Appl. Phys. B 68, 999–1005 (1999) / DOI 10.1007/s003409900041

Applied Physics B
Lasers
and Optics

Electromechanical and optical effects in photorefractive materials

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Received: 18 November 1998/Revised version: 18 February 1999/Published online: 12 April 1999

Abstract. From thermodynamic considerations, we derive a consistent set of equations coupling the steady-state photoinduced photorefractive space-charge field to mechanical deformations, dc permittivity, and refractive index changes. For the first time to our knowledge, these equations include piezoelectricity, electrostriction, the elasto-optic effect, the linear and quadratic electro-optic effects, as well as the influence of the volume forces and electric torques. We determine the conditions on the material parameters, for which volume forces and torques are of some importance on the optical properties.

These equations resulting from a macroscopic approach are valid whatever the physical microscopic origins of the various effects. Non centrosymmetrical and centrosymmetrical materials are considered. The order of approximation is the lowest possible able to describe the mentioned effects in both types of materials.

PACS: 77.84.-s; 42.70.Nq

The photorefractive effect is usually understood as the optically generated variation of the refractive index caused by an induced space-charge field through the Pockels or the Kerr effect [1], which are electro-optic effects originating from purely electronic processes. This definition was extended to include photorefractive polymers. In these materials, the chromophores have to be oriented under an applied electric field to break the inversion symmetry, thus allowing the linear electro-optic effect. The large diffraction efficiency and two-beam coupling gain observed in some of these organic materials were explained [2] by an orientational contribution caused by the birefringence of the chromophores, combined with the electro-optic effect. In organic glasses [3], the modulation of birefringence is the major mechanism giving rise to the spatial variation of the refractive index. In fact, these two contributions may formally be expressed in terms of quadratic electro-optic effect [4].

Electromechanical effects may also modulate the refractive index, through the elasto-optic effect. This was at the origin of the “clamped”, “unclamped” dilemma for the values of the electro-optic coefficients in photorefractive inorganic crystals. This has been clarified in crystals of infinite extension [5–7]: the sinusoidally modulated photorefractive space-charge field stresses and strains the material by piezoelectricity whereas the resulting elasto-optic effect modifies the induced variation of refractive index. These electromechanical effects could also be at the origin of surface reliefs observed in some materials.

In this paper, we intend to provide a consistent macroscopic description of the interactions between the space-charge field induced in photorefractive materials and the mechanical properties of these materials. Our purpose here is to avoid the usual phenomenological introduction of the various effects. The microscopic characteristics of the formation of the space-charge field are beyond the scope of this paper. The optical effects include elasto-optic, linear, and quadratic electro-optic effects. The static effects relate to the coupling between the mechanical deformations, the electric field, and the dc permittivity. This description simultaneously takes into account, for the first time to our knowledge, electrostriction, volume forces, and the equilibrium between mechanical and electrical torques. Electrostriction is the main electromechanical effect in centrosymmetrical materials, that are basically non piezoelectric. Volume forces describe the action of the electric field on charges and dipoles. Moreover, when a static electric field and a static polarization are present, a field of electrical torques is balanced by mechanical torques. These torques and volume forces are usually neglected. However, torques have been considered in liquid crystals [8] and their importance has been described in the case of photorefractive liquid crystals [9] where the induced birefringence results mostly from molecular orientation under these torques. They are to be considered as soon as the plasticity of the material does not allow the complete orientation of the dipoles (permanent or induced) in the direction of the internal field. Therefore, volume forces and torques will be

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We dedicate this paper to Prof. Eckard Krätzig on the occasion of his 60th birthday and in acknowledgement for his pioneering contributions to the physics of photorefractive materials.

considered in the model to establish in which type of materials they are finally negligible or not. We will discuss here non-centrosymmetrical and centrosymmetrical materials.

1 Mechanical, electrical, and optical responses

Various electromechanical effects couple the static electric field and polarization vectors to the displacement gradient tensor and to the stress tensor [10]. Once the mechanical and electrical responses of the material have been obtained for a given electric field, the optical response may be determined. It originates in the different susceptibilities associated with the static electric field (electro-optic effects) but also to the stress or the deformations (elasto-optic effect). We do not analyze here absorption effects.

In the text, the symbol associated with a tensor is written in square brackets if it does not indicate a tensor element. In this section, all the equations are written using uncontracted tensors and whenever necessary, the Einstein implicit summation is used.

1.1 *Electromechanical effects*

1.1.1 Equilibrium conditions. The material is in a thermodynamic equilibrium resulting from the effects coupling the electric fields and electric displacements to the mechanical deformations and stresses. The thermal effects (thermoelastic effect and pyroelectricity [11]) coupling those quantities to temperature and entropy are neglected.We describe the mechanical response, using the electric field $\boldsymbol{E}$ (as usual in the description of the photorefractive effect) and the displacement gradient $[u]$ as independent variables. The stresses $[T]$ will be expressed in terms of $[u]$, and the dc electric displacement $\boldsymbol{D}$, in terms of $\boldsymbol{E}$.

