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The cholesteric–smectic A transition

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Instead of studying the cholesteric–smectic A transition from the analogy with superconductors, we present a direct investigation of the properties of this transition. The transition is of first order and a very simple relationship between the four basic lengths (correlation length, penetration length, layer spacing of the smectic structure, and pitch of the cholesteric structure) exists at the transition temperature. We calculate the wall energy separating a cholesteric region from a smectic region in two different configurations. For one of them, we recover the definition of the type I (positive wall energy) and type II (negative wall energy) smectics A. We do not find a specific value of the Ginzburg–Landau parameter k_c which gives the distinction between the two types of smectics; k_c is a function of the product of the perpendicular correlation length and the wave vector of the smectic density modulation. We recover the well known value from the superconductor analogy, $k_c = 1/\sqrt{2}$, only if this product is large and the rotation of the director inside the wall is small. For the second configuration, the wall energy is always positive and there is no analogy with superconductors. Finally, we discuss briefly two different possibilities of mixed phases.

1. Introduction

The idea of writing an article on the cholesteric–smectic A transition arose when preparing a course on liquid crystals for graduate students. I asked myself if the best way to expose the properties of the Ch–SmA transition is to begin with the normal-superconductor transition, as is usually done in a textbook [1]. The beautiful analogy, made by de Gennes [2], between these two transitions contributed to the discovery of new smectic phases like the twist grain boundary (TGB) phases [3]. However, for those who want to learn about the properties of the Ch–SmA transition and do not have knowledge of superconductivity, it seems more logical to begin directly by the study of the Ch–SmA transition. Then, the analogy can be made, but now in the inverse direction.

One important point is to understand how non-homogeneous structures such as those of the TGB phases can exist. It is usually to distinguish between type I and type II smectics A and one of the purposes of this paper is to give their definition. Of course, we shall follow the same procedure as that used in the study of superconductors [4], but the results are not identical (as often assumed), and this study suggests some difference between smectics and superconductors.

This paper is organized as follows. First we shall derive the de Gennes free energy of smectics from the Landau theory of modulated systems. Then the thermodynamics of the Ch–SmA transition are presented. Since this transition is always first order, coexistence of the two phases is possible with a wall separating them. The energy of the wall (in two different configurations) is calculated and it is shown that in some circumstances the wall energy is negative, i.e. the appearance of non-homogeneous structures is energetically favourable. Finally, we shall discuss some possible structures for these particular phases.

Although the orginal motivation of this paper was pedagogical, in fact we have new results which we hope will contribute to a better understanding of the Ch–SmA transition.

2. The free energy

We shall begin with the SmA phase and give a derivation of the de Gennes free energy from the Landau theory of phase transitions. Although the de Gennes free energy is well known, some confusion still exists. The following derivation was presented very briefly by Chen and Lubensky [5]. The free energy of the cholesteric phase will be discussed later.

Since the SmA phase has a modulated structure, it is natural to apply the Landau theory of these structures [6]. Basically, there are two kinds of modulated phases: those for which the Lifshitz invariant is permitted by

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the symmetry and those for which it is forbidden. If one denotes by Ψ the complex order parameter, the Lifshitz invariant is $(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*)$. Its inclusion in the Landau free energy corresponds to structures for which the state defined by $-q$ (when q is the wave vector of the modulated structure) is not equivalent to the state q. Classical examples are helicoidal structures like helimagnetics or SmC* phases. Since in smectic A phases the states q and $-q$ are equivalent (this merely corresponds to change of the origin) the Lifshitz invariant is forbidden.

The Landau order parameter gives the change in the local density

$$\Psi(\mathbf{r}) = \Psi_0(\mathbf{r}) \exp(\mathrm{i}\mathbf{q}_\mathrm{s}\ \mathbf{r}). \tag{1}$$

In equation (1), **r** is the vector position, and $\mathbf{q}_\mathrm{s}$ the wave vector of the density modulation. In the following, we shall choose the z direction to be perpendicular to the smectic layers and the xy plane as that of the layer. The Landau free energy is a functional of the order parameter and of its derivatives up to second order [6]:

$$G = \frac{1}{2}\int [a|\Psi|^2 + u/2|\Psi|^4 + C_{//}|\partial\Psi/\partial z|^2 + D_{//}|\partial^2\Psi/\partial z^2|^2 + C_\perp(|\partial\Psi/\partial x|^2 + |\partial\Psi/\partial y|^2)]\,\mathrm{d}V. \tag{2}$$

The coefficients u, $D_{//}$ and $C_\perp$ are positive but, as shown below, $C_{//}$ must be negative in order that the modulated phase may be stable. As usual in the Landau theory, a is a linear function of the temperature, $a = a_0(T - T_0)$. We do not include second derivatives of Ψ relative to x and y since we chose $C_\perp$ positive (the case $C_\perp < 0$ corresponds to the SmC phase which is not considered here).

First, we shall consider a homogeneous smectic A sample, for which Ψ_0 is constant and the density modulation is in the z direction, $\Psi(z) = \Psi_0 \exp(\mathrm{i}q_\mathrm{s}z)$. Inserting $\Psi(z)$ in equation (2) gives the free energy (per unit volume)

$$G = \frac{1}{2}a\Psi_0^2 + \frac{1}{4}u\Psi_0^4 + \frac{1}{2}C_{//}q_\mathrm{s}^2\Psi_0^2 + \frac{1}{2}D_{//}q_\mathrm{s}^4\Psi_0^2. \tag{3}$$

From the condition of minimization relative to the wave vector q_s, one has

$$\Psi_0^2(2C_{//}q_\mathrm{s} + 4D_{//}q_\mathrm{s}^3) = 0$$

or

$$q_\mathrm{s}^2 = -C_{//}/(2D_{//}). \tag{4}$$

Now, we consider the general case where Ψ_0 varies in space. Inserting equation (1) into (2) gives G (some terms can be integrated by parts and the resultant surface terms are omitted):

$$\begin{aligned} G = \frac{1}{2}\int \{ & |\Psi_0|^2(a + C_{//}q_z^2 + D_{//}q_z^4) \\ & + \frac{1}{2}u|\Psi_0|^4 + |\partial\Psi_0/\partial z|^2(C_{//} + 6q_z^2D_{//}) \\ & + \mathrm{i}q_\mathrm{s}(C_{//} + 2q_z^2D_{//})(\Psi_0\partial\Psi_0^*/\partial z - \Psi_0^*\partial\Psi_0/\partial z) \\ & + D_{//}|\partial^2\Psi_0/\partial z^2|^2 \\ & + 2\mathrm{i}q_zD_{//}(\partial^2\Psi_0/\partial z^2\partial\Psi_0^*/\partial z - \partial^2\Psi_0^*/\partial z^2\partial\Psi_0/\partial z) \\ & + C_\perp[(q_x^2 + q_y^2)|\Psi_0|^2 + |\partial\Psi_0/\partial x|^2 + |\partial\Psi_0/\partial y|^2 \\ & + \mathrm{i}q_x(\Psi_0\partial\Psi_0^*/\partial x - \Psi_0^*\partial\Psi_0/\partial x) \\ & + \mathrm{i}q_\mathrm{s}(\Psi_0\partial\Psi_0^*/\partial y - \Psi_0^*\partial\Psi_0/\partial y)]\}\,\mathrm{d}V. \end{aligned} \tag{5}$$

