

Theory of electrostriction of liquid-crystalline blue phases I and II

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For the cubic lattices of the liquid-crystalline blue phases I and II electrostriction has been observed recently, i.e., a distortion of the crystal by an electric field in quadratic order. Here we investigate the characterizing fourth-order electrostriction tensor. Because electrostriction results from a competition between electric and elastic forces, the tensor is the quotient of the elasto-optic and the elastic tensor. The latter are derived from the Landau-de Gennes theory of phase transitions in liquid crystals within the model of rigid helices and are expressed as functionals of the alignment tensor for the undistorted system. Comparison is made with experimental data. The limitations of the model of rigid helices are discussed.

In the liquid-crystalline blue phases I and II (BP I and II) the molecular axes align to form a periodic long-range orientational order. The unit cell is cubic and contains about 10^7 molecules. Standard methods of crystallography, such as Bragg reflection and Kossel diagrams, have been applied to investigate this periodic structure with light in the *visible* range. Under the influence of a weak electric field, shifts in the Kossel diagrams and of the wavelengths of the Bragg peaks have been observed [1-4]. The variations are due to a distortion of the unit cell by the electric field. The process is called electrostriction; its characteristic measurable quantity is the fourth-order electrostriction tensor \mathbf{R} .

For the description of the orientational order of the

molecules the traceless and symmetric alignment tensor \mathbf{Q} is used, which is approximately proportional to the anisotropic part of the dielectric tensor [5]. The tensor field $\mathbf{Q}(\mathbf{r})$ is expanded into a Fourier series where the Fourier coefficients are written in a spherical tensor basis $\{\mathbf{M}_m(\mathbf{k})\}$ [6]:

$$\mathbf{Q}(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{m=-2}^{m=2} Q_m(\mathbf{k}) \mathbf{M}_m(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}).$$

The free enthalpy of blue phases in an applied homogeneous electric field \mathbf{E} is composed of the free enthalpy f^{LG} according to Landau-de Gennes theory and an electric free enthalpy f^E . It is expressed in scaled units [7]:

$$\begin{aligned} f &= f^{\text{LG}} + f^E = f_2^{\text{LG}} + f_3^{\text{LG}} + f_4^{\text{LG}} + f^E, \\ f_2^{\text{LG}} &= \frac{1}{2V} \int d^3\mathbf{r} \left(\frac{t}{2} Q_{ij}^2 + \frac{\kappa^2}{2q_c^2} Q_{ij,l}^2 + \frac{c_2}{c_1} \frac{\kappa^2}{2q_c^2} Q_{ij,i} Q_{ij,l} - \frac{\kappa^2}{q_c} \epsilon_{ijkl} Q_{in} Q_{ln,j} \right), \\ f_3^{\text{LG}} &= -\frac{\sqrt{6}}{V} \int d^3\mathbf{r} \text{tr} \mathbf{Q}^3, \\ f_4^{\text{LG}} &= \frac{1}{V} \int d^3\mathbf{r} (\text{tr} \mathbf{Q}^2)^2, \\ f^E &= -\delta \sqrt{\frac{3}{2}} \frac{1}{V} \int d^3\mathbf{r} \mathbf{Q} \cdot (\mathbf{E} \otimes \mathbf{E}) \\ &= -\delta \sqrt{\frac{3}{2}} \mathbf{Q}_0 \cdot (\mathbf{E} \otimes \mathbf{E}). \end{aligned} \tag{1}$$

Characteristic parameters are the chirality κ , the reduced temperature t , and the wave number q_c of the cholesteric helix. By ϵ_{ijkl} we denote the components of the Levi-Civita tensor. f^E contains the simplest SO(3) invariant, which can be constructed by \mathbf{Q} and \mathbf{E} . \mathbf{Q}_0 is the homogeneous part ($\mathbf{k} = \mathbf{0}$) of the order parameter. Symmetry makes it vanish in the *cubic* blue phases. The coefficient δ includes proportionality factors both between the order parameter and the anisotropic part of

the dielectric tensor as well as between the applied electric field and the internal electric field. This fact can be proven by comparing f^E with the electric-field term of the Maxwell theory.