The static mechanical equilibrium condition [10] accounts for the balance between the surface forces T_{ij} (stresses) and the volume forces. These forces are the actions of the electric field $\boldsymbol{E}$ on the charges (density ρ) and on the dc polarization $\boldsymbol{\mathcal{P}}$. Using the dipolar approximation for the latter contribution, the equilibrium condition is written as:

$$\frac{\partial T_{ij}}{\partial x_j} + \rho E_i + \boldsymbol{\mathcal{P}} \frac{\partial \boldsymbol{E}}{\partial x_i} = 0 . \tag{1}$$

These volume forces were usually not taken into account in this equation as we will justify in many materials (see Sects. 1.4 and 1.5). The stress tensor $[T]$ which appears in (1) is the sum of a symmetric part $[T]^{\mathrm{s}}$ and an antisymmetric part $[T]^{\mathrm{as}}$ which is also usually not taken into account. However $[T]^{\mathrm{as}}$ defines the mechanical torques which balance the field $\boldsymbol{\mathcal{P}} \times \boldsymbol{E}$ of electric torques appearing inside any material if $\boldsymbol{E}$ is not parallel to $\boldsymbol{\mathcal{P}}$ (with $\times$ denoting the vectorial product). The equilibrium of torques thus fully defines the antisymmetrical stress components such that [10]:

$$T_{ij} - T_{ji} = 2T^{\mathrm{as}}_{ij} = \mathcal{P}_i E_j - \mathcal{P}_j E_i . \tag{2}$$

$[T]^{\mathrm{s}}$ is expressed by Hooke's law [10] as a function of the rigidity $[c]$, the converse piezoelectric $[e]$, and the electrostrictive $[a]$ tensors:

$$T^{\mathrm{s}}_{ij} = c_{ijkl} u_{kl} - e_{kij} E_k - 0.5 a_{ijkl} E_k E_l . \tag{3}$$

This relation is a Taylor expansion of $[T]^{\mathrm{s}}$ in E_i and u_{ij}, limited to its first non-zero terms. The first term never vanishes so that the second-order term in u_{ij} is neglected. However, in centrosymmetrical materials, the second term is cancelled and the first non-zero electric term is a second-order effect in E_i, i.e. electrostriction. This is why it has been included in relation (3). For the same reason, in the case of centrosymmetrical materials, one could think of introducing second-order crossed terms in $E_j u_{kl}$. However, we will show in the discussion of relation (6) that it must be neglected at this order of the Taylor expansion. Equation (3) applies to a number of materials, but not to some liquid crystals where a major effect, flexoelectricity, depends on the derivatives of the strain [12].

1.1.2 Electric polarization. $\mathcal{P}_i$, or equivalently D_i, may be developed with respect to E_j and u_{jk}. In the acousto-optic literature [13], this expansion is usually limited to the first-order terms in E_j and u_{jk}, i.e. to the contributions of the linear dielectric polarization, proportional to the relative static dielectric constant $\varepsilon^{r(1)}_{ij}$, and to the direct piezoelectric effect, proportional to e_{ijk}. However, this expansion would only be consistent with a linear development of the stress in E_i and u_{ij}. To determine the correct expansion for $\boldsymbol{D}$, we use the thermodynamic approach, well known in the piezoelectric literature [14].

Let θ be temperature, S the entropy, and U the internal energy. Using the differential of the new state function $V = U - \boldsymbol{E}.\boldsymbol{D}$:

$$\mathrm{d}V = T_{ij}\,\mathrm{d}u_{ij} - D_k\,\mathrm{d}E_k + \theta\,\mathrm{d}S , \tag{4}$$

we get the thermodynamic relation,

$$\frac{\partial T_{ij}}{\partial E_k} = -\frac{\partial D_k}{\partial u_{ij}} . \tag{5}$$

Therefore, to be coherent with the expansion for T^{s}_{ij} (relation (3)), the expansion for D_i must include terms proportional to $E_j u_{kl}$ and additional terms proportional to u_{jk}, besides the usual linear orders in E_j and u_{jk}. Other terms in the expansion of D_i are not needed. In particular, the second-order terms in u_{ij} are only a small correction to the dielectric polarization that exists even in centrosymmetrical materials. We thus neglect it in the expansion of D_i. That is why, as a consequence of relation (5), the term in $E_j u_{kl}$ has been neglected in (3). Computing the derivative of D_i with the definitions (2) and (3), we get the consistent equation for D_i:

$$D_i = \varepsilon_0 E_i + \mathcal{P}_i = P_i + \varepsilon_0 \varepsilon^{r(1)}_{ij} E_j + e'_{ijk} u_{jk} + a'_{klij} E_j u_{kl} , \tag{6}$$

where

$$e'_{ijk} = e_{ijk} + e^{\mathrm{rot}}_{ijk} \quad \text{with} \quad e^{\mathrm{rot}}_{ijk} = -0.5 \left(P_j \delta_{ik} - P_k \delta_{ji} \right) , \tag{7}$$

and

$$a'_{klij} = a_{klij} + a^{\mathrm{rot}}_{klij} \quad \text{with}$$
$$a^{\mathrm{rot}}_{klij} = -0.5 \varepsilon_0 \left(\varepsilon^{r(1)}_{ki} \delta_{lj} + \varepsilon^{r(1)}_{kj} \delta_{li} - \varepsilon^{r(1)}_{li} \delta_{kj} - \varepsilon^{r(1)}_{lj} \delta_{ki} \right) . \tag{8}$$

