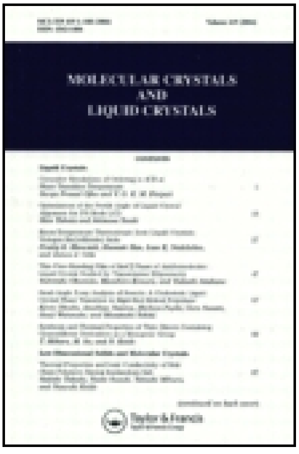

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Determination of Changes in Director Orientation with Temperature in Oriented Cholesteric Layers

H. Zink [a] & V. A. Belyakov [b c]
[a] Laboratorium voor Akoestiek en Thermische Fysica, Celestijnenlaan 200D, B-3001, Leuven, Belgium
[b] Scientific Research Center for Investigation of Surface and Vacuum, Andreevskaya nab 2, 117334, Moscow, Russia
[c] L.D. Landau Institute of Theoretical Physics Kosygin str. 2, 117334, Moscow, Russia
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DETERMINATION OF CHANGES IN DIRECTOR ORIENTATION WITH TEMPERATURE IN ORIENTED CHOLESTERIC LAYERS

H. ZINK
Laboratorium voor Akoestiek en Thermische Fysica, Celestijnenlaan 200D, B-3001 Leuven, Belgium
V.A. BELYAKOV*
Scientific Research Center for Investigation of Surface and Vacuum, Andreevskaya nab. 2, 117334 Moscow, Russia

Abstract The temperature dependence of the pitch in a planar oriented cholesteric layer has been examined and it is shown that, before the jump in the number of half-pitches in the sample changes by 1, the director orientation deviates from the alignment direction at the sample surface. The number of half-pitches changes into a noninteger number. This deviation angle depends on the strength of the anchoring at the surface and when the elastic constant K_{22} is known, the anchoring energy can be determined.

INTRODUCTION

For completely aligned CLC-samples in the cholesteric phase, the number of half-pitches in the layers depends on the temperature. Only at discrete values of the temperature an exact number of half-pitches fits in the sample thickness. We showed [1] that this can be seen in the transmission and reflection spectra of circularly polarized incident light. These spectra can be well described by the 4-wave model of Belyakov and Dmitrienko [2] in which 6 parameters are used to characterize the spectra. For temperatures in between, the spectra are distorted. We will demonstrate that these distortions can be explained by small rotations of the director at the surface of the sample when the temperature changes. In the calculations these small rotations of the director can be taken into account by a slight change of the angle between the director and the alignment direction at the sample surfaces as well as by a slight change of the number of half-pitches to a noninteger number.
By taking a superposition of 2 weighted spectra with N and N+1 half-pitches, the agreement with the experiments is very good.

EXPERIMENTAL

Transmission spectra are measured in a sample of a 60% chiral/racemic mixture of CE6 [BDH] (1). The molecules are planar oriented by means of a rubbed polyimide coating on both glass surface plates and the sample thickness is 4.8μm. The normal incident light on the sample is circularly polarized by means of a Glan-Thomson polarizer and a 1/4-wave plate.

As we scan through the visible light spectrum of a halogen light source,the polarization of the incident light on the sample will be elliptically polarized and the ellipticity will change with the wavelength.

The pitch of the sample diverges exponentially with decreasing temperature on approaching the Ch-S transition temperature.So the number of half-pitches in the sample can be varied by changing the temperature.

Integer number of half- pitches.

Only at specific temperatures, an integer number of half -pitches fit in to the sample thickness. In these cases the spectra are determined by 6 parameters.

1/ Sample thickness N [in number of half-pitches $N = 2 L/p$]

2/ Polarization of the incident light $e = \cos\alpha\ \chi_1 + i \sin\alpha\ \chi_2$.
χ_1, χ_2 are the linear polarization directions, with χ_1 making the angle ξ with the director orientation at the entrance surface of the layer. α is the ellipticity of the incident light.

3/ Dielectric anisotropy $\delta = (\epsilon_1 - \epsilon_2) / (\epsilon_1 + \epsilon_2)$, $\epsilon = (\epsilon_1 + \epsilon_2) / 2$, where ϵ_1, $\epsilon_2 = \epsilon_3$ are the principal values of the CLC dielectric tensor.

4/ r is the ratio of refractive indices of the external media and the CLC. $r = n_e/n$.

