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Cholesteric pitch divergence near smectic phase transitions

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The critical behavior of the pitch divergence of cholesteric liquid crystals in the vicinity to smectic-A^* (SmA^*) and smectic-C^* (SmC^*) phases is studied experimentally and compared with conflicting theoretical interpretations. Members of two homologous series were studied with varying polymorphism from N*-SmC^* to N*-SmA^*. A modified functionality of the temperature dependence of the pitch is introduced to determine the critical exponent, and it is shown that the latter is independent of sample geometry. In contrast to several earlier investigations aiming to determine the critical exponent, which were inconclusive, the results of our critical exponents for the pitch divergence provide evidence for the model by Chen and Lubensky which predicts a critical exponent of $\nu=1/2$ for the N*-SmA^* and $\nu=1$ for the N*-SmC^* transition. This specifically implies that fluctuations cannot be neglected in the consideration of the nature of the phase transition.

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I. INTRODUCTION

Liquid crystals are ordered fluids with well-known applications, especially in the area of flat panel display devices. A variety of different liquid crystalline phases exist, distinguished through the order that the molecules adopt. The microscopic structures have a strong influence on the bulk physical properties exhibited by the materials. Chiral nematic or cholesteric (N*) liquid crystals in particular have a helical superstructure, adopted as a result of the chiral interactions between the molecules. The helical pitch is often of the order of the wavelength of light, causing the selective reflection of visible light [1]. The strong temperature dependence of the cholesteric pitch and thus sensitivity of the selectively reflected light, have led to their use in thermometry devices and other applications that map temperature or stress fields [2]. The helical pitch, p, of the phase is related to the central wavelength of the selective reflection band (the center of the band gap), $\lambda_{\max}$, through the equation $\lambda_{\max}=\tilde{n}p$, where $\tilde{n}$ is the average refractive index. The bandwidth $\Delta\lambda$ of the reflection is proportional to the birefringence of the liquid crystal, $\Delta\lambda=\Delta np$. For bulk devices the pitch, and hence the wavelength of selectively reflected light change continuously with temperature. It is this property that makes chiral nematic liquid crystals especially useful in thermometry applications. Nevertheless, it has proven difficult to describe the exact temperature dependence of the selective reflection, especially in the vicinity to the transition to (fluid) smectic phases. This paper develops an approach that successfully describes the temperature dependence of the pitch in several different liquid crystalline materials across their full phase range, taking into consideration the added complexity of pitch jumps that occur in thin devices as they are commonly employed in experiment and applications.

The temperature dependence of the helical pitch in a cholesteric liquid crystal is frequently dominated by a critical divergence that occurs close to the transition from the chiral nematic to the smectic phase [2] [Fig. 1(a)]. The type of smectic phase that underlies the chiral nematic phase has an influence on the critical divergence. The most common underlying smectic phases are the orthogonal smectic-A^* (SmA^*) phase, where the average direction of the molecules is parallel to the smectic layer normal, and the smectic-C^* (SmC^*) phase where the molecules adopt a temperature-dependent tilt with respect to the smectic layer normal. Further, while the temperature dependence of the natural pitch of the bulk cholesteric phase is continuous as shown in Fig. 1(a), the pitch variation that is actually observed may become discontinuous when the material is constrained between two surfaces in a thin device with planar boundary conditions. This effect is illustrated in Fig. 1(b). In relatively

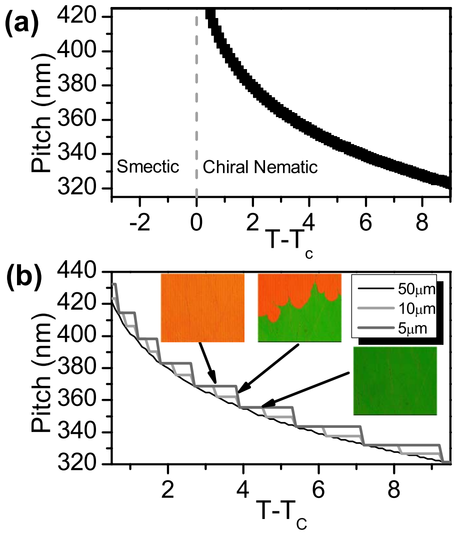

FIG. 1. (Color online) Typical examples of an experimentally determined pitch divergence (reduced temperature $T-T_c$ in K). (a) shows the continuous behavior observed in a thick bulk sample, while (b) shows the discontinuous pitch jumps observed in thin devices. The photographs in (b) show the microscopic appearance of pitch jumps; the green and orange domains differ in twist by a half turn, i.e., by a π twist.

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thin devices (e.g., below approximately 5 μm thickness, depending on cholesteric pitch), large, discrete pitch jumps can be observed, as the strong surface anchoring constrains the direction of the surface molecules and hence the helical pitch to values such that $2d/p=N$, with d the device thickness and N an integer. Pitch variations are, thus, limited to integer changes of π twists [3–5].

This paper considers the temperature dependence of cholesteric materials which exhibit both of the most common underlying smectic phases, SmA^* and SmC^*. Effects of confining devices are also considered. We briefly review the theoretical descriptions of the critical pitch divergence in the vicinity of low temperature smectic phases and argue that a different functionality needs to be introduced to adequately describe the temperature dependence of the cholesteric pitch across the entire temperature range, to deduce the critical exponent accurately.

