Open problems in the optics of crystals: The role of multiple scattering

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The thickness b of the transition boundary layer, always present in crystals and giving still unsolved problems for the boundary conditions, is shown to be essentially determined by the multiple scattering of light, due to the inhomogeneity of any periodic structure. The parameter b depends on the orientation ϑ of the boundary plane with respect to the crystal lattice, and diverges for some critical orientations where strong macroscopic effects are found, which cannot be interpreted by any macroscopic model based on bulk and boundary equations. Our analysis exhaustively defines the limits of validity of macroscopic models for periodic nanoscale structures and solid crystals.

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I. INTRODUCTION

The simplest approach to the optics of nonmagnetic media is based upon the local approximation, i.e., assuming the dielectric polarization in a volume V, whose radius is small with respect to the light wavelength λ, depends only on the electric field averaged over V (macroscopic field $\mathbf{E}$). Within this approximation the optical activity of chiral media and the other properties related to the spatial dispersion are lost. In the spite of the great effort done in the last decades to go beyond the local approximation, many important problems arising from the nonlocal interactions are not yet fully solved. In the presence of such interactions, the polarization at a given point $\mathbf{r}$ is given by the integral over $\mathbf{r}'$ of a function of the type $\chi(\mathbf{r},\mathbf{r}')\mathbf{E}(\mathbf{r}')$. In liquids and gases, which are homogeneous in the statistical sense [1], the function $\chi(\mathbf{r},\mathbf{r}')$ depends only on $\mathbf{r}-\mathbf{r}'$: Maxwell's equations admit plane wave solutions but the macroscopic permittivity $\tilde{\varepsilon}$ depends explicitly on the wave vector $\mathbf{k}$. The dependence of $\tilde{\varepsilon}$ on $\mathbf{k}$ is called spatial or wave-vector dispersion and is the spatial analog of the well known frequency dispersion. These simple considerations evidence the following important point. The integral over $\mathbf{r}'$ yields different results in the bulk and near the boundaries of the medium, giving rise to a transition boundary layer. In optics, the thickness b of the boundary layer is generally neglected because $b \ll \lambda$, where λ is the light wavelength. However, its presence gives difficult problems for the definition of the boundary conditions in chiral media and near isolated absorption lines [2–5]. An effective medium approximation can be usefully applied to finite sample only if a set of boundary conditions is found. If one considers the effective medium defined by the bulk equations as well as by the boundary conditions the best macroscopic model is still an *open and controversial problem* even if the range of the considered interactions is much smaller than λ.

Much more important problems arise for the definition of a macroscopic model for structurally inhomogeneous media. In fact, the internal multiple scattering acts as a nonlocal and very long range interaction. It plays a particularly important role in periodic media because the scattering centers are correlated over the entire sample, independently of its size. In solid crystals it is very difficult to include the multiple scattering in the usual microscopic approaches based on classical lattice dynamics or on quantum mechanics [2–6]. We consider therefore periodic nanoscale structures, but the multiple scattering is expected to play an important role in any periodic medium.

The main role of the multiple scattering in chiral structures has already been evidenced by numerical analysis [7–11]. In Ref. [9] it has been shown by experiments and by a theoretical analysis that in a particular optical geometry no effective medium accounts for the optical activity of short period liquid crystals. The presence of a "surface dead layer" in spatially dispersive crystals was suggested by Hopfield and Thomas [3], and the effects of a "surface transition layer" were discussed in Refs. [4,5,12]. A very general discussion of the limits of validity of macroscopic models for solid crystals has been done in Ref. [1], based on the following facts. In an homogeneous unlimited medium the plane waves are eigenmodes of the electromagnetic field, with field vectors proportional to $\exp(i\mathbf{k}\cdot\mathbf{r})$. In periodic structures the eigenmodes are Bloch waves and the factor $\exp(i\mathbf{k}\cdot\mathbf{r})$ is multiplied by a periodic function $P(\mathbf{r})$ having the periodicity of the crystal. The effective tensor $\tilde{\varepsilon}$, describing the bulk properties of the macroscopic model, is defined by simply neglecting the periodic modulation. This is equivalent to neglect the short-wavelength components obtained by expanding $P(\mathbf{r})$ in a Fourier series (method of long waves [13–15]). As shown in Ref. [1] on the basis of qualitative or semiquantitative arguments, the neglected components give, in general, small macroscopic effects. The particular case considered in Ref. [9] represents an exception to this general rule.