Taking into account that $q_x \cong q_zn_x$ and $q_y \cong q_zn_y$, where n_x and n_y are the components of the nematic director in the layer plane, the $C_\perp$ term can be written as

$$\begin{aligned} C_\perp[& (\partial/\partial x - \mathrm{i}q_zn_x)\Psi_0(\partial/\partial x + \mathrm{i}q_zn_x)\Psi_0 \\ & + (\partial/\partial y - \mathrm{i}q_zn_y)\Psi_0(\partial/\partial y + \mathrm{i}q_\mathrm{s}n_y)\Psi_0]. \end{aligned} \tag{6}$$

The minimization relatively to q_z seems now very complicated. We shall use a very convenient approximation, namely that the deformation of the layers is small. Consequently we have $q_z \cong q_\mathrm{s}$ given by equation (4). The final form for the free energy is

$$\begin{aligned} G = \frac{1}{2}\int \{ & |\Psi_0|^2(a - C_{//}^2/4D_{//}) + u/2|\Psi_0|^4 \\ & - 2C_{//}|\partial\Psi_0/\partial z|^2 + D_{//}|\partial^2\Psi_0/\partial z^2|^2 \\ & + \mathrm{i}C_{//}(\partial^2\Psi_0/\partial z^2\partial\Psi_0^*/\partial z - \partial^2\Psi_0^*/\partial z^2\partial\Psi_0/\partial z) \\ & + C_\perp[|(\partial/\partial x - \mathrm{i}q_\mathrm{s}n_x)\Psi_0|^2 \\ & + |(\partial/\partial y - \mathrm{i}q_\mathrm{s}n_y)\Psi_0|^2]\}\,\mathrm{d}V. \end{aligned} \tag{7}$$

This is the de Gennes free energy which is deduced from the Landau free energy from minimization relatively to q_z. In general, terms including second derivatives are not taken into account and we shall do the same in the following.

To conclude this section, two remarks are made. Firstly, the two order parameters, that of Landau $\Psi(r)$ and that of de Gennes $\Psi_0(r)$ are clearly not the same. The de Gennes order parameter is only the complex amplitude of the Landau order parameter. Secondly, even if Lifshitz terms can appear in the de Gennes free energy, in the Landau free energy they are forbidden.

3. The cholesteric–smectic A transition

We consider now a homogeneous sample and we suppose that it is cholesteric at high temperature and becomes smectic A at a lower temperature. The free energy per unit surface of the cholesteric phase is written [1] as

$$G_{\mathrm{Ch}}=\frac{1}{2}\int K_2(\mathbf{n}\ \operatorname{curl}\mathbf{n}-q_0)^2\,\mathrm{d}z$$

or

$$G_{\mathrm{Ch}}=\frac{1}{2}\int K_2(\mathrm{d}\theta/\mathrm{d}z-q_0)^2\,\mathrm{d}z \tag{8}$$

if one supposes that the helix axis is parallel to the z direction. K_2 is the twist elastic constant and q_0 is the wave vector of the helix structure. This energy is minimized by $\mathrm{d}\theta/\mathrm{d}z=q_0$, such that at equilibrium the cholesteric free energy is null.

Now in the smectic phase, we have to introduce the energy $1/2K_2q_0^2$ which is the energy necessary to unwind the cholesteric structure. The free energy used to describe the Ch–SmA transition is [r is equal to $a-C_{//}^2/4D_{//}$ of equation (7)]

$$G=\frac{1}{2}\int [r|\Psi_0|^2+u/2|\Psi_0|^4+K_2(\mathrm{d}\theta/\mathrm{d}z-q_0)^2]\,\mathrm{d}z. \tag{9}$$

In the cholesteric phase, $G=0$ and in the smectic A phase we have (per unit volume)

$$G_{\mathrm{A}}=\frac{1}{2}r|\Psi_0|^2+u/4|\Psi_0|^4+\frac{1}{2}K_2q_0^2 \tag{10}$$

where $r=r_0(T_0-T)$. From the minimization condition $\partial G_{\mathrm{A}}/\partial\Psi_0=0$, one gets $|\Psi_0|^2=-r/u$ and $G_{\mathrm{A}}=-r^2/4u+1/2K_2q_0^2$. The transition is given by $G_{\mathrm{A}}=0$, or $r^2=2K_2q_0^2u$ and the transition temperature is

$$T_{\mathrm{Ch\text{-}A}}=T_0-(2K_2q_0^2u)^{1/2}/r_0. \tag{11}$$

A nematic phase is the limit of a cholesteric phase for $q_0\to 0$, and in this case $T_{\mathrm{NA}}=T_0$. The first order character of the transition can be seen by comparison of the entropy S in the two phases at $T_{\mathrm{Ch\text{-}A}}$: in the Ch phase, $S_{\mathrm{Ch}}=0$ but in the SmA phase $S_{\mathrm{A}}=-\mathrm{d}G_{\mathrm{A}}/\mathrm{d}T$, or $S_{\mathrm{A}}=r_0(2K_2q_0^2)^{1/2}/2u$. The jump of the entropy at the transition is the clear indication of a first order transition. This can also be seen by the discontinuity of the smectic order parameter at the transition temperature:

$$\Psi_0(T_{\mathrm{Ch\text{-}A}})=(2K_2q_0^2/u)^{1/2} \tag{12}$$

which goes to zero with q_0.

It is important to emphasize even at this stage that the appearance of the various TGB phases is a direct consequence of the first order nature of the Ch–SmA transition, as we shall see below.

4. The wall energy

In all this section, we consider a sample which is exactly at the Ch–SmA transition temperature. Since the transition is first order, the system can exist either in the Ch phase or in the SmA phase. The case we shall study in detail is when one part of the sample is in the Ch phase and another is in the SmA phase and the two parts are separated by a wall in which there is a progressive passage from one structure to the other. This section is devoted to the calculation of the wall energy in two different configurations and this will give us the distinction between smectics of type I and type II relative to the twist.

One can imagine two different configurations for a wall. In the first (see figure 1), the side $y=-\infty$ is smectic with the layers parallel to the xy plane and on the side $y=\infty$, the sample is cholesteric with the helix axis parallel to the y axis. Passing from the side $y<0$ to the side $y>0$, the smectic order parameter decreases until it becomes zero when the director changes its direction from the z axis and begins rotating around the y axis. The nematic director always remains in the xz plan and its direction is given by the angle θ. In the second configuration (figure 2), the wall is perpendicular to the z direction when the side $z\to\infty$ is in the cholesteric state with the helix axis parallel to z. On the side $z\to-\infty$, the sample is smectic in the same situation as in the first configuration. Now the smectic order parameter decreases when passing from $z<0$ to $z>0$. At the same time the director begins to rotate and to change its direction. In this configuration, two angles (φ and θ) give the direction of $\mathbf{n}$.

