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# Multiple order light scattering by ringed spherulites

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## Abstract

The transmittivity [Point JJ. Bull Clas Sci Acad Roy Belg 1953;39:455; 1955;41:982. [1]] of light intensity through spherulitic films of poly(ethylene adipate) (PEA) is not uniform. These films may actually be used as multiple diffraction gratings. The intensity of the first order scattering depends reversibly on the temperature *T* of the film (between 10 and 59 °C). For sufficient film thickness (e.g. 30 μm), this intensity is an increasing function of *T*. It is, however, a decreasing function of *T* when the films are sufficiently thin (e.g. 2 μm). These, and other effects are explained by geometrical optics and by the electromagnetic theory of light. Evidently, these effects are not specific to PEA but are characteristic properties of ringed spherulites of polymers and other materials.

*Keywords:* Spherulites; Light scattering; Poly(ethylene adipate)

## 1. Introduction and background

The twisted crystal model of optically ringed spherulites examined in a polarizing microscope was accepted more than 50 years ago [1,2]. In the case of polyethylene, it was supported by:

- X-rays diffraction data [1] that show that the *b* axis is exactly parallel to the spherulite radius.
- Microscopic observation between linear or circular [2] crossed polars, that shows the regular rotation of the crystals along the spherulite radius.
- Microscopic observation using a universal stage tilting experiment [1,2].

At the same time, however, several other observations were not analyzed (or understood) in similar detail. Among other features, it was observed [1] that:

- – Films of crystallized polymers may be used as multiple-order diffraction gratings.
- – The transmittivity of natural light through 2D poly(ethylene adipate) spherulites (i.e. equatorial sections of spherulites produced by, e.g. growth in thin films) is not uniform; it is maximum through concentric circular lines.
- – The measured birefringence in spherulites is too low and cannot be correlated exactly with the crystallites' refractive indices.
- – Ringed polymer spherulites yield multiple order light scattering, whereas theoretical interpretations used so far in the polymer literature account for a single diffraction peak. Several accounts of this multiple order scattering exist in the literature [4–6]. Similar results were obtained in the author's laboratory by Goffin and Van Sinoy [3] (GV). In addition, GV observed and analyzed the $V_V$ scattering of films under various experimental conditions (a detailed account on these experimental results will be reported in the near future). The most unexpected results are the following:
    - (i) When the temperature of the sample is raised the intensity of the first scattering peak increases or decreases if the thickness of the studied film is large or small, respectively.
    - (ii) The ratio of the intensities the second and first scattering peaks depends on the wavelength of the light.

These observations could not be explained by available models and the multiple-order light scattering by polymer films made of ringed spherulites was usually explained by secondary and accidental circumstances, such as interference of light waves diffracted by several spherulites, or non-uniform twisting of the lamellae, etc. (cf. GV, Ref. [3] and Stein and Rhodes, Ref. [4]). In the present paper, we analyze these

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experimental observations and provide a theoretical approach to their interpretation. We show that multiple scattering of thin ringed spherulites is amenable to a better theoretical analysis by considering the ringed spherulites as phase objects rather than amplitude objects (as has been done so far).

At this point, exact definitions of the terms amplitude and phase objects are needed. Their introduction will also help to set the flow chart of the present contribution.

Let a polymer film cover a portion of a reference plane *Oxy* in a *Oxyz* system of coordinates and let illuminate it by a plane monochromatic wave incident in the *Oz*-direction. If no object were present the disturbance in the *Oxy* plane would be represented by the function $V_0(x,y)=A\ \exp(ikz)$, (the $\exp(i\omega t)$ factor is omitted as usual). Because the presence of the film the disturbance is modified. In the output plane of the film, it may be represented by some function which we denote $V(x,y)$. The transmittivity of the film is defined as $F(x,y)=V(x,y)/V_0(x,y)$. In general the function $F$ is complex since both amplitude and phase of the light may be altered on passing through the film. In the special case, when the film alters the amplitude and not the phase of the incident wave (i.e. $\arg(F)=0$) we speak of an amplitude object; if it alters the phase but not the amplitude (i.e. $|F|=1$) we speak of a phase object.

Assume that the experimental arrangement is that described in Fig. 1. The spherulitic film is in a plane parallel to *Oxy*. The incident polarized light beam (*E* vector || to *Oy*) has a diameter much smaller than the spherulite radius. It illuminates a small peripheral region in which the spherulite fibers are nearly parallel, and parallel also to *Ox*. They constitute a linear grating. The lines of this grating are parallel to *Oy* (Fig. 3).

In the models of Refs. [4–6], the polymer films is infinitely thin (in fact its thickness is assumed equal to zero). Therefore, $\arg(F)$ is equal to 0. If $F$ is proportional to $\cos(Kx)$ (where $\Lambda=2\Pi/K$ is the half-periodicity of the pitch), the object would appear as an amplitude grating. In its diffraction spectrum, only the first order would be observable because the Fourier transform of a cosine function is composed of two $\delta$ functions. This is essentially (but not exactly) the major reason why the Stein model does not predict multiple order scattering of significant intensity (Section 3.1).

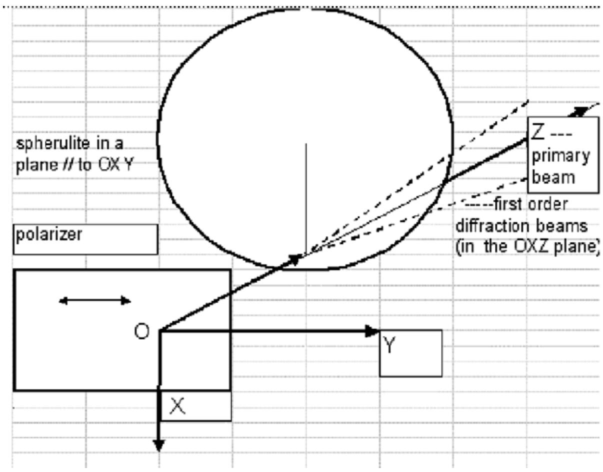

Fig. 1. Experimental arrangement.

The thickness of the ringed poly(ethylene adipate) spherulite, which give a scattering pattern of measurable intensity are larger than few microns. In such thick sample, microscopy shows (Fig. 3) that the condition $\arg(F)=0$ is not fulfilled. In a first approximation $\arg(F)$ is proportional to $\cos(Kx)$. The grating is then a phase grating, or a phase and amplitude grating and multiple order light scattering is expected.

In the present contribution, the experimental part deals with the light scattering by well ordered spherulites of PEA in order to identify the physical parameters that determine the diffraction spectra.

In the theoretical part, we study the diffraction by spherulites in which the refractive index for light polarized tangentially (i.e. with the electric vector parallel to *Oy*) is a periodic function of *x*.

According to this approach, thin spherulites are phase gratings whereas in thick films $|F|\neq 1$. This simple model accounts for the various experimental observations made on the PEA spherulites. It helps uncover the significant physical parameters at play in their light scattering.