II. THEORETICAL CONSIDERATIONS

The divergence of elastic constants near transitions from the nematic phase has been studied both theoretically [6–8] and experimentally [9–13]. There are three main theoretical approaches relevant to the discussion of the cholesteric pitch divergence: those by de Gennes [6], Chen and Lubensky [7], and Chu and McMillan [8]. The fact that some of these papers study the transitions between the achiral phases is not of principal concern, as thermodynamically the chiral (N^*) and achiral phases (N) are equivalent. De Gennes considered anomalies in the temperature regime close to the phase transition by examining both of the phase transitions relevant to this paper, N-SmA, and N-SmC [6]. Note that these phase transitions can be either of first or second order. De Gennes regarded the (second order) N-SmA transition in analogy to superconductivity in a metal, i.e the transition between the normally conducting metal and the Meissner phase. He predicted that the twist, K_{22}, and bend, K_{33}, elastic constants should diverge near the transition. In the analogy the liquid crystal twist corresponds to the magnetic induction in a superconductor. On the other hand, the N-SmC transition is more complex, and all elastic constants, K_{11}, K_{22}, and K_{33}, (splay, twist, and bend) should diverge near the transition as pretransitional anomalies. In his work, de Gennes employed the assumption that the two coherence lengths that describe the pretransitional smectic-like ordering, $\xi_{\perp}$ and $\xi_{\parallel}$ are isotropic, i.e., $\xi_{\perp} \cong \xi_{\parallel} \cong \xi$. The components, $\xi_{\perp}$ and $\xi_{\parallel}$, are the coherence lengths perpendicular to and along the optic axis of the smectic phase, appearing as cybotactic groups [14,15] (transient domains of smectic layerlike ordering) that occur in the pretransitional region. In the de Gennes model the coherence lengths vary as ξ^{1} at the N to SmA transition and as $\xi^{3/2}$ at the N to SmC transition [6].

Chen and Lubensky studied the nematic to smectic transition theoretically, introducing director fluctuations into the analysis [7]. They predicted that without director fluctuations the nematic to smectic transition would be of second order, while when considering fluctuations the transition can become first order. With respect to coherence lengths they predicted a variation as ξ^{1} at the nematic to SmA and ξ^{2} at the nematic to SmC transition.

TABLE I. The critical exponents predicted for the temperature dependence of the divergence of the cholesteric pitch by the three main theoretical approaches for materials exhibiting N^* to SmA or N^* to SmC^* transitions.

	Predicted critical exponent, ν	
Theoretical approach	N^*-SmA^* transition	N^*-SmC^* transition
De Gennes[a]	0.5	0.75
Chen and Lubensky[b]	0.5	1
Chu and McMillan[c]		0.5

[a] Reference [6].
[b] Reference [7].
[c] Reference [8].

Chu and McMillan studied the nematic to smectic-C transition employing a unified Landau theory [8]. As an initial condition, they introduced three order parameters, the (nematic) orientational order parameter, the smectic (layer) order parameter and a SmC dipolar order parameter. This approach is distinct from de Gennes' suggestion, as the latter introduced only two order parameters, the orientational and the smectic layer order parameter. Employing a three order parameter model, Chu and McMillan found the coherence length to vary as ξ^{1} at the nematic to smectic-C transition.

The coherence length varies with temperature according to the relationship, $\xi=\xi_0(T-T_c)^{-0.5}$. Thus, the power-law behavior deduced for the temperature-dependent divergence of the twist elastic constant (which is directly related to the helical pitch and, therefore, the selective reflection wavelength of the N^* phase), $\delta K_{22} \propto (T-T_c)^{-\nu}$ depends on the choice of theoretical model. The critical exponent for the cholesteric pitch divergence, ν, expected from the different approaches are summarized in Table I.

Several previous experimental studies [9–12] have compared the measured critical exponent with theoretical predictions using Eq. (1) to describe the temperature dependence of the pitch:

$$p(T) = p_0 + A(T - T_c)^{-\nu}. \tag{1}$$

Here, $p(T)$ is the pitch at a temperature T, T_c is a critical temperature (usually close to the phase transition temperature), p_0 is the pitch without pretansitional smectic ordering, and A is a constant. Equation (1) assumes implicitly that *all* of the temperature dependence of the pitch variation is due to a critical divergence in the pretransitional regime, and that the pitch takes a value p_0 in the absence of pretransitional effects. Dequidt and Oswald [13], adopted a slightly different approach and assumed a linear dependence of the pitch on temperature away from the pretransitional regime, as stated in Eq. (2),

$$p(T) = a + bT + c(T/T_C - 1)^{-\nu}. \tag{2}$$

Here, a, b, and c are empirical constants without a specific physical meaning, and T_C is the effective critical temperature. The results of various experiments based on these approaches are summarized in Table II. We note that none of

TABLE II. A summary of some critical exponents found experimentally for both the N^*-SmA^* and N^*-SmC^* transitions.

	Measured critical exponent, ν	
	N^*-SmA transition	N^*-SmC^* transition
Pindak *et al.*[a,b]	0.78	
Zhang and Yang[c]	0.67	
Lim and Ho[d]		0.82
Dequidt and Oswald[e]	0.41	

[a] Reference [9].
[b] Reference [10].
[c] Reference [11].
[d] Reference [12].
[e] Reference [13].

these experimental results coincide with any of the theoretical predictions.