5/ The amplitude of the Eigenwaves E_+, E_- is determined by the following expression:

$$E_\pm = \frac{1}{\sqrt{2}} (\cos\alpha \pm i\sin\alpha)(\cos\xi - i\sin\xi)$$

We started by determining these 6 parameters α, ξ, r, δ, N and Lp for the spectra at T = 40.41°C and T = 40.27°C. Only Lp is different for the 2 temperatures and N differs by 1.

In Fig. 1 the experimental and calculated spectra are shown for the two temperatures.

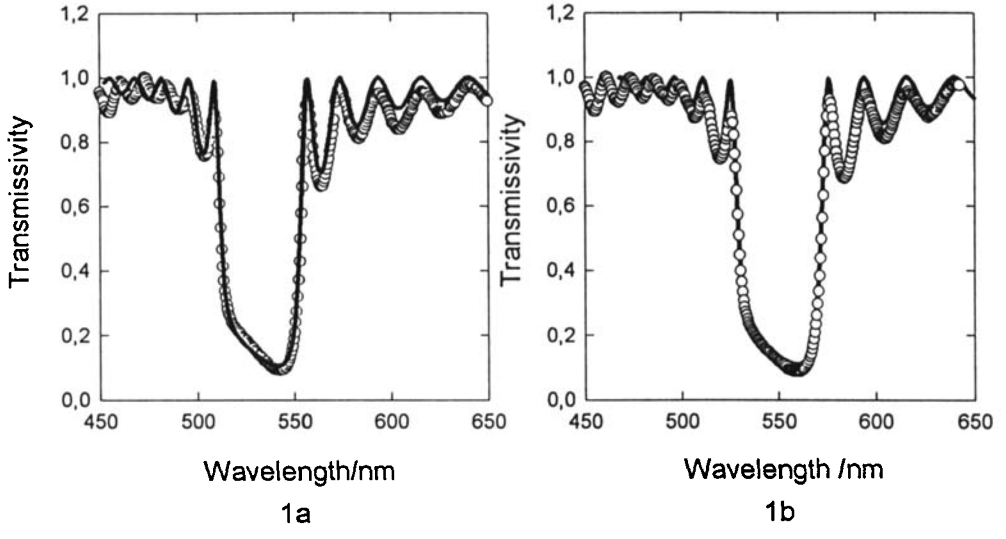

Figure 1 Transmission spectra (a) T = 40.41°C ; (b) T = 40.27°C
Exp (oooo) ; Calc (___)

The agreement is very good as we showed already in (1).

The values for the parameters of the calculated spectra are given in Table I.

The spectra at 40.39°C, 40.37°C and 40.34°C did not noticably differ from the one at 40.41°C.

Table I Parameters for the spectra of Figure 1 and Figure 2.

T/°C	α	ξ	Δφ	r	δ	N	w	L_p/nm
40.41	π/8	9π/16	0	1.19	0.061	30	1	532.5
40.39	π/8	9π/16	0	1.19	0.061	30	1	532.5
40.37	π/8	9π/16	0	1.19	0.061	30	1	532.5
40.34	π/8	9π/16	0	1.19	0.061	30	1	532.5
40.32	π/8	9π/16	-π/24 +π/24	1.19	0.061	30 29	5/9 4/9	532.5 550.5
40.30	π/8	9π/16	-π/24 +π/24	1.19	0.061	30 29	1/10 9/10	532.5 550.5
40.27	π/8	9π/16	0	1.19	0.061	29	1	550.5

Non-integer number of half-pitches.

To calculate the spectra at 40.32°C and 40.30°C a superposition of 2 spectra, with N differing by 1, has to be used together with the introduction of $\Delta\varphi$, ΔN and a weightingfactor w for the 2 constituing spectra. Here $\Delta\varphi$ is the deviation of the director orientation at the sample surface with respect to the alignment direction at the sample surface. ΔN is the non-integer part of the number of half pitches $N+\Delta N$. ($\Delta N = 2\Delta\varphi/\pi$ - see Theoretical background)

In Fig. 2 the spectra at 40.32°C and 40.30°C are shown and the parameters are again given in Table 1.