4.1. *The first configuration*

The free energy (per surface unit) adapted to the configuration shown in figure 1 is

$$G=\frac{1}{2}\int [r|\Psi_0|^2+u/2|\Psi_0|^4+C_{\perp}|(\mathrm{d}/\mathrm{d}y-\mathrm{i}q_sn_y)\Psi_0|^2 +K_2(\mathbf{n}\ \operatorname{curl}\mathbf{n}-q_0)^2]\,\mathrm{d}y \tag{13}$$

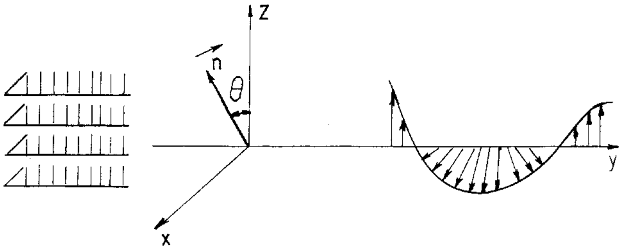

Figure 1. First configuration of a wall between a smectic structure ($y<0$) and a cholesteric structure ($y>0$) at the Ch–SmA transition. The director is parallel to the z axis in the smectic phase and rotates in the cholesteric phase.

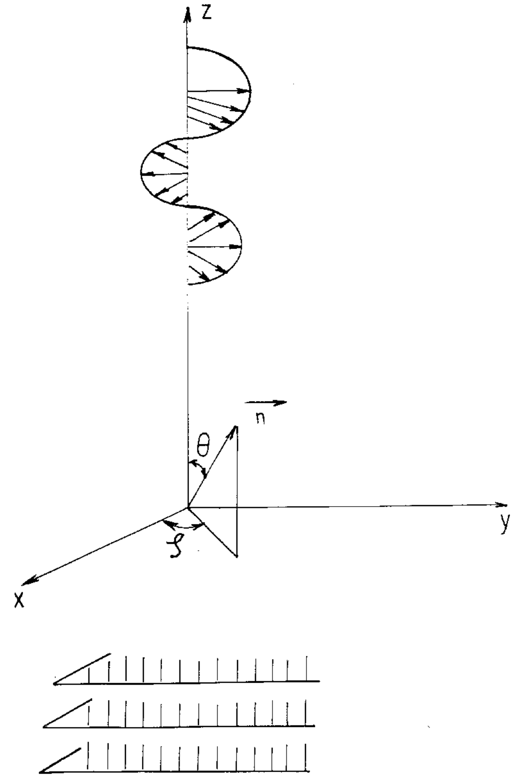

Figure 2. Second configuration of a wall between a smectic structure ($z<0$) and a cholesteric structure ($z>0$).

where Ψ_0 and θ are functions of y ($n_x=\sin\theta$, $n_y=0$, $n_z=\cos\theta$). Since the temperature is that of the transition, where both phases have zero free energy, G is in fact the energy of the wall. We have to determine the functions $\Psi_0(y)$ and $\theta(y)$ by minimizing expression (13) with the conditions of this configuration:

$$y\to-\infty,\quad \Psi_0^2=-r/u \text{ (as calculated above)},$$

$$\theta=0,\quad \mathrm{d}\theta/\mathrm{d}y=0;\quad y\to\infty,\quad \Psi_0=0,\quad \mathrm{d}\theta/\mathrm{d}y=q_0.$$

Before performing the minimization procedure with the help of the Euler–Lagrange equations, we shall normalize G, Ψ_0 and y. We write $G=(r^2/4u)g$, $\Psi_0^2=(-r/u)f^2$ and $y=\lambda_2 Y$, where λ_2 is a length which will be defined later. From equation (13), one obtains

$$g/4=\lambda_2/2\int\Bigg[-f^2+\frac{1}{2}f^4+(C_\perp q_\mathrm{s}^2/|r|)\sin^2\theta f^2 + (C_\perp/\lambda_2^2|r|)(\mathrm{d}f/\mathrm{d}Y)^2 + (K_2u/\lambda_2^2r^2)(\mathrm{d}\theta/\mathrm{d}Y-q_0\lambda_2)^2\Bigg]\mathrm{d}Y. \tag{14}$$

The quantity $(C_\perp/|r|)^{1/2}$ is well known; it is the perpendicular correlation length $\xi_\perp$. The quantity $K_2u/\lambda_2^2r^2$ must be dimensionless, and so we can write

$$K_2u/\lambda_2^2r^2=(K_2u/\lambda_2^2|r|C_\perp q_\mathrm{s}^2)(q_\mathrm{s}^2C_\perp/|r|) \tag{15}$$

and since $q_\mathrm{s}^2C_\perp/|r|$ is a pure number, one can choose λ_2 such that

$$K_2u/\lambda_2^2q_\mathrm{s}^2|r|C_\perp=1 \tag{16}$$

when one gets

$$\lambda_2^2=K_2u/C_\perp q_\mathrm{s}^2|r|. \tag{17}$$

One can write the free energy (14) in the following form

$$g/4=\lambda_2/2\int\Bigg[-f^2+\frac{1}{2}f^4+\xi_\perp^2q_\mathrm{s}^2\sin^2\theta f^2 + (1/k^2)(\mathrm{d}f/\mathrm{d}Y)^2+\xi_\perp^2q_\mathrm{s}^2(\mathrm{d}\theta/\mathrm{d}Y-q_0\lambda_2)^2\Bigg]\mathrm{d}Y \tag{18}$$

where k is equal to $\lambda_2/\xi_\perp$. In the frame of the theory of superconductors, it is called the Ginzburg–Landau parameter. Here we shall call it the perpendicular Ginzburg–Landau parameter; its importance is discussed below. Although $\xi_\perp$ and λ_2 are temperature dependent through r, their ratio is not.

Four characteristic lengths have been introduced:

(a) q_s^{-1}, the inverse of the wave vector of the density modulation of the smectic structure;
(b) q_0^{-1}, the inverse of the helix pitch of the cholesteric structure;
(c) $\xi_\perp$, the perpendicular correlation length;
(d) λ_2, the penetration length relative to the twist, justification of this name is given below.

There is a very simple relation between these four lengths at the Ch–SmA transition. We saw in the preceding section that at the transition,

$$-r^2/4u+\frac{1}{2}K_2q_0^2=0 \tag{19}$$

and with the help of the definitions of $\xi_\perp$ and λ_2 equation (19) becomes

$$2q_\mathrm{s}^2q_0^2\xi_\perp^2\lambda_2^2=1. \tag{20}$$

This important relationship will be used several times in the following.