Key to each of the investigations reviewed above are the assumptions made regarding the different contributions to the overall temperature dependence of the helical pitch. The theoretical approaches consider only the behavior in the pretransitional regime, i.e., the terms including T_C in Eqs. (1) and (2). However, it is also important to consider the underlying behavior of the pitch well away from pretransitional effects, i.e., the natural temperature dependence of the pitch of the cholesteric phase in the absence of any low temperature phase transitions. This issue has attracted little attention so far, but without using an appropriate form to describe the temperature dependence of the cholesteric pitch, unreliable values for the critical exponent will be obtained as two separate temperature dependencies are convoluted. In Eq. (1) the natural temperature dependence of the pitch is neglected, set to a constant value p_0. In Eq. (2) the temperature dependence is assumed to be linear. Nevertheless, it is well known that most cholesteric materials exhibit a $1/T$ dependence of the pitch on temperature, even without any pretransitional effects, which in its simplest form was described by Keating [16]. Below we suggest an alternative approach to describe the temperature dependence of the cholesteric pitch including the temperature regime in the vicinity to the transition into different smectic phases, and relate the respective critical exponents to theoretical predictions.

III. EXPERIMENTAL

We studied a commercial mixture and two homologs series that exhibit N^*-SmA^* and N^*-SmC^* transitions with two materials involving a N^* to twist grain boundary (TGBA*) transition. The phase transition temperatures of all the materials are summarized in Table III. We are not aware of any specific theory relating to pretransitional behavior in the N^* phase with an underlying TGBA* phase, though this phase transition naturally falls into the family of systems studied. Considering the structure of the TGBA* phase a similar pitch behavior may be expected for the N^*-TGBA* transition as that for a N^*-SmA^* transition. All but TM1001 are pure materials. TM1001 is a mixture designed by Merck for thermometry around body temperature, and has a N^*-SmA^* transition. The synthesis and diverse properties of the two homologous series have been reported elsewhere [17,18]. The series denoted as Mn [18] are 4-[(*S*)-2-chlor-3-methylbutanoyloxy]-4′-(4-*n*-alkyloxy-benzoyloxy)biphenyls. These materials exhibit N^*-SmC^* transitions for homologs M3-M9, and the N^*-SmA^* transition for the M10 homolog. The second homologous series are esters derived from D-valine, and are denoted as the Dn series [17]. These materials show a N^*-SmC^* transition for D5 and D6 and a N^*-TGB$_A^*$ transition for the D7 and D8 homologs [19].

Two different methods of measuring the pitch were employed. The pitch of TM1001 was measured directly from fits to the selective reflection spectra, as described in Refs.

TABLE III. Relevant phase transition temperatures of the materials employed in this study. Note that both the Mn and the Dn compounds exhibit a variety of hexatic and higher ordered phases at lower temperatures [17,18], which are not listed here.

Material				SmA^*-N^* (°C)	N^*-I (°C)
TM1001 (mixture from Merck)		SmC^*-N^* (°C)	TGB$_A$-N^* (°C)	27	44
Homologous 1 series Mn	$n=3$	110.2			201.3
	$n=4$	120.4			207.7
	$n=5$	128.9			197.5
	$n=6$	138.5			190.8
	$n=7$	142.3			183.6
	$n=8$	146.6			184.6
	$n=9$	153.7			179.9
	$n=10$			158.7	176.7
Homologous series Dn	$n=5$	106.7			134.1
	$n=6$	114.6			135.6
	$n=7$		121.1		133.2
	$n=8$		129.4		134.5

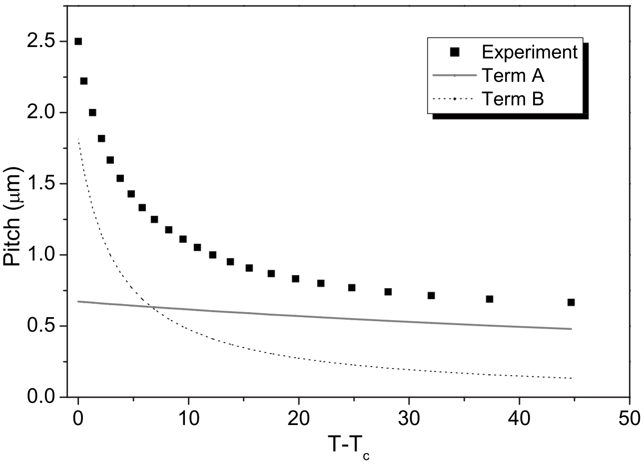

FIG. 2. Measurement of the pitch versus reduced temperature $T-T_c$ in K, for the material M4 (symbols). The lines refer to the fitting procedure adopted as discussed in the text, with the solid line describing the natural cholesteric pitch dependence (term A) and the dotted line describing pretransitional effects (term B) due to cybotactic smectic domains in the cholesteric phase.

[20,21]. The equipment consists of an Olympus polarizing microscope, a monochromator (Chromex 500IS), hot stage (Mettler) and temperature controller (Mettler). Reflection spectra were collected with 0.1nm resolution at temperatures across the N* phase range with a relative temperature resolution of ±0.1 K. We numerically fit the spectra and obtain the pitch (and other constants that define the spectrum) with an accuracy of ±0.1 nm. The temperature dependence of the pitch of the materials of the Mn and Dn homologous series were deduced from discontinuous color changes [22] and are consistent with values obtained by the Grandjean-Cano method.