Light scattering by spherulites of some nylons and polyesters has been investigated by Magill. These spherulites are more complex to analyze, because the angles between the spherulite radius and any axis of the indicatrix are much larger than in PEA (the observed value of the angle between the spherulite radial direction $a^*$ and the mean axis of the PEA indicatrix is 13° and is neglected in our analysis). Analysis of the light scattering of these nylons and polyesters spherulites requires more elaborated models that will be discussed in a forthcoming paper.

## 2. Experimental section

### 2.1. Introduction

As already indicated, a full account of the experimental work on diffraction of light by PEA spherulites will be reported in a forthcoming paper. In the present section, we limit ourselves to describe the most relevant results obtained by Goffin and Van Sinoy [3] (hereafter referred to as GV) in the author's laboratory back in 1975 and to the data given in Fig. 6).

GV determined how the intensity of the different orders of diffraction depends on the thickness of the sample. These observations could not be explained at the time by available models, although many similar observations had been reported in the literature (and many more have been reported more recently). GV, and the present author invoked uncontrolled and unidentified factors (irregularities of the helical structure of the sample, tangential cracking of the thick samples, etc.), in line with explanations available at that time in the literature [4–6]. These explanations were not, however, satisfactory, and publication of these results has been postponed until now.

GV also measured a highly characteristic and unusual dependence of the spectra on the temperature of the film: the scattering angles do not vary and the intensities change reversibly for temperatures ranging from −10 °C up to the melting temperature of PEA (59 °C).

We have reanalyzed these data and found a reasonable interpretation for the observed phenomena. This explanation is developed in the last section of this paper. First, however, we provide some data on PEA. PEA was used as a test polymer sample because of our familiarity with this material when the experimental work was performed. Again, the exact nature of the polymer is not an essential ingredient in the analysis, provided of course that spherulites are ringed. We then provide the major experimental observations needed to set the background of the theoretical interpretation.

### *2.2. Ringed spherulites of poly(ethylene adipate): some properties*

Upon isothermal crystallization between $T_c=19$ and 36 °C, films of melted PEA give large and well ordered two-dimensional double ringed spherulites [1,7]. The distance between equivalent rings is a measure of the half-periodicity of the pitch of the twisting lamellae (twist axis radial). The variation of the half-pitch distance is represented in Fig. 2.

In the 19–30 °C temperature range, the half-pitch of the helical lamellae does not vary much, but increases sharply above 32–33 °C. No optical banding (concentric rings) is observed at temperatures higher than 36 °C: the structure of the spherulites is different (e.g. different radial growth axis). Note also that the periodicity of the rings depends solely on the crystallization temperature that fixes the frame of twisting lamellae. Later changes of the temperature do not significantly affect this periodicity (except for thermal expansion). Even partial melting and recrystallization (if it maintains this lamellar framework) does not significantly affect the ring spacing.

Ringed PEA spherulites crystallized at or around ambient temperature are, therefore, good candidates for the study of light scattering, and indeed multiple-order light scattering by such spherulites has been observed from the early beginning [1]. Since, they are our main experimental material, the structure of these spherulites needs to be described in more detail.

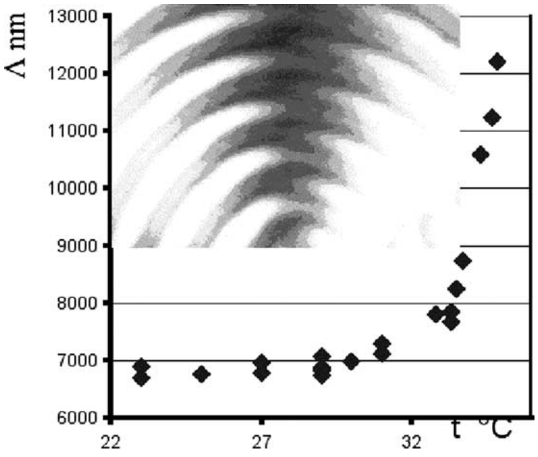

Fig. 2. Periodicity of the refractive index variation along a spherulite radius versus the temperature of crystallization $T_c$. Insert: optical micrograph between crossed polars of part of a typical ringed spherulite.

PEA has, as most aliphatic polyesters, a monoclinic unit-cell [8] with parameters $a=0.547$ nm, $b=0.723$ nm, $c$ (chain axis) $=1.172$ nm, $\beta=113.5°$. Microbeam X-ray indicates that the $a^*$-axis is radial in the ringed spherulites.

Since, we are dealing with optical properties, the optical indicatrix must be determined. The principal refractive indices, the angle $V$ and the angle $\delta$ between the $a^*$-axis and the medium axis of the optical indicatrix have been calculated by the method of Bunn and Daubeny [9]. The numerical values are:

$$\alpha = 1.554,\quad \beta = 1.606,\quad \gamma = 1.685,\quad V = 40.75°,\quad \delta = 12.75°$$

The half-axes $\alpha$ and $\beta$ of the indicatrix are in the (010) plane (normal to the unique axis $b$ of the unit-cell), and the axis $\gamma$ is parallel to that $b$ axis.

It is clear that, given the fact that the radial growth direction is parallel to $a^*$, the medium axis $\beta$ of the indicatrix is not exactly radial: it should make an angle of $\delta=12.75°$ (or even smaller, since the samples are not completely crystalline). This slight 'misorientation' is, however, of little consequence in the following. It can be neglected in a first approximation since the refractive indices obey locally the equations given later, in Section 3.2. In retrospect, it appears that a polymer with an orthorhombic unit-cell would be a better test compound, since a crystallographic axis and the medium axis of the indicatrix would both be exactly radial. This is the case for polyethylene (orthorhombic unit-cell, biaxial but numerically nearly uniaxial optical indicatrix) that also displays ringed spherulites [1,2].

### *2.3. A brief account of experimental results obtained by Goffin and Van Sinoy*

GV observed and analyzed the $V_V$ scattering of PEA spherulites under two different experimental conditions. They first recorded the scattering of films (of undetermined thickness) at different temperatures crystallized at $T_c=25$, 29 and 30 °C, and observed multiple-order scattering (but we hasten to underline that similar observations had been made by other authors [4–6]). In a second set of experiments, they determined the scattering of films with controlled thickness and as a function of the temperature—actually up to the melting range of PEA (Fig. 3).

