3} = 70 \cdot 529^\circ. \tag{3.60}$$

The quartic invariant consists again of the square of the quadratic piece

$$\left(12\varphi^{(2)^2}\right)^2. \tag{3.61}$$

Next there are the contributions of pairs of different momenta of the type (3.39). A short look at Table 1 shows that these are

$$\varphi^{(2)^4}\left\{12\left[\left(\frac{3}{4}\right)^4+\left(\frac{1}{4}\right)^4\right]+3\left[\left(\frac{1}{2}\right)^4+\left(\frac{1}{2}\right)^4\right]\right\}=\frac{135}{8\cdot 4}\varphi^{(2)^4} \tag{3.62}$$

the first 12 coming from adjacent, the last three from non-adjacent pairs of momenta in the tetrahedron (see Fig. 1).

Finally there are new contributions which were absent before: They come from closed quadrangles the momenta of which add up to zero: ($1\bar{6}43$), ($23\bar{5}6$), ($4\bar{5}\bar{1}\bar{2}$). They enter the quartic invariant as

$$\begin{aligned} I_4\colon 8\varphi_1{}^{(2)}\varphi_6{}^{(2)}\varphi_4{}^{(2)}\varphi_3{}^{(2)}\big[&\mathrm{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_1)\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_6)\right)\mathrm{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_4)\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_3)\right)\\ &+\mathrm{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_1)\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_3)\right)\mathrm{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_4)\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_6)\right)\\ &+\mathrm{tr}\left(\varepsilon^{(2)}(\hat{\boldsymbol{q}}_1)\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_4)\right)\mathrm{tr}\left(\varepsilon^{(-2)}(\hat{\boldsymbol{q}}_6)\,\varepsilon^{(2)}(\hat{\boldsymbol{q}}_3)\right)+\text{c.c.}\big]\\ =8\varphi_1{}^{(2)}\varphi_6{}^{(2)}\varphi_4{}^{(2)}\varphi_3{}^{(2)}&[(\boldsymbol{l}_1\boldsymbol{l}_6{}^*)^2\,(\boldsymbol{l}_4\boldsymbol{l}_3)^2+(\boldsymbol{l}_1\boldsymbol{l}_3)^2\,(\boldsymbol{l}_4\boldsymbol{l}_6{}^*)^2+(\boldsymbol{l}_1\boldsymbol{l}_4)^2\,(\boldsymbol{l}_6{}^*\boldsymbol{l}_3)^2+\text{c.c.}]. \end{aligned} \tag{3.63}$$

Alltogether there are 24 combinations for each quadrangle apart from the total reversal of all momenta. Inserting the vectors from Table 1 we see the square bracket to become

$$\begin{aligned} &(1\bar{6}43)\colon && \left[\left(\frac{3}{4}\right)^4 e^{-4i\alpha}+\left(\frac{3}{4}\right)^4 e^{4i\alpha}+\left(\frac{1}{2}\right)^4\right]e^{i(\gamma_1+\gamma_3+\gamma_4-\gamma_6)}+\text{c.c.}\\ &(23\bar{5}6)\colon && \left[\left(\frac{3}{4}\right)^4 e^{4i\alpha}+\left(\frac{3}{4}\right)^4 e^{-4i\alpha}+\left(\frac{1}{2}\right)^4\right]e^{i(\gamma_2+\gamma_3-\gamma_5+\gamma_6)}+\text{c.c.}\\ &(4\bar{5}\bar{1}\bar{2})\colon && \left[\left(\frac{3}{4}\right)^4 e^{-4i\alpha}+\left(\frac{3}{4}\right)^4 e^{4i\alpha}+\left(\frac{1}{2}\right)^4\right. e^{i(-\gamma_1-\gamma_2+\gamma_4-\gamma_5)}+\text{c.c.} \end{aligned} \tag{3.64}$$

such that for all equal $\varphi_i{}^{(2)}$'s:

$$\begin{aligned} I_4\colon\ \varphi^{(2)^4}\left(1+\frac{81}{8}\cos 4\alpha\right)[&\cos(\gamma_1+\gamma_3+\gamma_4+\gamma_6)\\ &+\cos(\gamma_2+\gamma_3-\gamma_5+\gamma_6)\\ &+\cos(-\gamma_1-\gamma_2+\gamma_4-\gamma_5)]. \end{aligned} \tag{3.65}$$

Because of (3.60) we may calculate $\cos 2\alpha = 2\cos^2\alpha - 1 = -7/9$, $\cos 4\alpha = 17/81$

$$\left(1+\frac{81}{8}\cos 4\alpha\right)=\frac{25}{8}. \tag{3.66}$$

The six phase angles in (3.59) and (3.65) are not independent. If we call the three combinations in (3.65) successively $2\chi_1$, $2\chi_2$, $2\chi_3$, then the bracket (3.59) simplifies to

$$\begin{aligned} [&\cos(3\alpha+\chi_1+\chi_2+\chi_3)+\cos(3\alpha-\chi_1+\chi_2-\chi_3)\\ &+\cos(3\alpha+\chi_1-\chi_2-\chi_3)+\cos(3\alpha-\chi_1-\chi_2+\chi_3)]. \end{aligned} \tag{3.67}$$

In the normalization (3.8), the final energy has the form:

$$f_{\text{bcc}} = 6\tau y^2 + \frac{27}{32}\sqrt{3}\, y^3 [\cos(3\alpha + \chi_1 + \chi_2 + \chi_3) + \cos(3\alpha + \chi_1 - \chi_2 - \chi_3) + \cos(3\alpha - \chi_1 + \chi_2 - \chi_3) + \cos(3\alpha - \chi_1 - \chi_2 - \chi_3)] + \frac{y^4}{8}\left[36 + \frac{135}{16} + \frac{25}{32}(\cos 2\chi_1 + \cos 2\chi_2 + \cos 2\chi_3)\right]. \tag{3.68}$$

The quartic terms can be collected to

$$\frac{y^4}{16^2}[1422 + 25(\cos 2\chi_1 + \cos 2\chi_2 + \cos 2\chi_3)]. \tag{3.69}$$

The most precocious onset of this phase is reached for the maximum of the first bracket which lies at $\chi_1 = \chi_2 = \chi_3 = \pi$ with the value

$$-4\cos 3\alpha = 4\,\frac{23}{27} \approx 3.41 \tag{3.70}$$

which is quite close to the upper bound 4. We therefore take this choice of angles such that

$$f_{\text{bcc}} \approx 6\tau y^2 + \frac{23}{8}\sqrt{3}\, y^3 + \frac{499\cdot 3}{16^2}\, y^4. \tag{3.71}$$

This phase sets in at (see (3.48))

$$\tau_0^{\text{bcc}} = \frac{1}{6}\,\frac{23^2}{499} \approx .177 \tag{3.72}$$

with

$$y_0^{\text{bcc}} = \frac{23\cdot 16}{3\cdot 499}\sqrt{3} \approx .426. \tag{3.73}$$

Asymptotically it behaves as

$$f_{\text{bcc}} \xrightarrow[\tau\to-\infty]{} -\frac{a^2}{4c}\tau^2 = -\frac{4^4\cdot 3}{499}\tau^2 \approx -1.539\tau^2. \tag{3.74}$$

Thus, ultimately, it falls off slower than the hexagonal energy. This behaviour is, however, academic since the transition to the cholesteric phase takes place much before this can become relevant:

$$\tau_{\text{bcc}\leftrightarrow\text{chol}} \approx -21. \tag{3.75}$$

Actually, as far as the low temperature limit is concerned, the phase choice $\chi_i = \pi$ is not optimal. If one uses $\chi_i \equiv \pi/2$, the asymptotic energy (3.74) can be lowered by a factor (see (3.69))

$$\frac{1422 + 75}{1422 - 75} \approx 1.11 \tag{3.76}$$

i.e. by 11%. The total energy reads

$$f_{\text{bcc}} \approx 6\tau y^2 + \frac{10\sqrt{6}}{8} y^3 + \frac{449 \cdot 3}{16^2} y^4 \tag{3.77}$$

such that, indeed,

$$f_{\text{bcc}} \xrightarrow[\tau \to -\infty]{} -\frac{4^4 \cdot 3}{449} \tau^2 \approx -1.71\tau^2. \tag{3.78}$$

This form would have a phase transition only at $\tau = 0.74$ its energy being larger than (3.71) for small τ. It would intersect the cholesteric phase at $\tau \approx 24.5$, i.e. after the first version has made the transition. Thus this second form cannot be realized in the laboratory[5]).

The contour plots, in the bcc phase, for energy (3.71) and for the parameter y of reflection of circularly polarized light are given in Figs. 1 and 3.

The optical isotropy makes the bcc phase a possible candidate for the blue phase. There is, however, a serious quantitative problem: By comparing the three calculated energies we see that only for $\alpha \gtrsim 1.3$, bcc is the only phase between normal and cholesteric. This value corresponds to a rather narrow pitch much smaller than that of the experimental samples. Moreover, the second blue phase which is see experimentally does not appear in this calculation. The ansatz (3.54) will need some refinement[6]) in order to accommodate

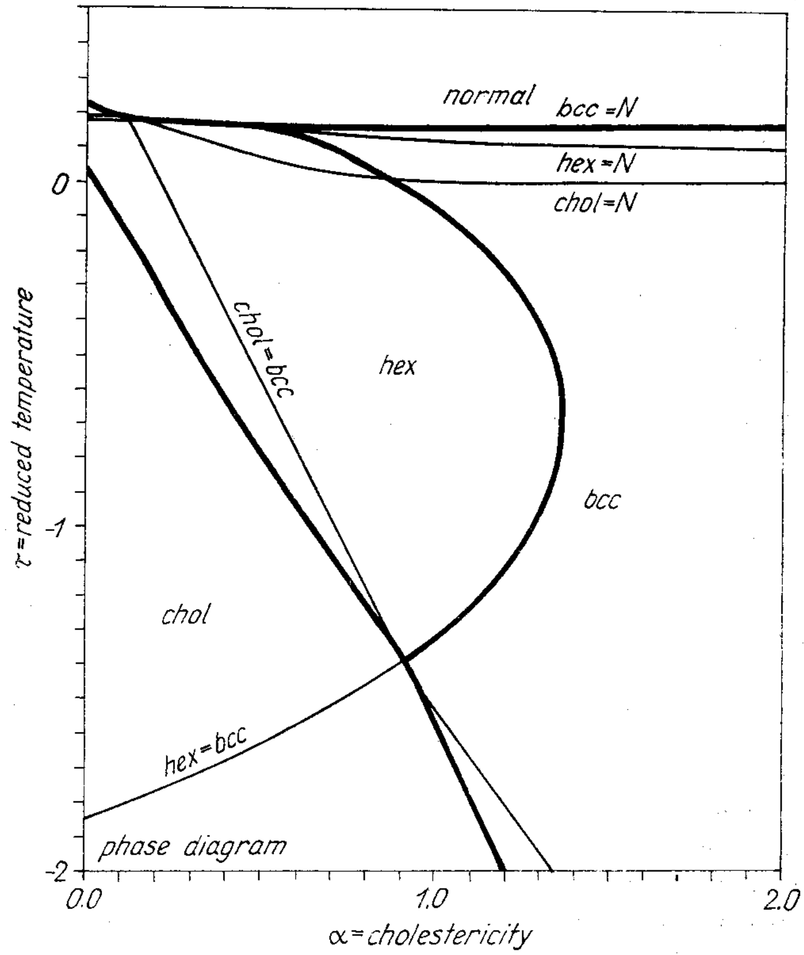


Fig. 5

[5]) Otherwise it would have explained the existence of two blue phases.