In devices with strong unidirectional boundary conditions the pitch of the chiral nematic phase changes discontinuously whenever the temperature dependence allows for a half turn change. For all materials the devices were sufficiently thin (<10 μm) and well aligned so that pitch jumps were clearly observed. In this case, the pitch divergence can be monitored by allowing discrete pitch changes of π-twists to occur. Different alignment materials were used for different cells; 2.5 μm thick in-house devices used polyvinyl alcohol (PVA) as an alignment material, and 5 and 10 μm commercial devices had different polyimides as alignment layers as well as an indium tin oxide (ITO) electrode (which is not of relevance to this study). In all cases strong anchoring was observed, so that the alignment layer does not play a decisive role for the determination of the critical pitch divergence exponents.

IV. RESULTS AND DISCUSSION

A. Homologous series with varying smectic polymorphy

Typical results for measurements of the cholesteric pitch as a function of temperature are shown in Fig. 2. As already mentioned in order to obtain a realistic value for the critical exponent, it is important to include an appropriate term that describes the underlying temperature dependence of the cholesteric pitch in the absence of pretransitional effects. In contrast to Eq. (1), which assumes a temperature independent pitch in the absence of pretransitional effects, and Eq. (2), which assumes a linear temperature dependence of the pitch, we suggest a different form of the temperature dependence:

$$p(T) = a(T-T_0)^{-1} + b(T-T_C)^{-\nu}. \tag{3}$$

Here, a and b are constants, T_C is the critical temperature associated with the phase transition from the N* to the smectic phase, ν is the critical exponent and T_0 is a virtual temperature at which the pitch of the system would diverge in the absence of any transition to a smectic phase. The physical basis for the suggested temperature dependence of the pitch in the absence of the phase transition relies on the fact that for the great majority of cholesteric systems the pitch is actually inversely proportional to temperature, even in systems with a nonstandard pitch behavior, such as helix inversion compounds [3–5]. This can be understood by the arguments going back to Keating [16] who treated the temperature dependence of the pitch as a torsional analogy to thermal expansion. Quasi-molecular nematic layers carry out torsional vibrations in an anharmonic potential $V(\psi)$:

$$V(\psi) = V_0 + A\psi^2 + B\psi^3 \tag{4}$$

where ψ is the angle between adjacent quasinematic layers. Introducing the moment of inertia J for a quasinematic layer, Keating derived the potential as:

$$V(\psi) = V_0 + \frac{1}{2}J\omega_0^2\psi^2 - \frac{1}{6}JA\psi^3 \tag{5}$$

where ω_0 is the Eigenfrequency of the torsional vibrations, and A is a factor that describes the anharmonicity of the potential. Calculating the thermal average $\langle\psi\rangle$ via Boltzmann statistics, and taking into account that the pitch P must be inversionaly proportional to $\langle\psi\rangle$, $P=2\pi d/\langle\psi\rangle$, where d is the distance between the quasinematic layers, the intrinsic, noncritical temperature dependence of the cholesteric pitch becomes:

$$P = \frac{4\pi dJ\omega_0^4}{AkT} \tag{6}$$

This physically motivates the introduced $P \sim T^{-1}$ proportionality for the noncritical part of the temperature dependence of the cholesteric pitch at high temperatures, as employed in the fitting procedure of Eq. (3).

We thus would like to point out that our fitting procedure combines a physically established description of the temperature dependence of the cholesteric pitch with that of the critical behavior near phase transitions to smectic phases. For convenience, we will call the two terms in Eq. (3) term A and B, where term A describes the temperature dependence of the pitch in the absence of a phase transition and term B describes the pretransitional effects determining the critical exponent. An illustrative example is shown in Fig. 2, where the dashed line represents term A, the dotted line term B, and the solid line the sum of both according to Eq. (3), which very well describes the experimental data depicted as symbols.

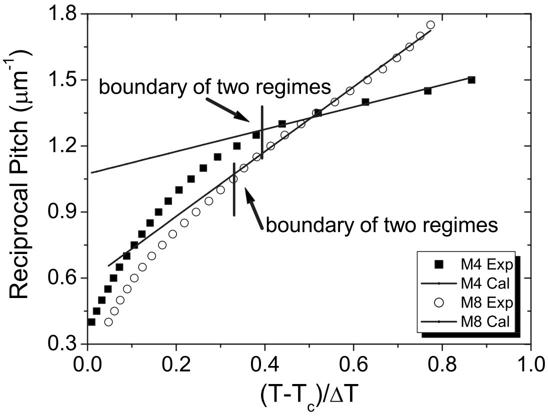

FIG. 3. Illustration of the pitch fitting procedure to evaluate term A, the noncritical part of the temperature dependence of the cholesteric pitch. This is determined by fitting the high temperature linear part of the inverse pitch P^{-1}. The temperature range of the noncritical part comprises approximately 60% of the cholesteric phase regime in all cases investigated. Shown here is exemplary data for the compounds M4 and M8.