The quantity, which is measured in field experiments and which is therefore defined on a *macroscopic* scale, is the electrostriction tensor \mathbf{R} . It consists of an elastic and an electric part. In this paper we develop an analytical *mesoscopic* theory by expressing both contributions to

\mathbf{R} in terms of the undistorted order parameter field $\mathbf{Q}(\mathbf{r})$ that describes the orientational order of the molecules inside the unit cell on a mesoscopic scale.

We start with a review of the definition and of experimental results for the electrostriction tensor \mathbf{R} . The distortion of the cubic unit cell of the BP I and II under the influence of an electric field is characterized by the strain tensor ϵ expanded into a power series of the applied electric field \mathbf{E} :

$$\epsilon = \mathbf{R}(\mathbf{E} \otimes \mathbf{E}), \quad \epsilon_{ij} = R_{ijkl} E_k E_l = \epsilon_{ji}.$$

The linear piezoelectric term vanishes due to the cubic point symmetry of the undistorted BP I and II. For the same reason the electrostriction tensor \mathbf{R} has only three independent components, denoted by

$$R_1 = R_{1111}, \quad R_2 = R_{1122}, \quad R_3 = 2R_{2323}.$$

(In the following we deal with several fourth-order tensors of cubic point symmetry whose three independent components are denoted accordingly.) When the volume

of the unit cell is conserved, and hence $\text{tr} \epsilon = 0$, then the following relation must be fulfilled:

$$R_1 = -2R_2.$$

Two groups [1–4] have carried out electrostriction measurements using cholesteric mixtures with a nematic component of a high dielectric anisotropy $\Delta\kappa = \kappa_{\parallel} - \kappa_{\perp}$. Kitzerow and co-workers [3, 4] found a conservation of volume of the unit cell, whereas Porsch and Stegemeyer [1, 2] measured $R_1 \approx -2.6R_2$. The ratio R_1/R_3 has been found in a range between 0.4 and 1.0 for BP II and between -0.1 and -0.4 for BP I. The signs of the electrostriction coefficients R_i depend in a characteristic way on the sign of the dielectric anisotropy (see Table I). The negative sign of R_1/R_3 in BP I is denoted “anomalous electrostriction.”

The theory of the electrostriction tensor in cubic blue phases is usually formulated on a *macroscopic* scale by a free enthalpy in scaled units [in accordance with Eq. (1)] which is expanded into a power series of the strain tensor ϵ and the applied electric field \mathbf{E} [8]:

$$F(\epsilon, \mathbf{E}) = \frac{1}{2} \lambda \cdot (\epsilon \otimes \epsilon) - \sqrt{\frac{3}{2}} [\kappa_0 E^2 + \mathbf{p} \cdot (\mathbf{E} \otimes \mathbf{E} \otimes \epsilon) + \frac{1}{6} \chi^{(4)} \cdot (\mathbf{E} \otimes \mathbf{E} \otimes \mathbf{E} \otimes \mathbf{E})]. \quad (2)$$

The first term, the elastic free enthalpy, takes into account the distortion of the lattice of the BP I and II. The stability conditions require that

$$\lambda_1 - \lambda_2 > 0, \quad \lambda_1 + 2\lambda_2 > 0, \quad \lambda_3 > 0.$$

The remaining terms lead to the dielectric tensor

$$\kappa = -\frac{1}{\sqrt{6}} \frac{\partial^2 F}{\partial \mathbf{E} \partial \mathbf{E}} = \kappa_0 \mathbf{1} + \mathbf{p} \epsilon + \chi^{(4)} (\mathbf{E} \otimes \mathbf{E}).$$