They also observed that the thickness of the sample affects the intensity of the different orders non-linearly with respect to the film thickness. The amplitude of the first order reflection is not proportional to the film thickness (only a qualitative statement can be made, since the film thickness is difficult to assess precisely). For the thin films, a second order reflection is often observed, but higher orders are absent (it could be argued that the intensity is too weak due to the limited film thickness. This weakness has, however, a theoretical justification, as examined later). Beyond a 'threshold' film thickness, intense higher orders can often be observed (up to five or six orders), and their intensity can either increase or decrease with the film

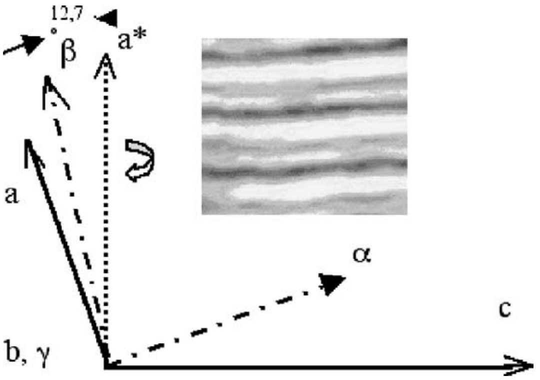

Fig. 3. Orientation of the slow ($\alpha$) and medium ($\beta$) refractive indices in the 010 plane of poly(ethylene adipate). Insert: optical micrograph taken between crossed polars of a peripheral part of a spherulite of poly(ethylene adipate). The axis of rotation of the indicatrix along a spherulite radius is $a^*$ (see also Ref. [18]).

thickness. GV were, therefore, led to classify the films as 'thin films' (say up to 2 μm thickness) or 'two orders-films' and 'thick films' or 'multiple orders films' (e.g. 20 μm thick films). The intensity ratio of the first and second order reflections varies considerably for thin and thick films. It is 20 and 1.1 in the spectra of Figs. 4 and 5, respectively (the appellation 'two orders-film' and the assumption of a 'threshold thickness' were used and are discussed in the caption of Fig. 8).

Temperature cycling (partial melting followed by recrystallization)—up to the melting temperature, where most of the sample is melted, does not modify significantly the recorded patterns. The data are given in Table 1.

This observation simply tells that recrystallization is confined within the framework left by the unmelted lamellae and does not modify the optical properties of the spherulite (although lamellar thickness etc of the lamellae recrystallized at a higher temperature probably differ from the initial ones).

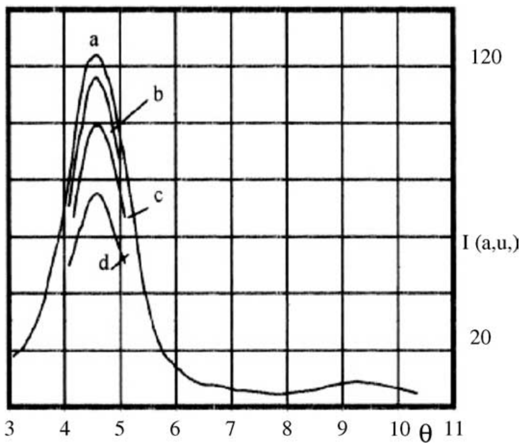

Fig. 4. Thermal dependence of the diffraction spectra by a 'thin two orders' film crystallized at 25 °C. The spectrometer (Bleeker) uses the mercury-vapor line at 5460 nm. Curves a, b, c, d are for observation temperatures of 25, 40, 45 and 50 °C, respectively. Note that at 25 °C, the ratio of the peaks heights for the first to the second order is large. Higher orders are not observed. Note also that the intensity of both orders decreases when the temperature of the film is increased (not shown in the figure, for the too small second order). Annealing for a long time at high-temperature would modify the intensities and has been avoided.

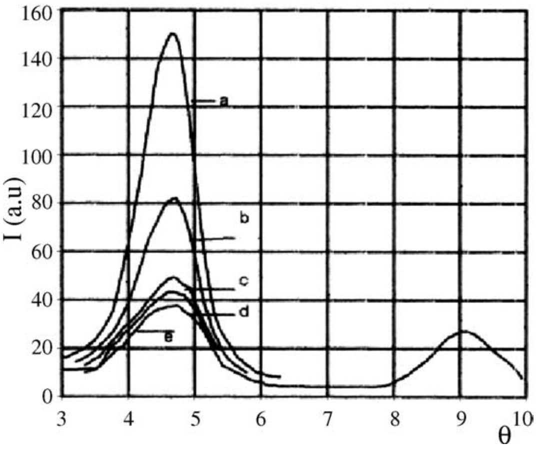

Fig. 5. Thermal dependence of the diffraction spectra by a 'thick multiple-order' film crystallized at 25 °C. Same experimental set-up as in Fig. 3 (mercury-vapor line at 5460 nm). Spectra a, b, c, d and e are recorded at 49.5, 42.5, 33, 30 and 25 °C, respectively. Note that at 25 °C the ratio of the heights of the first to the second order peaks is 1.5. Higher orders 3, 4 and 5 (not shown in the figure) are clearly observed. Note also that the intensity of first order increases when the temperature of the film is increased. On raising the temperature, the intensity of the second order first increases (until 35 °C) and decreases thereafter.

Note that in these temperature cycling experiments, the film thickness and the film structure remain nearly constant. Only the birefringence of the rings varies as the material is progressively melted, which implies that the refractive index must feature in any analysis of the scattered light.

These thick and thin films differ also markedly when investigating the diffracted intensity as a function of temperature, as observed in a second set of experiments in which the temperature is varied step by step. A crystalline framework of the spherulite remains and GV observed that temperature changes result in nearly reversible changes of the scattering intensities while the peak angular positions remain unchanged.

Figs. 4 and 5 show in details the effect of the temperature on the light scattering by a 'two-orders-film' and by a 'multiple-orders-film'. These very representative data are extracted from a significantly larger and consistent set of data.

Strikingly, upon raising the temperature, the intensity of the first order decreases for thin films but increases for thick films. This variation in intensity is most pronounced for the first order and affects most the variation of intensity ratios between the first and higher orders, which explains an apparently 'erratic' variation of these intensity ratios.

To summarize this brief experimental results section, we recall that isothermal crystallization of PEA films, at temperature between 19 and 36 °C results in double ringed spherulites. Temperature cycling between −10 and 60 °C of

Table 1
Cycling the temperature of a thick sample

| | | | | | | |
|---|---|---|---|---|---|---|
| Extrema of the temperatures (°C) and intensity of the first order | 22 | 50 | 22 | 52 | 22 | 53 |
| | 5.8 | 23 | 4.7 | 21 | 5.1 | 23.8 |

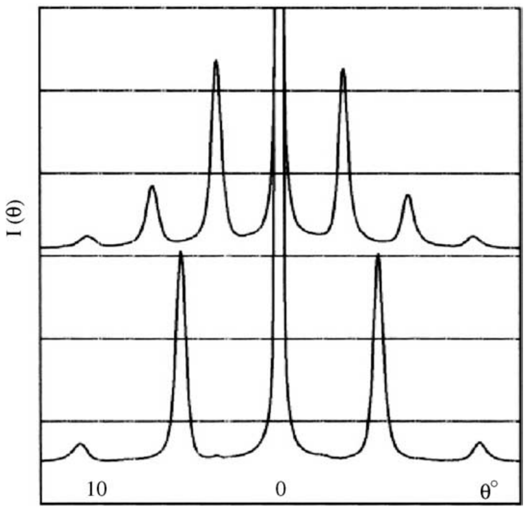

Fig. 6. Diffraction of light with 450 and 700 nm wavelength (upper and lower spectra, respectively). The other parameters (refractive indices, crystallinity, thickness, temperature…) remain unchanged. Indeed in both the experiments, the primary light beam is incident on the same sample at the same location.

these spherulites results in their partial melting and recrystallization, and also in a nearly reversible evolution of their light diffraction spectra. The pitch of the helical organization of the crystals along the spherulites radii remains constant. When the temperature of the sample is raised, the value of the intensity of the first scattering peak increases or decreases if the thickness of the studied film is large or small, respectively. In the following, these films will be referred to as ‘thin films’ and ‘thick films’, respectively. Also, at a constant temperature, the intensities of the second and higher orders are increasing functions of the thickness of the film.