Any homogeneous approximation of inhomogeneous media is useful for the solution of optical problems if it provides not only the bulk equations and the boundary conditions defining the effective medium, but also the limits of validity of the model. The aim of this paper is to discuss this last point, and more precisely the assumptions required to define the macroscopic model for periodic structures. This will be done on the basis of a fully quantitative analysis able to take into account the multiple scattering and the presence of the boundaries.

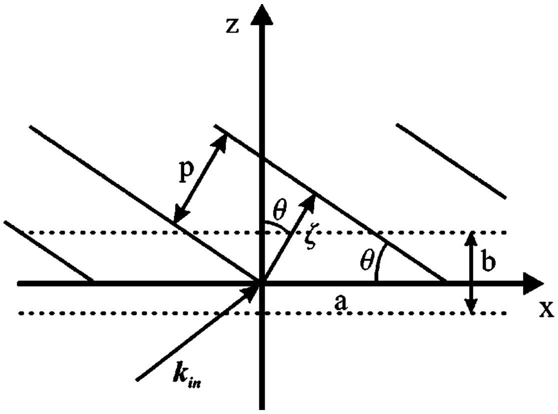

FIG. 1. Sample geometry. A 1D nanoscale medium fills the half space $z>0$. The periodicity direction ζ is parallel to the incidence plane (x,z) of the external wave; p is the period of the medium, ϑ is the angle between ζ and z, b is the thickness of the boundary layer, and $a=p/\sin\vartheta$ is the periodicity along x of the semi-infinite structure.

II. THE BOUNDARY LAYER

In order to evidence the presence of a boundary layer and to evaluate its thickness we consider a plane wave incident on a nanoscale structure filling the half space $z>0$. For simplicity, we assume that the medium is periodic in only one direction ζ parallel to the incidence plane (x,z) of the external wave [see Fig. 1], and that its optical properties are fully defined by the field $\varepsilon(\zeta)$ providing the local permittivity, that will be considered $\mathbf{k}$ independent. Under such assumption, the unique source of nonlocality is the multiple scattering [8–11]. In any effective medium the external wave generates only two internal waves with different polarizations. In the periodic medium, instead, it generates an infinite number of Bloch modes. In general, only two of such modes are running. Their long wave components define the effective tensor $\tilde{\varepsilon}$, a fact that requires the approximations already discussed in the Introduction. However, the most important discrepancies between the actual periodic medium and its homogeneous approximation are due to the presence of the additional modes. The starting point of our analysis is the evaluation of the Bloch vector $\mathbf{k}_m$ of the mode of order m, where $m=0,\pm1,\pm2,\ldots$. The tangential components of the vectors $\mathbf{k}_m$ satisfy the exact relation

$$k_{m,x}=k_{in,x}+mk_p\sin\vartheta; \tag{1}$$

where $\mathbf{k}_{in}$ is the incidence wave vector, $k_p=2\pi/p$, and p is the periodicity of the structure. Equation (1) is a simple consequence of the Bloch-Floquet theorem and of the fact that the semi-infinite structure is periodic along x with period $p/\sin\vartheta$, and it can be considered as an extension to periodic media of the phase matching condition at the boundary between homogeneous media.