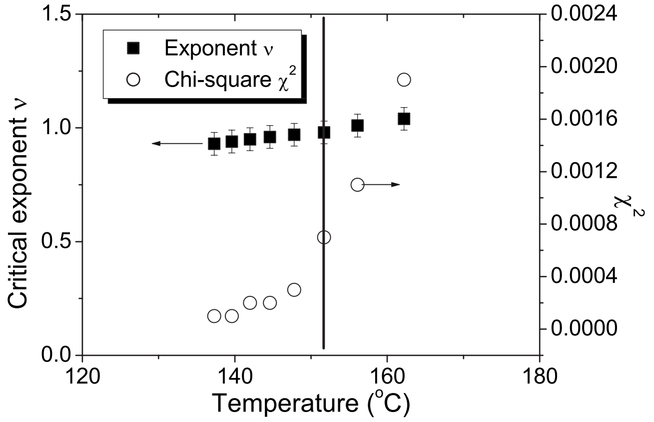

FIG. 4. Exemplary data to verify the robustness of the fitting procedure employed to determine the critical exponent. The compound chosen is M4 with a rather large existence range of the cholesteric phase from approximately 120–190 °C. The critical exponent was determined by varying the pretransitional temperature regime through approximately 30K. Variations of the critical exponent are rather small (closed symbols), within the range of error of about ±5%. Respective values of χ^2 are also shown as open symbols. The solid vertical line indicates the chosen temperature regions for the reported final data, with a similar behavior being observed for all compounds under investigation.

It should be noted that Eq. (3) contains five independent fit parameters, while only limited experimental data is available for the temperature dependence of the cholesteric pitch. We thus on occasion experienced difficulties when fitting Eq. (3) directly to all data of the cholesteric temperature range, obtaining unphysical results. Therefore, the fitting procedure was adjusted to make it more robust. We started by fitting only the high-temperature data to term A, in the region of absence of pretransitional effects. This was determined by plotting the reciprocal pitch $1/P$ as a function of temperature, and fitting this regime to a linear equation. Such a procedure naturally defines the two temperature regimes of the noncritical (term A) and the critical (term B) part of the temperature dependence of the pitch. In all cases the former contribution comprises approximately 60% of the cholesteric phase regime toward higher temperatures, while the latter, critical part comprises the 40% of the cholesteric temperature range toward the low temperature phase transition. This is demonstrated in Fig. 3 for the arbitrarily chosen compounds M4 and M8. The initial procedure largely determines the parameters a and T_0 of Eq. (3), i.e., the natural temperature dependence of the cholesteric pitch. In a subsequent fit to all experimental data over the entire N* range the parameter T_0 is allowed to only vary slightly within confined boundaries. The constant a of Eq. (3) may vary by up to 35% in the fit to obtain the critical exponent, but it should be kept in mind that the former is by no means the factor one is interested in, because it only describes in part the noncritical behavior, besides T_0. In the figures presented below, it may appear that the fits to Eq. (3) are not very good. The reason for this is that we deliberately show the noncritical and the critical regimes of the behavior as originally fitted. We believe that this gives an absolutely honest account of the experimental analysis, rather than superpositioning terms A and B for temperature regions chosen. This procedure ensures a robust fitting mechanism for the critical exponent from low-temperature data close to the transition into the smectic phases, which is the main parameter of interest in this study. It also is the reason for the occasional deviations of the fits at high temperatures, especially for materials with very large N* temperature range. A further concern could be a possible variation of the determined critical exponent with the temperature ranges chosen for fitting the regimes of terms A and B. We have taken specific care of this issue and varied these regimes over approximately one third of the whole existence region of the cholesteric phase, without finding any significant changes in the critical exponent, i.e., less than the error margin, which is about ±5%. A detailed example of such an analysis is shown in Fig. 4, for the compound M4, which has a temperature region of the cholesteric phase between 120 and 190 °C. For the critical exponent (solid symbols), it is clear that variations are rather small, despite changing the temperature regions of fitting through nearly 30K in a 70K region. The solid vertical line depicts the temperature that was chosen for the above outlined analysis and final results, as was done for all other compounds investigated. We note that this roughly coincides with an inflection point of the values of χ^2 (open symbols), while a further reduction or increase of the critical regime surely is not physically reasonable.

Critical exponents were evaluated for two homologous series, Mn and Dn, whose data and fits are shown in Figs. 5 and 6, respectively. Term A was preliminarily evaluated from the temperature dependence of the pitch at high temperatures (to the right of the vertical dashed lines in Figs. 5 and 6). With only slight variations allowed in term A, the critical exponents were then determined by fitting all terms of Eq. (3) (solid line). Tables IV and V summarize the resultant parameters for the Mn and the Dn homologous series,