In these experiments, features were noticed that could not be explained by then available theories.

Fig. 6 shows the change of the diffraction spectra with the light wavelength. Note the change of the ratio of the intensities of the first to the second order peaks. The largest orders of the observable peaks are 2 and 5 for light with 700 and 450 nm wavelengths, respectively.

## 3. Theoretical section

### 3.1. Introduction

A natural (non-polarized) light beam used to illuminate a film made of ringed poly(ethylene adipate) spherulites yields a pattern that displays several diffraction orders. Locally, (i.e. at any one point of the spherulite) the light beam may be considered as the sum of two linearly polarized beams: one is oriented parallel to the spherulite radius, the other is tangential to the rings. The former is not diffracted, since the refractive index along the radius is constant. The tangential component encounters a periodic variation of the refractive index along the spherulite radius (linked with the twisting geometry of the lamella). It is diffracted, but its direction of polarization remains that of the latter beam, as in the so-called $V_V$ mode.

The above data were at first explained tentatively by us (GV and JJP) using the then available theoretical expression of the scattering intensity. This expression proposed by Stein and Rhodes [4] is still widely used to interpret the light scattering of polymeric systems.

But it does not account for the multiplicity of diffraction orders. Second, it does not explain the variation of the diffracted peaks with the temperature and, third, with the thickness of the film. Rhodes and Stein [4] pointed out the first weakness (absence of multiple diffraction orders) in their initial paper, as have later on Clough and Stein [5,10], Dausher et al. [6]; Moore also raised this issue [11].

In the following, we present alternative analyses of the diffraction of light by ringed polymer spherulites.

In Ref. [4] and in this paper, the diffracted intensity is calculated using Fresnel integrals. The light sources that are considered in the integral are located the output plane of the sample. In Ref. [4] there are all in phase because the thickness of the film is assumed to be equal to zero. In an alternative calculation, we introduce variations in the phase of the emerging light rays due to the differences in light retardation linked with the local variations of refractive index (Section 2.1). This is the essential difference between our approach and that of Ref. [4].

### 3.2. Physical basis of the theory

The data obtained by microscopy between crossed polarizers and summarized in the introduction are not only indication but actually proof that the light scattering by two-dimensional ringed spherulites is a phase, or a phase and amplitude effect. Indeed, examination of ringed spherulites of PEA in polarized light and using a $\lambda$ wave plate yields first order yellow and second order blue rings. It illustrates the variation of the relative retardations in the positive and negative bands and the spatial dependence of the phase of the light waves in the polymer film. This simple observation justifies the study of phase gratings as models for ringed spherulites.

In the analysis developed next, the phase grating is supposed to be linear. It does not, therefore, take into account the symmetry of the spherulite examined in the optical microscope: this symmetry is roughly cylindrical (equatorial section of a spherulite). It is, however, a suitable model for the scattering by small peripheral regions of the spherulite that can be investigated by using a primary light beam of small cross-section. In such regions, the plane of the polymer film is denoted by $xOz$, and (by a suitable choice of the co-ordinate system $Oxyz$) the refractive indices are

$$n_x, \quad n_y = n_0 + n_1 f(x), \quad n_z$$

where $f(x)$ is a periodic function of wavelength $\Lambda$ (half the pitch of the helical crystal arrangement) and $n_x$, $n_y$, $n_0$, $n_1$, $n_z$ are constants. The primary light wave propagates along $Oz$ and the $E$ vector is parallel to $Oy$.

Diffraction spectra obtained for peripheral regions of spherulites are made of arcs (instead of circles) but the angular dependence of the scattered intensity is similar to that obtained from a large film area including several full spherulites [1].

In a broader perspective, it should be stressed that the present development has many similarities with the classical analysis of light scattering by a column of fluid submitted to ultrasonic waves. In this fluid, the ultrasonic wave propagates in the $Ox$ direction. This compressive wave modifies the refractive index according to

$$n = n_0 + n_1 \cos(2\pi x/\wedge + 2\pi\omega t)$$

where $\Lambda = 2\pi/K$ is the wave length and $\omega$ is the circular frequency.

A light beam propagates along the $Oz$ direction through this column and is scattered by this grating. In this experiment (but not in the study of scattering of light by polymer spherulites), the refractive index is a scalar rather than a tensor. Also, the wave that modulates the refractive index is progressive (therefore, when dealing with light scattering by ultrasonic waves, Doppler effects are predicted and observed).

The problem of scattering light by ultrasonic waves [12] has been extensively studied in the 1930s by Debye and Sears [13], Raman and Nath [14], Lucas and Biquard [15], and others. A comprehensive analysis of these works can be found in Born's book: 'principles of optics' [16].

### 3.3. Very thin films. The simplest model

The light propagates through a polymer film so thin that neither the amplitude nor the direction of propagation of the beam are significantly modified.

The polymer film is parallel to the $xOz$ plane and its assumed refractive indices are

$$n_y = n_0 + n_1 \cos(Kx), n_x, n_z$$

where $n_y$, $n_x$, $n_z$, $n_0$, $n_1$ are constants. $\Lambda = 2\pi/K$ is the periodicity of the grating. $d$ is the thickness of the film.

We start with the study of the diffraction of an incident light beam of sufficient lateral size and of wavelength $\lambda$, polarized with its electric polarization direction along $Oy$. Locally, the light is considered as a plane wave. When it propagates along $Oz$ through the film, its phase change is equal to

$$n_0 + n_1 \cos(2\pi x/\wedge) 2\pi d/\lambda$$

or

$$2\pi n_0 d/\lambda + \xi \cos(\theta) \quad \text{if} \quad \xi = 2\pi d n_1/\lambda \quad \text{and} \quad \theta = 2\pi x/\wedge$$

The directions in which there is an appreciable intensity of diffracted light are determined by the condition that the optical path difference between the rays from successive abcissae $\Lambda$ apart are an integral multiple of $\lambda$.

Consider the order $m$ of diffraction and two rays coming from points of abcissae 0 and $x$; the condition of diffraction introduces an additional difference of phase equal to $m2\pi x/\Lambda$ or $m\theta$ (Fig. 7).

The contribution to the diffracted complex amplitude arising from a whole period of the grating is proportional to

$$\int_{-\pi}^{\pi} \exp - i(m\theta + \xi \cos(\theta)) \mathrm{d}\theta$$

or, if $\eta = \pi/2 - \theta$ and if $J_m(\xi)$ is the Bessel function of integer order $m$ [17].

$$i^m \int_{-\pi}^{\pi} \exp - i(m\eta + \xi \sin(\eta)) \mathrm{d}\eta = i^m J_m(\xi)$$

The intensity of the $m$th order is proportional to $J_m(\xi)^2$. The difference between the phases of two consecutive orders is $\pi/2$. On the other hand, polarized light with electric vector parallel to $Ox$, propagating along $Oz$, is not diffracted since the refractive index $n_x$ is constant.