In (6), P_i accounts for the permanent polarization as in ferroelectric materials, high glass transition temperature (T_{g})

polymers or ferroelectric liquid crystals. The following term is the usual first-order expansion in the electric field. The last two terms are a consequence of equality (5). They represent the direct piezoelectric effect and electrostriction modified by the torques as follows:

e_{ijk} is symmetrical in the last two indices so that $e_{ijk}u_{jk} = e_{ijk}u^{\mathrm{s}}_{jk}$, it describes the usual direct piezoelectric effect; $[u^{\mathrm{s}}]$ being the strain tensor, symmetrical part of $[u]$.

e^{rot}_{ijk} is antisymmetrical in the last two indices so that $e^{\mathrm{rot}}_{ijk}u_{kl} = e^{\mathrm{rot}}_{ijk}u^{\mathrm{as}}_{kl}$, it describes the additional polarization resulting from a rotation of the permanent polarization $\boldsymbol{P}$; $[u^{\mathrm{as}}]$ being the antisymmetrical part of $[u]$.

a_{klij} is symmetrical in the first two indices so that $a_{klij}E_j u_{kl} = a_{klij}E_j u^{\mathrm{s}}_{kl}$, it represents the direct electrostrictive effect [10] (polarization induced by electrostriction);

a^{rot}_{klij} is antisymmetrical in the first two indices so that $a^{\mathrm{rot}}_{klij}E_j u_{kl} = a^{\mathrm{rot}}_{klij}E_j u^{\mathrm{as}}_{kl}$, it represents an additional polarization.

As the charge density ρ may be calculated from Poisson's equation, these equations (1), (2), (3), and (6), combined with the conditions on the surfaces, form a set of electromechanical equations that completely determines the deformations and stresses everywhere in the material, taking into account the existence of volume forces, electrical and mechanical torques.

1.2 *Optical effects*

The definition of the electric displacement $\boldsymbol{D}(\omega)$ at optical frequencies is also derived from thermodynamical considerations. The energy of the optical field should be included in the expression of U, thus introducing in (4) the additional term $-D_k(\omega)\,\mathrm{d}E_k(\omega)$. A thermodynamical relation similar to (5) is obtained:

$$\frac{\partial T_{ij}}{\partial E_k(\omega)} = -\frac{\partial D_k(\omega)}{\partial u_{ij}}\,. \tag{9}$$

This introduces in the expression of $\boldsymbol{D}(\omega)$ an additional term $a'_{klij}(\omega)E_j(\omega)u_{kl}$ similar in shape to the last term of (6) and given by (8). Its value at optical frequencies has no direct connection with its static value. In terms of variation of the optical relative permittivity, this corresponds to:

$$\delta\varepsilon^{r\,\mathrm{elasto}}_{ij} = \left(a_{klij}(\omega) + a^{\mathrm{rot}}_{klij}(\omega)\right) u_{kl}/\varepsilon_0\,. \tag{10}$$

In the expansion of $D_i(\omega)$, this is the only term related to T_{ij}, by the relation (9). At optical frequencies, there is no constant term, nor any term in u_{jk}. The first non-zero electric term, proportional to $\varepsilon^{r(1)}_{ij}(\omega)$, accounts for birefringence. One should add the first non-vanishing and nonlinear terms in the electric field, in order to describe the optical nonlinearities: the linear (Pockels) or possibly the quadratic (Kerr, or orientational) electro-optic effect, when the optical properties of centrosymmetrical materials are to be described:

$$\delta\varepsilon^{r\,\mathrm{electro}}_{ij} = \chi^{(2)}_{ijk}(-\omega;\,\omega,0)E_k + \chi^{(3)}_{ijkl}(-\omega;\,\omega,0,0)E_k E_l\,. \tag{11}$$

$\chi^{(2)}_{ijk}$ and $\chi^{(3)}_{ijkl}$ are the nonlinear susceptibilities associated with the Pockels and Kerr effects. We thus write:

$$\begin{aligned} D_i(\omega) &= \varepsilon_0\varepsilon^r_{ij}(\omega)E_j(\omega) \\ &= \varepsilon_0\left[\varepsilon^{r(1)}_{ij}(\omega) + \delta\varepsilon^{r\,\mathrm{electro}}_{ij} + \delta\varepsilon^{r\,\mathrm{elasto}}_{ij}\right]E_j(\omega)\,, \end{aligned} \tag{12}$$