The Euler–Lagrange equations $[\partial/\partial\theta=\partial(\partial/\partial\theta')/\partial Y$, $\partial/\partial f=\partial(\partial/\partial f')/\partial Y$, where $\theta'=\mathrm{d}\theta/\mathrm{d}Y$ and $f'=\mathrm{d}f/\mathrm{d}Y]$ are:

$$-f+f^3+\xi_\perp^2q_\mathrm{s}^2f\sin^2\theta-1/k^2(\mathrm{d}^2f/\mathrm{d}Y^2)=0 \tag{21a}$$

$$\xi_\perp^2q_\mathrm{s}^2(f^2\sin\theta\cos\theta-\mathrm{d}^2\theta/\mathrm{d}Y^2)=0. \tag{21b}$$

From these two equations it is possible to find a first integral. Multiplying equation (21 a) by $\mathrm{d}f/\mathrm{d}Y$ and (21 b)

by $\mathrm{d}\theta/\mathrm{d}Y$, summing and integrating gives:

$$f^2+\frac{1}{2}f^2-1/k^2(\mathrm{d}f/\mathrm{d}Y)^2 + \xi_\perp^2 q_s^2[f^2\sin^2\theta-(\mathrm{d}\theta/\mathrm{d}Y)^2]=C_s. \qquad (22)$$

The unknown constant C_s is easily determined by one of the following conditions: on the smectic side ($Y=-\infty$) $f=1$ and $\theta=0$, $\mathrm{d}\theta/\mathrm{d}Y=0$, or on the cholesteric side ($Y=\infty$), $f=0$ and $\mathrm{d}\theta/\mathrm{d}Y=q_0\lambda_2$. In both cases, one finds $C_s=-1/2$. With the help of equation (20), the first integral (22) can be written as

$$-f^2+\frac{1}{2}f^4+\xi_\perp^2 q_s^2 f^2\sin^2\theta=1/k^2(\mathrm{d}f/\mathrm{d}Y)^2 + \xi_\perp^2 q_s^2[(\mathrm{d}\theta/\mathrm{d}Y)^2-q_0^2\lambda_2^2]. \qquad (23)$$

In principle, to calculate g, it is necessary to find $f(Y)$ and $\theta(Y)$ [using two of the three equations (21 *a*), (21 *b*) and (23)], then to introduce them in (18) and to perform the integration. For the time being, we shall not consider the most general case, but only show that in the two extreme cases $k^2 \gg 1$ and $k^2 \ll 1$ the sign of the wall energy g is different. Afterwards we shall calculate explicitly g, $f(Y)$ and $\theta(Y)$ in these two limiting cases. Finally, numerical calculations will be presented.

With the help of equations (21 *a*), (21 *b*) and (23), there are several possible ways to write the free energy g. For the present purpose, it is convenient to replace the three first terms of the integral (18) by the right side of (23) and g is now:

$$g/4=\lambda_2\int[1/k^2(\mathrm{d}f/\mathrm{d}Y)^2 + \xi_\perp^2 q_s^2(\mathrm{d}\theta/\mathrm{d}Y)(\mathrm{d}\theta/\mathrm{d}Y-q_0\lambda_2)]\,\mathrm{d}Y. \qquad (24)$$

If $k^2 \gg 1$, the first term in equation (24) is negligible and g reduces to

$$g/4=\lambda_2\int \xi_\perp^2 q_s^2(\mathrm{d}\theta/\mathrm{d}Y)(\mathrm{d}\theta/\mathrm{d}Y-q_0\lambda_2)\,\mathrm{d}Y. \qquad (25)$$

The derivative $\mathrm{d}\theta/\mathrm{d}Y$ is an increasing function from 0 in the smectic region to the value $q_0\lambda_2$ in the cholesteric region; thus we have the inequality $\mathrm{d}\theta/\mathrm{d}Y<q_0\lambda_2$ (this is also shown in Appendix A). Consequently the wall energy g is negative.

Now if $k_2 \ll 1$, the first term $1/k^2(\mathrm{d}f/\mathrm{d}Y)^2$ in equation (24) is the most important and this shows that the wall energy is positive. This is the distinction between the type II smectic A for which the wall energy is negative and the type I smectic A for which the wall energy is positive. In the first case (type II), the wall is stable and there is a tendency for the system to form mixed phases like the TGB phases. In the second case (type I) the wall is unstable and tends to disappear.

In the Appendices A (type II) and B (type I), the calculations of g, $f(Y)$ and $\theta(Y)$ are included, and here we shall give only the results. For type II, an easy calculation can be made if one supposes that inside the wall (i.e. in the region where $\mathrm{d}f/\mathrm{d}Y$ is different from 0) the angle θ remains small. The criterion for the smallness of θ is that $\xi_\perp^2 q_s^2 \ll 1$ which is not a very strong condition since near the transition the correlation length $\xi_\perp$ is often much larger than the layer spacing $d=2\pi/q_s$. In this approximation (which we shall call the superconductor approximation, because the analogy with superconductors is complete) the wall energy g is equal to $-1.1\ \lambda_2$ and the variations of f and θ near $Y \leqslant 0$ are given by (we chose $Y=0$ as the end of the wall, i.e. $f=0$ for $Y>0$):

$$\theta \cong \theta_m \exp(Y/\sqrt{2})=\theta_m\exp(y/\lambda_2\sqrt{2}) \qquad (26)$$

$$f=1-\xi_\perp^2 q_s^2\theta^2 \qquad (27)$$

where $\theta_m=1/(\xi_\perp q_s)$ is the value of θ at the end of the wall. The variations of θ and f are given schematically in figure 3. It is noted that inside the wall, one has $f\neq 0$ and also $\theta>0$. This can be seen as the penetration of the cholesteric structure into the smectic structure. This is the reason for calling λ_2 the penetration length and it is the characteristic length of the wall. If the superconductor approximation is not valid, the expressions (26) and (27) are still correct, but the wall energy is given by a complicated expression in which the product $\xi_\perp q_s$ appears explicitly.

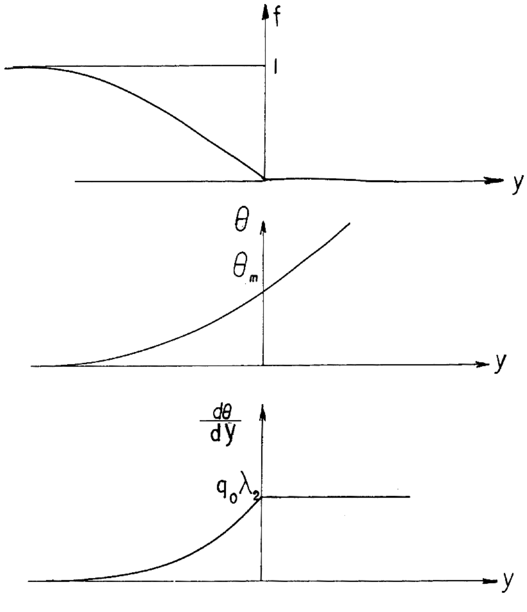

Figure 3. Schematic variations of the normalized smectic order parameter f, the angle θ (see figure 1) and its derivative $\mathrm{d}\theta/\mathrm{d}y$ in the case of a type II smectic A.

For type I, the wall energy is $g=(4\sqrt{2/3})\lambda_2/k$ $k=(4\sqrt{2/3})\xi_\perp$. The structure of the wall is without penetration: on the side $Y<0$, f is different from 0 but $\theta=0$ and on the side $Y>0$, $f=0$ and $\theta=q_0\lambda_2 Y=q_0 y$. This discontinuity in $\mathrm{d}\theta/\mathrm{d}Y$ means that the director begins to rotate only from the point $Y=0$. The schematic variations of f and θ are given in figure 4. From Appendix B, one has

$$\begin{aligned} f(Y)&=0 &&\text{for } Y>0\\ f(Y)&=\mathrm{th}[(|Y|k/2)^{1/2}] &&\text{for } Y<0. \end{aligned} \tag{28}$$

The characterisic length is now the perpendicular correlation length (since $Yk=y/\xi_\perp$) while it is the penetration length in the case of type II smectics A. The structure of the wall for type I is very similar to that at a wall at a first order nematic–smectic transition.