[6]) See Ref. [7].

both facts. With the bcc phase setting in before in hexagonal at larger α (compare (3.50) and (3.72)) we may wonder whether for small α the latter can move up to higher temperature such that it is reached before the bcc phase. The additional degree of freedom in x certainly helps to lower the energy. For large $\tau + 2\alpha$, x is small of the order $1/(\tau + 2\alpha)$ and we may approximate the energy (3.42) by

$$f_{\text{bcc}} \approx (\tau + 2\alpha)\left(x - \frac{3}{4(\tau + 2\alpha)}\, y^2\right)^2 + 3\tau y^2 + \frac{27}{32}\sqrt{3}\, y^3 + \frac{699}{8^3}\, y^4 - \frac{9}{16(\tau + 2\alpha)}\, y^4 \tag{3.79}$$

such that we can use formula (3.48) for the onset of this phase

$$\tau_0 = \frac{b^2}{4ac} = \frac{1}{4}\,\frac{27}{(23)^2}\,\frac{1}{\frac{699}{8^3} - \frac{9}{16(\tau + 2\alpha)}} \tag{3.80}$$

or

$$\tau_0 = -\alpha + \frac{3 \cdot 337}{16 \cdot 233} + \sqrt{\left(\alpha + \frac{5 \cdot 105}{16 \cdot 233}\right)^2 + \left(\frac{54}{233}\right)^2}\,. \tag{3.81}$$

For $\alpha \approx .7$, this becomes equal to τ_0^{bcc} such that below this value the hexagonal phase is reached before bcc. The full numeric calculation moves this α value somewhat to the left ($\rightarrow \alpha \sim .4$) as can be seen on the diagrams of Figs. 1, 5.

IV. Candidates for Second Blue Phase

In this section we shall investigate three textures which have an a priori chance of being related to the second blue phase. The first and algebraically simplest one consists in giving the bcc texture the freedom of becoming asymmetric in the amplitudes of the six momenta. This phase would be an interpolation between hexagonal and bcc and might appear where these phases meet, i.e. around $\alpha \approx 0.6$, $\tau \approx 0.1$. If such an Ansatz fails to provide for a lower energy it serves as a useful check for the stability of the symmetric bcc texture. Certainly, the optical anisotropy of any distorted bcc texture would be non-zero. But when cooling the sample, the second blue phase is passed so rapidly that it may well be possible that the short temperature interval of optical unisotropy has been missed.

The second option is a further study of other isotropic momentum configurations. Apart from the tetrahedron the only other Platonic solids with equilateral triangles are the octahedron and the icosahedron. The momenta associated with the first coincide exactly with those of the tetrahedron such that no new texture is obtained. The second appears, at first sight, quite promising and we shall study its free energy in detail.

For completeness we also investigate the properties of a phase interpolating between cholesteric and hexagonal. It consists of a triangle of momenta plus a forth momentum vertical to it. Obviously these are the reciprocal lattice vectors of a three dimensional hexagonal close-packed texture which could, in principle, be observable in a certain range of temperature and cholestericity. Before going to the calculations it is useful to give a summary of all energy terms which contribute to an arbitrary momentum configuration:

$$F_2 = \frac{a}{2}\,\varphi^{(0)^2} + \left(a - \frac{d^2}{b}\right) \sum_i \varphi_i^{(2)^2}, \tag{4.1}$$

$$F_3 = \frac{\lambda_3}{3!}\left\{\varphi^{(0)^3}\frac{1}{\sqrt{6}} + 3\sqrt{6}\,\varphi^{(0)}\sum_i \varphi_i^{(2)^2}\left(|\boldsymbol{l}_i\boldsymbol{n}|^2 - \frac{1}{3}\right)\right.$$
$$\left. + 6\sum_{\Delta}\varphi_i^{(2)}\varphi_j^{(2)}\varphi_k^{(2)}[(\boldsymbol{l}_i\boldsymbol{l}_j)\,(\boldsymbol{l}_j\boldsymbol{l}_k)\,(\boldsymbol{l}_k\boldsymbol{l}_i) + \text{c.c.}]\right\}, \qquad (4.2)$$

$$F_4 = \frac{\lambda_4}{4!}\left\{\left(\varphi^{(0)^2} + 2\sum_i \varphi_i^{(2)^2}\right)^2 + 12\varphi^{(0)^2}\sum_i \varphi_i^{(2)^2}|\boldsymbol{l}_i\boldsymbol{n}|^4\right.$$
$$+ 4\sqrt{6}\,\varphi^{(0)}\sum_{\Delta}\varphi_i^{(2)}\varphi_j^{(2)}\varphi_k^{(2)}[(\boldsymbol{l}_i\boldsymbol{n})^2\,(\boldsymbol{l}_j\boldsymbol{l}_k)^2 + 3\text{ cyclic permutations} + \text{c.c.}]$$
$$+ 8\sum_{i>j}\varphi_i^{(2)^2}\varphi_j^{(2)^2}[|\boldsymbol{l}_i\boldsymbol{l}_j|^4 + |\boldsymbol{l}_i\boldsymbol{l}_j^*|^4]$$
$$\left. + 8\sum_{\square}\varphi_i^{(2)}\varphi_j^{(2)}\varphi_k^{(2)}\varphi_l^{(2)}[(\boldsymbol{l}_i\boldsymbol{l}_j)^2\,(\boldsymbol{l}_k\boldsymbol{l}_l)^2 + (\boldsymbol{l}_i\boldsymbol{l}_l)^2\,(\boldsymbol{l}_j\boldsymbol{l}_k)^2 + (\boldsymbol{l}_i\boldsymbol{l}_k)^2\,(\boldsymbol{l}_i\boldsymbol{l}_l)^2 + \text{c.c.}]\right\} \qquad (4.3)$$

with the normalization (3.8) this may be written as

$$f = (\tau + 2\alpha)\,x^2 + \tau\sum_i y_i^2$$
$$+ \frac{x^3}{3} + 3x\sum_i y_i^2\left((\boldsymbol{l}_i\boldsymbol{n})^2 - \frac{1}{3}\right) + \sqrt{3}\sum_{\Delta} y_iy_jy_k[(\boldsymbol{l}_i\boldsymbol{l}_j)\,(\boldsymbol{l}_j\boldsymbol{l}_k)\,(\boldsymbol{l}_k\boldsymbol{l}_i) + \text{c.c.}]$$
$$+ \frac{1}{8}\left(x^2 + \sum_i y_i^2\right)^2 + \frac{3}{4}\,x^2\sum_i y_i^2|\boldsymbol{l}_i\boldsymbol{n}|^4$$
$$+ \frac{1}{4}\sqrt{3}\,x\sum_{\Delta} y_iy_jy_k[(\boldsymbol{l}_i\boldsymbol{n})\,(\boldsymbol{l}_i\boldsymbol{l}_k)^2 + \text{cycl.} + \text{c.c.}] + \frac{1}{4}\sum_{i>j} y_i^2y_j^2[|\boldsymbol{l}_i\boldsymbol{l}_j|^4 + |\boldsymbol{l}_i\boldsymbol{l}_j^*|^4]$$
$$+ \frac{1}{4}\sum_{\square} y_iy_jy_ky_l[(\boldsymbol{l}_i\boldsymbol{l}_j)^2\,(\boldsymbol{l}_k\boldsymbol{l}_l)^2 + (\boldsymbol{l}_i\boldsymbol{l}_l)^2\,(\boldsymbol{l}_j\boldsymbol{l}_k)^2 + (\boldsymbol{l}_i\boldsymbol{l}_k)^2\,(\boldsymbol{l}_j\boldsymbol{l}_l)^2 + \text{c.c.}]. \qquad (4.4)$$

1. Asymmetric BCC Texture

We shall assume a limited asymmetry by putting the direction $\boldsymbol{n}$ orthogonal to the 123 triangle, i.e.

$$\boldsymbol{n} = \frac{1}{\sqrt{3}}\,(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}}) \qquad (4.5)$$

and assigning to the sides 123 and 456 a different amplitudes y and z, respectively. The quadratic energy is then

$$F_2 = (\tau + 2\alpha)\,x^2 + 3\tau(y^2 + z^2). \qquad (4.6)$$

For the cubic energy we have to evaluate

$$3x\left[y^2\sum_{i=1,2,3}\left(|\boldsymbol{l}_i\boldsymbol{n}|^2 - \frac{1}{3}\right) + z^2\sum_{i=4,5,6}\left(|\boldsymbol{l}_i\boldsymbol{n}|^2 - \frac{1}{3}\right)\right]. \qquad (4.7)$$

Using (3.55) we find

$$3x\left[y^2 3\left(\frac{1}{2} - \frac{1}{3}\right) - z^2 3\left(\frac{1}{6} - \frac{1}{3}\right)\right] = \frac{3}{2}\,x(y^2 - z^2) \qquad (4.8)$$

which vanishes for the symmetric bcc texture, as it should.

In the triangular parts we have to distinguish between one triangle 123 and the three others ($1\bar{6}5$), ($\bar{6}4\bar{2}$), ($3\bar{5}4$) which give

$$2\left(\frac{3}{4}\right)^3 \sqrt{3}\,\{y^3 \cos(3\alpha + \gamma_1 + \gamma_2 + \gamma_3) + yz^2[\cos(-3\alpha + \gamma_1 + \gamma_5 - \gamma_6) + \cos(3\alpha - \gamma_2 + \gamma_4 - \gamma_6) + \cos(-3\alpha + \gamma_3 + \gamma_4 - \gamma_5)]\}\,. \tag{4.9}$$

Thus the cubic terms together are

$$f_3 = \frac{1}{3}x^3 + \frac{3}{2}x(y^2 - z^2) + \frac{27}{32}\sqrt{3}\,y[y^2\cos(3\alpha + \chi_1 + \chi_2 + \chi_3) + z^2\cos(3\alpha - \chi_1 + \chi_2 - \chi_3) + z^2\cos(3\alpha + \chi_1 - \chi_2 - \chi_3) + z^2\cos(3\alpha - \chi_1 - \chi_2 + \chi_3)] \tag{4.10}$$

which may be compared with (3.68) in the symmetric case. Consider now the quartic pieces. First there is $1/8(x^2 + 3y^2 + 3z^2)^2$. For the next term we find

$$\frac{3}{4}x^2\left[y^2\sum_{i=1,2,3}|\boldsymbol{l}_i\boldsymbol{n}|^4 + z^2\sum_{i=4,5,6}|\boldsymbol{l}_i\boldsymbol{n}|^4\right] = \frac{3}{4}x^2\left(y^2\frac{3}{4} + z^2\frac{3}{36}\right) = \frac{x^2}{16}(9y^2 + z^2). \tag{4.11}$$

Then we evaluate the triangular contributions. For the triangle (123) we find

$$\frac{\sqrt{3}}{4}xy^3\,3\left(\frac{3}{4}\right)^2\frac{1}{2}\,e^{3i\alpha + i(\gamma_1+\gamma_2+\gamma_3)} + \text{c.c.} \tag{4.12}$$

while the triangles ($1\bar{6}5$), ($\bar{6}4\bar{2}$), (354) give

$$\frac{\sqrt{3}}{4}xz^3 3\left(\frac{3}{4}\right)^2\frac{1}{6}\,[e^{-3i\alpha + i(\gamma_1+\gamma_5-\gamma_6)} + \text{c.c.} + e^{3i\alpha + i(-\gamma_2+\gamma_4-\gamma_6)} + \text{c.c.} + e^{-3i\alpha + i(\gamma_3+\gamma_4-\gamma_5)} + \text{c.c.}] \tag{4.13}$$

such that together

$$\frac{9}{64}\sqrt{3}\,xy[3y^2\cos(3\alpha + \chi_1 + \chi_2 + \chi_3) - z^2\cos(3\alpha - \chi_1 + \chi_2 - \chi_3) - z^2\cos(3\alpha + \chi_1 - \chi_2 - \chi_3) - z^2\cos(3\alpha - \chi_1 - \chi_2 + \chi_3)]\,. \tag{4.14}$$