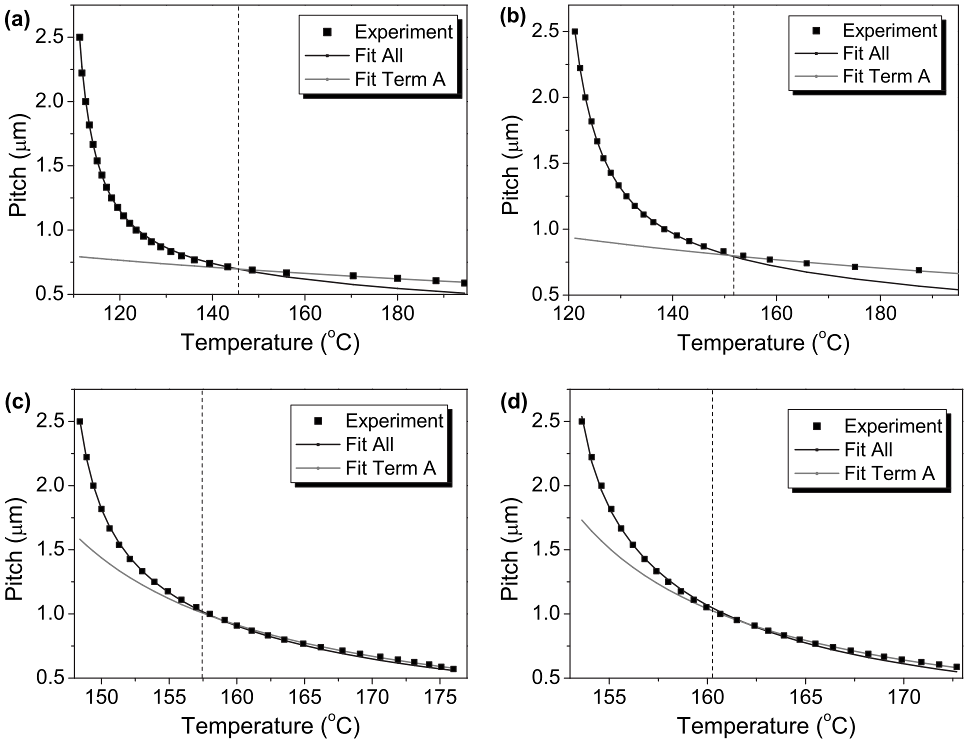

FIG. 5. Exemplary fitting results by the separation to two regions, pretransitional area (left of the dashed line) and pretransition-free regime (right of the dashed line). Compounds are: (a) M3, (b) M4, (c) M8, and (d) M9.

respectively. We note that the parameters of term A for the pretransitional-free-temperature dependence of the pitch, a and T_0, indeed only change slightly for the full fit. The critical temperatures T_C are close to the observed phase transition temperatures, which makes physical sense and is as expected. Finally, the critical exponents ν for the transitions N*-SmC^* are equal to $\nu \approx 1$ within the limits of error, while for the N*-SmA^* transitions they are found to be $\nu \approx 1/2$ for both homologous series. Only for M8 and M9 we observe values in between as the critical exponent crosses over from $\nu = 1 \rightarrow 1/2$ as the phase transition changes from N*-SmC^* (M3-M7) to N*-SmA^* (M10) (see Fig. 7). It may be interesting to notice that the tilt angle of the low-temperature smectic phase decreases with increasing carbon chain-length, while also the phase transition behavior changes from a first order N*-SmC^* transition for short chain homologs to a sec-

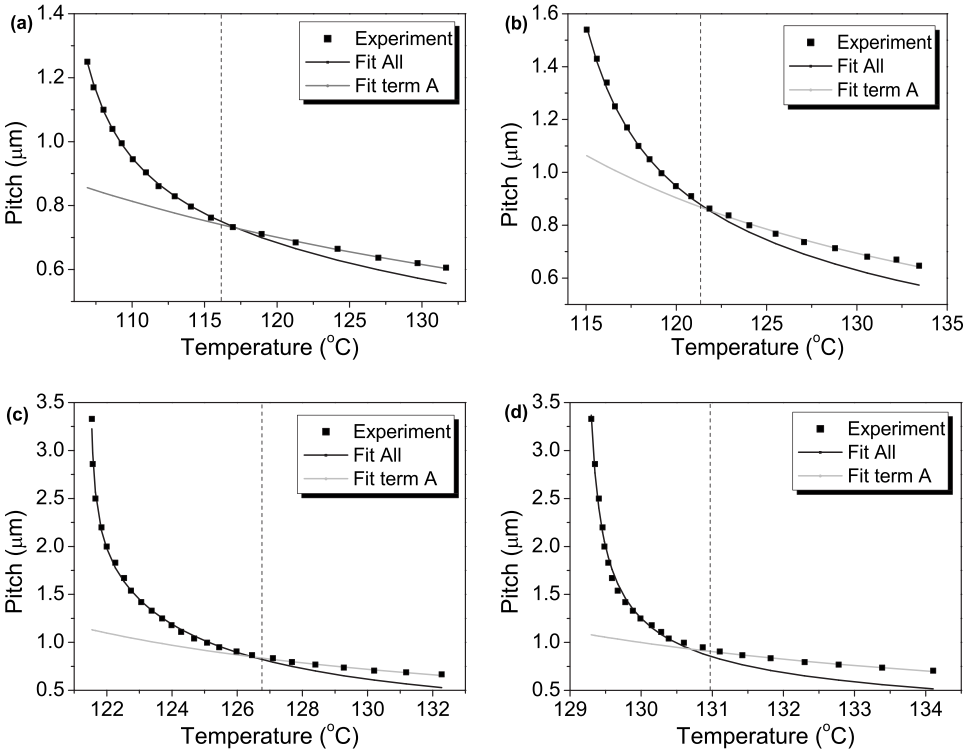

FIG. 6. Fitting results for the homologous series Dn: (a) D5, (b) D6, (c) D7, and (d) D8.

TABLE IV. Evaluation results for homologous Mn series. Term A is fitted first for the high temperature regimes of Fig. 3. These are then allowed to vary only slightly when fitting the pretransitional regime (term B).