Since for $k^2\gg 1$, the wall energy is negative and for $k^2\ll 1$ it is positive, we shall try to find the value of k for which $g=0$. First, we shall write g in a new form (of course, equivalent to those we proposed above). In Appendix C, we show that

$$g/4=\lambda_2/2\int[-f^4/2+\xi_\perp^2 q_s^2(\mathrm{d}\theta/\mathrm{d}Y-q_0\lambda_2)^2]\,\mathrm{d}Y. \tag{29}$$

This expression is interesting since it shows how g can be positive or negative as it is the difference of two positive quantities. Writing $g=0$ gives from (29)

$$f^4=2\xi_\perp^2 q_s^2(\mathrm{d}\theta/\mathrm{d}Y-q_0\lambda_2)^2. \tag{30}$$

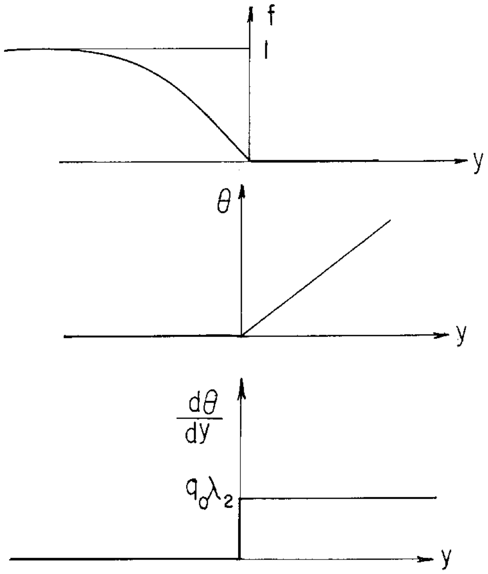

Figure 4. Schematic variations of the normalized smectic order parameter f, the angle θ, and its derivative $\mathrm{d}\theta/\mathrm{d}y$ in the case of a type I smectic A.

This means that in order to calculate the two functions $f(Y)$ and $\theta(Y)$, we now have three equations: as above, the two Euler–Lagrange equations (or one of them and the first integral) and the equation (30). This is possible only for a particular choice of k that we shall try to determine. We shall calculate the first integral (23) using (30) and the following relationship is deduced from (30):

$$f^2(\mathrm{d}f/\mathrm{d}Y)^2=\frac{1}{2}\xi_\perp^2 q_s^2(\mathrm{d}^2\theta/\mathrm{d}Y^2)^2. \tag{31}$$

One gets

$$f^4\sin^2\theta=1/(2k^2)(\mathrm{d}^2\theta/\mathrm{d}Y^2)^2. \tag{32}$$

This last expression can be compared with the second Euler–Lagrange equation (21 *b*) that we write in the following form

$$f^4\sin^2\theta\cos^2\theta=(\mathrm{d}^2\theta/\mathrm{d}Y^2)^2. \tag{33}$$

The expressions (32) and (33) are compatible only if $2k^2=\cos^2\theta$. In other words k must be a function of θ in order that the wall energy g will be zero. This seems paradoxical since we saw above the two limits of k for which there is a change of sign of g. However, in the superconductor approximation, the angle θ is small and $\cos\theta\cong 1$ and one recovers the superconductor result, $k_c=1/\sqrt{2}$.

To solve this paradox we have to pay attention to how the condition $g=0$ was reached. We put the integrand in equation (29) equal to zero and consequently $g=0$. But there is another possibility, namely that the integral giving g is null without the integrand being null also, clearly, this is the more general way to solve the problem, but it can be done only numerically.

We performed a numerical resolution of the Euler–Lagrange equations (21 *a*) and (21 *b*) and also calculated numerically the wall energy g from (18). We chose a series of values of k and also of the second parameter $\xi_\perp q_s$ that we shall call a for convenience (for details on the numerical calculations, see Appendix D). The results are given in figures 5 and 6.

In figure 5 the quantity g/λ_2 is plotted as a function of k for $a=1$ and $a=10$. The curve corresponding to $a=10$ crosses the k axis at $k_c=0.7$, very near the superconductor value $k_c=1/\sqrt{2}=0.707$. This means that, as mentioned above, we recover the superconductor approximation if a is large enough. However, for $a=1$, the critical k is now larger and is close to 1.25. In the strong type II region ($k>5$), g/λ_2 is equal to -1.1, in excellent agreement with the value found above, independently of the value of a.

In figure 6, the same quantity as in figure 5 is plotted as a function of a, for $k=1$. For large values of a, we are in the type II regime, as in the superconductor approximation, but for smaller values one enters the

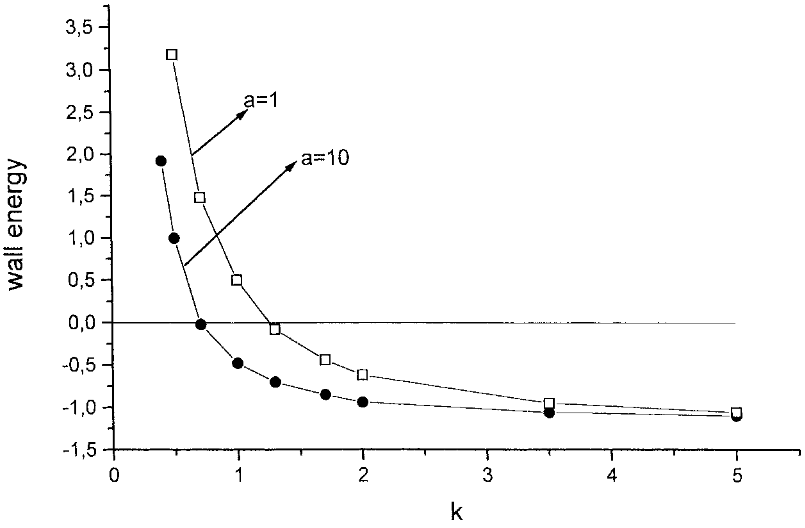

Figure 5. Variation of the wall energy divided by the penetration length (g/λ_2) with the Ginzburg–Landau parameter k for two different values of the product $a=\xi_\perp q_s$ (perpendicular correlation length × smectic wave vector).

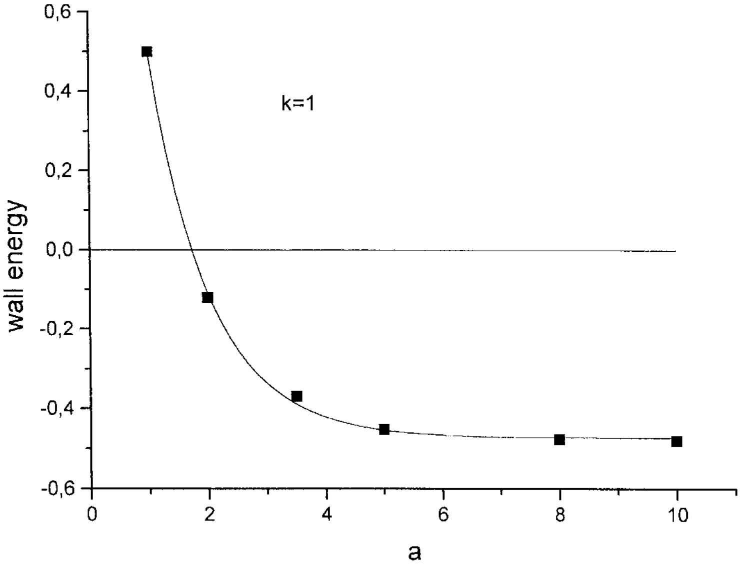

Figure 6. Variation of the ratio g/λ_2 with a for $k=1$. This curve shows that one can pass from type I to type II by varying the product $\xi_\perp q_s$ while keeping k constant.

type I region. For given k, it is also possible to find a critical a_c which separates the two types. In our example ($k=1$), a_c is close to 1.5.