It is composed of a linear isotropic contribution $\kappa_0 \mathbf{1}$, an *elasto-optic* contribution $\mathbf{p} \epsilon$, which describes the coupling between the strain tensor ϵ and the electric field \mathbf{E} , and a nonlinear dielectric contribution. If we assume that any distortion ϵ of the blue phase unit cell only changes the orientational order and not the density of the molecules (see below), then the isotropic part of κ ($\text{tr} \kappa = \kappa_{ii}$) is constant. Therefore also the isotropic part of the elasto-optic contribution ($\text{tr} \mathbf{p} \epsilon$) must vanish which implies the important relation for the elasto-optic coefficients:

$$p_1 = -2p_2. \quad (3)$$

To calculate the equilibrium strain tensor ϵ we minimize $F(\epsilon, \mathbf{E})$ for a given electric field \mathbf{E} :

$$\left. \frac{\partial F}{\partial \epsilon} \right|_{\mathbf{E}} = \lambda \epsilon - \sqrt{\frac{3}{2}} \mathbf{p} (\mathbf{E} \otimes \mathbf{E}) = 0$$

and obtain the electrostriction tensor \mathbf{R} :

$$\epsilon = \mathbf{R}(\mathbf{E} \otimes \mathbf{E}), \quad \mathbf{R} = \sqrt{\frac{3}{2}} \lambda^{-1} \mathbf{p},$$

in terms of the tensor λ^{-1} of the elastic compliances and the elasto-optic tensor \mathbf{p} . Obviously electrostriction results from a competition between elastic (λ) and electric (\mathbf{p}) forces. The relation $p_1 = -2p_2$ leads to the electrostriction coefficients

$$R_1 = \sqrt{\frac{3}{2}} \frac{p_1}{\lambda_1 - \lambda_2} = -2R_2, \quad (4)$$

$$R_3 = \sqrt{\frac{3}{2}} \frac{p_3}{\lambda_3}. \quad (5)$$

From these equations it is clear that the sign of the R_i depends on the sign of the p_i because the elastic constants have to satisfy the stability conditions above. Further, we conclude that a constant density of the molecules [$p_1 = -2p_2$, Eq. (3)] results in a conservation of volume of the unit cell ($R_1 = -2R_2$). This statement is trivial for a crystal but not for the blue phases where the unit cell is not formed by the centers of mass of the molecules but by the periodicity of their orientational order.

In a first article on the theory of electrostriction, Lubin

TABLE I. The characteristic signs of the electrostriction coefficients depending on the sign of $\Delta\kappa$.

	$\Delta\kappa > 0$		$\Delta\kappa < 0$	
	BP I	BP II	BP I	BP II
R_1	–	+	+	–
R_2	+	–	–	+
R_3	+	+	–	–

and Hornreich [7] minimized the free enthalpy f for different electric-field strengths. The authors used an order parameter that was composed of the energetically preferred tensor modes [6] of helicity $m = 2$ (or -2) and a homogeneous part. The mode amplitudes and the lattice constants served as variational parameters. The numerical calculations, however, were so extensive that only parts of the electrostriction tensor could be determined and the structure of O_c^8 , which is the favored candidate for BPI, could not be studied.

Therefore we now present a simpler mesoscopic theory of \mathbf{R} using for the elastic deformation of the order parameter field $\mathbf{Q}(\mathbf{r})$ the model of "rigid helices." Inserting the model order parameter field into the mesoscopic free enthalpy f (in terms of \mathbf{Q} and \mathbf{E}) we derive a macroscopic free enthalpy $F(\boldsymbol{\epsilon}, \mathbf{E})$, which allows us to calculate \mathbf{R} in terms of the undistorted order parameter field $\mathbf{Q}(\mathbf{r})$.

We formulate our model in two steps. The first step follows an idea of Dmitrienko [9]. A distortion of the lattice in real space corresponds to the inverse deformation of the reciprocal lattice. The wave vectors of the distorted reciprocal lattice are $\tilde{\mathbf{k}} = (1 - \boldsymbol{\epsilon})\mathbf{k}$. In the model of rigid helices the distorted order parameter field is a superposition of tensor modes of helicity $m = 2$ (or $m = -2$) propagating along the distorted wave vectors $\tilde{\mathbf{k}}$ without change of amplitude:

$$\sum_{\tilde{\mathbf{k}}} Q_2(\mathbf{k}) \mathbf{M}_2(\tilde{\mathbf{k}}) \exp(i\tilde{\mathbf{k}} \cdot \mathbf{r}).$$