Two forward Bloch modes with different polarizations correspond to each m value (for finite slabs the presence of the second boundary generates two backward Bloch modes). The z components of $\mathbf{k}_m$ are approximately given by the equation

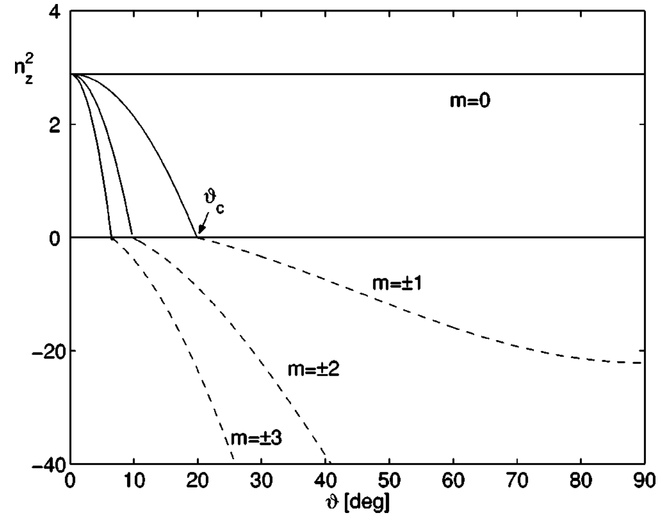

FIG. 2. Plot of $n_z^2\equiv(k_z/k_0)^2$ versus ϑ for the modes of order $m=0,\pm1,\pm2,\pm3$, for $p=\lambda/5$, $\overline{n}=1.7$ and for normally incident light. Positive and negative values of n_z^2 correspond to waves running over the entire half space $z>0$ (continuous lines) and to evanescent waves (dashed lines), respectively. For $\vartheta=\vartheta_c$ the quantity k_z is zero for $m=\pm1$ and the thickness of the boundary layer is infinite. Notice the scale change on the vertical axis.

$$k_{m,z}^2=(\overline{n}k_0)^2-k_{m,x}^2, \tag{2}$$

where $k_0=2\pi/\lambda$ and $\overline{n^2}$ coincides with a suitably chosen average $\overline{\varepsilon}$ of the function $\varepsilon(\zeta)$. Equation (2) can be considered as the lowest order approximation in a perturbative approach where the periodic modulation $\varepsilon(\zeta)-\overline{\varepsilon}$ is the perturbing term. In fact, the quantity $\overline{n}k_0$ is the modulus of the wave vector within the unperturbed average medium.

The most important parameter in our analysis is the angle ϑ between ζ (the periodicity direction) and z (the boundary normal). If $p\ll\lambda$ and the angle ϑ is not too small then the quantity $k_{m,z}^2$ appearing in Eq. (2) is negative and $k_{m,z}$ is purely imaginary for any $m\neq0$, as shown in Fig. 2, where the square of the reduced components $n_{m,z}=k_{m,z}/k_0$ of the modes is plotted versus ϑ. Thus, only the two modes corresponding to $m=0$ are running and propagate over the whole half space, as already stated. The field vectors of the other modes are different from zero only in a transition boundary layer. In principle, a boundary layer is associated to any one of such modes, referred in what follows as surface modes. The thickness of the layers can be identified with $|k_{m,z}|^{-1}$. In the interval $\vartheta>\vartheta_c$, where only the modes of order $m=0$ are running the periodic medium is expected to be well approximated by the homogeneous model defined using the Bloch method [8–11]. However, the presence of the transition layers can give problems for what concerns the boundary conditions, as stated in the Introduction.