The pairs of momenta give simply

$$\frac{1}{4}\left\{(y^4 + z^4)\,3\cdot\left[\left(\left(\frac{3}{4}\right)^4 + \left(\frac{1}{4}\right)^4\right)\right] + y^2z^2\left[6\left(\left(\frac{3}{4}\right)^4 + \left(\frac{1}{4}\right)^4\right) + 3\left(\left(\frac{1}{2}\right)^4 + \left(\frac{1}{2}\right)^4\right)\right]\right\} = \frac{3}{8^3}[41(y^4 + z^4) + 98y^2z^2]. \tag{4.15}$$

In the quadrangles one always has two sides of type y and z, respectively. Apart from this the terms are the same as in the symmetric case:
Collecting all quartic terms we have the free energy

$$f_4 = \frac{1}{8} x^4 + \frac{21}{16} x^2y^2 + \frac{13}{16} x^2z^2$$
$$+ \frac{9}{8^2} \sqrt{3}\, xy[3y^2 \cos(3\alpha + \chi_1 + \chi_2 + \chi_3)$$
$$- z^2 \cos(3\alpha - \chi_1 + \chi_2 - \chi_3)$$
$$- z^3 \cos(3\alpha + \chi_1 - \chi_2 - \chi_3)$$
$$- z^2 \cos(3\alpha - \chi_1 - \chi_2 + \chi_3)]$$
$$+ \frac{699}{8^3} (y^4 + z^4) + \frac{y^2 \cdot z^2}{8^3} [1446 + 50(\cos 2\chi_1 + \cos 2\chi_2 + \cos 2\chi_3)]. \tag{4.16}$$

The agreement with the symmetric bcc phase was noted along the way. As an additional check we see that for $z = 0$ and $\chi_1 + \chi_2 + \chi_3 = \pi - 3\alpha$ we reobtain the hexagonal energy (3.42). With this expression interpolating between hexagonal and bcc textures there is a chance of finding a lower energy in a region close to their respective phase transition line. Since the general expression is hard to handle analytically, let us try for a configuration close to bcc by setting $\chi_1 = \chi_2 = \chi_3 = \pi$. Then the energy is

$$f = (\tau + 2\alpha)\, x^2 + 3\tau(y^2 + z^2) + \frac{x^3}{3} + \frac{3}{2} x(y^2 - z^2) + \frac{23}{32} \sqrt{3}\, y(y^2 + 3z^2)$$
$$+ \frac{1}{8} x^4 + \frac{21}{16} x^2y^2 + \frac{13}{16} x^2z^2 + \frac{23}{8^2} \sqrt{3}\, xy(y^2 - z^2)$$
$$+ \frac{699}{8^3} (y^4 + z^4) + \frac{399 \cdot 4}{8^3} y^2z^2. \tag{4.17}$$

In the limit of large α we may freeze $x \to 0$. In order to see the deviations from bcc let us set

$$z^2 = y^2 + d^2. \tag{4.18}$$

Then the energy reads

$$f = f_{\text{bcc}} + 3\tau d^2 + \left(\frac{499 \cdot 3}{16^2} y^2 + \frac{23}{8} \sqrt{3} \cdot \frac{3}{4} y\right) d^2 + \frac{699}{8^3} d^4. \tag{4.19}$$

But due to the extremality of bcc, the d^2 term vanishes. There remains only the quartic term in d which is positive definite. Thus for $\alpha \to \infty$, the distortion of the bcc phase leads to an increase in energy. If is easy to see that this conclusion remains unaltered by taking the next leading corrections $O(1/(\tau + 2\alpha))$ into account. Keeping terms in x and x, the energy has a slightly reduced coefficient of d^4:

$$\left(\frac{699}{8^3} - \frac{9}{16} \frac{1}{\tau + 2\alpha + \frac{17}{8} y^2 + \frac{13}{16} d^2} \left(1 + \frac{23}{96} y^2\right)^2\right) d^4 \tag{4.20}$$

which at the level of this approximation is far from changing sign. There is however a tendency towards destabilization such that a numerical search for smaller α seems indicated. Similarly we may discuss the neighbourhood of the hexagonal phase. There we can write for large $\tau + 2\alpha$

$$f \approx f_{\text{hex}} - \frac{3}{2} xz^2 + \frac{17}{32} \sqrt{3}\, yz^2 - \frac{17}{8^2 \cdot 3} xz^3 + \frac{699}{8^3} z^4 + \frac{997 \cdot 4}{8^3 \cdot 3} y^2 z^2 \tag{4.21}$$

where $x \approx -(3/4)\, y^2/(\tau + 2\alpha)$ is the asymptotic form of x in the hexagonal phase. Consider the point $\alpha \sim 0.7$, $\tau \sim 0.177$ where, in this approximation, $y \sim -0.723$, $x \sim 0.248$ meets with the onset of the bcc phase. There the coefficient of z^2 is

$$0.37 - 0.67 + 1.35$$

which is stable but goes in the direction of destabilization due to the negative y term. We have performed a detailed numerical search for minima of the asymmetric bcc phase but found none which lies lower than bcc or planar hexagonal as shown in our phase diagram.

3. The Isocahedral Texture

There are fiften independent vectors. Because of cubic symmetry we may take the order parameter without $\varphi^{(0)}$:

$$Q_{\alpha\beta}(x) = \sum_{i=1}^{15} \varepsilon_{\alpha\beta}^{(2)}(\hat{\boldsymbol{q}}_i)\, e^{i\boldsymbol{q}_i \boldsymbol{x}} + \text{c.c.} \tag{4.22}$$

Aligning the coordinates as shown in Fig. 6 we have with $k = 1, 2, \ldots, 5$

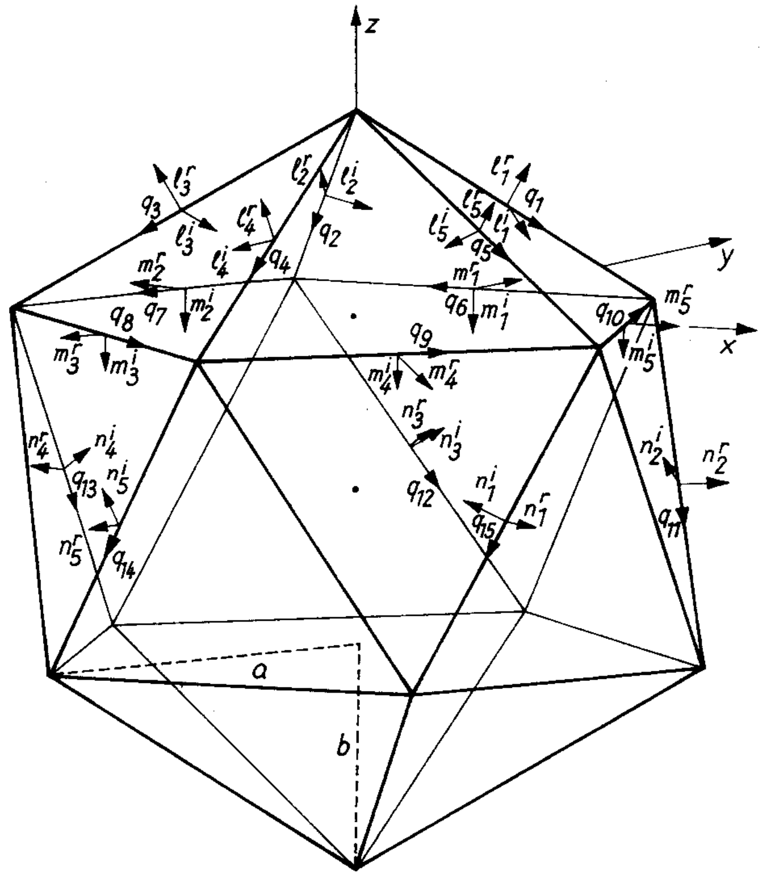
$$\begin{aligned} \hat{\boldsymbol{q}}_k &= a\big(\cos{(2k-1)}\,\alpha\, \hat{\boldsymbol{x}} + \sin{(2k-1)}\,\alpha\, \hat{\boldsymbol{y}}\big) - b\hat{\boldsymbol{z}} \\ \hat{\boldsymbol{q}}_{5+k} &= -\sin 2k\alpha\, \hat{\boldsymbol{x}} + \cos 2k\alpha\, \hat{\boldsymbol{y}} \\ \hat{\boldsymbol{q}}_{10+k} &= b\big(\cos 2(k-2)\,\alpha\, \hat{\boldsymbol{x}} + \sin 2(k-2)\,\alpha\, \hat{\boldsymbol{y}}\big) - a\hat{\boldsymbol{z}} \end{aligned} \tag{4.23}$$

where

$$\begin{aligned} \alpha &= \frac{\pi}{5}, \quad a = \frac{1}{2\cos\frac{3\pi}{10}} = \frac{1}{2\sin\alpha} = \sqrt{\frac{5+\sqrt{5}}{10}} \approx 0{,}8507 \\ b &= \sqrt{1-a^2} = 2a\sin\frac{\pi}{10} = \frac{1}{2\cos\frac{\pi}{10}} = \frac{1}{2\sin 2\alpha} = \sqrt{\frac{5-\sqrt{5}}{10}} = 0{,}5257\,. \end{aligned} \tag{4.24}$$

The polarization vectors associated with these momenta may be chosen as

$$\begin{aligned} \boldsymbol{l}_k &= \frac{1}{\sqrt{2}}\Big[b\big(\cos{(2k-1)}\,\alpha\, \hat{\boldsymbol{x}} + \sin{(2k-1)}\,\alpha\, \hat{\boldsymbol{y}}\big) + a\hat{\boldsymbol{z}} \\ &\quad + i\big(\sin{(2k-1)}\,\alpha\, \hat{\boldsymbol{x}} - \cos{(2k-1)}\,\alpha\, \hat{\boldsymbol{y}}\big)\Big] \\ \boldsymbol{m}_k &= \frac{1}{\sqrt{2}}\left[\cos 2k\alpha\, \hat{\boldsymbol{x}} + \sin 2k\alpha\, \hat{\boldsymbol{y}} - i\hat{\boldsymbol{z}}\right] \\ \boldsymbol{n}_k &= \frac{1}{\sqrt{2}}\Big[a\big(\cos{(2k-1)}\,\alpha\, \hat{\boldsymbol{x}} + \sin{(2k-1)}\,\alpha\, \hat{\boldsymbol{y}}\big) - b\hat{\boldsymbol{z}} \\ &\quad + i\big(\sin{(2k-1)}\,\alpha\, \hat{\boldsymbol{x}} - \cos{(2k-1)}\,\alpha\, \hat{\boldsymbol{y}}\big)\Big]. \end{aligned} \tag{4.25}$$


z
y
x
q_1
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q_3
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q_8
q_9
q_{10}
q_{11}
q_{12}
q_{13}
q_{14}
q_{15}
l_1^r
l_1^i
l_2^r
l_2^i
l_3^r
l_3^i
l_4^r
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m_5^r
m_5^i
n_1^r
n_1^i
n_2^r
n_2^i
n_3^r
n_3^i
n_4^r
n_4^i
n_5^r
n_5^i
a
b