Electro-optic and elasto-optic effects are more often described as a change $[\delta\eta]$ in the impermeability tensor $[\eta] = [\varepsilon^r(\omega)]^{-1}$ under the form:

$$\delta\eta_{ij} = r_{ijk}E_k + g_{ijkl}E_k E_l + p_{ijkl}u^{\mathrm{s}}_{kl} + p^{\mathrm{rot}}_{ijkl}u^{\mathrm{as}}_{kl}\,. \tag{13}$$

The clamped Pockels tensor $[r]$, the Kerr tensor $[g]$, the usual elasto-optic tensor $[p]$, and the roto-optic tensor $[p^{\mathrm{rot}}]$ are related, in the principal axes of the material, to the definitions (10) and (11) by:

$$\begin{cases} \varepsilon^{r(1)}_{ii}(\omega)\varepsilon^{r(1)}_{jj}(\omega)r_{ijk} = -\chi^{(2)}_{ijk}(-\omega;\,\omega,0)\,, \\ \varepsilon^{r(1)}_{ii}(\omega)\varepsilon^{r(1)}_{jj}(\omega)g_{ijkl} = -\chi^{(3)}_{ijkl}(-\omega;\,\omega,0,0)\,, \\ \varepsilon_0\varepsilon^{r(1)}_{ii}(\omega)\varepsilon^{r(1)}_{jj}(\omega)\,p_{ijkl} = -a_{ijkl}(\omega)\,, \\ \varepsilon_0\varepsilon^{r(1)}_{ii}(\omega)\varepsilon^{r(1)}_{jj}(\omega)\,p^{\mathrm{rot}}_{ijkl} = -a^{\mathrm{rot}}_{ijkl}(\omega)\,. \end{cases} \tag{14}$$

The expression of a^{rot}_{klij} was previously obtained [15] by considering the effect of a rotation on the index ellipsoid. It is derived here from thermodynamic considerations. The roto-optic tensor may be expressed in the principal axes of the material. The obtained expression is identical to the one given in [13]:

$$p^{\mathrm{rot}}_{ijkl} = \frac{1}{2}\left[\left(\frac{1}{n_j^2}\right) - \left(\frac{1}{n_i^2}\right)\right](\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})\,. \tag{15}$$

$[p^{\mathrm{rot}}]$ has non-zero coefficients if the material is birefringent.

1.3 *The space charge field*

The permittivity at optical frequency, (12) or (13), can be determined if both the displacement gradient and the electric field are known. To compute their values one should simultaneously solve the set of mechanical equations (1), (2), (3), (6), and the set of equations of the charge transport model describing the photorefractive effect. In the photorefractive band transport model [16, 17], the space-charge electric field depends on the static dielectric tensor, through Poisson's equation. It is also a function of the conductivity tensor $[\sigma]$ through the mobility of the charge carriers. Strictly speaking, as $[\varepsilon^r]$ and $[\sigma]$ both depend on the displacement gradient and on the electric field, the charge transport equations are coupled to the static electromechanical equations. This coupling has been considered in liquid crystals [8] taking into account torques only. These torques introduce two additional contributions to the photorefractive space-charge field as usually calculated. They originate from the anisotropies of the conductivity and dielectric permittivity. Although these effects occur in all photorefractive materials, they have only been described in the case of photorefractive nematic liquid crystals [9].

Here, we take into account the contribution of the dielectric anisotropy in (12) or (13) but ignore the effect of the anisotropic conductivity. In general, the charge transport and mechanical equations are nonlinear. However in an infinite medium the spatially periodic illumination generates a periodic structure. For low modulations of the sinusoidal illumination pattern, the equations may be linearized as usually done [17] for the photorefractive effect. We therefore limit our analysis to the first-order terms (spatial wave number K)

and we develop all the space varying quantities with this first order Fourier expansion:

$$Q(\boldsymbol{r}) = Q^{\langle 0\rangle} + 0.5(Q^{\langle 1\rangle} \exp \mathrm{i}\boldsymbol{K}.\boldsymbol{r} + \mathrm{c.c})\,. \tag{16}$$

By solving the set of (1), (2), (3), and (6), one finds that the displacement gradient at wave number K is related to the space-charge field by a linear relation:

$$u_{jk}^{\langle 1\rangle} = \alpha_{jkl} E_l^{\langle 1\rangle}\,. \tag{17}$$

This approach, similar to the method derived in photorefractive crystals [5–7], leads to the definition of an effective dielectric tensor $[\varepsilon^{r\,\mathrm{eff}}]$ taking into account the dielectric, piezoelectric, electrostriction effects and the torques:

$$\begin{aligned} D_i^{\langle 1\rangle} &= \varepsilon_0 \varepsilon_{ij}^{r\,\mathrm{eff}} E_j^{\langle 1\rangle} \\ &= \varepsilon_0 \varepsilon_{ij}^{r(1)} E_j^{\langle 1\rangle} + e'_{ijk} u_{jk}^{\langle 1\rangle} + a'_{klij} \left[E_j^{\langle 1\rangle} u_{kl}^{\langle 0\rangle} + E_j^{\langle 0\rangle} u_{kl}^{\langle 1\rangle} \right]. \end{aligned} \tag{18}$$