For $\vartheta<\vartheta_c$ also modes of order $m\neq0$ become running. Figure 2 refers to normally incident light, but a ϑ interval always exists where any external wave generates running modes which are absent in the effective (homogeneous) medium. The homogeneous model can be usefully applied to describe the macroscopic properties of the actual periodic structure *if and only if* the additional running modes have negligibly small macroscopic effects. In the following section we shall show that this is not true for ϑ values very close to the angle ϑ_c, that plays the role of a *critical angle* for all macroscopic properties of the periodic structure. This will be done by considering a well defined periodic medium and using the exact equations. However, the simple analysis given in this section, based on the approximate equation (2), evidences the following facts: (i) When ϑ approaches ϑ_c from above, $k_{1,z}$ goes to zero and the thickness of the boundary layer diverges, so that *it becomes impossible to separate bulk and boundary*; (ii) Effects related to the presence of waves with $m \neq 0$ are expected if the orientation of the boundary plane is such that its normal is contained in a solid angle that includes the periodicity direction ζ. The actual shape of this angle depends on the direction of the external wave, but in any case a critical cone where more than two Bloch waves become running always exists; (iii) For 2D and 3D periodic structures a critical cone is associated to any vector of the reciprocal lattice. In fact, it is very easy to extend to such structures of the exact equation (1) and the approximate equation (2).

III. CRITICAL ORIENTATIONS OF THE BOUNDARY PLANE

For a fully quantitative and exact analysis we consider a periodic medium made of isotropic and achiral layers having different refractive indexes and thickness $\lambda/10$. The period is therefore $p=\lambda/5$. We have purposely considered an achiral medium in order to evidence that the failure of the homogeneous models for $\vartheta \approx \vartheta_c$ involves any optical properties. In fact the difficulties to define homogeneous models for chiral crystals have already been discussed in the past. In particular, the failure of the homogeneous model evidenced in Ref. [9] involves only the optical activity of chiral media.

The real part of the quantities $n_{m,z}$ for $m=0\pm1,\pm2$ are plotted in Fig. 3. They have been computed using the coupled-wave method [14], which is numerically exact. However, the value of ϑ_c is very close to the value given by approximate equation (2).

The very critical role played by the angle ϑ_c is clearly illustrated by Fig. 4. It shows that the energy transferred by the external wave to the modes of order $m=\pm1$, neglected by the macroscopic models, becomes dominant at $\vartheta=\vartheta_c$ for TE polarization. Indeed, for this polarization the electric fields of the external and internal waves are parallel and strongly coupled. The shape of the peak in Fig. 4 critically depends on the optical parameters (ratio of refractive indexes, incidence angle, lattice period).

The waves of order $m=\pm1$ give strong macroscopic effects, as shown by Figs. 5, 6, and 7, referring to the more realistic case of a sample confined between parallel planes. For $\vartheta<\vartheta_c$ the sample acts as a diffraction grating, which generates diffracted beams of order $m\neq0$. We observe that: (i) the grating period is equal to $p/\sin\vartheta$ and the quantity $k_p \sin\vartheta$ appearing in Eq. (1) is the wave vector of the grating; (ii) Eq. (2) gives *exactly* the components $k_{m,z}$ of the beams of order m generated by the grating in an external medium with refractive index $n=\overline{n}$; (iii) the Bragg conditions are never met for $p<\lambda/2$, so that the grating acts in the Raman-Nath regime.

Figures 5(a) and 5(b) show the transmittance and the reflectance of the beams of orders $m=0,\pm1$ in two different samples. Obviously, no homogeneous model accounts for this behavior. Figure 6 gives the reflected intensity of the beam of order $m=0$ in a slab between glasses whose refractive index is such that the internal plane waves correspond-