Fig. 6a

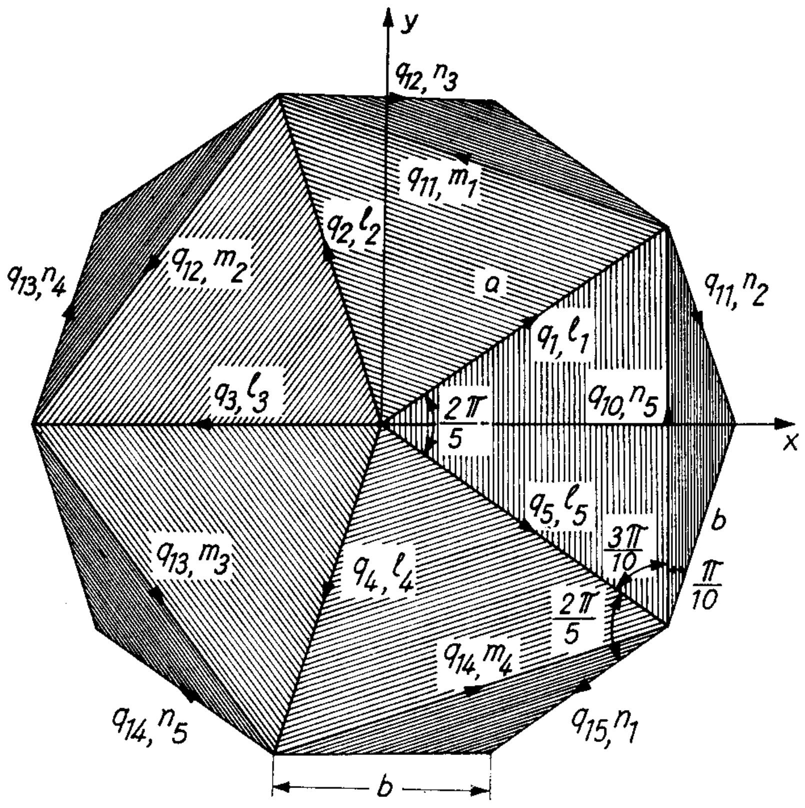
y
x
q_{12}, n_3
q_{11}, m_1
q_{13}, n_4
q_{12}, m_2
q_2, l_2
a
q_{11}, n_2
q_1, l_1
q_3, l_3
$\frac{2\pi}{5}$
q_{10}, n_5
q_5, l_5
b
q_{13}, m_3
q_4, l_4
$\frac{3\pi}{10}$
$\frac{\pi}{10}$
$\frac{2\pi}{5}$
q_{14}, m_4
q_{14}, n_5
q_{15}, n_1
b

Fig. 6b

The quadratic energy is simply

$$f_2 = (\tau + 2\alpha)\, x^2 + 15\tau y^2. \tag{4.26}$$

In the cubic term we have to form (see (4.4))

$$f_3 = \sqrt{3}\, y^3 \sum_{\Delta} [(\boldsymbol{l}_i\boldsymbol{l}_j)\,(\boldsymbol{l}_j\boldsymbol{l}_k)\,(\boldsymbol{l}_k\boldsymbol{l}_i) + \text{c.c.}] \tag{4.27}$$

with a sum over all triangles. There are 10 of these (see Fig. 6) with polarization vectors

$$l_1 m_1 l_2^* \qquad + 5 \text{ cyclic terms}$$

$$m_1 n_3 n_5^* \qquad + 5 \text{ cyclic terms}.$$

Using the scalar products of Table 2 we find

$$\begin{aligned} (l_1 m_1)\,(m_2 l_2^*)\,(l_2^* l_1) &= \left(\frac{3}{4}\right)^3 e^{-3i\beta} \\ (m_1 n_3)\,(n_3 n_5^*)\,(n_5^* m_1) &= \left(\frac{3}{4}\right)^3 e^{3i\beta} \end{aligned} \tag{4.28}$$

where

$$\beta \equiv \operatorname{arc\,tan}\frac{2}{\sqrt{5}}, \quad \cos\beta = \frac{\sqrt{5}}{3}, \quad \cos 2\beta = \frac{1}{9}, \quad \cos 3\beta = -\frac{7\sqrt{5}}{27}, \quad \cos 4\beta = -\frac{79}{81}. \tag{4.29}$$

For symmetry reasons, we allow only for a common additional phase for each group of vectors l, m, and n, respectively, such that (4.27) becomes

$$\begin{aligned} f_3 &= -\sqrt{3}\, y^3 5 \left(\frac{3}{4}\right)^3 2\,[\cos(3\alpha + \gamma_m) + \cos(3\alpha - \gamma_m)] \\ &= -\sqrt{3}\, y^3 5 \left(\frac{3}{4}\right)^3 4 \cos 3\alpha \cos\gamma_m. \end{aligned} \tag{4.30}$$

The most precocious onset of this phase is obtained by choosing $\gamma_m = 0$ where f_3 is maximal:

$$f_3 = \sqrt{3}\, y^3 20 \left(\frac{3}{4}\right)^3 \frac{7}{27}\sqrt{5} \approx 8.47 y^3. \tag{4.31}$$

The quartic energy contains again the square of the quadratic piece

$$\frac{1}{8}\,(15y^2)^2 \approx 28.13. \tag{4.32}$$

Next, there is the sum (see (4.4))

$$\frac{1}{4}\, y^4 \sum_{i<j} (|\boldsymbol{l}_i\boldsymbol{l}_j|^4 + |\boldsymbol{l}_i\boldsymbol{l}_j^*|^4). \tag{4.33}$$

Table 2

The scalar products between the polarisation vectors of the icosahedral texture (see Fig. 6). The lower elements in each box correspond to the column vector being complex conjugate. The indices can be any number from 1 to 5 modulo 5. The square brackets in the exponent are a short form for the function arctan.

$(l_i l_j)$ etc. $(l_i l_j^*)$	l_i, l_i^*	m_i, m_j^*	n_i, n_i^*
l_i	0	$3/4\, e^{-i[2/\sqrt{5}]}$ $1/4$	$i/2$
l_{i+1}	$1/4$ $3/4\, e^{i[2/\sqrt{5}]}$	$1/4$ $3/4\, e^{i[2/\sqrt{5}]}$	$(5-\sqrt{5})/8\, e^{i[2]}$ $-(3+\sqrt{5})/8$
l_{i+2}	$(3+\sqrt{5})/8$ $-(5-\sqrt{5})/8\, e^{-i[2]}$	$-(3-\sqrt{5})/8$ $(5+\sqrt{5})/8\, e^{i[2]}$	$(3-\sqrt{5})/8$ $-(5+\sqrt{5})/8\, e^{i[2]}$
l_{i+3}	$(3+\sqrt{5})/8$ $-(5-\sqrt{5})/8\, e^{i[2]}$	$\mp i/2$	$-(3-\sqrt{5})/8$ $(5+\sqrt{5})/8\, e^{-i[2]}$
l_{i+4}	$1/4$ $3/4\, e^{-i[2/\sqrt{5}]}$	$(5+\sqrt{5})/8\, e^{-i[2]}$ $-(3-\sqrt{5})/8\, e$	$-(5-\sqrt{5})/8\, e^{-i[2]}$ $(3+\sqrt{5})/8$
m_i	$3/4\, e^{-i[2/\sqrt{5}]}$ $1/4$	0	$(5-\sqrt{5})/8\, e^{-i[2]}$ $-(3+\sqrt{5})/8$
m_{i+1}	$(5+\sqrt{5})/8\, e^{-i[2]}$ $-(3-\sqrt{5})/8$	$-(5-\sqrt{5})/8\, e^{i[2]}$ $(3+\sqrt{5})/8$	$-1/4$ $-3/4\, e^{i[2/\sqrt{5}]}$
m_{i+2}	$-i/2$	$-(5+\sqrt{5})/8\, e^{i[2]}$ $(3-\sqrt{5})/8$	$\pm i/2$
m_{i+3}	$-(3-\sqrt{5})/8$ $(5+\sqrt{5})/8\, e^{-i[2]}$	$-(5+\sqrt{5})/8\, e^{i[2]}$ $(3-\sqrt{5})/8$	$3/4\, e^{i[2/\sqrt{5}]}$ $-1/4$
m_{i+4}	$1/4$ $3/4\, e^{-i[2/\sqrt{5}]}$	$-(5-\sqrt{5})/8\, e^{i[2]}$ $(3+\sqrt{5})/8$	$(3+\sqrt{5})/8$ $-(5-\sqrt{5})/8\, e^{-i[2]}$
n_i	$\pm i/2$	$(5-\sqrt{5})/8\, e^{-i[2]}$ $-(3+\sqrt{5})/8$	0
n_{i+1}	$-(5-\sqrt{5})/8\, e^{-i[2]}$ $(3+\sqrt{5})/8$	$(3+\sqrt{5})/8$ $-(5-\sqrt{5})/8\, e^{i[2]}$	$-(3-\sqrt{5})/8$ $(5+\sqrt{5})/8\, e^{i[2]}$
n_{i+2}	$-(3-\sqrt{5})/8$ $(5+\sqrt{5})/8\, e^{i[2]}$	$3/4\, e^{i[2/\sqrt{5}]}$ $-1/4$	$-1/4$ $-3/4\, e^{-i[2/\sqrt{5}]}$
n_{i+3}	$(3-\sqrt{5})/8$ $-(5+\sqrt{5})/8\, e^{-i[2]}$	$i/2$	$-1/4$ $-3/4\, e^{i[2/\sqrt{5}]}$
n_{i+4}	$(5-\sqrt{5})/8\, e^{i[2]}$ $-(3+\sqrt{5})/8$	$-1/4$ $-3/4\, e^{-i[2/\sqrt{5}]}$	$-(3-\sqrt{5})/8$ $(5+\sqrt{5})/8\, e^{-i[2]}$

This may be calculated as follows

$$
\begin{aligned}
&ll: \quad 5\left(\frac{1}{4^4}+\frac{81}{4^4}\right)+5\left(\left(\frac{3+\sqrt{5}}{8}\right)^4+\left(\frac{5-\sqrt{5}}{8}\right)^4\right)\\
&lm: \quad 10\left(\frac{1}{4^4}+\frac{81}{4^4}\right)+5\left(\frac{1}{2^4}+\frac{1}{2^4}\right)+10\left(\left(\frac{3-\sqrt{5}}{8}\right)^4+\left(\frac{5+\sqrt{5}}{8}\right)^4\right)\\
&ln: \quad 5\left(\frac{1}{2^4}+\frac{1}{2^4}\right)+10\left(\left(\frac{3+\sqrt{5}}{8}\right)^4+\left(\frac{5-\sqrt{5}}{8}\right)^4\right)+10\left(\left(\frac{3-\sqrt{5}}{8}\right)^4+\left(\frac{5+\sqrt{5}}{8}\right)^4\right)\\
&mm: \quad 5\left(\left(\frac{3+\sqrt{5}}{8}\right)^4+\left(\frac{5-\sqrt{5}}{8}\right)^4\right)+5\left(\left(\frac{3-\sqrt{5}}{8}\right)^4+\left(\frac{5+\sqrt{5}}{8}\right)^4\right)\\
&nm: \quad 10\left(\frac{1}{4^4}+\frac{81}{4^4}\right)+5\left(\frac{1}{2^4}+\frac{1}{2^4}\right)+10\left(\left(\frac{3+\sqrt{5}}{8}\right)^4+\left(\frac{5-\sqrt{5}}{8}\right)^4\right)\\
&nn: \quad 5\left(\frac{1}{4^4}+\frac{81}{4^4}\right)+5\left(\left(\frac{3-\sqrt{5}}{8}\right)^4+\left(\frac{5+\sqrt{5}}{8}\right)^4\right)
\end{aligned}
\tag{4.34}
$$

such that (4.33) becomes

$$
\frac{1}{4}y^4\left[30\,\frac{82}{4^4}+15\,\frac{1}{8}+30\left(\left(\frac{3+\sqrt{5}}{8}\right)^4+\left(\frac{3-\sqrt{5}}{8}\right)^4+\left(\frac{5-\sqrt{5}}{8}\right)^4+\left(\frac{5+\sqrt{5}}{8}\right)^4\right)\right]
$$

$$
\frac{75}{8}\,y^4 \approx 9.375y^4. \tag{4.35}
$$

It remains to evaluate the quadrangle contributions

$$
\frac{1}{4}\,y^4\sum_{\square}\left[(\boldsymbol{l}_i\boldsymbol{l}_j)^2\,(\boldsymbol{l}_k\boldsymbol{l}_l)^2+(\boldsymbol{l}_i\boldsymbol{l}_l)^2\,(\boldsymbol{l}_j\boldsymbol{l}_k)^2+(\boldsymbol{l}_i\boldsymbol{l}_k)^2\,(\boldsymbol{l}_j\boldsymbol{l}_l)^2\right] \tag{4.36}
$$

where l stands collectively for l, m, or n vectors in each of the 5 different quadrangles. These may be grouped into three different combinations together with their cyclic permutations

$$
\begin{aligned}
&l_1 n_5 n_4{}^* l_2{}^* + 4 \text{ cyclic}\\
&l_1{}^* m_5 l_4 m_4 + 4 \text{ cyclic}\\
&m_4 n_4 m_2 n_3 + 4 \text{ cyclic}.
\end{aligned}
\tag{4.37}
$$