To conclude this section, it can be said that, as in the case of superconductors, it is possible to define two types of smectic A. However, the classification depends on two parameters and not just one as for supercondutors. Contrarily to superconductors, there is no universal value of k separating the two types. However, one finds the superconductor approximation when the parameter $a=\xi_\perp q_s$ is large enough.

4.2. *The second wall configuration*

In this configuration, shown in figure 2, the free energy is much more complicated than in the preceding case. Besides the appearance of the twist of the director when passing from the smectic side to the cholesteric side, there is also bending characterized by the elastic constant K_3. The direction of $\mathbf{n}$ is given by two angles θ and φ (see figure 2). We have now three functions which describe the system (Ψ_0, θ, φ) and these functions are functions of z only. The free energy is†:

$$\begin{aligned} G=\frac{1}{2}\int & [r|\Psi_0|^2+u/2|\Psi_0|^4+C_{//}|\mathrm{d}\Psi_0/\mathrm{d}z|^2 \\ & + C_\perp q_s^2(n_x^2+n_y^2)|\Psi_0|^2+K_2(\mathbf{n}\ \mathrm{curl}\ \mathbf{n}-q_0)^2 \\ & + K_3(\mathbf{n}\times\mathrm{curl}\ \mathbf{n})^2]\,\mathrm{d}z \end{aligned} \qquad (34)$$

and the components of $\mathbf{n}$ are: $n_x=\cos\varphi\sin\theta$, $n_y=\sin\varphi\sin\theta$ and $n_z=\cos\theta$. The free energy written as a

---

† In equation (34) $C_{//}$ is chosen positive, contrary to the choice in the section on the free energy.

function of Ψ_0, θ, φ is:

$$
\begin{aligned}
G=\frac{1}{2}\int & [r|\Psi_0|^2+u/2|\Psi_0|^4+C_{//}|\mathrm{d}\Psi_0/\mathrm{d}z|^2 \\
& + C_{\perp}q_s^2\sin^2\theta|\Psi_0|^2+K_3\cos^2\theta(\mathrm{d}\theta/\mathrm{d}z)^2 \\
& + (K_3\cos^2\theta+K_2\sin^2\theta)\sin^2\theta(\mathrm{d}\varphi/\mathrm{d}z)^2 \\
& + 2K_2q_0\sin^2\theta(\mathrm{d}\varphi/\mathrm{d}z)+K_2q_0^2]\,\mathrm{d}z. \qquad (35)
\end{aligned}
$$

We follow exactly the same procedure as above to normalize the free energy. For that we define: $\xi_{//}=[C_{//}/|r|]^{1/2}$, parallel correlation length, $\lambda_3^2=(K_3u/C_{\perp}|r|q_s^2)$, the penetration length relative to the bend, $k_2=\lambda_2/\xi_{//}$, the parallel Ginzburg–Landau parameter and $Z=z/\lambda_2$. One gets:

$$
\begin{aligned}
g/4=\frac{1}{2}\lambda_2\int & \Big\{-f^2+\frac{1}{2}f^4+1/k_2^2(\mathrm{d}f/\mathrm{d}Z)^2 \\
& + \xi_{\perp}^2q_s^2[f^2\sin^2\theta(\lambda_3/\lambda_2)^2\cos^2\theta(\mathrm{d}\theta/\mathrm{d}Z)^2 \\
& + (\lambda_3/\lambda_2\cos^2\theta+\sin^2\theta)\sin^2\theta(\mathrm{d}\varphi/\mathrm{d}Z)^2 \\
& + 2q_0\lambda_2\sin^2\theta(\mathrm{d}\varphi/\mathrm{d}Z)+q_0^2\lambda_2^2]\Big\}\mathrm{d}Z. \qquad (36)
\end{aligned}
$$

For the normalization of the length, we take the same penetration length as above. It is also possible to define another one by replacing $C_{\perp}$ in equation (16) by $|C_{//}|$. As a consequence, it is necessary to replace $\xi_{\perp}$ by $\xi_{//}$ in (36), but the results are clearly unchanged. As above, we have in principle to find the three functions which minimize expression (36). But it is possible to show without solving all the Euler–Lagrange equations that the wall energy is always positive. We shall do that in the approximation $K_2\cong K_3$ and $\lambda_2\approx\lambda_3$.

The first step is to write the Euler–Lagrange equation for $\varphi(Z)$, that is $\partial/\partial\varphi=\partial(\partial\partial\varphi')\partial Z$, $\varphi'=\partial\varphi/\partial Z$—and to solve this equation. One gets $\mathrm{d}\varphi/\mathrm{d}Z=q_0\lambda_2$ when θ is different from zero. The second step is to introduce this value of φ' in equation (36) and to write the two Euler–Lagrange equations for f and θ. Applying the same method as above it is possble to get a first integral:

$$
\begin{aligned}
& -f^2+f^4+\xi_{\perp}^2q_s^2[f^2\sin^2\theta-\cos^2\theta(\mathrm{d}\theta/\mathrm{d}Z)^2] \\
& \quad -1/k_2^2(\mathrm{d}f/\mathrm{d}Z)^2+1/2\cos^2\theta=0. \qquad (37)
\end{aligned}
$$

With the help of equation (37), one may write the free energy g as

$$
g/4=\frac{1}{2}\lambda_2\int[1/k_2^2(\mathrm{d}f/\mathrm{d}Z)^2+\xi_{\perp}^2q_s^2\cos^2\theta(\mathrm{d}\theta/\mathrm{d}Z)^2]\,\mathrm{d}Z \qquad (38)
$$

which is always positive. So in this configuration there is no place for distinction between type I or type II. The physical reason for that is the gradual change in the direction of **n**, as θ passes from 0 to $\pi/2$. From the point of view of the energy cost, this is very expensive. The structure of the wall is quite different from that in the preceding case. On the side $Z<0$, f decreases until it is equal to zero, with or without penetration of the cholesteric structure, depending on the value of k_2. On the side $Z>0$, the director rotates as in a cholesteric phase, but it makes with the helix axis an angle θ smaller than $\pi/2$. The angle θ increases linearly with a slope equal to $q_0/\sqrt{2}$ until it becomes equal to $\pi/2$.

To conclude this section, we emphasize that the choice of the temperature as equal to $T_{\text{Ch–A}}$ makes the calculations relatively easy because it is possible to use the relation (20) which is valid only at $T_{\text{Ch–A}}$.