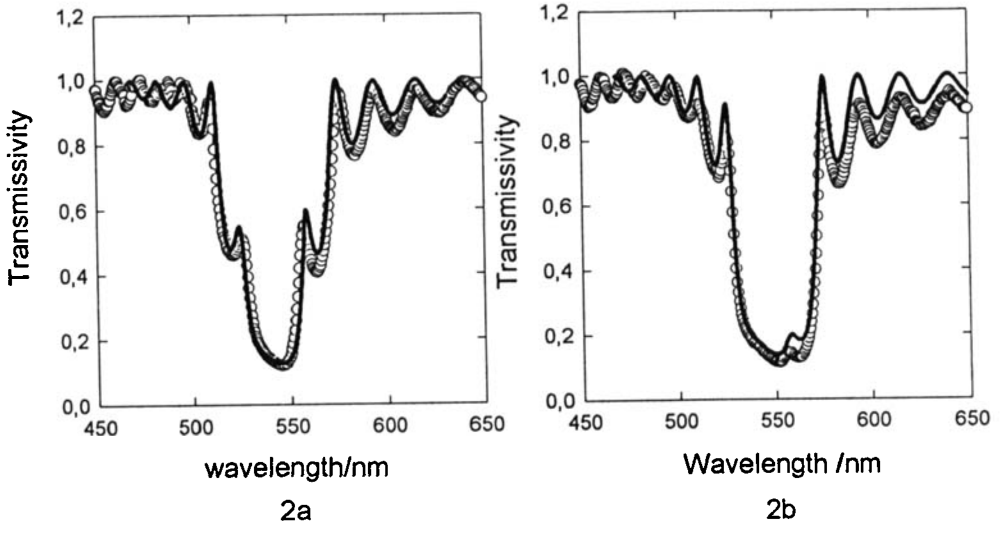

Figure 2 Transmission spectra (a) T = 40.32°C ; (b) T = 40.30°C
Exp (oooo) ; Calc (___)

A second series of measurements, also taken at decreasing temperatures, is given in Fig.3.