These results (which may be used to interpret the findings of GV) are commented at the end of the next section. We observe, however, that the index gradients are so large that using geometrical optics may be questionable. In order to confirm our conclusions, we treat the same problem in the formalism of the Maxwell equations.

### 3.4. Discussion using the Maxwell equations

In this section, the results of Section 3.2 are analyzed on the basis of a mathematical development made in association with my colleague Ceuleneer, University of Mons.

Let the incident monochromatic plane wave be linearly polarized with its electric vector along the $y$-axis.

From the symmetry of the problem, $E_x = 0$ and $E_z = 0$. Because there are no free charge and because $n$ depends only on $x$, $E_y$ is independent of the $y$ coordinate.

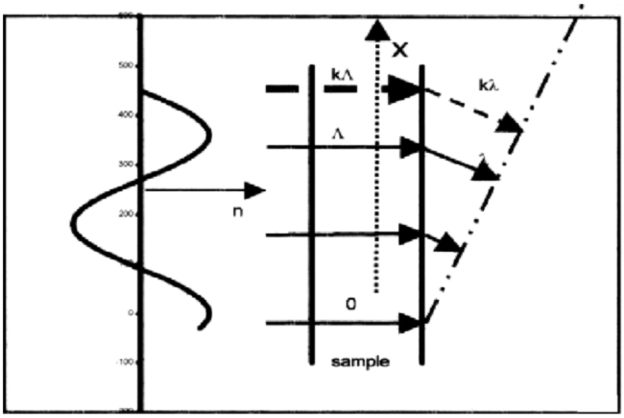

Fig. 7. The simplest model: when the plane polarized incident light crosses the polymer film, it is assumed that its amplitude and direction are not modified. The change of phase depends on $x$ and $z$. If the area of the film is large, the angles between the incident and diffracted beams are $\arcsin(m\lambda/\Lambda)$ where $m = 0, 1, -1, 2, \ldots$ is the order.

Because $E_x = E_z = 0$ and $\partial E_y/\partial y = 0$ | Because $B = 0$ and $E_x = E_z = 0$

$$\partial E_y/z = -ikB_x, \qquad \partial B_z/\partial_y = 0,$$

$$0 = ikB_y \quad | \quad \partial B_x/\partial z - \partial B_z/\partial x = ikn^2 E_y$$

$$\partial E_y/\partial x = ikB_z \quad | \quad \partial B_x/\partial y = 0$$

In conclusion, $E_y$ must satisfy the boundary condition $E_y(0) = 1$ and the equation:

$$\partial^2 E_y/\partial x^2 + \partial^2 E_y/\partial z^2 + k^2 n^2 E_y = 0 \qquad (1)$$

The trial function $E_y = \exp(iknz)$ gives when introduced in (1) three terms:

$$(\partial^2 E_y/\partial z^2 + k^2 n^2 E_y)\ (-k^2 \sin^2(Kx)[n_1^2(Kz)^2])\ (-ik^2\cos(Kx)[(K/k)n_1 Kz]$$

The absolute values of each of the two last terms of this sum are, for not too large a value of $z$, much smaller than each of the two terms of $(\partial^2 E_y/\partial z^2 + k^2 n^2 E_y)$.

Indeed, $n_1 \ll n_0$ (for instance, $n_1 = n_0/25$) and $K \ll k$ (for instance, $K = k/10$). The trial function may thus be retained tentatively.

It yields for the intensity of the $m$th order of diffraction a value proportional to the square of the Bessel function of integer order $J_m(kn_1 z)$.

Several authors have obtained improved solutions of Eq. (1) in the form of slowly converging series (the reader is referred to Born's book [16]). However, these solutions do not modify significantly the calculated intensities. Since also the parameters that characterize our samples are not known exactly, these mathematical developments are not pursued now. And the obtained expression of the intensities is accepted.

A different, and more critical problem relates, however, the non-uniform transmission of the light through the polymer film. This leads to a discussion of the trajectory of the light rays. In such calculation it may be that more exact solution of the Maxwell equation is needed.

From the approximate solution of Eq. (1) the components of the magnetic induction and of the Poynting vectors are

$$B_x = -(n_0 + n_1 \cos Kx)E_y \qquad P_z = c/8\pi(n_0 + n_1 \cos Kx)E_y$$

$$B_z = Kn_1 \sin(Kx)zE_y \qquad P_x = c/8\pi Kzn_1 \sin(Kx)E_y$$

These further calculations from the approximate solution of Eq. (1) cannot be retained. Indeed, the integration along a ray of

$$\partial z/\partial x = P_z/P_x = n_0/(n_1 Kz \sin(Kx)) + 1/(Kz\, tg(Kx))$$

leads to

$$z = [2n_0/(n_1 K)\ln((tg(Kx/2)/tg(Kx_i/2)) + (2/K)\ln((\sin Kx)/(\sin Kx_i))]^{1/2} \qquad (2)$$

Such an equation expresses the fact that the light comprised in a strip limited by two abcissae which are consecutive integer multiples of $\Lambda/2$ (i.e. $i/2\Lambda$ and $(i+1)\Lambda/2$) remains confined in that strip. In addition, such curves present an inflexion point at some location comprised between these two abcissae. This cannot be accepted because light rays bend towards the region of higher refractive index and because in any single strip, the gradient of refractive index has everywhere the same direction.

Determination of the trajectories of the light rays, from the approximate solutions of the Maxwell equation may be retained solely for very low values of $z$. More exact calculations from series expressing the values of $E_y$ are cumbersome. The simplest way to solve the problem is, as shown by Lucas and Bicquart [15] in a closely related problem, to resort to calculation by geometrical optics (Section 3.6).

### 3.5. Comparison with the data of GV

The results of the above calculations, although still approximate, explain the observations made by Goffin and VanSinoy and justify a posteriori their empirical classification of the polymer films as 'two-orders-films' and 'multiple-orders films' (Fig. 8). This figure explains the a priori unexpected different response of 'thin two orders' and 'thick multiple orders' films.