5. MGB phase versus TGB phase

We now wish to discuss briefly the existence of mixed phases which are neither homogeneous cholesteric nor smectic. Although the calculation of the wall energy was made only at $T_{\text{Ch–A}}$, the results are valid in the vicinity of this temperature. In the case of type II smectics, one can understand that, since the energy of a wall is negative (comparatively to the zero free energy of the cholesteric phase), the system may prefer a state which is a mixture of smectic and cholesteric (to have the possibility of creating walls). Two structures have been proposed for the mixed state: the melt grain boundary phase [7] (MGB phase) and the twist grain boundary phase [3] (TGB phase). In both cases, the sample is divided into smectic regions and the director rotates by a small angle when passing from one smectic region to the neighbouring smectic region. The difference in the two models lies in the nature of the interface between two smectic regions.

In the MGB phase, the smectic order parameter decreases from its value in a smectic region to zero inside the interface and increases again in the neighbouring smectic region. The director rotates in the interface such that the interface is exactly the wall described in the preceding section. It is not excluded that there is also a small rotation of the director inside the smectic region. This is because near $T_{\text{Ch–A}}$ the smectic order parameter is small, and also because in this range of temperatures the penetration length is large. Slightly above $T_{\text{Ch–A}}$, but below T_0 (where the smectic phase becomes stable) the system finds advantage by creating walls with negative energy, even if the free energy of the smectic regions is positive. However, below $T_{\text{Ch–A}}$ the free energy of the smectic regions becomes negative, and at low enough temperatures the smectic free energy density is lower than that of a wall and a mixed state is not energetically advantageous. This explains, in a qualitative way, how an MGB phase can appear between the cholesteric phase and a smectic phase.

In the case of the TGB phase, the interface is made up by a line of screw dislocations. The advantage of a screw dislocation is that it is possible to increase the ratio of the surface free energy to the bulk free energy. However, it costs energy to make a dislocation and this must be taken into account. The argument developed above for the MGB phase can be repeated here without change.

Calculations of the free energy of the MGB phase have not been made, so that it is impossible, at the present stage, to determine which phase is the more stable. Renn and Lubensky [3] presented calculations of the transition temperatures between the cholesteric and the TGB phases and between the TGB and smectic A phases. They made the assumption that the superconductor–smectic A is perfect so that they would use all the results known for superconductors. In particular, it was established in 1969 [4] that the equivalent of an MGB phase (the laminar phase) is less stable than the Abrikosov phase made up of an array of vortices. Dozov [7] claimed that the TGB phase is more stable than the MGB phase in the case of a smectic A phase. However, if it is a smectic C* phase, an MGB phase is the more stable. The properties of the smectic C* phase are beyond the scope of this paper and we shall not deal with them.

As a final remark about the existence of the TGB phase, we refer to the experimental results of Goodby *et al.* [8]. These authors determined the phase diagram of a homologous series of compounds which may exhibit one of the two sequences of phases: I–SmA–SmC* or I–SmA*–SmC* where the SmA* phase is the TGB phase. It should be interesting to check if the appearance of one or the other sequence is related to the change from type I to type II, because of the change of the relevant characteristic lengths.

6. Conclusion

We have studied the cholesteric–smectic A phase transition without using the analogy with superconductors. We have presented the definition of type I and type II smectics A and the criterion for their distinction. The analogy with superconductors is not always perfect. A strict parallelism exits only under a particular condition: $\xi_\perp^2 q_s^2 \gg 1$ or $q_0^2\lambda_2^2 \ll 1$ at the Ch–SmA transition. In general, the Ginzburg–Landau parameter which gives the distinction between the two types is dependent on the product $\xi_\perp q_s$ (or the product $q_0\lambda_2$). Finally we have discussed briefly how mixed states between cholesteric and smectic phases can appear.

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Appendix A

In this Appendix, calculations of the wall properties of type II smectics A are presented. We shall follow the program indicated above: solve the Euler–Lagrange equations, insert the solutions in the free energy and calculate the integral. We again write the Euler–Lagrange equations (21 *a*) and (21 *b*) using the condition $k^2 \gg 1$:

$$-f+f^3+\xi_\perp^2 q_s^2 \sin^2\theta = 0 \qquad (A1)$$

$$f^2 \sin\theta\cos\theta = \mathrm{d}^2\theta/\mathrm{d}Y^2. \qquad (A2)$$

From equation (A1) we get (in the region where $f \neq 0$)

$$f^2 = 1-\xi_\perp^2 q_s^2 \sin^2\theta. \qquad (A3)$$

Since f^2 cannot be negative, we find that f is zero for θ larger than a specific value θ_m given by $\sin\theta_m = 1/(\xi_\perp q_s)$. We can now insert equation (A3) into (A2) to give a differential equation for $\theta(Y)$:

$$\mathrm{d}^2\theta/\mathrm{d}Y^2 = \sin\theta\cos\theta(1-b^2\sin^2\theta) \qquad (A4)$$

with $b=\xi_\perp^2 q_s^2$. It is possible to integrate equation (A4) once multiplying the two sides of (A4) by $\mathrm{d}\theta/\mathrm{d}Y$ and taking into account the condition that for $\theta=\theta_m$, $\mathrm{d}\theta/\mathrm{d}Y = q_0\lambda_2$. This condition is related to the fact that f is null (i.e. the structure is that of the cholesteric phase) for $\theta \geqslant \theta_m$. We choose also $Y=0$ at the point where f becomes null. We then get (again using relation (20) to show that the integration constant is null):

$$\mathrm{d}\theta/\mathrm{d}Y = \pm\sin\theta\left(1-\frac{1}{2}\sin^2\theta/\sin^2\theta_m\right)^{1/2}. \qquad (A5)$$

From equation (A5), one sees that when $\mathrm{d}\theta/\mathrm{d}Y > 0$ (see figure 3) then

$$\mathrm{d}\theta/\mathrm{d}Y < \frac{1}{2}\sin\theta_m = 1/(2\xi_\perp q_s) = (q_s\lambda_2)/\sqrt{2} < q_0\lambda_2 \qquad (A6)$$

which is another justification of the negative value of g; see equation (25). The integration of equation (A5) is straightforward if one assumes θ_m to be small, i.e. if $\xi_\perp q_s \gg 1$. If one takes, as an example, $\xi_\perp \cong 50$ Å and for the layer spacing 25 Å, one gets $\xi_\perp q_s = 4\pi$ which is enough for the above condition to be fulfilled. Equation (A5) can be written in the following form which makes it possible to calculate $Y(\theta)$:

$$\mathrm{d}Y/\mathrm{d}\theta = \theta^{-1}\left[1-\frac{1}{2}(\theta/\theta_m)^2\right]^{-1/2}. \qquad (A7)$$

The solution of equation (A7) is

$$Y=\log\frac{1+[1-(\theta/2\theta_{\mathrm{m}})^2]^{1/2}}{(\theta/\theta_{\mathrm{m}}\sqrt{2})}+C \tag{A8}$$

which on inversion gives

$$\theta=(\theta_{\mathrm{m}}\sqrt{2})(2C\exp Y)/(1+C^2\exp 2Y),\quad (Y<0). \tag{A9}$$

The integration constant C is determined by the condition $Y=0$, $\theta=\theta_{\mathrm{m}}$ and one has $C=\sqrt{2}\pm 1$. The good choice of the sign is $+$ as can be seen by the fact that Y is an increasing function of θ (since we chose $\mathrm{d}\theta/\mathrm{d}Y>0$). Near $Y=0$ we develop the function $\theta(Y)$ and find

$$\theta\cong\theta_{\mathrm{m}}(1+Y/\sqrt{2})\cong\theta_{\mathrm{m}}\exp(Y/\sqrt{2}). \tag{A10}$$