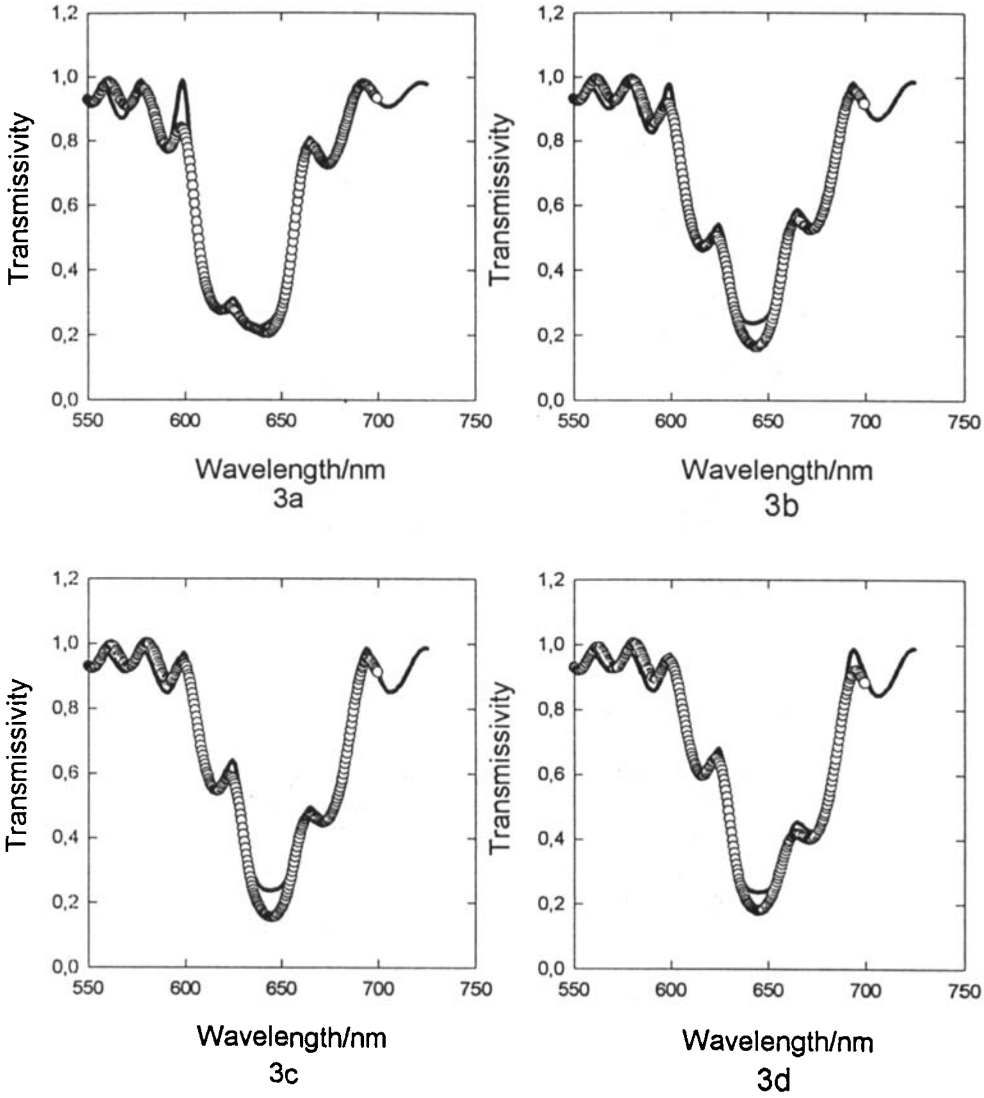

Figure 3 Transmission spectra
(a) T = 39.86°C; (b) T = 39.84°C; (c) T = 39.83°C; (d) T = 39.81°C

It is obvious that these spectra can too be reproduced very well by a change in the director orientation with respect to the surface alignment and a superposition of 2 spectra with respectively N+ΔN, and N+1-ΔN half-pitches. The weightingfactor w changes with temperature.

The parameters are given in Table 2.

Table 2 Parameters for the spectra of Figure 3

T/°C	α	ξ	Δξ	r	δ	N	w	L_p/nm
39.88	11π/32	11π/16	0	1.25	0.061	24	1	630.5
39.86	11π/32	11π/16	-π/10 +π/10	1.25	0.061	24 23	0.8 0.2	625.2 663.7
39.84	11π/32	11π/16	-π/10 +π/10	1.25	0.061	24 23	0.52 0.48	625.2 663.7
39.83	11π/32	11π/16	-π/10 +π/10	1.25	0.061	24 23	0.4 0.6	625.2 663.7
39.81	11π/32	11π/16	-π/10 +π/10	1.25	0.061	24 23	0.35 0.65	625.2 663.7

As the spectra in the second series of measurements were taken at a lower temperature,the values for L_p , α and N differ from the values in Table 1. A different value for ξ means that the sample has been rotated around the normal to the sample surface in between the 2 series of measurements. Finally Δφ has changed because the number of half-pitches has decreased.

THEORETICAL BACKGROUND

Analysis of the layer optical characteristics dependence on temperature shows that just before the change of the number of half-pitches by one the director direction at the surface essentially differs from the alignment direction. It is naturally to suppose that the value of the corresponding angle is dependent on the force of molecular anchoring at the surface and therefore the corresponding measurements can be used to obtain information about the anchoring forces [4][5][6]. Examine this problem more in detail.

Examine a thin enough plane-parallel optical cell of thickness d with a planar cholesteric texture and coinciding alignment directions at both its surfaces. It is well known that in a such cell the the cholesteric pitch (and the number of half turns of cholesteric helix) changes by a jump when the temperature changes at some temperature T_j and the number of half-turns changes by one at these temperatures. The most simple temperature dependence of the pitch in the cell reveals itself in the idealized case of a cell with infinite anchoring energy. In this case the director orientation at the cell surfaces remains unchanged and coincides with the alignment direction. The cholesteric pitch and the number of half-turns at the cell thickness d changes by a jump (Fig.4, curve 2). In the opposite limiting case of zero anchoring energy the pitch in the cell changes continuously with temperature (Fig.4, curve 1) and the corresponding temperature dependence is simple the one for a bulk cholesteric material i.e. for an equilibrium cholesteric pitch.

In the case of infinite anchoring energy the temperature (and equilibrium pitch value) at which the number of half-turns changes by one is determined by an equality of the volume elastic free energies of the director structure with N and

N+1 half-turns. For our purpose it is enough to take, in the expression for the elastic free energy, only the term responsible for twist deformations into consideration :

$$F = K_{22}(rotn - q(T))^2 \tag{1}$$

where q(T) is the equilibrium value of the pitch of bulk cholesteric for the temperature T.

The condition of equality of the volume elastic free energies of the director structure with N and N+1 half turns can be presented, with the help of (1) in the following relation:

$$(1/p_N - 1/p_T)^2\, p_N N = (1/p_{N+1} - 1/p_T)^2\, p_{N+1}\,(N + 1) \tag{2}$$

where p_N is the pitch in the cell with N half-turns of the director.

The relation (2) determines the equilibrium value of the pitch of a bulk cholesteric L.C. (i.e. the temperature T_j) for which a jump of the number of half-turns from N to N+1, and of the pitch, takes place in the cell:

$$P_{Tj} = 2d\ /\ (N + 1/2\ ) \tag{3}$$

Examine now a more realistic situation when the anchoring energy is a finite quantity. To be specific assume that the anchoring is identical at both surfaces of the cell.