		$a/\mu\mathrm{m}\ ^\circ\mathrm{C}$	$T_0/^\circ\mathrm{C}$	$b/\mu\mathrm{m}\ ^\circ\mathrm{C}$	$T_c/^\circ\mathrm{C}$	ν
$M=3$	Term A	198 ± 20	-138 ± 29			
	All	139 ± 2	-142 ± 4	6.98 ± 0.1	107.5 ± 0.2	0.96 ± 0.05
$M=4$	Term A	170 ± 17	-61 ± 27			
	All	101 ± 2	-63 ± 4	10.6 ± 0.1	115.5 ± 0.2	0.97 ± 0.05
$M=5$	Term A	88 ± 4	44 ± 5			
	All	61 ± 2	46 ± 4	5.0 ± 0.1	125.6 ± 0.2	0.90 ± 0.05
$M=6$	Term A	50 ± 1	99 ± 1			
	All	30 ± 2	98 ± 4	6.7 ± 0.1	135.0 ± 0.2	0.94 ± 0.05
$M=7$	Term A	33.0 ± 0.5	121.1 ± 0.6			
	All	14 ± 2	121 ± 4	6.6 ± 0.1	140.2 ± 0.2	0.89 ± 0.05
$M=8$	Term A	25.1 ± 0.3	132.5 ± 0.3			
	All	16 ± 2	130 ± 4	2.4 ± 0.1	146.7 ± 0.2	0.72 ± 0.05
$M=9$	Term A	16.7 ± 0.1	143.9 ± 0.1			
	All	12 ± 2	146 ± 4	1.0 ± 0.1	152.6 ± 0.2	0.73 ± 0.05
$M=10$	Term A	6.0 ± 0.1	151.0 ± 0.1			
	All	12 ± 2	151 ± 4	0.9 ± 0.1	158.4 ± 0.2	0.44 ± 0.05

ond order N*-SmA^* transition for M10. Detailed tilt angle data is published in Ref. [18].

The results of the Dn and Mn series show very good agreement with the predictions by Chen and Lubensky [7] (see Fig. 7). Within limits of error the critical exponents are equal to $\nu=1$ for a N*-SmC^* transition and $\nu=1/2$ for a N*-SmA^* transition. The $n=8$ and $n=9$ homologs of the Mn series appear to mark a transition from a strong SmC^* behavior to the strong SmA^* behavior of the $n=10$ homolog. The results of the Dn series imply that in terms of pretransitional behavior the TGBA* phase can be treated like a SmA^* phase, which intuitively is sensible, since it indeed exhibits the local smectic-A^* layering.

B. Pitch divergence in thin planar devices with discontinuous pitch jumps

When measurements are made in a thin planar device with strong anchoring, the equation used to describe the temperature dependence of the pitch needs to be modified to account for the discrete values that the pitch can take between pitch jumps. In such devices, the pitch can take discrete values defined by the cell gap $d=\mathrm{N}p/2$, where d is the device thickness and N is an integer. Thus an integer number of half turns (π twists) fits into the device thickness. Taking this discrete variation into account modifies Eq. (3) to give Eq. (7) or in terms of the number of π-twists Eq. (8).

$$p(T)=\frac{2d}{a'(T-T_0)}+\frac{2dc'}{(T-T_C)^{-\nu}} \tag{7}$$

$$N(T)=\mathrm{int}\left\{\frac{a'}{[(T-T_0)-1+a'c'(T-T_c)^{-\nu}]}\right\}, \tag{8}$$

where $p(T)$ is the pitch at a temperature T, $N(T)$ is the number of π twists at temperature T, a' and c' are constants, and d, T_0, T_c, and ν are as defined previously.

TABLE V. Summary of the evaluation results for the homologous series Dn. The fitting procedure was the same as for the Mn series and as discussed in the text.

		$a/\mu\mathrm{m}\ ^\circ\mathrm{C}$	$T_0/^\circ\mathrm{C}$	$b/\mu\mathrm{m}\ ^\circ\mathrm{C}$	$T_c/^\circ\mathrm{C}$	ν
$D=5$	Term A	51 ± 3	48 ± 5			
	All	40 ± 2	49 ± 4	1.6 ± 0.1	103.9 ± 0.2	0.91 ± 0.05
$D=6$	Term A	30 ± 1	87 ± 1			
	All	24 ± 2	80 ± 4	4.1 ± 0.1	111.1 ± 0.2	1.13 ± 0.05
$D=7$	Term A	17 ± 1	107 ± 1			
	All	5 ± 2	118 ± 4	0.5 ± 0.1	121.5 ± 0.2	0.48 ± 0.05
$D=8$	Term A	9.5 ± 0.5	120.5 ± 0.6			
	All	3 ± 2	119 ± 4	0.9 ± 0.1	129.2 ± 0.2	0.56 ± 0.05

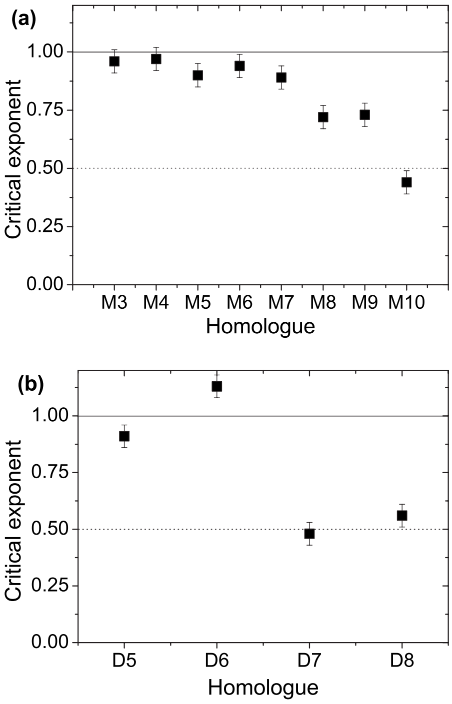

FIG. 7. Critical exponents ν for the two homologous series (a) Mn and (b) Dn. The $\nu=1$ and $\nu=0.5$ values are indicated by the two horizontal dashed lines to guide the eye.