The free energy g of the wall is given by equation (25) reproduced below

$$g/4=\lambda_2\xi_{\perp}^2q_{\mathrm{s}}^2\int\mathrm{d}\theta/\mathrm{d}Y(\mathrm{d}\theta/\mathrm{d}Y-q_0\lambda_2)\,\mathrm{d}Y \tag{A11}$$

which can also be written

$$g/4=\lambda_2\xi_{\perp}^2q_{\mathrm{s}}^2\int[(\mathrm{d}\theta/\mathrm{d}Y)-q_0\lambda_2]\,\mathrm{d}\theta \tag{A12}$$

when the integraton limits are from $Y=-\infty$ to $Y=\infty$ in (A11) and from $\theta=0$ to $\theta=\theta_{\mathrm{m}}$ in (A12). The integral (A12) can be calculated with the help of (A7) and one obtains a cumbersome expression. However in the limit of small θ_{m} ($\theta_{\mathrm{m}}<0.1$) one finds that g is equal to $-1.1\lambda_2$. For larger θ_{m}, the wall energy g is also dependent on θ_{m} or on the products $\xi_{\perp}^2q_{\mathrm{s}}^2$ or $\lambda_2^2q_0^2$ which makes the analogy with superconductors less strong.

Appendix B

Among the solutions of the Euler–Lagrange equations (21 *a*) and (21 *b*), there is one in which the two functions $f(Y)$ and $\theta(Y)$ are such that where f is different from 0, $\theta=0$ and where θ is different from 0, $f=0$. One can see that there is complete absence of penetration, since the two structures (cholesteric and smectics A) coexist without a region where a mixture of both phases is present. In such a case (in our choice of the geometry), θ is null for $Y<0$ and for $Y>0$ increases linearly with the slope λ_2q_0. On the other hand ($Y<0$) f decreases when Y increases from $-\infty$ until it becomes null for $Y\geqslant 0$. The wall energy given by equation (24) reduces to

$$g/4=\lambda_2\int 1/k^2(\mathrm{d}f/\mathrm{d}Y)^2\,\mathrm{d}Y \tag{B1}$$

which is just the limit of g when $k^2\ll 1$. The system of differential equations (21 *a,b*) reduces to one equation for $f(Y)$ which can be written as

$$-f+f^3-1/k^2(\mathrm{d}^2f/\mathrm{d}Y^2)=0. \tag{B2}$$

In a less formal way, it is possible to see that the limit $k^2\ll 1$ corresponds to the non-penetration of the cholesteric structure into the smectic A region. Since $k=\lambda_2/\xi_{\perp}$, very small values of k are obtained as a result of the small value of the penetration length relative to the correlation length; this also means small penetration of the cholesteric structure as given by the particular solution we discussed at the beginning of this Appendix.

Thus for type I smectics A, one has only to solve equation (B2) and calculate (B1). The solution of (B2) is found in two steps: in the first, one multiplies (B2) by $\mathrm{d}f/\mathrm{d}Y$ and integrates (taking into account the limits that we chose)

$$1/4-f^2/2+f^4/4=(1/2k^2)(\mathrm{d}f/\mathrm{d}Y)^2 \tag{B3}$$

or

$$(k^2/2)(1-f^2)^2=(\mathrm{d}f/\mathrm{d}Y)^2 \tag{B4}$$

which has the following solution (the second step)

$$f(Y)=-\mathrm{th}(\sqrt{\ }\,Yk/2). \tag{B5}$$

The calculation of (B1) is easy using equation (B4) and one obtains $g=(4\sqrt{2}/3)\xi_{\perp}$.

Appendix C

In this Appendix, we shall briefly indicate how one passes from the original expression (18) for the wall energy g to that given by equation (29). One multiplies the first Euler–Lagrange equation (21 *a*) by f and uses the following identity

$$f(\mathrm{d}^2f/\mathrm{d}Y^2)=\mathrm{d}(f\,\mathrm{d}f/\mathrm{d}Y)/\mathrm{d}Y-(\mathrm{d}f/\mathrm{d}Y)^2 \tag{C1}$$

giving

$$1/k^2(\mathrm{d}f/\mathrm{d}Y)^2=f^2-f^4-\xi_{\perp}^2q_{\mathrm{s}}^2f^2\sin^2\theta+1/k^2\,\mathrm{d}(f\,\mathrm{d}f/\mathrm{d}Y)/\mathrm{d}Y. \tag{C2}$$

One then replaces $1/k^2(\mathrm{d}f/\mathrm{d}Y)^2$ in (18) by the right side of equation (C2) and performs the integration of the term $\mathrm{d}(f\,\mathrm{d}f/\mathrm{d}Y)/\mathrm{d}Y$ which is zero because of the integration limits: for $Y=-\infty$, $\mathrm{d}f/\mathrm{d}Y=0$ and for $Y=\infty$, $f=0$. In this way, one obtains the final expression (29).

Appendix D

To solve numerically the Euler–Lagrange equations (21 *a,b*) we used an iteration method. We chose 101 points on the Y axis equivalent to 10 times the penetration length, i.e. Y varies between 0 and 10 and the interval h between two points is 0.1. The equations (21 *a*) and

(21 *b*) are replaced by

$$-f_j+f_j^3+a^2(\sin\theta_j)^2 f_j=(f_{j+1}-2f_j+f_{j-1})/(k^2h^2) \quad \text{(D1)}$$

$$f_i^2\sin\theta_j\cos\theta_j=(\theta_{j+1}-2\theta_j+\theta_{j-1})/h^2. \quad \text{(D2)}$$

The equations (D1) and (D2) can be also written as

$$f_j=\frac{1}{2}[f_{j+1}+f_{j-1}-h^2k^2(-f_j+f_j^3+a^2(\sin\theta_j)^2 f_j)] \quad \text{(D3)}$$

$$\theta_{j+1}=2\theta_j-\theta_{j-1}+h^2 f_j^2\sin\theta_j\cos\theta_j. \quad \text{(D4)}$$

We take a trial function for f having values 1 and 0 at the two ends of the chosen interval of Y, i.e. we chose the 101 initial values for f_j. The simple choice is a linear variation. We chose also the two initial values for the angle θ on the side where $f=1$, $\theta_0=0$ and $\theta_1=10^{-5}$. We verified that the results are independent of this initial choice of θ values provided that they are very small and that $\theta_0<\theta_1$. We also impose that the two final values of θ_{j} ($j=99$ and 100) are such that the final slope $(\theta_{100}-\theta_{99})/h$ is equal to $q_0\lambda_2=1/(a\sqrt{2})$; see equation (20).

The calculation is performed for each pair of k and a. We calculate a new value of f_j using equation (D3) and a value of θ_{j+1} using (D4). The process is repeated until convergence is reached. This is checked by calculating after each iteration the difference between the mean values of the two sides of the first integral (23). The number of iterations may vary from 100 to 1000.

Once we have the list of the f_j and θ_j values, the calculation of the integral (18) is trivial.

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