In the case of a finite anchoring energy, the director deviates little from the alignment direction during the temperature change before the jump and correspondingly the pitch before the jump is subjected to smooth changes. It is clear, from general considerations, that the corresponding angle of deviation and the point of the jump should be dependent on the strength and the shape of anchoring potential. Now searching the jump point one should add to the free energy (1) the surface energy $W_s(\varphi)$ where φ is the angle of director deviation from the alignment direction. Under the natural assumption that the surface energy $W_s(\varphi)$ is an even function of the angle φ one finds that the equilibrium value of the pitch (and consequently the jump temperature) does not depend on the anchoring energy and is determined by the formula (3) found for the case of infinitely strong anchoring forces.

The change of the director deviation with temperature before the jump is determined by a minimum of the free energy relative to the deviation angle φ, which now takes into account the anchoring energy $W_s(\varphi)$

$$F = 2W_s(\varphi) + K_{22}\left[\, 2\pi/p_{N+\Delta N} - 2\pi/p(T)\right]^2 p_{N+\Delta N}\,(N + \Delta N)/2 \tag{4}$$

where ΔN is the noninteger constituent of the half-turn number connected with the director deviation, i.e. $\Delta N = 2\varphi/\pi$. Therefore the minimum condition takes the form

$$2\partial W_s(\varphi)/\partial\varphi + 4K_{22}\left[2\pi/p_{N\cdot\Delta N} - 2\pi/p(T)\right] = 0 \qquad (4')$$

i.e. $2\pi/p_{N\cdot\Delta N} = \pi(N+2\varphi/\pi)/d = 2\pi/p(T) - (\partial W_s(\varphi)/\partial\varphi)/2K_{22}$. Therefore the smooth prejump director rotation (pitch change) is determined by Eq.(4) which being expressed as the rotation angle results in:

$$\varphi = [\,2\pi(d/p(T) - N/2) - d(\partial W_s(\varphi)/\partial\varphi)/2K_{22}\,]\,/\,2 \qquad (5)$$

To find the director deviation at the jump point one should insert into (4, 5) the p(T) value corresponding to the jump, i.e. p(T) = 2d / (N + 1/2). The expression for the deviation angle at the jump φ_j takes the form

$$\varphi_j = \pi/4 - d(\partial W/\partial\varphi)/4K_{22} = \pi/4 - (d/p)(\partial W_s/\partial\varphi)/(4K_{22}/p) \qquad (6)$$

Not specifying the form of anchoring potential one gets from (4 - 6) for the limiting cases of infinitely strong and weak anchoring $\varphi_j = 0$ and $\varphi_j = \pi/4$. The value $\varphi_j = 0$ corresponds to the curve 2 on Fig.1 and the value $\varphi_j = \pi/4$ corresponds to the condition $p_{N\cdot\Delta N} = p_{N+1\cdot\Delta N} = p_j$ (i.e. absence of the jump) to the curve 1 on Fig. 4.

Note that the value of φ_j, as it follows from (6) is dependent on the number of half-turns N at the cell thickness d. Therefore measurements of φ_j for different values of N give a direct opportunity to determine from the experiment the derivative of the anchoring potential for the corresponding values of φ_j, i.e. such kind of measurements may serve as a base for direct experimental determination of the anchoring potential W_s. In the limit of large N φ_j approaches zero. The maximum value of φ_j corresponds to N = 1.

To find the explicit form of the temperature dependence of φ and φ_j, and the form of the temperature dependence of the ratio of the anchoring energy to the characteristic twist energy, one should specify the form of the anchoring potential W_s. If one assumes that W_s is described by the Rapini potential $W = -(W/2)\cos^2\varphi$ [7] the equation (4) takes the form:

$$\sin 2\varphi + (4\pi K_{22}/pW_s)\,[(N+2\varphi/\pi) - 2d/p(T)]\,(p/d) = 0 \qquad (7)$$

Note, that $4\pi K_{22}/pW_s$ is the ratio of elastic twist energy for a half-turn to the anchoring energy.