Only the first in each group has to be calculated separately. We see

$$
(l_1 n_5)^2 = \left(\frac{5-\sqrt{5}}{8}\right)^2 e^{2i\arctan 2}
$$

$$
(n_3{}^* l_2{}^*)^2 = \left(\frac{5-\sqrt{5}}{8}\right)^2 e^{2i\arctan 2} \tag{4.38}
$$

$$
\begin{aligned}
(l_1n_3^*)^2 &= \left(\frac{5+\sqrt{5}}{7}\right)^2 e^{-2i\arctan 2} \\
(n_5l_2^*) &= \left(\frac{5+\sqrt{5}}{8}\right)^2 e^{-2i\arctan 2} \\
(l_1l_2^*) &= \left(\frac{3}{4}\right)^2 e^{-2i\arctan 2/\sqrt{5}} \\
(n_5n_3^*)^2 &= \left(\frac{3}{4}\right)^2 e^{-2i\arctan 2/\sqrt{5}}
\end{aligned}
\tag{4.38}
$$

such that the first five quadrangles give

$$
\frac{1}{4}\,y^4\cdot 5\cdot 2\left[-\left(\frac{3}{4}\right)^4\frac{79}{81}-\left(\left(\frac{5-\sqrt{5}}{8}\right)^4+\left(\frac{5+\sqrt{5}}{8}\right)^4\right)\frac{7}{25}\right]. \tag{4.39}
$$

Fortunately, our final phase choice is symmetric enough to give the same result also for the second group

$$
\begin{aligned}
(l_1^*m_5)^2 &= \left(\frac{3}{4}\right)^2 e^{-2i\arctan 2/\sqrt{5}} \\
(m_4l_4)^2 &= \left(\frac{3}{4}\right)^2 e^{-2i\arctan 2/\sqrt{5}} \\
(l_1^*m_4)^2 &= \left(\frac{5+\sqrt{5}}{8}\right)^2 e^{-2i\arctan 2} \\
(m_5l_4)^2 &= \left(\frac{5+\sqrt{5}}{8}\right)^2 e^{-2i\arctan 2} \\
(l_1^*l_4)^2 &= \left(\frac{5-\sqrt{5}}{8}\right)^2 e^{2i\arctan 2} \\
(m_5m_4)^2 &= \left(\frac{5-\sqrt{5}}{8}\right)^2 e^{2i\arctan 2}
\end{aligned}
\tag{4.40}
$$

as well as the third group of quadrangles

$$
\begin{aligned}
(m_4n_4)^2 &= \left(\frac{5-\sqrt{5}}{8}\right)^2 e^{-2i\arctan 2} \\
(m_2n_3^*)^2 &= \left(\frac{5-\sqrt{5}}{8}\right)^2 e^{-2i\arctan 2} \\
(m_4m_2)^2 &= \left(\frac{5+\sqrt{5}}{8}\right)^2 e^{2i\arctan 2} \\
(n_4n_3^*)^2 &= \left(\frac{5+\sqrt{5}}{8}\right)^2 e^{2i\arctan 2}
\end{aligned}
\tag{4.41}
$$

$$(m_4 n_3{}^*)^2 = \left(\frac{3}{4}\right)^2 e^{2i\arctan 2/\sqrt{5}}$$

$$(m_5 m_2)^2 = \left(\frac{3}{4}\right)^2 e^{2i\arctan 2/\sqrt{5}}. \tag{4.41}$$

Thus the quartic terms add up to

$$f_4 = \left(\frac{225}{8} + \frac{75}{8} - \frac{30}{8}\right) y^4 \tag{4.42}$$

such that the full icosahedral energy reads

$$f = 15y^2 + \frac{35}{16}\sqrt{15}\, y^3 + \frac{270}{8}\, y^4. \tag{4.43}$$

We now see that this phase has no chance of being realized in nature. Its onset temperature would be

$$\tau_0 = \frac{7^2 \cdot 5}{2^8 \cdot 3} \approx .035 \tag{4.44}$$

such that at moderate τ the system prefers to be in the bcc phase. Asymptotically, the energy falls off faster, namely with

$$f \xrightarrow[\tau \to -\infty]{} -\tau^2 \frac{5}{6} \tag{4.45}$$

but before the two phases can become equal, which would happen at around

$$\tau_{\text{bcc=icos}} \approx -44.7, \tag{4.46}$$

the system has already made its transition into the cholesteric phase. One may wonder wether there exists an intelligent choice of polarization phases which could succeed in pressing the icosahedral texture energetically below the bcc phase. It is, however, easy to see that this cannot be true.

For suppose we would succeed in increasing the angular factor in the cubic term to unity and simultaneously give all quadrangular contributions (4.38), (4.40), (4.41) a negative phase (-1), then (4.39) would double. This procedure would *decrease* the energy to

$$f_{\text{l.b.}} = 15y^2 + \frac{23}{8}\sqrt{3}\,\frac{27}{23}\,\frac{10}{4}\, y^3 + \frac{1}{8}\,(15^2 + 15)\, y^4 \tag{4.47}$$

where we have written the coefficients in such a way as to permit a fast comparison with the bcc expression (3.68) (with the numbers 15, 10 counting the number of lines and triangles as compared to 6 and 4 in the bcc phase). Even this lower bound would, at moderate τ, lie above the bcc phase since the onset temperature would be

$$\tau_0 = \frac{3^5}{2^{11}} \approx .119 \tag{4.48}$$

i.e. below $\tau_0{}^{\text{bcc}}$ and the two energies would not intersect after the cholesteric phase has been reached.

4. The Hexagonal Close-Packet Texture

With many liquids crystallizing into a hexagonal close-packed texture we find it worthwhile to investigate the free energy also for this texture. In real space, this is generated by in the x, y plane by the primitive translation vectors

$$\boldsymbol{a}_1 = a\left(\frac{1}{2}\,\hat{\boldsymbol{y}} + \frac{\sqrt{3}}{2}\,\hat{\boldsymbol{x}}\right)$$
$$\boldsymbol{a}_2 = a\hat{\boldsymbol{y}} \tag{4.49}$$

just as in the planar hexagonal case. The vertical array follows from multiples of the third vector

$$\boldsymbol{a}_3 = c\hat{\boldsymbol{z}} \tag{4.50}$$

plus a shift by $\boldsymbol{d} = \boldsymbol{a}_1/2 + \boldsymbol{a}_2/2 + \boldsymbol{a}_3/3$. The reciprocal lattice concists of

$$\boldsymbol{b}_1 = \frac{2}{\sqrt{3}\,a}\,\hat{\boldsymbol{x}}$$
$$\boldsymbol{b}_2 = \frac{2}{\sqrt{3}\,a}\left(-\frac{\hat{\boldsymbol{x}}}{2} + \frac{\sqrt{3}}{2}\,\hat{\boldsymbol{y}}\right) \tag{4.51}$$
$$\boldsymbol{b}_3 = \frac{1}{c}\,\hat{\boldsymbol{z}}$$

such that there is again a triangle of momentum vectors $q_{1,2,3}$ as in (3.25) plus a forth momentum orthogonal to it

$$\boldsymbol{q}_4 = \frac{\sqrt{3}\,a}{2c}\,\hat{\boldsymbol{z}}\,. \tag{4.52}$$

For the particular ratio $\sqrt{3}/2\,a = c$ (not ideally packed) this is of the same length as the others and contributes to the ground state energy.
The order parameter is now taken as

$$Q_{\alpha\beta} = \varphi^{(0)}\varepsilon_{\alpha\beta}^{(0)}(\boldsymbol{n}) + \sum_{i=1}^{4} \varphi_i^{(2)}\varepsilon_{\alpha\beta}^{(2)}(\hat{\boldsymbol{q}}_i) \tag{4.53}$$

with $\boldsymbol{l}_4 = 1/\sqrt{2}\,(\hat{\boldsymbol{x}} + i\hat{\boldsymbol{y}})$ and the reduced amplitudes x, $y_{1,2,3}$, z. For symmetry reasons we shall assume all y's to be the same.
Obviously, such an ansatz interpolates between the cholesteric and simple hexagonal phase and may give a lower energy in the boundary region between them. The quadratic energy can directly be taken from (4.4)

$$f_2 = (\tau + 2\alpha)\,x^2 + \tau(3y^2 + z^2)\,. \tag{4.54}$$

For the cubic term we have the hexagonal contribution (3.42) plus the cholesteric piece

$$3xz^2\left(|\boldsymbol{l}_4\boldsymbol{n}|^2 - \frac{1}{3}\right) = 3xz^2\left(\frac{1}{2}\,(n_x{}^2 + n_y{}^2) - \frac{1}{3}\right) = 3xz^2\left(\frac{1}{2}\sin^2\theta - \frac{1}{3}\right) \tag{4.55}$$

such that

$$f_3 = \frac{x^3}{3} + x\left(\frac{3}{2}y^2 - z^2\right)\left(1 - \frac{3}{2}\sin^2\theta\right) - \frac{27}{32}\sqrt{3}\,y^3\cos(\gamma_5 + \gamma_2 + \gamma_3). \quad (4.56)$$

In the quartic energy, the following new pieces have to be added to the hexagonal expression (3.42):

1.) From

$$I_2^2 = (x^2 + 3y^2 + z^2)^2$$

there is an additional

$$f_4\colon \frac{1}{8}(2x^2z^2 + 6y^2z^2 + z^4) \quad (4.57)$$

2.) Since

$$|\boldsymbol{l}_i\boldsymbol{n}|^4 = \sin^4\theta$$

there is a term

$$f_4\colon \frac{3}{4}x^2z^2\sin^4\theta \quad (4.58)$$

3.) Using

$$(\boldsymbol{l}_4\boldsymbol{l}_1) = \frac{i}{2},\quad (\boldsymbol{l}_4{}^*\boldsymbol{l}_1) = -\frac{i}{2}$$

$$\left(\boldsymbol{l}_4\boldsymbol{l}_{\substack{2\\3}}\right) = \mp\frac{1}{2}e^{\pm i\arctan 1/\sqrt{3}} = -\left(\boldsymbol{l}_4{}^*\boldsymbol{l}_{\substack{3\\2}}\right) \quad (4.59)$$

one has

$$\frac{1}{4}y^2z^2\sum_{i=1}^{3}\left(|\boldsymbol{l}_4\boldsymbol{l}_i|^4 + |\boldsymbol{l}_4\boldsymbol{l}_i{}^*|^4\right) = \frac{3}{32}y^3z^2. \quad (4.60)$$

Alltogether, the quartic energy becomes

$$f_4 = \frac{1}{8}x^4 + \frac{21}{16}x^2y^2\left[1 + \frac{1}{3}\sin^2\theta\left(\frac{1}{2}\sin^2 2\varphi\sin^2\theta + \cos^2\theta\right)\right]$$
$$+ \frac{699}{8^3}y^4 - \frac{27}{8^2}\sqrt{3}\,xy^3\left(1 - \frac{3}{2}\sin^2\theta\right)\cos(\gamma_1 + \gamma_2 + \gamma_3)$$
$$+ \frac{1}{8}z^4 + \frac{1}{4}x^2z^2 + \frac{27}{32}y^2z^2 + \frac{3}{4}x^2z^2\sin^4\theta. \quad (4.61)$$

The cubic energies are maximized by setting $\gamma_i \equiv \pi$, $\theta = 0$ such that we can restrict our attention to the expression

$$f_{\text{hcp}} = (\tau + 2x)\,x^2 + \tau(3y^2 + z^2) + \frac{x^3}{3} + x\left(\frac{3}{2}y^2 - z^2\right) + \frac{27}{32}\sqrt{3}\,y^3$$
$$+ \frac{1}{8}x^4 + \frac{21}{16}x^2y^2 + \frac{699}{8^3}y^4 + \frac{27}{8^2}\sqrt{3}\,xy^3 + \frac{1}{8}z^4 + \frac{1}{4}x^2z^2 + \frac{27}{32}y^2z^2. \quad (4.62)$$

There is one observation which can be made immediately:
For large α, f_{hcp} has the asymptotic form

$$f_{\text{hcp}} \to \tau(3y^2 + z^2) + \frac{27}{32}\sqrt{3}\,y^3 + \frac{699}{8^3}y^4 + \frac{1}{8}z^4 + \frac{27}{32}y^2z^2. \quad (4.63)$$

With respect to z, there are two minima: $z = 0$ which is the hexagonal phase, and

$$z^2 = -4\tau - \frac{27}{8} y^2 \tag{4.64}$$

which is the candidate for the hcp phase if $y \neq 0$. This solution can exist only for sufficiently negative $\tau < -27/32y^2$. But inserting (4.64) into (4.63) we find only $y = 0$ as a possible minimum of f_{hcp} which corresponds to the cholesteric phase. Thus only the influence of x gives a chance to stabilize an intermediate hcp phase with y and $z \neq 0$. A computer search for minima, however, eliminates also this possibility.