Therefore, the effective dielectric tensor to be used to determine the fundamental frequency of the space-charge field is:

$$\varepsilon_0 \varepsilon_{ij}^{r\,\mathrm{eff}} = \varepsilon_0 \varepsilon_{ij}^{r(1)} + \left(e'_{ikl}\alpha_{klj} + a'_{klij} u_{kl}^{\langle 0\rangle} + a'_{klim}\alpha_{klj} E_m^{\langle 0\rangle} \right). \tag{19}$$

For an infinite medium, one should first literally calculate the expression for $u_{kl}^{\langle 0\rangle}$ (or $u_{kl}^{\langle 1\rangle}$) as a function of $\boldsymbol{E}^{\langle 0\rangle}$ (or $\boldsymbol{E}^{\langle 1\rangle}$), from the electromechanical (1), (2), (3), (6) and conditions on stresses or strains (for example clamped or unclamped samples). Next, the value of the electric field $\boldsymbol{E}^{\langle 1\rangle}$ can be computed using the effective dielectric tensor (19), in the charge transport equations. Once this electric field has been determined, one finds the numerical values for $u_{kl}^{\langle 1\rangle}$ from the literal expression (17) previously calculated. Finally, the optical effects are computed reporting these values in (12) or (13).

In the following, we discuss the relative importance of the different effects. For specific materials, some terms may be neglected in (1), (2), (3), (6), and (19). We separate the case of non-centrosymmetrical materials from that of centrosymmetrical ones. We show that they may both be described by similar equations.

1.4 Non-centrosymmetrical materials

In these materials, such as high-T_g polymers and some crystals, one may usually neglect the effects of electrostriction ($[a]$, second-order effect) compared to those of piezoelectricity ($[e]$, first-order effect).

1.4.1 Determination of the space-charge field. From (8) one sees that a_{ijkl}^{rot} is of the order of $\varepsilon_0\varepsilon_{ij}^{r(0)}$ so that in relation (6), then in the definitions (18) or equivalently (19), one should neglect the terms proportional to a_{klij}^{rot} compared to the terms proportional to $\varepsilon_0\varepsilon_{ij}^{r(1)}$. Therefore, because we have also disregarded electrostriction, the expression of the effective permittivity may be expressed as:

$$\varepsilon_0 \varepsilon_{ij}^{r\,\mathrm{eff}} \approx \varepsilon_0 \varepsilon_{ij}^{r(1)} + e'_{ikl}\alpha_{klj}\,. \tag{20}$$

It differs from the usual expressions [6, 7] by the term $e_{ikl}^{\mathrm{rot}}\alpha_{klj}$, which only exists in ferroelectric materials. As e_{ikl}^{rot} is of the same order of magnitude as P (see relation (7)), this term $e_{klj}^{\mathrm{rot}}\alpha_{klj}$ may be neglected if $P \ll |e_{ijk}|$. This is the case for example in BaTiO$_3$ (symmetry 4 mm), where the relevant parameters in $e_{ikl}^{\mathrm{rot}}\alpha_{klj}$ are P and e_{15} (see Table 1 for numerical values). This is found to be still true, although less marked, in a ferroelectric liquid crystal [18] where the polarization is 10% to 20% of the piezoelectric modulus ($1.5\times10^{-4}\,\mathrm{C/m^2}$ for the latter).

1.4.2 Determination of the deformations. Once again, because electrostriction is neglected, (3) reduces to:

$$T_{ij}^{\mathrm{s}} \approx c_{ijkl}u_{kl} - e_{kij}E_k\,. \tag{21}$$

Equation (6) has already been used to determine $\varepsilon_{ij}^{r\,\mathrm{eff}}$, but it is needed here again to compute the displacement gradient. In that case, different approximations for the electric displacement may be stated. Because first, e_{ijk}^{rot} is of the order of P and second, we deal in this paper with small values of deformations in the limit of elasticity, $e_{ijk}^{\mathrm{rot}}u_{jk}$ is only a small correction to P_i. e_{ijk}^{rot} can thus be neglected in the expression (6). Similarly, a_{ijkl}^{rot} being of the order of $\varepsilon_0\varepsilon_{ij}^{r(1)}$, one should neglect $a_{klij}^{\mathrm{rot}}u_{kl}$ compared to $\varepsilon_0\varepsilon_{ij}^{r(1)}$. The remaining terms in (6), the piezoelectric terms proportional to e_{ikl}, can also be neglected. Indeed, this expression (6) is now used to solve (1) by inserting the value of $\mathscr{P}_i$ in (1) and (2). The piezoelectric terms $e_{ijk}u_{jk}$ from (6) thus introduce, in (1), terms proportional to $e_{ijk}u_{kl}E_j$ which can be neglected compared to the terms $e_{kij}E_k$ originating from (3). Therefore, the electric displacement can be approximated by:

$$D_i \approx P_i + \varepsilon_0\varepsilon_{ij}^{r(1)}E_j\,. \tag{22}$$

From the same reasons, the expressions (2) for the stress tensors can be simplified as:

$$\begin{aligned} 2T_{ij}^{\mathrm{as}} &= \left(P_i + \varepsilon_0(\varepsilon_{ik}^{r(1)} - \delta_{ik})E_k \right) E_j \\ &\quad - \left(P_j + \varepsilon_0(\varepsilon_{jk}^{r(1)} - \delta_{jk})E_k \right) E_i\,. \end{aligned} \tag{23}$$

Using these simplified expressions (21) to (23), one may compute the displacement gradients with (1). However, in most previous analyses, volume forces and torques are neglected in (1). Let us examine the relative contributions of these terms for the spatial wave number K. For this comparison, we do not consider the exact values for the parameters and we note X for the average values of the non-zero coefficients of any tensor $[X]$. The volume forces induced by the electric field on the polarization and the influence of T^{as} have the same order of magnitude in (1):

$$\boldsymbol{\mathscr{P}}\frac{\partial \boldsymbol{E}}{\partial x} \approx \frac{\partial T^{\mathrm{as}}}{\partial x} \approx K E^{\langle 1\rangle}\left(P + \varepsilon_0(\varepsilon^r - 1)E^{\langle 0\rangle} \right). \tag{24}$$

These values should be compared to the two contributions originating from T^{s}, for example the piezoelectric part:

$$e\frac{\partial E}{\partial x} \approx K E^{\langle 1\rangle} e\,. \tag{25}$$

Table 1. Numerical values used for tensors in $BaTiO_3$ and $Bi_{12}TiO_{20}$

Tensor	Value	Reference
$BaTiO_3$		
Clamped dielectric constant	$\varepsilon_{11}^{r(1)} = 2180$, $\varepsilon_{33}^{r(1)} = 56$	[22]
Rigidity tensor (10^{10} N/m^2)	$c_{11} = 22.2$, $c_{13} = 11.1$, $c_{33} = 15.1$, $c_{55} = 6.1$	[22]
Piezoelectric tensor (C/m^2)	$e_{15} = 34.2$, $e_{31} = -0.7$, $e_{33} = 6.7$	[22]
Spontaneous polarization (C/m^2)	$P = 0.28$	[23]
Clamped electro-optic tensor (pm/V)	$r_{13} = 10.2$, $r_{33} = 40.6$, $r_{51} = 730$ at 633 nm	[22]
$Bi_{12}TiO_{20}$		
Clamped dielectric constant	$\varepsilon_{11}^{r(1)} = 47$	[24]
Rigidity tensor (10^{10} N/m^2)	$c_{11} = 13.7$, $c_{12} = 2.8$, $c_{33} = 14.8$, $c_{44} = 2.6$	[5]
Piezoelectric tensor (C/m^2)	$e_{14} = 1.1$	[5]
Clamped electro-optic tensor (pm/V)	$r_{41} = 4.75$ at 633 nm	[5]

Therefore, both torques and the volume forces $\boldsymbol{\mathcal{P}}\,\partial \boldsymbol{E}/\partial x$ may be neglected in (1), as soon as:

$$P \ll |e| \quad \text{and } \varepsilon_0 \varepsilon^{r(1)} E^{\langle 0\rangle} \ll |e| \,. \tag{26}$$

Similarly we estimate the magnitude of the volume forces ρE from Poisson's equation as:

$$\rho E \approx K E^{\langle 1\rangle} E^{\langle 0\rangle} \varepsilon_0 \varepsilon^{r\,\mathrm{eff}} \quad \text{with } \varepsilon^{r\,\mathrm{eff}} = \left(\frac{\boldsymbol{K}}{K}\right)^t \left[\varepsilon^{r\,\mathrm{eff}}\right] \left(\frac{\boldsymbol{K}}{K}\right) . \tag{27}$$

Comparing this force to the main contribution given by (25), we thus find that ρE is negligible if the following condition is satisfied:

$$\varepsilon_0 \varepsilon^{r\,\mathrm{eff}} E^{\langle 0\rangle} \ll |e| \,. \tag{28}$$

Therefore, we can neglect volume forces and torques in (1), as usually done, if conditions (26) and (28) are simultaneously satisfied. As a matter of fact, given that $\varepsilon^{r\,\mathrm{eff}}$ is usually of the order of $\varepsilon^{r(1)}$, condition (28) is often included in condition (26). Eventually, if conditions (26) and (28) do not hold, volume forces and torques have to be taken into account, unless the piezoelectric effect may be neglected for both static and optical quantities. This is the case if the clamped and unclamped values of the dielectric tensor (or the electro-optic tensor) are very close to each other.