The corresponding equation for the deviation angle at the jump point φ_j is of the form

$$\sin 2\varphi_j + (4\pi K_{22}/pW_s)\,[(2\varphi_j/\pi) - 1/2]\,(p/d) = 0 \qquad (8)$$

Because in the general case equations (7,8) can not be solved analytically it should be solved by numerical methods. However in the limiting cases of a strong and weak anchoring and large N approximate analytical solutions can be easily found.
Weak anchoring ($4\pi K_{22}/pW_s >> 1$). In this case $\varphi_j = \pi/4 + \Delta\varphi_j$, where $\Delta\varphi_j << 1$, and one finds

$$\Delta\varphi_j = (N + 1/2)\ (W_s p_j/\pi K_{22})\ /\ 8 \qquad (9)$$

In the case of a strong anchoring ($4\pi K_{22}/pW_s << 1$) and in the case of large N, $\varphi_j << 1$ and therefore in (8) $\sin 2\varphi_j$ may be substituted by $2\varphi_j$. So, finally one gets

$$\varphi_j = \pi\,(\pi K_{22}/W_s p_j)\ /\ 2(N+1/2) \qquad (10)$$

The expressions (9,10) give the dependencies of the pitch p on the temperature in the cell. The qualitative forms of these dependencies are presented on Fig 4 by curves 3 and 4.

From the expression (10) using a measured value of φ_j we can estimate the anchoring energy for the cell used in the experiment. The obtained value is $W = 10^{-2}$ erg/cm^2 (for K_{22} we accepted 5.10^{-7} dyne).

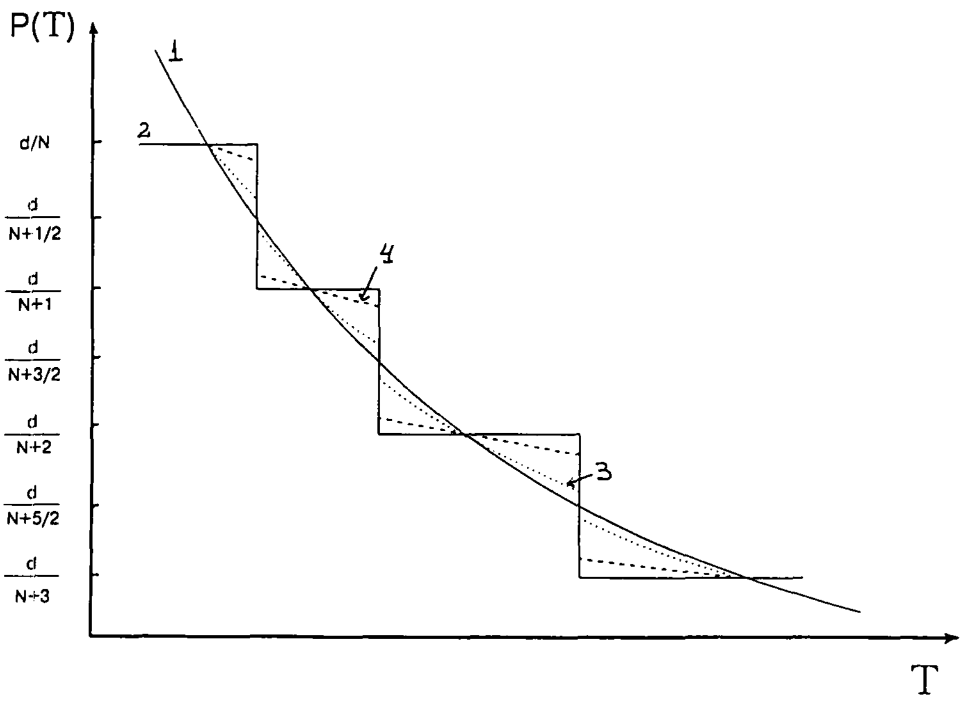

Fig. 4 Qualitative form of the temperature dependence of the pitch for a thin cell with different anchoring strength.

1. Absence of anchoring
2. Infinitely strong anchoring
3. Weak anchoring ($4\pi K_{22}$ / pW_sN >> 1)
4. Strong anchoring or a large half-turn number N for a weak anchoring ($4\pi K_{22}$ / pW_sN << 1)

Discussion

Note, that the formulas obtained above not only allow one to determine the ratio of anchoring and twist energies from the deviation angle φ_j at the jump but also to predict the temperatures of the pitch jump if the temperature behavior of the pitch in bulk cholesteric is known. These formulas can also be useful for the study of the temperature dependence of the anchoring energy through the measurements of the director deviation angle φ_j at the jump points for various numbers of half-turns and thicknesses of the cell.

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* Present address:
L.D. Landau Institute of Theoretical Physics
Kosygin str. 2
117334 Moscow
Russia