V. Comparison with the Bilocal Field Formalism

The approach used in this work took advantage of the simple decomposition (2.17) of the spin 2 polarization tensors $\varepsilon^{(2)}(\hat{q})_{\alpha\beta}$ into polarization vectors l. This gives a considerable calculational advantage over the method of HS which employed an expansion in spherical harmonics and had to rely on Clebsch-Gordan coefficients of angular momentum $I = 2$. For completeness, it may be useful to give the translation between the two methods. For this we multiply our tensor fields $Q_{\alpha\beta}$ by an arbitrary unit vector and introduce the bilocal super-field

$$\Phi(\boldsymbol{n}, \boldsymbol{x}) \equiv \sqrt{\frac{15}{8\pi}}\, n_\alpha n_\beta Q_{\alpha\beta}(\boldsymbol{x}) = \sum_m \sqrt{\frac{15}{8\pi}}\, n_\alpha n_\beta \varepsilon_{\alpha\beta}^{(m)}(\hat{\boldsymbol{q}}_i)\, e^{i\boldsymbol{q}_i\boldsymbol{x}} + \text{c.c.} \tag{5.1}$$

Instead of the polarization tensors there are now bilocal polarization functions

$$Y_2^{(m)}(\boldsymbol{n}, \hat{\boldsymbol{q}}) = \sqrt{\frac{15}{8\pi}}\, n_\alpha n_\beta \varepsilon_{\alpha\beta}^{(m)}(\hat{q})\,. \tag{5.2}$$

These can depend only on the polar coordinates θ and φ of n in the $\hat{\boldsymbol{q}}$ dependent frame $\boldsymbol{l}^r, \boldsymbol{l}^i, \hat{\boldsymbol{q}}$. If these axes are rotated into $\hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}, \hat{\boldsymbol{z}}$ directions such that

$$\boldsymbol{n} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta) = (x, y, z) \tag{5.3}$$

we see from (2.17) that $Y_2^{(m)}$ reduce to spherical harmonics:

$$\begin{aligned} Y_2^{(2)}(\theta, \varphi) &= \sqrt{\frac{15}{8\pi}}\, \frac{1}{2}\, (x + iy)^2 = Y_2^{(-2)}(\theta, \varphi)^* \\ Y_2^{(1)}(\theta, \varphi) &= \sqrt{\frac{15}{8\pi}}\, (x + iy)^z = Y_2^{(-1)}(\theta, \varphi)^* \\ Y_2^{(0)}(\theta, \varphi) &= \sqrt{\frac{5}{4\pi}}\, \frac{1}{2}\, (3z^2 - 1) \end{aligned} \tag{5.4}$$

in the normalization

$$\int d\cos\theta d\varphi\, Y_2^{(m)}(\theta, \varphi)\, Y_2^{(m')*}(\theta, \varphi) = \delta_{mm'}\,. \tag{5.5}$$

This can also be verified directly by using the angular average relation

$$\int \frac{dn}{4\pi}\, n_\alpha n_\beta n_\gamma n_\delta \equiv t^{(4)} = \frac{1}{15}\, (\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} + \delta_{\alpha\gamma}\delta_{\beta\delta}) \tag{5.6}$$

and calculating

$$\int dn Y_2^{(m)}(\boldsymbol{n}, \hat{\boldsymbol{q}})\, Y_2^{(m')*}(\boldsymbol{n}, \hat{\boldsymbol{q}})$$
$$= \frac{15}{2}\left[\int \frac{dn}{4\pi}\, n_\alpha n_\beta n_\gamma n_\delta\right] \varepsilon_{\alpha\beta}^{(m)}(\hat{\boldsymbol{q}})\, \varepsilon_{\gamma\delta}^{(m')*}(\hat{q}) = \mathrm{tr}\left(\varepsilon^{(m)}(\hat{\boldsymbol{q}})\, \varepsilon^{(m')*}(\hat{\boldsymbol{q}})\right) = \delta_{mm'} \tag{5.7}$$

due to the orthonormality relation (2.18).
The super-field $\Phi(\boldsymbol{n}, \boldsymbol{x})$ can now be employed to construct the free energy (2.1)—(2.3). Let us start with the invariants I_3, I_4, I_5. Then, certainly,

$$\int dx \int dn\Phi^2(\boldsymbol{n}, \boldsymbol{x}) = \int dx\, \frac{15}{2}\, t^{(4)}_{\alpha\beta\gamma\delta} Q_{\alpha\beta} Q_{\gamma\delta} = \int dx \left(\mathrm{tr}\, Q^2 + \frac{1}{2}\,(\mathrm{tr}\, Q)^2\right) = I_2. \tag{5.8}$$

The cubic energy can be obtained from

$$\int dx\, dn\, \Phi^3(\boldsymbol{n}, \boldsymbol{x})$$
$$= \int dx \left[\int \frac{dn}{4\pi}\, n_{\alpha_1} \cdots n_{\alpha_6}\right) 4\pi \left(\frac{15}{8\pi}\right)^{3/2} Q_{\alpha_1\alpha_2} Q_{\alpha_3\alpha_4} Q_{\alpha_5\alpha_6}$$
$$= \int dx\, \frac{1}{7}\, [\delta_{\alpha_1\alpha_2} t^{(4)}_{\alpha_3\alpha_4\alpha_5\alpha_6} + \delta_{\alpha_1\alpha_3} t^{(4)}_{\alpha_2\alpha_4\alpha_5\alpha_6} + \delta_{\alpha_1\alpha_4} t^{(4)}_{\alpha_2\alpha_3\alpha_5\alpha_6} + \delta_{\alpha_1\alpha_5} t^{(4)}_{\alpha_2\alpha_3\alpha_4\alpha_6} + \delta_{\alpha_1\alpha_6} t^{(4)}_{\alpha_2\alpha_3\alpha_4\alpha_5}]$$
$$\times\, 4\pi \left(\frac{15}{8\pi}\right)^{3/2} Q_{\alpha_1\alpha_2} Q_{\alpha_3\alpha_4} Q_{\alpha_5\alpha_6}$$
$$\equiv \int dx\, t^{(6)}_{\alpha_1\cdots\alpha_6}\, 4\pi \left(\frac{15}{8\pi}\right)^{3/2} Q_{\alpha_1\alpha_2} Q_{\alpha_3\alpha_4} Q_{\alpha_5\alpha_6}$$
$$= \int dx\, 4\pi \left(\frac{15}{8\pi}\right)^{3/2} \frac{1}{105}\left(8\, \mathrm{tr}\,(Q^3) + 6\, \mathrm{tr}\,(Q^2)\, \mathrm{tr}\, Q + (\mathrm{tr}\, Q)^3\right) = 4\pi \left(\frac{15}{8\pi}\right)^{3/2} \frac{8}{105}\, I_3. \tag{5.9}$$

Similarly, the quartic energy follows from

$$\int dx\, dn\, \Phi^4(\boldsymbol{n}, \boldsymbol{x})$$
$$= \int dx \left[\int \frac{dn}{4\pi}\, n_{\alpha_1} \cdots n_{\alpha_8}\right] 4\pi \left(\frac{15}{8\pi}\right)^2 Q_{\alpha_1\alpha_2} \cdot \cdots \cdot Q_{\alpha_7\alpha_8}$$
$$= \int dx\, \frac{1}{9}\, [\delta_{\alpha_1\alpha_2} t^{(6)}_{\alpha_3\cdots\alpha_8} + \cdots + \delta_{\alpha_1\alpha_8} t^{(6)}_{\alpha_2\cdots\alpha_7}]\, 4\pi \left(\frac{15}{8\pi}\right)^2 Q_{\alpha_1\alpha_2} \cdot \cdots \cdot Q_{\alpha_7\alpha_8}$$
$$\equiv \int dx\, 4\pi \left(\frac{15}{8\pi}\right)^2 \frac{1}{3\cdot 5\cdot 7\cdot 9}$$
$$\times\, [48\, \mathrm{tr}\,(Q^4) + 32\, \mathrm{tr}\,(Q^3)\, \mathrm{tr}\, Q + 12\,(\mathrm{tr}\, Q^2)^2 + 12\, \mathrm{tr}\,(Q^2)\,(\mathrm{tr}\, Q)^2 + (\mathrm{tr}\, Q)^4]$$
$$= 4\pi \left(\frac{15}{8\pi}\right)^2 \frac{36}{945}\, I_4 \tag{5.10}$$

where we have taken advantage of the identity (2.5). The derivative terms can be obtained along the same lines: The c term is directly

$$\int dn\, \partial\Phi\, \partial\Phi = \partial_\alpha Q_{\beta\gamma}\, \partial_\alpha Q_{\beta\gamma}. \tag{5.11}$$

For the remaining two pieces we introduce the spin operator in the $\boldsymbol{n}$ representation

$$\boldsymbol{S} \equiv -i\boldsymbol{n} \times \partial_n . \tag{5.12}$$

Then the d term is found as

$$-i \int dn \Phi \boldsymbol{S}\, \partial \Phi = -2\varepsilon_{\alpha\beta\gamma} Q_{\alpha\delta}\, \partial_\gamma Q_{\beta\delta} . \tag{5.13}$$

Finally, by using $\boldsymbol{S}\partial$ twice we obtain

$$\int dn (\boldsymbol{S}\partial\Phi)^2 = 4(\partial_\alpha Q_{\beta\gamma}\, \partial_\alpha Q_{\beta\gamma} - 6\partial_\alpha Q_{\beta\gamma}\, \partial_\beta Q_{\alpha\gamma}) \tag{5.14}$$

which combines b and c terms. Thus we arrive at the following alternative way of writing our free energy (2.1)—(2.3) in terms of the super-field

$$F_2 = \int dx\, dn \left(\frac{a}{2} \Phi^2 + \frac{b + 2c/3}{2} (\partial\Phi)^2 - \frac{c}{12} (\boldsymbol{S}\, \partial\Phi)^2 - id\Phi \boldsymbol{S}\, \partial\Phi \right) \tag{5.15}$$

$$F_3 = \frac{\lambda_3}{3!} \frac{105}{8} \frac{2}{15} \sqrt{\frac{8\pi}{15}} \int dx\, dn \Phi^3 \tag{5.16}$$

$$F_4 = \frac{\lambda_4}{4!} \frac{945}{36} \frac{2}{15} \frac{8\pi}{15} \int dx\, dn \Phi^4 \tag{5.17}$$

which, may be compared with HS.