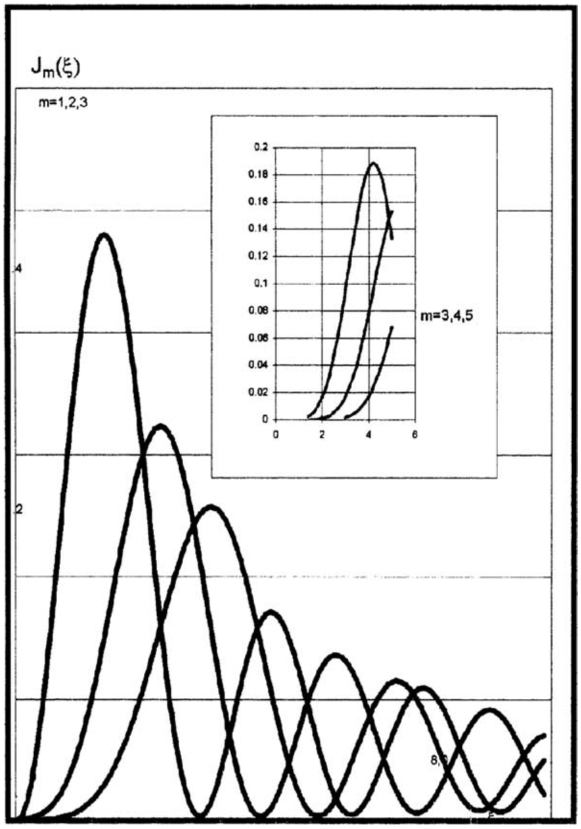

Fig. 8. Dependence on $\xi$ of the square of the Bessel functions of integer orders $J_n(\xi)$. This figure explains the a priori unexpected different response of 'thin two orders' and 'thick multiple orders' films. For low values of $\xi$, the values of $J_1^2$ and $J_2^2$ are much larger than the values of $J_3^2, J_4^2, J_5^2$. However, for values of $\xi$ between 1.0 and 2.0, the values of $J_n^2$ for $n = 3, 4, 5$ are (usually) are larger and if not equal, at least of the same order of magnitude (we recall that the thickness of a film is not rigorously constant). However, strictly speaking $\xi = 2$ cannot be considered as a 'threshold'. Note also that the derivatives of $J_2, J_3, J_4, \ldots$ are zero for $\xi = 0$ while that of $J_1$ is positive. In order to take into account the finite cross section of the incident light beam, the calculated intensities would have to be convoluted by an appropriate form factor (for instance by an Airy function). Such complications would introduce, without great profit, additional parameters.

Table 2
Numerical values of the square of Bessel functions of integer order

| $\xi$ | $J_1(\xi)^2$ | $\xi$ | $J_2(\xi)^2$ | $\xi$ | $J_3(\xi)^2$ |
|---|---|---|---|---|---|
| 0.0000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 1.8412 | 0.337 | 3.0542 | 0.236 | 2.000 | 0.017 |
| 3.8317 | 0.000 | 5.1356 | 0.000 | 4.200 | 0.189 |
| 5.3314 | 0.121 | – | – | – | – |

(1) The theoretical values of the successive orders intensities are proportional to $J_m(\xi)^2$. These functions are represented in Fig. 8. The values of some of their local maxima and zeros are indicated in Table 2.

(2) In the useful range of variation of $\xi$ and $m$, the squares of the Bessel functions of larger integer orders are increasing functions of $\xi$. If $m<n$, the value of $J_m(\xi)^2$ is (for sufficiently low values of $\xi$, lower than that of $J_n(\xi)^2$.

(3) Assuming that the range of variation of $\xi$ for the thin 'two-orders-films' and thick 'multiple-orders-films' of Goffin and VanSinoy are (0, 1.841) and (1.841, 5.33), respectively, or, more precisely, that the $\xi$ values of the films giving the spectra of Figs. 3 and 4 are 0.9 and 2.0 leads to the following conclusions:
    - The higher orders are seen only in the 'multiple-order-films' because their intensity is given by the square of Bessel functions of higher order and for relatively low $\xi$ values (i.e. for values lower than $\xi$ corresponding to the first local maximum of these functions).
    - The fact that, at 25 °C, the intensity of the first order in spectra 3 and 4 are nearly equal in spite of the different film thickness may be due to the fact that their $\xi$ value are below and above 1.8415, respectively (this value corresponds to the first local maximum of $J_1$).
    - On heating, the films of PEA are partially melted. Their $\xi$ parameter (equal to $2\pi dn_1/\lambda$ decreases. A straightforward but unexpected consequence is that the intensity of the first order maximum decreases for the thin film but paradoxically increases for the thick sample. These effects are represented by the arcs $X'Y'$ and $XY$ in Fig. 12.
    - Simultaneously, the intensity of the second order decreases for the thin film (Fig. 4). A small increase and then a decrease are observed for the thick film (Fig. 5).

### 3.6. Further comments

There is a qualitative agreement with the prediction of intensities of the $m$th order proportional to the square of $J_m(\xi)$. The Bessel functions of integer order have zeros and local maxima and minima. GV were able to prepare films of sufficient thickness to illustrate the occurrence of the first maximum of $J_1$. However, it would be interesting to investigate samples characterized by larger values of $\xi$. Let us consider different experimental means (and associated difficulties) that may be used (and encountered) to measure or change the value of $\xi$.

The most elegant method to change $\xi$ is to change $\lambda$, by use either of lasers with different wavelengths or of a low-pressure mercury-vapor lamp (the emission spectrum of the latter is made of many well separated lines) (Fig. 6).

- Evaluation of $n_1$ is possible only if the crystallinity is known exactly and if the problem raised by Keith [18] about the possible existence of two populations of crystals were definitely solved.
- The thickness $d$ of the film may be determined by weighing a known area of the film. It may be also obtained by interferometry of the air film between the microscopic slide and cover all around the polymer film. Note that the object and cover slides do not have optical surfaces. It is possible that the data of GV do not correspond to exact values of $d$, but represent some average value of $d$.
- The value of $\xi$ depends on the product $dn_1$. This product is the sum of the absolute values of the retardation in the center of the positive and negative bands of the spherulites. However, complications arising from the curvature of the light rays are very likely, and measuring the retardations with compensators is not an easy task (Section 3.6).
- The dependence of the sample structure as a function of $d$ must also be taken into account. Nucleation of the spherulitic fibers occurs frequently at the glass polymer interface. Therefore, the obliquity of these fibers with respect to the film plane depends on $d$. The nucleation may also occur in the bulk. In that case, the number of nuclei per unit surface and the average spherulitic diameter depend on $d$. Again, the fibers are variously tilted with respect to the light beam. Changing the film thickness while maintaining constant the values of the other parameters would be problematic. An easy way out (at least for thin polymer films) is, however, to record the light scattered from the exterior of big spherulites, where growth is essentially parallel to the plane of the film.

### 3.7. Curvature of the light rays

The study of the scattering of light by ultrasonic waves propagating in a liquid medium, light focalization was observed [15]. This effect was not explicitly considered in the previous sections although it does also occur when light is scattered by polymer spherulites (as reported, but not further commented on, in our early paper [1] on PEA spherulites). In order to illustrate and quantify this effect, let us return to the geometrical optics approach, but taking into account the curvature of the light rays.

A light ray linearly polarized along $Oy$ propagates in the $Oz$ direction and enters the polymer film at the abcissa $x_i$ where $n_y=n_0+n_1\cos(Kx_i)$. The external parts of the trajectory are in a plane $\Pi$ parallel to $xOz$. The gradient of the refractive index $n_y$ is everywhere parallel to $Ox$. At the abcissa $x_i$, $Oxz$ is the osculating plane of the trajectory and the light ray and the gradient of refractive index remain in this plane.