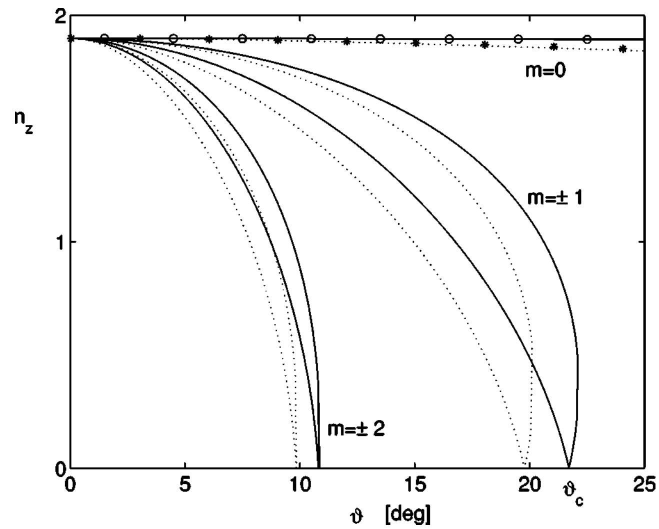

FIG. 3. Components n_z of the Bloch vectors $\mathbf{n}=\mathbf{k}/k_0$ versus ϑ for normally incident light. Here and in the following figures the periodic medium is made of isotropic layers with thickness $\lambda/10$ and refractive indices $n_1=1.3$, $n_2=2.1$. The full and dashed lines refer to the TE and TM modes, respectively. The symbols *, ○ refer to the n_z values given by the macroscopic model defined by the Bloch wave method [10].

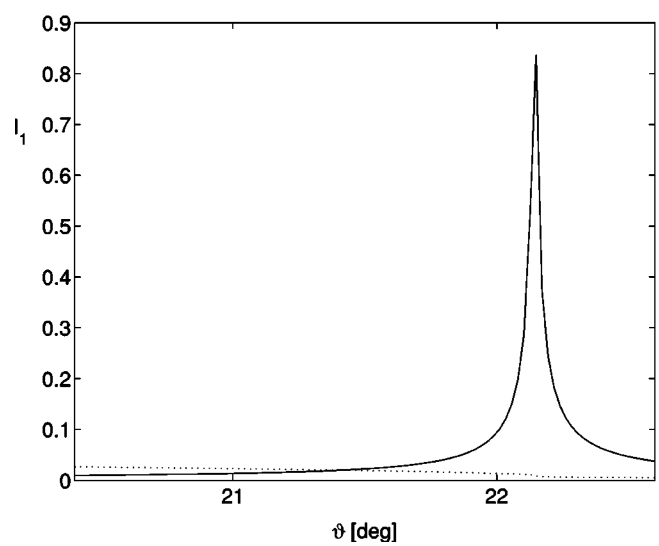

FIG. 4. Relative energy I_1 transferred to the modes of order $m=\pm1$ versus ϑ for the same medium as in Fig. 3, for half space geometry and normal incidence. The refractive index of the external medium is $n=1.885$.