$$\frac{a}{2} = \alpha_0 \tag{5.18}$$

$$\frac{\lambda_3}{3!} = \sqrt{\frac{5}{\pi}} \frac{1}{7} \beta_0 \equiv \beta \sqrt{6} \tag{5.19}$$

$$\frac{\lambda_4}{4!} = \frac{15}{28\pi} \gamma_0 \equiv \gamma . \tag{5.20}$$

In principle, the calculation of the free energy in terms of Φ fields should, of course, give the same results as ours. But it proceeds along somewhat different intermediate steps. For example, the cubic contribution of $\varphi^{(2)}$ involves the integral

$$\int dn\, Y_2^{(2)}(\boldsymbol{n}, \hat{\boldsymbol{q}}_1)\; Y_2^{(2)}(\boldsymbol{n}, \hat{\boldsymbol{q}}_2)\; Y_2^{(2)}(\boldsymbol{n}, \hat{\boldsymbol{q}}_3) . \tag{5.21}$$

If $D^2_{mm'}(\boldsymbol{l}, \boldsymbol{q})$ denotes the rotation matrix from $\hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}, \hat{\boldsymbol{z}}$ to the $\hat{\boldsymbol{q}}$ dependent frame $\boldsymbol{l}^r, \boldsymbol{l}^i, \hat{\boldsymbol{q}}$, this can be written as

$$\left[\int dn\, Y_2^{m_1}(\boldsymbol{n})\; Y_2^{m_2}(\boldsymbol{n})\; Y_2^{m_3}(\boldsymbol{n})\right] D^2_{m_1 2}(\boldsymbol{l}_1, \hat{\boldsymbol{q}}_1)\; D^2_{m_2 2}(\boldsymbol{l}_2, \hat{\boldsymbol{q}}_2)\; D^2_{m_3 2}(\boldsymbol{l}_3, \hat{\boldsymbol{q}}_3) . \tag{5.22}$$

The remaining angular average over ordinary spherical harmonics leads to $3j$ symbols:

$$\sqrt{\frac{5^3}{4\pi}} \begin{pmatrix} 2 & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 2 & 2 & 2 \\ m_1 & m_2 & m_3 \end{pmatrix} D^2_{m_1 2}(\boldsymbol{l}_1, \hat{\boldsymbol{q}}_1)\; D^2_{m_2 2}(\boldsymbol{l}_2, \hat{\boldsymbol{q}}_2)\; D^2_{m_3 2}(\boldsymbol{l}_3, \hat{\boldsymbol{q}}_3) . \tag{5.23}$$

This is the expression which has to be evaluated in HS for each triangle instead of our simple scalar products of polarization vectors (3.29). A certain simplification may be reached by a common rotation which brings $\boldsymbol{l}_3$, into the $\hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}, \hat{\boldsymbol{z}}$ direction. However, we have found it extremely hard to keep track of all relative phases. Since HS do not report any details of their calculations while changing results as time proceeds it appears that they have had the same difficulty. The direct assignment of polarization vectors as in our Fig. 3, however, is quite simple and takes care of all relative phases when inserted into (3.29). We leave it up to the reader to identify the correct terms in HS's free energy.

VI. Summary

We have performed an systematic investigation of the free energies of several lattice textures in cholesteric liquid crystals. The phase diagram shows that for large cholestericity α, the system passes through a region of bcc texture before entering the cholesteric phase. For lower α, an interval of planar hexagonal texture appears inserted into the bcc phase which should be observables via its optical unisotropy. Finally, for even smaller $\alpha < 0.3$, it is the hexagonal texture which sets in first and from which the system passes directly into the cholesteric phase without intermediate bcc. The appearence of the hexagonal phase for low cholestericity would be an important confirmation of this type of calculation.

No theoretical indication has been found for a second optically isotropic phase. Thus, the experimentally observed transition within the blue phase remains unexplained at this level of approximation.

A second fact which the present calculation cannot account for is the temperature dependence of the wavelength in the reflection of circularly polarized light [*1*].

The inclusion of higher harmonics will be necessary in order to accomodate either of these phenomena [*7*].

It is hoped that this work may supply a useful technical framework for other more detailed considerations.

Note added in proof: After completion of this work a paper appeared by D. L. Johnson, J. H. Flack and P. V. Crooker with very beautiful Bragg reflexes of the bcc type for both blue phases as well as more details on the temperature dependence of the textural lattice [*8*].

Acknowledgement

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Appendix

Scalar Products for Icosahedral Polarization Vectors

From the vectors (4.25) we obtain

$$l_{i+n}l_i = l_{n+1}l_1 = \frac{1}{2}\{b^2[\cos(2n+1)\alpha\cos\alpha + \sin(2n+1)\alpha\sin\alpha]$$

$$+ a^2 \mp \sin(2n+1)\alpha\sin\alpha \mp \cos(2n+1)\alpha\cos\alpha + i(\pm ib + b)$$

$$-i(\pm b - b)[\sin(2n+1)\alpha\cos\alpha - \cos(2n+1)\alpha\sin\alpha]\}$$

$$= \frac{1}{2}(b^2\cos 2n\alpha + a^2 \mp \cos 2n\alpha) + \begin{Bmatrix} 0 \\ ib\sin 2n\alpha \end{Bmatrix}$$

$$= \frac{a^2}{2}(1 - \cos 2n\alpha) + \begin{Bmatrix} 0 \\ \cos 2n\alpha + ib\sin 2n\alpha \end{Bmatrix} \tag{A.1}$$

where here and in the following equations the lower alternative refers to the right hand factor (here l_i) being complex conjugate. Using

$$a^2 = \frac{\sqrt{5}+1}{2\sqrt{5}}, \quad \cos 2\alpha = \frac{\sqrt{5}-1}{4}, \quad \cos 5\alpha = -\cos\alpha = -\frac{\sqrt{5}+1}{4},$$
$$\cos 6\alpha = -\cos\alpha, \ \cos 8\alpha = \cos 2\alpha \tag{A.2}$$

we see directly for $n = 0, 1, \ldots, 4$:

$$l_{i+n}l_i = 0, \ \frac{1}{4}, \ (3+\sqrt{5})/8, \ (3+\sqrt{5})/8, \ \frac{1}{4}. \tag{A.3}$$

If l_i is complex conjugate, a little more work is necessary. With

$$b^2 = \frac{\sqrt{5}-1}{2\sqrt{5}}, \quad \sin 2\alpha = \frac{\sqrt[4]{5}}{2}\sqrt{\frac{\sqrt{5}+1}{2}}, \quad \sin 4\alpha = \sin\alpha = \frac{\sqrt[4]{5}}{2}\sqrt{\frac{\sqrt{5}-1}{2}},$$
$$\sin 6\alpha = -\sin\alpha \qquad \sin 8\alpha = -\sin 2\alpha \tag{A.4}$$

we evaluate:

$$l_i l_i^* = 1$$

$$l_{i+1}l_i^* = \frac{a^2}{2}(1-\cos 2\alpha) + \cos 2\alpha + ib\sin 2\alpha = \frac{1}{2}\left(\frac{1}{2} + \frac{\sqrt{5}-1}{2} + i\right)$$
$$= \frac{3}{4}\, e^{i\arctan 2/\sqrt{5}}$$

$$l_{i+2}l_i^* = \frac{a^2}{2}(1+\cos\alpha) - \cos\alpha + ib\sin\alpha = \frac{1}{2}\left(\frac{3+\sqrt{5}}{4} - \frac{\sqrt{5}+1}{2} + i\,\frac{\sqrt{5}-1}{2}\right)$$
$$= -\frac{\sqrt{5}-1}{8}\sqrt{5}\, e^{-i\arctan 2} \tag{A.5}$$

$$l_{i+3}l_i^* = \frac{a^2}{2}(1 + \cos\alpha) - \cos\alpha - ib\sin\alpha = (l_{i+2}l_i^*)^*$$
$$l_{i+4}l_i^* = \frac{a^2}{2}(1 - \cos 2\alpha) + \cos 2\alpha - ib\sin 2\alpha = (l_{i+1}l_i^*)^*. \tag{A.5}$$

The scalar products among m vectors are very simple:

$$m_{i+n}m_i = m_n m_0 = \frac{1}{2}(\cos 2n\alpha \mp 1)$$
$$= \begin{Bmatrix} 0 & -\frac{5-\sqrt{5}}{8} & -\frac{5+\sqrt{5}}{8} & -\frac{5+\sqrt{5}}{8} & \frac{5-\sqrt{5}}{8} \\ 1 & \frac{3+\sqrt{5}}{8} & \frac{3-\sqrt{5}}{8} & \frac{3-\sqrt{5}}{8} & \frac{3+\sqrt{5}}{8} \end{Bmatrix}. \tag{A.6}$$

For the n vectors we can take the same formulas as for the l's, except that we have to substitute $b \to a$ and $a \to -b$. Therefore

$$n_{i+n}n_i = \frac{b^2}{2}(1 - \cos 2n\alpha) + \begin{Bmatrix} 0 \\ \cos 2n\alpha + ia\sin 2n\alpha \end{Bmatrix}. \tag{A.7}$$

The upper elements are simply $b^2/a^2 = (3 - \sqrt{5})/2$ times the corresponding $l_{i+n}l_i$, i.e.

$$n_{i+n}n_i = 0\,,\ \frac{3-\sqrt{5}}{8},\ \frac{1}{4}\,\frac{1}{4},\ \frac{3-\sqrt{5}}{8}. \tag{A.8}$$

The lower parts need some calculation:

$$n_i n_i^* = 1$$
$$n_{i+1}n_i^* = \frac{b^2}{2}\big((1 - \cos 2\alpha) + \cos 2\alpha + ia\sin 2\alpha\big) = \frac{1}{2}\left(\frac{3-\sqrt{5}}{4} + \frac{\sqrt{5}-1}{2} + i\,\frac{\sqrt{5}+1}{2}\right)$$
$$= \frac{\sqrt{5}+1}{8}\sqrt{5}\, e^{i\arctan 2}$$
$$n_{i+2}n_i^* = \frac{b^2}{2}(1 + \cos\alpha) - \cos\alpha + ia\sin\alpha = \frac{1}{2}\left(\frac{1}{2} - \frac{\sqrt{5}+1}{2} + \frac{i}{2}\right)$$
$$= -\frac{3}{4}\, e^{-i\arctan 2/\sqrt{5}} \tag{A.9}$$
$$n_{i+3}n_i^* = (n_{i+2}n_i^*)^*$$
$$n_{i+4}n_i^* = (n_{i+1}n_i^*)^*.$$

Let us now turn to the mixed products.

$$l_{i+n}m_i = l_n m_0 = \frac{1}{2}[b\cos(2n-1)\alpha \mp ia + i\sin(2n-1)\alpha]. \tag{A.10}$$