- Denote by $x=g(z)$ the equation of the light ray and by $S(x,z)$ the optical path. Because $n_y$ depends solely on $x$, the eikonal equation

$$(\partial S/\partial x)^2 + (\partial S/\partial z)^2 = n_y^2(x)$$

gives $\partial S/\partial z = C$ where $C$ is a constant, and

$$\partial S/\partial x = (n_y^2 - C^2)^{1/2}$$

For $x=x_i$ $\partial S/\partial x=0$. Therefore, $C=n_i$

- The gradient of $S$ is tangent to the ray. As a consequence, the differential equation of the ray is

$$g'(\partial S/\partial x)/(\partial S/\partial z) = (n_y^2 - n_i^2)^{1/2}/n_i$$

- Finally, we get

$$(n_y/n_i)^2 = 1 + g'^2 \quad (3)$$

which is approximated by $g' = (2(n_y/n_i - 1))^{1/2}$

If $n_y = n_0 + n_1 \cos(Kx) = n_0 + n_1(1 - 2\sin^2(Kx/2))$ the differential equation of the trajectory is

$$g' = (2n_1/n_i)^{1/2}(\sin^2(Kx_i/2) - \sin^2(Kx/2))^{1/2} \quad (4)$$

or

$$dz = 1/K(n_i/n_1)^{1/2} d\varphi/(1 - k^2\sin^2\varphi)^{1/2} \quad (5)$$

If the constants $k$ and $\alpha$ and the variable $\varphi$ are defined by

$$Kx_i/2 = \alpha, \quad k = \sin\alpha \quad \text{and} \quad \sin(Kx/2) = k\sin\varphi,$$

Therefore, $z$ is proportional to the elliptic integral [17] of the first kind $F(\varphi|\alpha)$. In conclusion, (sn being the sinus amplitude of Jacobi), two (equivalent) equations of the light rays are obtained

$$z = 1/K(n_i/n_1)^{1/2}(F(\Pi/2|\alpha) - F(\varphi|\alpha))$$

and

$$\sin(\Pi x/\wedge) = \sin(\Pi x_i/\wedge)\ \mathrm{sn}(F(\Pi/2|\alpha) + (2\Pi/\wedge\,(n_1/n_i)^{1/2})z) \quad (6)$$

Fig. 9 illustrates accordingly the curvature of the light rays towards the regions of large refractive index. It is drawn for a particular value of the parameter $(n_i/n_1)^{1/2}$ (see caption of Fig. 9). If the polymer film is thick, i.e. when $((n_1/n_i)^{1/2})z$ is larger than 1.57 (the value of $F(\Pi/2,|\Pi/2)$), rays cross the $z$-axis and cross also the rays coming from the negative abcissae. The light beam is more or less focalized. For instance if $2\Pi d/\Lambda = 8.0$ at the film output, a band of width $\Lambda/3$, receives a very large part of the intensity.

From the very beginning [1], it was reported that the transmissivity of natural light through thick spherulitic films of PEA was maximum along regularly spaced circular lines. Fig. 10 shows this effect for linearly polarized light. The transmissivity is maximum at the center of the negative bands in sectors of spherulites in which the electrical vector is tangential to the rings. This is precisely the effect predicted and illustrated in Fig. 9.

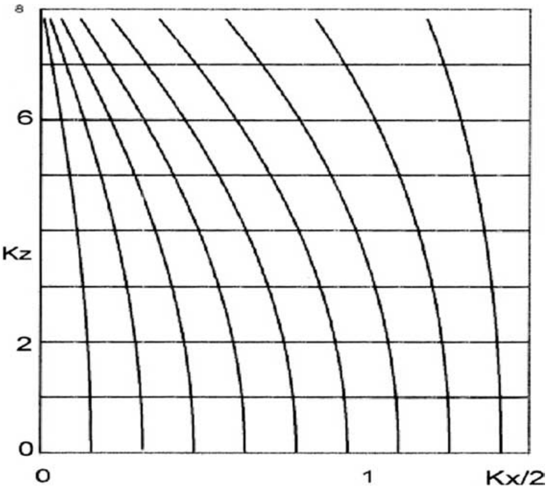

Fig. 9. Curvature of the light rays.

### 3.8. Consequences of the curvature of light rays on observations between crossed polarizers

Eq. (6) gives the trajectories of the light rays and allows calculation of the amplitude and phase at any point of the film output plane, which is the ultimate goal we wish to achieve through this mathematical analysis.

Let us for instance calculate the path of a ray propagating through the thickness of the sample, from $z=0$ to $z=d$. The geometric length of the path is larger than the film thickness because the light path is curved. Also, along the ray, the refractive index $n_x$ increases, as the ray is bent towards regions of higher refractive indices.

The length $L$ of the optic path is given by integration of Eq. (7) [14]

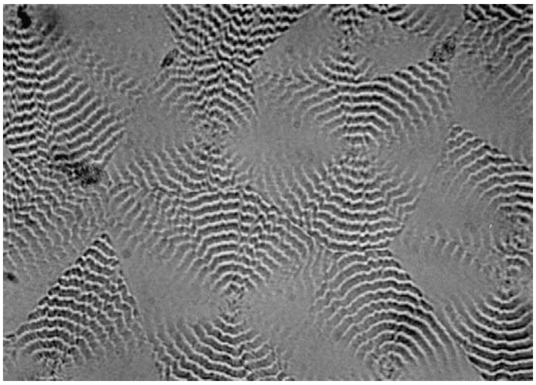

Fig. 10. Optical micrograph of a PEA spherulite observed in plane polarized light. The electric vector is horizontal. Along any given radius, the tangential component of the incident light beam is focused at the center of the negative bands. The transmission factor of the radial component of the incident light is uniform.

$$L = \int n(1 + g'^2)^{1/2}\mathrm{d}z \tag{7}$$

$$L = (F(\Pi/2|\alpha) - F(\varphi|\alpha))(a + bk^2) + (E(\Pi/2|\alpha) - E(\varphi|\alpha))(c + dk^2) + \mathrm{e}\,\sin(2\varphi)k^2\varDelta$$

where $a = n_0^2 - 2n_1n_0 - n_1^2/3$; $c = 4n_0n_1 + 4/3n_1^2$; $d/2 = 4/3n_1^2$; $\varDelta = (1 - k^2\sin\varphi)^{1/2} - (1 - k^2)^{1/2}$

The apparent index is defined as $n_{\mathrm{ap}} = \int nds/d$ and is represented in Fig. 11 as a function of the actual value of the index $n_y(x)$. It is smaller than $n_y(x)$ except for $x = 0$ and $x = \varLambda/2$. Consequently, if the thickness of the film increases, the centers of the negative and positive bands of the spherulite are not affected by a change of $(n_i/n_1)$ and/or by the curvature of the light ray. However, the width of the negative bands increases at the expense of that of positive ones. This calculation shows that the effect of curvature of the light rays in polymer films (for film thicknesses commonly used, i.e. 10–40 μm) may complicate the evaluation of the relative retardation, of the birefringence and of the 2*V* angle between the optic axes. For future reference, we note that it may also modify the shape of the extinction lines. These topics will be studied in a forthcoming paper.