The new base tensor $\mathbf{M}_2(\tilde{\mathbf{k}})$, now orientated along $\tilde{\mathbf{k}}$, results from a rotation of $\mathbf{M}_2(\mathbf{k})$ along a rotation axis perpendicular to \mathbf{k} and $\tilde{\mathbf{k}}$. Such a rotation does not include a rotation along the wave vector $\tilde{\mathbf{k}}$ and hence causes the smallest possible change of the base tensor. A subsequent expansion of $\mathbf{M}_2(\mathbf{k})$ into a power series of the strain tensor $\boldsymbol{\epsilon}$ yields

$$\mathbf{M}_2(\tilde{\mathbf{k}}) = \mathbf{M}_2(\mathbf{k}) + \mathbf{m}(\mathbf{k})\boldsymbol{\epsilon} + \mathbf{n}(\mathbf{k})(\boldsymbol{\epsilon} \otimes \boldsymbol{\epsilon}) + O(\boldsymbol{\epsilon}^3),$$

$$\mathbf{v}^{(4)} = -\frac{4}{3\sqrt{6}} \sum_{\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0} Q_2(\mathbf{k}_1) Q_2(\mathbf{k}_2) Q_2(\mathbf{k}_3) \times \{ \text{tr}[\mathbf{M}_2(\mathbf{k}_2) \mathbf{M}_2(\mathbf{k}_3)] \mathbf{M}_1(\mathbf{k}_1) \otimes \mathbf{M}_1(\mathbf{k}_1) + 2 \text{tr}[\mathbf{M}_2(\mathbf{k}_2) \mathbf{M}_1(\mathbf{k}_3)] \mathbf{M}_2(\mathbf{k}_1) \otimes \mathbf{M}_1(\mathbf{k}_3) \}.$$

$\boldsymbol{\lambda}^{(i)}$ results when the inhomogeneous part of $\tilde{\mathbf{Q}}(\mathbf{r})$ is inserted into f_i^{LG} . The first term $\boldsymbol{\lambda}^{(2)}$ was already derived by Dmitrienko [9]. It satisfies the Cauchy relation $\lambda_2^{(2)} = \lambda_3^{(2)}$. Our calculations show that $\boldsymbol{\lambda}^{(2)}$ must be corrected by additional contributions of the higher-order terms in the free enthalpy according to Landau-de Gennes and further terms where the homogeneous part $\mathbf{b}\boldsymbol{\epsilon}$ appears both in first and in second order. As a result the Cauchy relation is broken.

Comparison of the second term of $f(\boldsymbol{\epsilon}, \mathbf{E})$ with $F(\boldsymbol{\epsilon}, \mathbf{E})$ shows that \mathbf{b} is proportional to the elasto-optic tensor

$$\mathbf{p} = \delta \mathbf{b}.$$

where $\mathbf{m}(\mathbf{k})$ and $\mathbf{n}(\mathbf{k})$ are tensors of ranks 4 and 6, respectively, which can be expressed as tensor products of the base tensors $\mathbf{M}_m(\mathbf{k})$.

In a second step we add a constant term $\mathbf{Q}_0 = \mathbf{b}\boldsymbol{\epsilon}$ to the order parameter field since a finite distortion breaks the cubic point symmetry of the BPI and II and allows a homogeneous part. In a first approximation we assume \mathbf{Q}_0 proportional to the strain tensor $\boldsymbol{\epsilon}$; \mathbf{b} is an unknown tensor of rank 4. Since for arbitrary distortions the trace of the contribution \mathbf{Q}_0 must vanish, we conclude that

$$b_1 = -2b_2$$

and remain with only two independent coefficients b_1 and b_3 . In the spirit of Landau we regard \mathbf{b} as a further order parameter that must be determined by minimization of a free enthalpy (see below). The complete distorted order parameter $\tilde{\mathbf{Q}}(\mathbf{r})$ is now

$$\tilde{\mathbf{Q}}(\mathbf{r}) = \mathbf{b}\boldsymbol{\epsilon} + \sum_{\tilde{\mathbf{k}}} Q_2(\mathbf{k}) \mathbf{M}_2(\tilde{\mathbf{k}}) \exp(i\tilde{\mathbf{k}} \cdot \mathbf{r}).$$