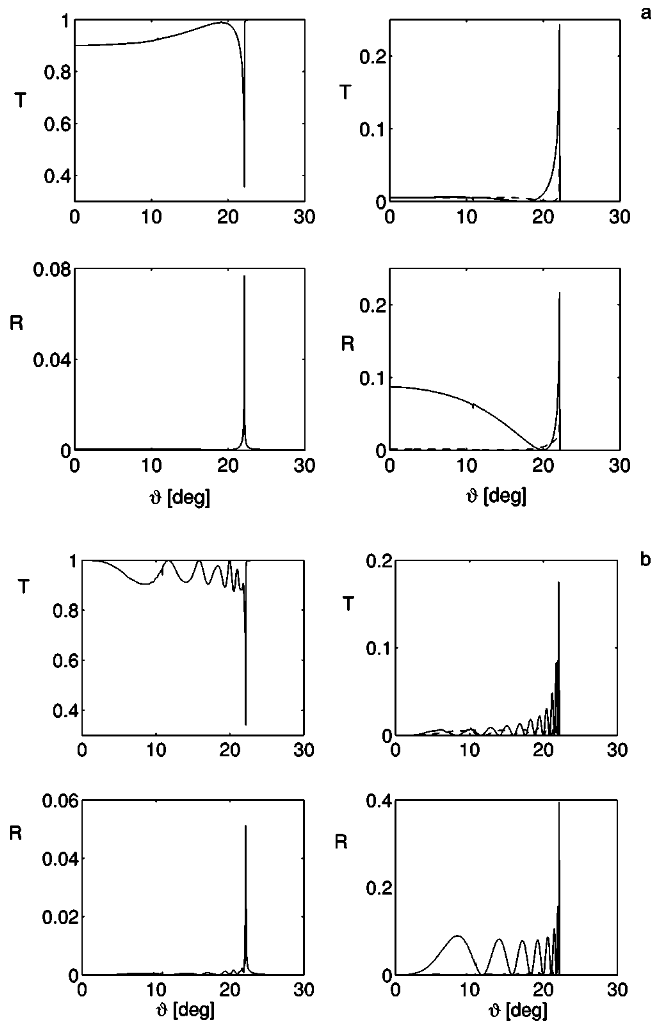

FIG. 5. Transmittance T and reflectance R vs ϑ of the TE polarized beams of order $m=0$ (left hand figures) and $m=\pm1$ (right hand figures), for light normally incident on samples with thickness $d=\lambda/2$ (a) and $d=5\lambda$ (b), between glasses with $n=1.885$. The continuous lines in the right hand figures refer to $m=-1$, the dashed lines to $m=+1$.

ing to $m=\pm1$ are totally reflected at the boundaries. They are coupled to that corresponding to $m=0$, thus giving rise to a guided mode that plays the role of a *resonance* of the periodic structure. Therefore, its width and amplitude depend on the actual shape and size of the crystal sample. However, Fig. 7 shows that for samples between parallel planes the maxima of reflectance are practically independent of the sample thickness.

Let us summarize some additional points evidenced by our numerical analysis for $\vartheta>\vartheta_c$, $\vartheta\sim\vartheta_c$, and for the particular case $\vartheta=0$.

(1) For $\vartheta>\vartheta_c$ the optical properties of the periodic medium considered here are rather well described by the macroscopic model, at least for the bulk properties. On the basis of the analysis given in Refs. [5,10,16] it seems reasonable to presume that difficult problems arise for the boundary conditions if the wave-vector dispersion is taken into account. We recall that the optical activity of chiral media is always a **k**-dependent property.

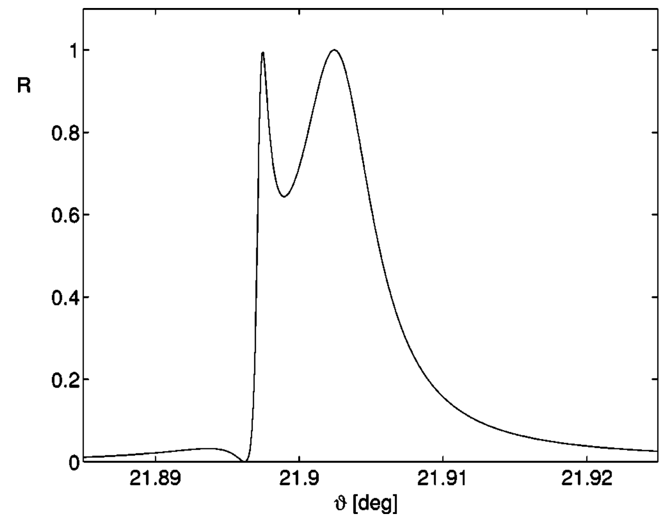

FIG. 6. Reflectance vs ϑ of the TE polarized beam of order $m=0$ for a sample with $d=5\lambda$ between glasses with $n=1.8$.

(2) Critical effects are present near the conical surfaces $\vartheta=\vartheta_{m,c}$, where $\vartheta_{m,c}$ are the critical angles for the Bloch modes of order $m=\pm2,\pm3,\ldots$. For the periodic medium considered here they are not very enhanced because the dominant Fourier components corresponding to $m=\pm1$ of $\varepsilon(\zeta)$ are dominant. For 3D periodic structures, *a critical cone is associated to any vector* $\mathbf{k_q}$ *of the reciprocal lattice*, but strong effects are present only for the $\mathbf{k_q}$ vectors corresponding to the dominant Fourier components of the function $\varepsilon(\mathbf{r})$. For solid 3D crystals having a lattice period of the order of 10^{-9} m or less, the angle ϑ_c becomes smaller than 0.1 deg. Thus, it is difficult to detect the critical effects through experiments, but it is not excluded that some of them will be observed in the future.