### *3.9. Fresnel integral by numerical calculation*

Knowing the amplitude and phase at any point of the output plane of the films also allows us to calculate the Fresnel integrals and the diffraction spectra. The values of the intensities of the successive orders were computed by assuming a constant value of the inclination factor of the Fresnel theory. The Fig. 12 shows the dependence on d of the diffracted intensity for the first order. The intensities of the successive orders are found to be nearly proportional to the square of the corresponding Bessel function. In line with Sections 1 and 4, these functions are closed expressions of the intensities, expressed in arbitrary units.

To sum up this theoretical analysis, we have first used a simplified approach to account for the light scattered by ringed spherulites. This approach leads to the Bessel functions that show that the energy shifts from one maximum of the diffraction pattern to the neighbor ones for increasing film thickness. As a consequence, the maximum scattered intensity is not necessarily observed for the lower orders of the pattern (this trend would continue when using even thicker samples). Using a more sophisticated approach that involves Maxwell equations does not improve matters much. It is still an idealized model and leads ultimately to using also Bessel functions, as a simplified solution of a more complex, hardly tractable mathematical problem. In simple terms, this analysis amounts to considering that the bending light rays, when they reach the areas of maximum refractive index, travel parallel to that plane of maximum refractive index. This is not physically realistic, which also tells that the Bessel solution is not correct when $z$ is large. In effect, the light rays cross the plane of maximum refractive index, and bend backwards again towards this plane. This geometrical approach of the trajectory of the light rays is (or would lead to) an exact solution of the scattering of light.

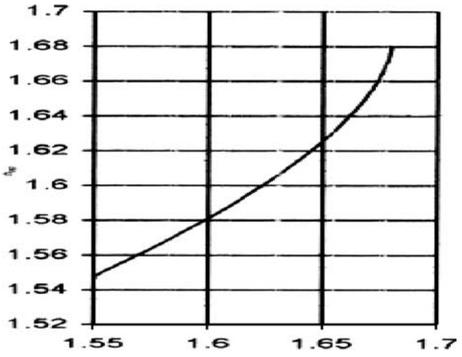

Fig. 11. Apparent refractive index at the output of the film ($z = d$) is defined as the ratio between the optical path within the film and the film thickness *d*. It is given here as a function of the actual index $n_0 + n_1\cos(Kx)$ (the parameters used are: $n_0/n_1 = 25$; $2\Pi z/\varLambda = 4$).

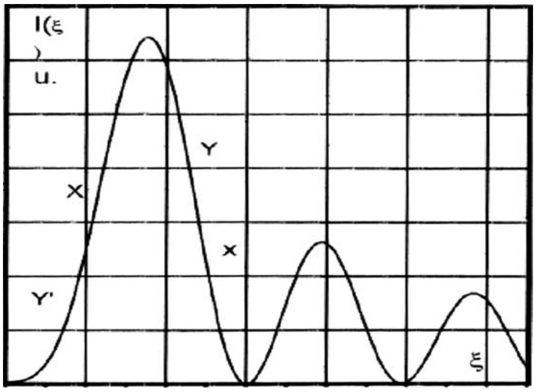

Fig. 12. Intensity of the first order as a function of $\xi$ obtained by Fresnel integration. The arcs $XY$ and $X'Y'$ show the variation of this intensity when the crystallinity of a thick sample decreases. The arcs $X'Y'$ shows this intensity and its variation when the crystallinity of a thin sample decreases.

## 4. Summary and conclusions

In this contribution, we have studied the multiple order scattering of light waves by films made of banded (ringed) spherulites. Observed from the early beginning, this effect has conventionally been attributed to irregularities of the structure of the spherulites. We propose an alternative explanation that is supported by results of Goffin and Van Sinoy obtained many years ago in our laboratory.

Observed between crossed nicols, ringed spherulites show that the relative retardation of light polarized radially is constant whereas for light polarized tangentially, this relative retardation is significant and varies periodically along the radius. These observations indicate that the scattering by ringed spherulites is a phase or a phase and amplitude effect—in effect, the ringed spherulite is a phase object. This feature is not usually taken into account in the analyses used so far in the polymer literature. In particular, the 'standard' theory accounts only for one order of diffraction, and does not take into account the variations of the refractive index in the film.

The present contribution has approached the issue of scattering and multiple scattering of polymer films following different paths, some of which only can be brought to (near) completion. Other approaches must be abandoned because exceedingly sophisticated mathematical developments would be required, and probably would not be worth the effort—if only because a simplified model for the spherulite structure is always assumed.

In a first model, valid for very thin spherulites, multiple orders scattering are predicted when a plane wave is normally incident to the spherulitic sample. Such spherulites act as phase gratings. If the tangential refractive index has a sinusoidal dependence on $r$ (the radius of the spherulite), Bessel functions come naturally into play. The angles of the diffracted beam with the normal to the film are $\arcsin(m\lambda/\Lambda)$ with $m=1, 2, 3$, etc. and their intensities are proportional to the square of the Bessel functions of integer orders $m$. The argument of the Bessel functions depends on the difference between extreme values of the optical paths (that themselves depend on the local refractive index) divided by $\lambda$. Two successive orders have phases differing by $\pi/2$. In a second model, valid for samples of finite thickness, we use the Maxwell equations that lead to similar conclusions. The main merit of this second approach is to help analyze the unavoidable approximations made in the first model and to define the range of validity of the mathematical development. It leads again to the Bessel functions considered in the above analysis, but the approach is still insufficient. It would lead, however, if performed correctly, to a complex mathematical development.

In a third part, we have considered yet a different approach to account for observed variations of the transmission factor of the films, a phenomenon that was observed early on. The variation in transmittance results from the partial focalization experienced by light propagating through the spherulitic film. The Bessel functions used above do not predict or consider the trajectory of the light rays in the polymer film. This third approach is thus based on geometrical optics. The underlying principle is that, since the refractive index gradients are large, it is necessary to take into account the curvature of the light rays (which, therefore, travel through parts of the sample that have different refractive indices). Interestingly, this approach explains and accounts for both the focalization of the light beams and for the amplitude and phase of the light in the output plane of the film. Moreover, the numerical calculation of the Fresnel integrals leads to scattering spectra in accordance with the results given by the two first models used in the present contribution (simplified model and Maxwell equations). For all practical purposes, the latter approach should be recommended to analyze the light scattered by spherulitic films.

The developments provided in this contribution help put in perspective several earlier experimental results. In some of these former studies, temperature and film thickness were assumed to be separate variables (more or less explicitly, and in accordance with an erroneous theoretical approach [4]). This explains why the observations seemed erratic and were assumed to result from hidden parameters. The experimental results briefly reported here show that the physical parameters are indeed numerous but show also that they are not separate variables. For instance, raising the temperature of the sample, considering higher orders of diffraction, or studying thicker films, or using a smaller wave length may result in an increase or in a decrease of the scattered intensity Moreover, reduced variables such as $n_0/n_1$, $n_1d/\lambda$, $\lambda/\Lambda$, $d/\Lambda$ and $m$ (the order of the diffraction peak)) are significant variables.

This study suggests strategies for future work and methods for non-destructive monitoring of thickness or crystallinity of very minute samples in real time. Finally, we wish to point out that thin spherical parts of spherulites are very likely wave guides.

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