We evaluated the critical exponent from Eq. (8) with the experiments depicted in Fig. 8 for TM1001 in cells of different thickness of 2.5, 5, and 10 μm. TM1001 exhibits a N*-Sm*A** transition which is exemplified by the a critical exponent of $\nu \approx 1/2$. Note that this critical exponent is independent of cell gap, as summarized in Table VI.

We note that in thin devices the temperature dependence of the cholesteric pitch is realized via discontinuous pitch jumps whenever the number of π-twist that fits into the constant cell gap changes. Figure 8 and the fitting constants listed in Table VI verify that the fundamental parameters to describe the pretransitional twist divergence, the critical exponent ν and the temperatures T_0 and T_C, are independent of the device thickness. Only the proportionality constants a' and c' obviously need to change.

V. CONCLUSIONS

The divergence of the cholesteric pitch when approaching different fluid smectic phases was studied experimentally and compared to theoretical predictions. To measure this we introduced a modified formula to describe the temperature dependence of the helical pitch of the cholesteric phase, including the natural temperature dependence in superposition with pretransitional effects. In contrast to previous experimental investigations which gave no conclusive indication of the correct theory and their critical exponents, our results clearly favor the description by Chen and Lubensky [7] over other theories, for most materials. For homologs, in the crossover region from cholesteric transitions into Sm*A** to transitions into Sm*C**, we observe critical exponents different from the Chen and Lubensky predictions, which we attribute to a simple transient behavior from a strongly N*-Sm*A** transition to a strongly N*-Sm*C** transition as the length of the flexible end chain is changed. The critical ex-

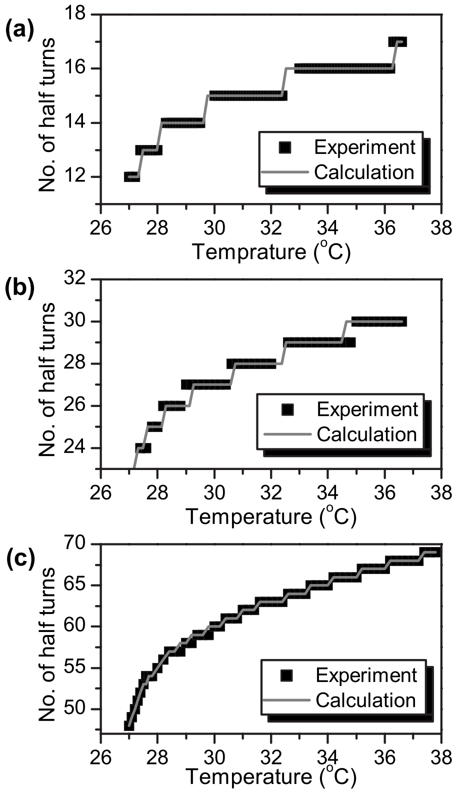

FIG. 8. Experimentally determined number of half turns (π twists) as a function of temperature for TM1001 and fitting to Eq. (5). Cell gaps employed are (a) 2.5 μm, (b) 5 μm, and (c) 10 μm. The values from the fitting procedure are given in Table IV.

TABLE VI. Summary of the results from measurements on thin cells with discontinuous pitch jumps.

Sample Parameters	TM1001; 2.5 μm	TM1001; 5 μm	TM1001; 10 μm
Constant a'	0.2 ± 0.01	0.36 ± 0.01	0.81 ± 0.01
Constant c'	0.013 ± 0.002	0.0061 ± 0.0002	0.0036 ± 0.0002
$T_0/\,^\circ$C	-55.1 ± 0.3	-54.5 ± 0.3	-54.5 ± 0.3
$T_c/\,^\circ$C	26.6 ± 0.3	26.6 ± 0.3	26.6 ± 0.3
Critical exponent ν	0.54 ± 0.03	0.54 ± 0.02	0.54 ± 0.02

ponents for the pitch divergence of the cholesteric phase are thus given by $\nu=1$ for the N*-SmC^* transition and $\nu=1/2$ for the N*-SmA^* transition. This indicates that in the description of this phenomena director fluctuations have to be taken into account. Investigations on two homologous series with varying polymorphism directly show the crossover from $\nu=1$ to $\nu=1/2$ for a changing phase sequence from N*-SmC^* to N*-SmA^*. In this context, we show that the twist grain boundary TGBA* phase acts to the same effect as a SmA^* phase, due to its local smectic-A^* layering. Investigations on very thin devices with discrete pitch changes verify the obtained results and indicate that the fundamental parameters in our pitch description, the critical exponent ν, and the two critical temperatures T_0 and T_C are independent of sample geometry.

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