To derive a free enthalpy in terms of $\boldsymbol{\epsilon}$ and \mathbf{E} we insert the distorted order parameter $\tilde{\mathbf{Q}}(\mathbf{r})$ into the mesoscopic free enthalpy $f[\mathbf{Q}(\mathbf{r}), \mathbf{E}]$ and expand it up to quadratic terms in the strain tensor $\boldsymbol{\epsilon}$:

$$\begin{aligned} f(\boldsymbol{\epsilon}, \mathbf{E}) &= f[\tilde{\mathbf{Q}}(\mathbf{r}), \mathbf{E}] - f[\mathbf{Q}(\mathbf{r}), \mathbf{E} = 0] \\ &\approx \frac{1}{2} \boldsymbol{\lambda} \cdot (\boldsymbol{\epsilon} \otimes \boldsymbol{\epsilon}) - \delta \sqrt{\frac{t}{2}} \mathbf{b} \cdot (\mathbf{E} \otimes \mathbf{E} \otimes \boldsymbol{\epsilon}). \end{aligned}$$

We identify $\boldsymbol{\lambda}$ with the elastic tensor in $F(\boldsymbol{\epsilon}, \mathbf{E})$ [see Eq. (2)]. It has a very complicated structure but fulfills the stability conditions; $\boldsymbol{\lambda}$ consists of fourth-order tensors $\boldsymbol{\lambda}^{(i)}$, $\mathbf{v}^{(i)}$, and \mathbf{w} and the scalar Q :

$$\begin{aligned} \boldsymbol{\lambda} &= \boldsymbol{\lambda}^{(2)} + \boldsymbol{\lambda}^{(3)} + \boldsymbol{\lambda}^{(4)} - 6\sqrt{6} \mathbf{b}(\mathbf{v}^{(3)} + \mathbf{v}^{(4)}) \\ &\quad + \left(\frac{t}{2} + 4Q \right) (\mathbf{b}\mathbf{b}) + 8(\mathbf{b}\mathbf{w}\mathbf{b}). \end{aligned}$$

A typical expression is, for example,

We calculate \mathbf{b} in terms of the undistorted order parameter by minimization of the elastic free enthalpy for arbitrary distortions $\boldsymbol{\epsilon}$:

$$\frac{\partial \boldsymbol{\lambda} \cdot (\boldsymbol{\epsilon} \otimes \boldsymbol{\epsilon})}{\partial \mathbf{b}} = 0.$$

In Table II the relevant components of the tensors $\boldsymbol{\lambda}$, \mathbf{b} , and \mathbf{R} are listed ($R_2 = -\frac{1}{2}R_1$ being omitted). As input data points of the phase diagram calculated by Hornreich and co-workers without electric field [10, 11] have been used. The table shows that for decreasing κ and increasing t both BPI and BPII become softer, i. e., λ_i decreases.

TABLE II. Relevant components of the tensors λ , \mathbf{b} , and \mathbf{R} for different values of the parameters κ and t .

κ	t	b_1	b_3	λ_1	λ_2	λ_3	R_1/δ	R_3/δ	R_1/R_3
BP II									
1.10	1.00	0.037	0.11	0.17	-0.036	0.23	0.22	0.60	0.37
1.50	1.00	0.037	0.11	0.36	-0.057	0.48	0.11	0.28	0.39
1.90	1.00	0.036	0.10	0.70	-0.084	0.88	0.06	0.14	0.40
1.50	0.40	0.040	0.11	0.43	-0.073	0.62	0.10	0.22	0.44
1.50	1.60	0.034	0.10	0.29	-0.041	0.34	0.13	0.38	0.34
BP I									
1.60	0.10	0.12	0.09	0.79	-0.21	0.59	0.14	0.19	0.73
2.00	-0.60	0.12	0.09	1.53	-0.37	1.13	0.08	0.10	0.79
2.40	-1.50	0.12	0.08	2.70	-0.60	1.98	0.04	0.05	0.86