$BaTiO_3$ is an example of ferroelectric material matching these conditions (26) and (28) for the usual values of the electric field (a few kV/cm) (see the tensor elements of Table 1). In the non-ferroelectric crystal $Bi_{12}TiO_{20}$ (BTO), volume forces and torques are also negligible (see Table 1). Surface gratings induced by piezoelectricity were recently observed in BTO [19]. We performed numerical simulations neglecting volume forces and torques in the configuration used for that experiment. The calculation is complicated by the cut of the crystal in that experiment. We computed the first harmonic Δh of the surface relief after simulating the deformations using the numerical values of the material parameters given in [5] and the electric field and grating spacing given in [19]. Our simulation gives $\Delta h = 0.33$ nm. The agreement with the experimental result $\Delta h = 0.26$ nm obtained from [19] is better than the rough approximation $\Delta h = 2.2$ nm given in the same paper.

In the ferroelectric liquid crystal mentioned above [18], we have already seen that $P < |e|$. Assuming $\varepsilon^{r(1)} \approx 3$ and considering $E^{\langle 0\rangle} \approx$ a few 10^5 V/m as in [18], we also have $\varepsilon_0 \varepsilon^{r(1)} E^{\langle 0\rangle} \ll |e|$. Condition (26) is matched in this material as well.

These values therefore fully justify the omission of volume forces and torques for these materials as done in previous analyses [5–7]. One should recall [7] that the effect of rotations, $[u^{\mathrm{as}}]$, were omitted in [6]. However, this complete analysis had to be performed and the order of magnitude of the effects given in order to lawfully neglect volume forces and torques in the materials known up to now. We have no indication of the existence of non-centrosymmetrical materials where torques and volume forces would have to be taken into account.

1.5 Centrosymmetrical materials

For centrosymmetrical materials such as low-T_g polymers, the Pockels effect, the piezoelectric tensor $[e]$ and tensor $[e^{\mathrm{rot}}]$, the permanent polarization vanish in all equations.

Determination of the space charge field. Similarly to non centrosymmetrical materials, one should neglect the terms proportional to a_{klij}^{rot} in the expression of the effective dielectric permittivity (19) so that:

$$\varepsilon_0 \varepsilon_{ij}^{r\,\mathrm{eff}} \approx \varepsilon_0 \varepsilon_{ij}^{r(1)} + \left(a_{klij} u_{kl}^{\langle 0\rangle} + a_{klim} \alpha_{klj} E_m^{\langle 0\rangle} \right) . \tag{29}$$

Determination of the deformations. As the piezoelectric tensor vanishes, (2) is:

$$T_{ij}^{\mathrm{s}} \approx c_{ijkl} u_{kl} - 0.5 a_{ijkl} E_k E_l \,. \tag{30}$$

In the expression of the electric displacement (6) we once again neglect the contribution of a_{ijkl}^{rot} for the same reason as the one discussed above. The contribution of a_{ijkl} must also be neglected. Indeed, it introduces in the expression of T_{ij}^{as}, and thus in (1), a term proportional to $a_{klij} E_j u_{kl} E_m$ which is much smaller than the contribution $0.5 a_{klij} E_j E_m$ introduced in (1) by T_{ij}^{s}. Therefore one should write:

$$D_i \approx \varepsilon_0 \varepsilon_{ij}^{r(1)} E_j \,, \tag{31}$$

so that the antisymmetrical part of the stress is,

$$2 T_{ij}^{\mathrm{as}} = \varepsilon_0 (\varepsilon_{ik}^{r(1)} - \delta_{ik}) E_k E_j - \varepsilon_0 (\varepsilon_{jk}^{r(1)} - \delta_{jk}) E_k E_i \,. \tag{32}$$

These equations demonstrate that if the applied electric field is much stronger than the space-charge field, then the centrosymmetrical materials may be treated in the same way as non-centrosymmetrical materials, with $P_i = 0$ and provided that one introduces the following equivalent tensors e^{eq}_{ijk}, $\chi^{(2)\mathrm{eq}}_{ijk}$, and r^{eq}_{ijk} in place of e_{ijk}, $\chi^{(2)}_{ijk}$, and r_{ijk}:

$$\begin{cases} e^{\mathrm{eq}}_{ijk} \equiv a_{jkil} E^{\langle 0\rangle}_l \,, \\ \chi^{(2)\mathrm{eq}}_{ijk}(-\omega;\, \omega, 0) \equiv 2\chi^{(3)}_{ijkl}(-\omega, \omega, 0, 0) E^{\langle 0\rangle}_l \\ \text{or } r^{\mathrm{eq}}_{ijk} \equiv 2 g_{ijkl} E^{\langle 0\rangle}_l \,. \end{cases} \tag{33}$$

With these equivalent tensors, we may discuss the importance of taking into account the volume forces and torques in (1) exactly as done in Sect. 1.4. Condition (26) simply reduces to:

$$\varepsilon_0 \varepsilon^{r(1)} \ll |a| \,. \tag{34}$$

Although we do not have exact parameters for photorefractive materials, we suspect this condition is not always fulfilled. Indeed, an estimate using Lorenz–Lorentz relation indicates that in an isotropic material, $\varepsilon_0 \varepsilon^{r(1)} \approx |a|$ [20].