(3) By decreasing the period p, the angle ϑ_c decreases, and for $p\ll\lambda$ it becomes nearly equal to p/λ. The maxima of

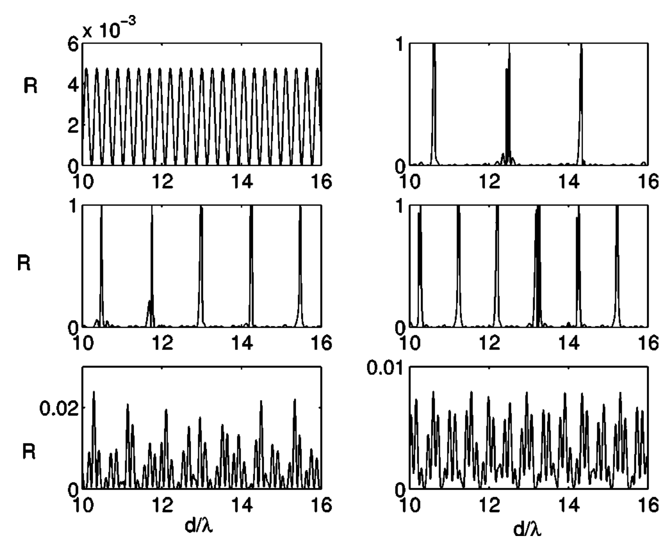

FIG. 7. Reflectance vs the sample thickness d of the TE polarized beam of order $m=0$ for a sample between glasses with $n=1.8$, for $\vartheta=22.2°$ and 21.9° (upper figures); 21.6° and 21.3° (middle figures); 21.0° and 20.7° (lower figures).

the peaks shown in Figs. 5 and 6 are not strongly p dependent, whereas their width decreases with p, as it is expected.

(4) The case $\vartheta = 0$ deserves a particular attention. In spite of the fact that all the Bloch waves become running in the limit $\vartheta \rightarrow 0$, the macroscopic model works well for many optical properties. As a possible explanation of this fact, we observe that for $\vartheta \rightarrow 0$ and for a given polarization all the Bloch vectors k_m and the corresponding Bloch waves become identical. In other words, the external wave generates only two independent modes. Nevertheless, some difficulties arise for $\vartheta = 0$ in short period cholesteric and chiral smectic liquid crystals. In fact, it has been shown both theoretically [11,17] and experimentally [9] that no macroscopic model is able to account for the optical rotation given by a sample between two planes cut orthogonally to the periodicity direction.

IV. CONCLUDING REMARKS

The nonlocal interactions give boundary effects which are not yet completely understood and which are particularly important in periodic media. They make difficult the definition of an effective medium for the periodic structure. We have shown that among the nonlocal interactions the multiple scattering plays a unique role. Due to the very long range of such interaction the optical properties of a finite sample could depend on its shape, independently of its size. Here, we have (i) focused the conditions under which the macroscopic models could seriously fail, (ii) evidenced the critical role played by the orientation of the boundary planes, and (iii) described some of the possible macroscopic effects, which are unexpectedly large, by explaining their origin and estimating their orders of magnitude.

The main motivation of our research refers to basic optics, but the results given here could be of interest for new applications of periodic nanoscale structures and photonic crystals, owing to the critical dependence of the reflectance and transmittance from external parameters (direction of periodicity, wavelength, sample thickness, incidence angle, . . .). To this purpose we observe that it is not difficult to prepare liquid crystal samples which are periodic in any given direction with respect to the boundaries and to electrically control this direction, for instance, using the electroclinic effect [18,19]. Applications of the effects discussed here are expected also outside optics. To this purpose we observe that the phonon scattering at the boundary plane between two different grains in solid crystals depends strongly on its orientation, and that the diffracted waves of order $m \neq 0$ give a non-negligible contribution to the thermal conductivity [20].

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