For the BP II the signs of R_1 and R_3 agree with experiment. The reversal of sign with a reversal of the dielectric anisotropy can be understood if we assume $\delta \sim \Delta\kappa$ which is well established in the nematic phase [12]. A comparison of the absolute values of R_1 and R_3 with experiment is not possible because there are no complete experimental data on the Landau coefficients for cholesteric liquid crystals. These coefficients cancel in the ratio R_1/R_3 , which is in good agreement with the measured values. While the coefficient R_3 cannot be extracted from the data of Lubin and Hornreich [7], their calculated value of R_1 is larger by a factor of 2.5. This difference may be due to the fact that Lubin and Hornreich also allow variations of the *mode amplitudes* and that they introduce the homogeneous part \mathbf{Q}_0 as a completely free variational parameter. Note that the ansatz for \mathbf{Q}_0 in the present theory allows a calculation of this homogeneous part exclusively from the elastic part of the free enthalpy. A completely free variation of \mathbf{Q}_0 would also include the feedback of \mathbf{E} onto the local rearrangement of the molecules in the unit cell, as is suggested by experiments of Heppke, Kitzerow, and Krumrey [13]. This local rearrangement under the influence of an elec-

tric field can be studied by a comparison of the model of rigid helices and a detailed investigation of the numerical calculations of Lubin and Hornreich [7].

The problem of negative ratios R_1/R_3 is still unresolved. The sign of R_1/R_3 equals the one of the ratio p_1/p_3 [Eqs. (4) and (5)] of the elasto-optic coefficients. Anomalous electrostriction has its origin beyond the model of rigid helices.

In summary, using a macroscopic free enthalpy we have decomposed the tensor of electrostriction into its elastic and elasto-optic part and have drawn conclusions concerning the observed conservation of volume and the signs of the electrostriction coefficients. With the help of the model of rigid helices we are able to give analytical expressions for the elastic tensor, the elasto-optic tensor, and the tensor of electrostriction in terms of the undisturbed order parameter. For BP II the model well describes the experiments. For BP I it must be extended to explain anomalous electrostriction.

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- [1] F. Porsch, in *Bericht zum Doktorandenkolloquium*, edited by H. Kitzerow and F. Oestreicher (Technische Universität, Berlin, 1988).
- [2] F. Porsch and H. Stegemeyer, *Chem. Phys. Lett.* **155**, 620 (1989).
- [3] G. Heppke, B. Jérôme, H.-S. Kitzerow, and P. Pieranski, *J. Phys. (Paris)* **50**, 549 (1989).
- [4] G. Heppke, B. Jérôme, H.-S. Kitzerow, and P. Pieranski, *J. Phys. (Paris)* **50**, 2991 (1989).
- [5] V. A. Belyakov and V. E. Dmitrienko, *Usp. Fiz. Nauk [Sov. Phys.—Usp.]* **28**, 535 (1985).
- [6] R. M. Hornreich and S. Shtrikman, *Mol. Cryst. Liq. Cryst.* **165**, 183 (1988).
- [7] D. Lubin and R. M. Hornreich, *Phys. Rev. A* **36**, 849 (1987).
- [8] V. E. Dmitrienko, *Liq. Cryst.* **5**, 853 (1989).
- [9] V. E. Dmitrienko, *Pis'ma Zh. Eksp. Teor. Fiz. [JETP Lett.]* **43**, 419 (1986).
- [10] H. Grebel, R. M. Hornreich, and S. Shtrikman, *Phys. Rev. A* **28**, 1114 (1983).
- [11] H. Grebel, R. M. Hornreich, and S. Shtrikman, *Phys. Rev. A* **30**, 3264 (1984).
- [12] W. H. de Jeu, *Physical Properties of Liquid Materials* (Gordon and Breach Science, New York, 1980).
- [13] G. Heppke, H.-S. Kitzerow, and M. Krumrey, *Mol. Cryst. Liq. Cryst. Lett.* **2**, 59 (1985).