Moreover, in case an electric field is applied to the material, the boundary conditions depend on the electrode attraction T^{elec} for a centrosymmetrical material. Its knowledge is required to calculate $u^{\langle 0\rangle}$ (see Sect. 1.3). It is also negligible, as soon as:

$$\left|T^{\mathrm{elec}}\right| \approx \left|0.5 \varepsilon_0 \varepsilon^{r(1)} (E^{\langle 0\rangle})^2\right| \ll \left|a (E^{\langle 0\rangle})^2\right| , \tag{35}$$

which is the same condition as (34).

As an example, we give the equivalent tensors for an isotropic material.

$[e^{\mathrm{eq}}]$ is a third-rank tensor, symmetrical with respect to its two last indices, as a piezoelectric tensor. From (33) and choosing the direction of $\boldsymbol{E}^{\langle 0\rangle}$ for the z axis we obtain in contracted notations:

$$\begin{bmatrix} 0 & 0 & 0 & 0 & e^{\mathrm{eq}}_{15} & 0 \\ 0 & 0 & 0 & e^{\mathrm{eq}}_{15} & 0 & 0 \\ e^{\mathrm{eq}}_{31} & e^{\mathrm{eq}}_{31} & e^{\mathrm{eq}}_{33} & 0 & 0 & 0 \end{bmatrix} \text{ with } \begin{cases} e^{\mathrm{eq}}_{15} = 0.5(a_{33} - a_{13}) E^{\langle 0\rangle} \\ e^{\mathrm{eq}}_{31} = a_{13} E^{\langle 0\rangle} \\ e^{\mathrm{eq}}_{33} = a_{33} E^{\langle 0\rangle} \,. \end{cases} \tag{36}$$

Using (33) and Kleinmann symmetry, the equivalent Pockels tensor $[r^{\mathrm{eq}}]$ is found to be:

$$\begin{bmatrix} 0 & 0 & r^{\mathrm{eq}}_{13} \\ 0 & 0 & r^{\mathrm{eq}}_{13} \\ 0 & 0 & 3r^{\mathrm{eq}}_{13} \\ 0 & r^{\mathrm{eq}}_{13} & 0 \\ r^{\mathrm{eq}}_{13} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \text{ with } r^{\mathrm{eq}}_{13} = 2 g_{13} E^{\langle 0\rangle} (g_{13} \text{ is defined in (14)}) \,. \tag{37}$$

This is identical to the result obtained for the $C_{\infty v}$ symmetry with Kleinmann symmetry in the case of axial molecules.

In photorefractive organic materials elastic enough so that the dipoles are able to move and align close to the total electric field, equations are simplified as well, as the electric torque is zero. In these materials, refractive index changes induced by electrostriction may be observed. Electrostriction has recently been evidenced in low-T_{g} photorefractive polymers [21].

2 Conclusion

We analyzed the electromechanical (stress, strain, polarization) and optical responses (electro-optic and elasto-optic effects) to a possibly modulated electric field, in photorefractive materials. It applies to many materials such as crystals, solgel films, low- or high-glass-transition-temperature polymers, multiple quantum wells, or photorefractive liquid crystals, as far as absorption effects are not concerned.

The electromechanical effects and their consequences on optical properties are formalized including electrostriction in centrosymmetrical materials. This had not been done before. The equations are shown to be formally the same as for non-centrosymmetrical materials. However the data available at this date do not allow us to draw reliable conclusions on the relevant electromechanical effects in these materials. Numerical data about both elasticity and electrostriction, and possibly the elasto-optic effect, in a given photorefractive polymer are needed to estimate the influence of electromechanical effects on the optical effects observed in these materials.

The conditions when the volume forces and torques are effectively negligible are discussed here for the first time to our knowledge. It seems that in many materials, their contribution is negligible compared to that of the symmetrical stress T^{s}_{ij}. The equilibrium condition on forces (1) may then be simplified as:

$$\frac{\partial T^{\mathrm{s}}_{ij}}{\partial x_j} = 0 \,, \tag{38}$$

T^{s}_{ij} given by Hooke's law (20) or by (29) depending if the material is centrosymmetrical or not. From a theoretical point of view, this justifies previous works about inorganic crystals [5–7].

However, the equilibrium condition on torques (2):

$$2T^{\mathrm{as}}_{ij} = \mathcal{P}_{\,i} E_j - \mathcal{P}_{\,j} E_i \tag{39}$$

always has to be kept to account for the molecular orientation at steady state, as done for example in liquid crystals [9].

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