Here we use

$$a = \frac{1}{2\sin\alpha} = \frac{\cos\alpha}{\sin 2\alpha}, \quad \cos 3\alpha = \cos 7\alpha = -\cos 2\alpha = -\frac{\sqrt{5}-1}{4}, \quad \cos 5\alpha = -1, \tag{A.11}$$

$$\sin 3\alpha = -\sin 7\alpha = \sin 2\alpha = \frac{\sqrt{5}}{2}\,a, \quad \sin 5\alpha = 0$$

and find

$$\begin{aligned} l_i m_i &= \frac{1}{2}(b\cos\alpha \mp ia - i\sin\alpha) \\ &= \frac{1}{2}\sqrt{b^2\cos^2\alpha + (a \pm \sin\alpha)^2}\exp\left(-i\arctan\frac{\sin\alpha \pm a}{b\cos\alpha}\right) \\ &= \frac{1}{2}(1 \pm a\sin\alpha)\exp\left(-i\arctan\frac{2\sin^2\alpha \pm 1}{b\sin 2\alpha}\right) \\ &= \frac{1}{2}\left(1 \pm \frac{1}{2}\right)\exp\left(-i\arctan\begin{Bmatrix}4 - 2\cos 2\alpha \\ -2\cos 2\alpha\end{Bmatrix}\right) = \begin{cases}\dfrac{1}{4}\exp\left(-i\arctan\dfrac{9-\sqrt{5}}{2}\right) \\ \dfrac{3}{4}\exp\left(i\arctan\dfrac{\sqrt{5}-1}{2}\right)\end{cases} \end{aligned} \tag{A.12}$$

$$l_{i+1}m_i = \frac{1}{2}(b\cos\alpha \mp ia + i\sin\alpha) = (l_i n_i^*)^*$$

$$\begin{aligned} l_{i+2}m_i &= \frac{1}{2}(-b\cos 2\alpha \mp ia + i\sin 2\alpha) \\ &= -\frac{1}{2}\sqrt{b^2\cos^2 2\alpha + (a \mp \sin^2\alpha)^2}\exp\left(-i\arctan\frac{\sin 2\alpha \mp a}{b\cos 2\alpha}\right) \\ &= -\frac{1}{2}(1 \mp a\sin 2\alpha)\exp\left(-i\arctan 2\,\frac{\sin^2 2\alpha \mp \cos\alpha}{\cos 2\alpha}\right) \\ &= \begin{cases} -\dfrac{3-\sqrt{5}}{8}\exp\left(-i\arctan\dfrac{\sqrt{5}-1}{2}\right) \\ -\dfrac{5+\sqrt{5}}{8}\exp\left(-i\arctan\dfrac{5\sqrt{5}+11}{2}\right)\end{cases} \end{aligned}$$

$$l_{i+3}m_i = \frac{1}{2}(-b \mp ia) = -\frac{1}{2}\exp\left(\pm i\arctan\frac{\sqrt{5}+1}{2}\right)$$

$$l_{i+4}m_i = \frac{1}{2}(-b\cos 2\alpha \mp ia - i\sin 2\alpha) = (l_{i+2}n_i^*)^*.$$

By changing $b \to a$ and $a \to -b$ we recover

$$n_{i+n}m_i = \frac{1}{2}[a\cos(2n-1)\alpha \pm ib + i\sin(2n-1)\alpha] \tag{A.13}$$

such that

$$n_i m_i = \frac{1}{2}(1 \mp b \sin\alpha) \exp\left(-i \arctan \frac{\sin\alpha \mp b}{a\cos\alpha}\right)$$

$$= \begin{cases} \dfrac{5-\sqrt{5}}{8} \exp\left(-i \arctan \dfrac{5\sqrt{5}-11}{2}\right) \\ \dfrac{3+\sqrt{5}}{8} \exp\left(-i \arctan \dfrac{\sqrt{5}+1}{2}\right) \end{cases}$$

$$n_{i+1} m_i = (n_i m_i{}^*)^*$$

$$n_{i+2} n_i = -\frac{1}{2}(1 \pm b \sin 2\alpha) \exp\left(-i \arctan \frac{\sin 2\alpha \pm b}{a \cos 2\alpha}\right)$$

$$= \begin{cases} -\dfrac{3}{4} \exp\left(-i \arctan \dfrac{9+\sqrt{5}}{2}\right) \\ -\dfrac{1}{4} \exp\left(-i \arctan \dfrac{\sqrt{5}+1}{2}\right) \end{cases} \tag{A.14}$$

$$n_{i+3} m_i = \frac{1}{2}(-a \pm ib) = -\frac{1}{2} \exp\left(\mp i \arctan \frac{\sqrt{5}-1}{2}\right)$$

$$n_{i+4} m_i = (n_{i+2} m_i{}^*)^*.$$

Finally, we may calculate

$$\begin{aligned} l_{i+n} n_i = l_{n+1} n_1 = \frac{1}{2} \{ & ba[\cos(2n+1)\alpha\cos\alpha + \sin(2n+1)\alpha\sin\alpha] \\ & -ba \mp [\sin(2n+1)\alpha\sin\alpha + \cos(2n+1)\alpha\cos\alpha] \\ & + i(a \mp b)[\sin(2n+1)\alpha\cos\alpha - \cos(2n+1)\alpha\sin\alpha]\} \end{aligned} \tag{A.15}$$

such that we find, with

$$b = \frac{\cos 2\alpha}{\sin\alpha}, \quad ba = \frac{1}{\sqrt{5}}, \quad ba(\cos\alpha + 1) = \cos\alpha, \quad (a+b)\sin\alpha = \cos\alpha, \tag{A.16}$$

the scalar products between l and n:

$$l_i n_i = \mp \frac{1}{2}$$

$$\begin{aligned} l_{i+1} n_i &= \frac{1}{2}[ba(\cos 2\alpha - 1) \mp \cos 2\alpha + i(a \mp b)\sin 2\alpha] \\ &= \frac{1}{2}\left[-\mathrm{b}\sin\alpha \mp \cos 2\alpha + i\left(\cos\alpha \mp \frac{1}{2}\right)\right] \\ &= \begin{Bmatrix} -\cos 2\alpha + i\,\dfrac{\cos\alpha - 1/2}{2} \\ i\,\dfrac{\cos\alpha + 1/2}{2} \end{Bmatrix} = \begin{cases} -\dfrac{\sqrt{5}-1}{8}\sqrt{5}\, e^{-i\arctan 1/2} \\ i\,\dfrac{3+\sqrt{5}}{8} \end{cases} \end{aligned} \tag{A.17}$$

$$l_{i+2}n_i = \frac{1}{2}\,[ba(-\cos\alpha - 1) \pm \cos\alpha + i(a \mp b)\sin\alpha]$$

$$= \begin{Bmatrix} \frac{i}{2}\,(a-b)\sin\alpha \\ -\cos\alpha + \frac{i}{2}\,(a+b)\sin\alpha \end{Bmatrix} = \begin{cases} i\,\frac{3-\sqrt{5}}{5} \\ -\frac{5+\sqrt{5}}{8}\,e^{-i\arctan 1/2} \end{cases}$$

$$l_{i+3}n_i = \frac{1}{2}\,[ba(-\cos\alpha - 1) \pm \cos\alpha - i(a \mp b)\sin\alpha] = (l_{i+2}n_i)^*$$

$$l_{i+4}n_i = \frac{1}{2}\,[ba(\cos 2\alpha - 1) \mp \cos 2\alpha - i(a \mp b)\sin 2\alpha] = (l_{i+1}n_i)^*.$$

The results can be brought to a more symmetric form by multiplying all m vectors with a phase factor

$$m_i \to m_i \exp\left(i\arctan\frac{\sqrt{5}-1}{2}\right) \tag{A.18}$$

and by changing all n vectors according to

$$n_i \to -in_i. \tag{A.19}$$

This has the effect of making all real parts of the polarisation vectors point in radial direction out of the icosahedron. The final form of all scalar products are shown on Table 2. The simplification follows from these phase relations:

$$\begin{aligned} \arctan\frac{\sqrt{5}-1}{2} + \arctan\frac{\sqrt{3}+1}{2} &= \frac{\pi}{2}, \\ \arctan\frac{\sqrt{5}-1}{2} - \arctan\frac{5\sqrt{5}-11}{2} &= \frac{\pi}{2} - \arctan 2, \\ \arctan\frac{\sqrt{5}-1}{2} - \arctan\frac{9+\sqrt{5}}{2} &= -\frac{\pi}{2} + \arctan\frac{2}{\sqrt{5}}, \\ \arctan\frac{\sqrt{5}-1}{2} + \arctan\frac{5\sqrt{5}+11}{2} &= \pi - \arctan 2. \end{aligned} \tag{A.20}$$

Erratum

Polarization Phenomena in Elastic Electron-Proton Scattering: by M. Kobayashi, Fortschritte der Physik 27 (1979) 463)

The signs of $K^{(i)}_{PK}$ with $i = 1, 2$ should be minus instead of plus in Eqs. (28) and (29). Corresponding to this correction, Fig. 10 should be replaced by the new one the paragraph (c) at the end of Subsection E of Section 3 should be replaced by the following:
"The other types of polarization transfer in the scattering plane are smaller than one percent at s higher than 2 GeV^2, except $A_t{}^{(2)}$ and $R_t{}'^{(1)}$ with involve the longitudinal polarization of electrons in the initial and final states respectively. $A_t{}^{(2)}$ and $R_t{}'^{(1)}$ are significant at medium angles ($\theta = 60° \sim 120°$) and is as large as $0.1 \sim 0.2$ at high energies."
The author would like to thank Drs. C. E. Carlson and F. L. Gross of The College of William and Mary for pointing-out an erroneous feature in Fig. 10, which has led the author to correct in the above error.

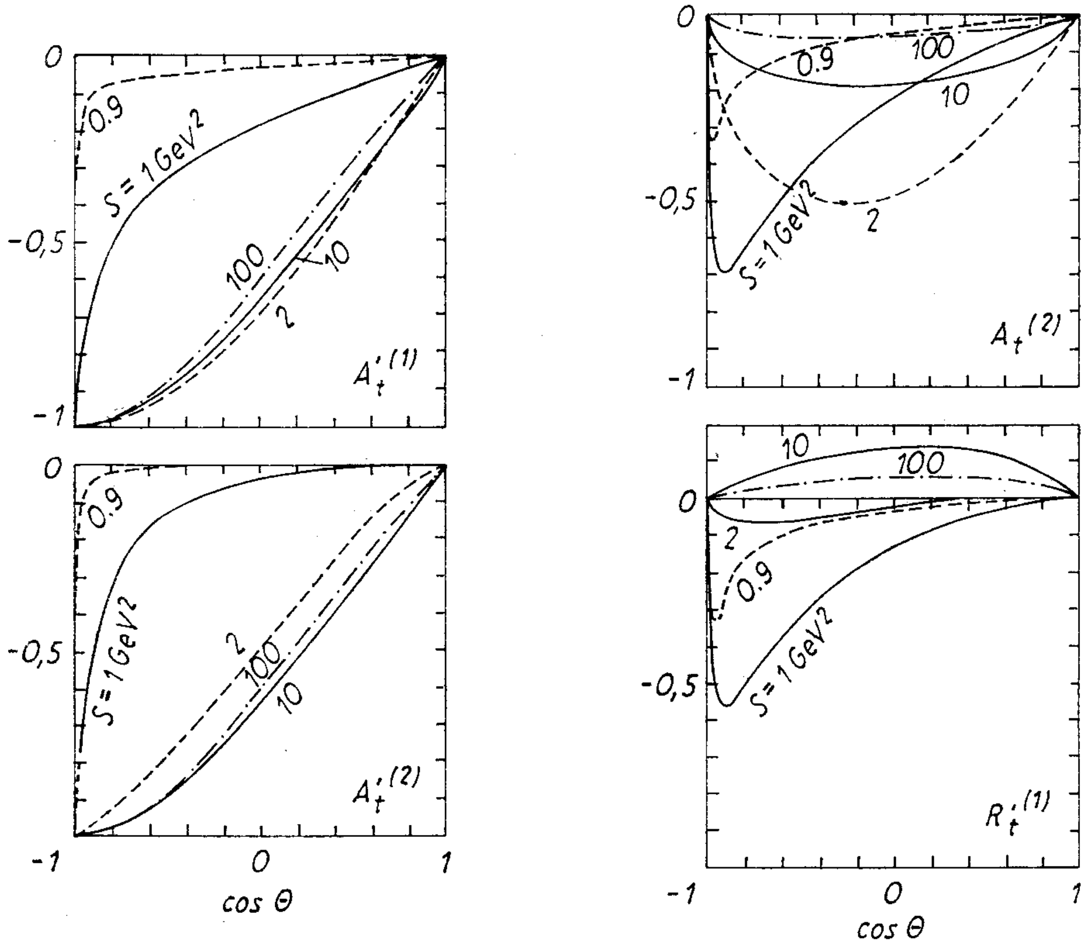

Fig. 10. Polarization transfer parameters referred to the laboratory system and evaluated in the one photon exchange approximation. A_t, A_t' and R_t'. θ: the CMS scattering angle.