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ON SOME FLOW PROPERTIES OF SMECTICS A

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Résumé. — Suivant le type d'expériences, un smectique A se comporte soit comme un liquide isotrope usuel, soit comme un milieu poreux solide. Nous discutons ici ces deux aspects, en tenant compte de la perméation, concept introduit par Helfrich. Nous étudions plus particulièrement:

a) les propriétés d'ondulations de couches dans un échantillon d'épaisseur finie;
b) les ondes de surface;
c) le comportement d'un smectique comprimé entre deux plaques. Ce dernier point pourrait se révéler important pour la compréhension du mécanisme de stabilisation d'émulsions ou de savons par des smectiques.

Abstract. — In certain experiments a smectic A is not very different from an isotropic liquid; in other experiments it may resemble a porous solid. We discuss here some aspects of this remarkable behavior, starting from the permeation concept of Helfrich, and introducing the notion of smectic boundary layers. The main present applications include:

a) the properties of layer undulations in a sample of finite thickness;
b) surface waves;
c) the effects occurring when a smectic film is squeezed between two plates. The latter may be of importance in understanding the stabilizing effect of smectic mesophases on emulsions or foams.

1. Permeation. — The smectics with which we are concerned here are layered materials, each layer being a two dimensional fluid [1]. These phases fall into different types: we shall consider only the simplest type (smectic A) and also, sometimes, the cholesteric phases, where one dimensional stratification is also found, but on a much larger scale (∼ 1 μ). All these systems have very anisotropic mechanical properties [2]. The layers can slide on each other quite easily as is clear from optical observations of the free surface [1]: the corresponding viscosity \( \eta \) is comparable to that of an ordinary fluid. On the other hand, if the layers are fixed in space (e.g. attached to the walls of the capillary as shown in figure 1) then, as first observed by Helfrich [3], a pressure gradient \( p' = \partial p/\partial z \) normal to the layers induces only a very weak flow, of velocity

\[
v_z = - \lambda_p p'. \tag{1.1}\]

There are only a few direct measurements giving the permeation constant \( \lambda_p \) but dimensional arguments suggest that

\[
\lambda_p = c/b^2 \eta^* \tag{1.2}\]

where \( c \) is a numerical constant of order unity, \( b \) is the small dimension of the constituent molecules, and \( \eta^* \) is a viscosity for molecular motion normal to the layers.

Of course the flow field \( v_z \) does not extend exactly up to the wall, but drops in fact near the wall, inside a small adjustment layer of thickness \( \kappa^{-1} \) where \( \kappa \) is given by:

\[
\kappa = (\lambda_p \eta)^{-1/2}. \tag{1.3}\]

On the whole, the Helfrich permeation process, where the same molecules play both the role of the filter and of the filtered species, is quite remarkable. Its conceptual similarity with the motion of vacancies in a crystal has been pointed out in a fundamental article by Martin, Parodi and Pershan [5]. The capillary experiment of figure 1 is the simplest theoretical

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example of permeation: but in practice it does involve some complications, which we shall present now.

a) How are the smectic planes anchored at the walls? Rugosities of the limiting surface, comparable in size to the interlayer distance \( d \), will probably cause rather strong anchoring. Irregularities on this scale are easy to obtain when \( d \sim 30 \) Å (smectics) but much less pronounced when \( d \sim 1 \) µ (cholesterics). For the latter it is tempting to use as walls optical gratings with a repeat period comparable to \( d \). However, even with this trick, all attempts to observe permeation in cholesteric single domains have apparently failed.

b) The reason for this is probably related to the deformability of the layers [7]. We shall now analyse the displacement \( u(r) \) of the smectic layers (measured along the capillary axis \( z \)) under an imposed pressure gradient \( p' \). For a non constant \( u \), the layers are tilted by an angle \( \theta = du/dr \) (Fig. 1). The distance between them is reduced by a factor \( \cos \theta \sim 1 - \theta^2/2 \). Thus we have a negative dilation \( \gamma = - \theta^2/2 \) and an elastic energy per cm\(^3\) [2, 8]:

\[
\frac{1}{2} By^2 = \frac{1}{8} B \theta^4
\]

(1.4)

where \( B \) is an isothermal rigidity coefficient.

The free energy per unit length along \( z \) may then be written simply as

\[
F = \int_0^R 2 \pi r dr \left( p' + p'' u(r) + \frac{1}{8} B \left( \frac{du}{dr} \right)^4 \right)
\]

(1.5)

where \( p' \) is the imposed pressure gradient and \( R \) is the radius of the tubes. Eq. (1.5) omits the curvature energy of the smectic [2]: the latter can be shown to be negligible (in most of the sample volume) whenever the layer displacement \( u \) in the center is large when compared to \( d \); this will be the case for the applications which we have in mind. Writing that (1.5) is a minimum leads to the equation

\[
p' B = \frac{1}{8} \left( \frac{du}{dr} \right)^3
\]

(1.6)

or

\[
u = \left( \frac{p'}{B} \right)^{1/3} \frac{3}{4} \left( -R^{4/3} + r^{4/3} \right).
\]

(1.7)

The parameter which is most accessible to optical observation is the tilt angle

\[
\theta = \frac{du}{dr} = \left( \frac{p'}{B} \right)^{1/3}.
\]

(1.8)

The \( 1/3 \) power occurring in (1.8) has remarkable consequences: although the pressure gradient \( p' \) is very small on a molecular level, \( \theta \) may be sizable. In contrast with the \( \sim 10^3 \) CGS units (corresponding roughly to a smectic falling under its own weight), \( r = 1 \) mm, and \( B = 10^8 \) ergs/cm\(^3\), we are led to \( \theta \sim 10^{-2} \) rad \( \sim 1/2 \) degree. In cholesterics, the situation is much more spectacular, because \( B \) is small [9]:

\[
B \rightarrow K_2 q_0^2
\]

(1.9)

where \( K_2 \) is the Frank constant for twist, and \( q_0 \) the wavevector of the cholesteric helix. With \( K_2 = 10^{-6} \) dynes and \( q_0 = 10^2 \) cm\(^{-1}\), \( B = 10^4 \), and (keeping \( r = 1 \) mm) \( \theta \sim 0.2 \) rad: even under its own weight, the cholesteric will distort its planes very strongly. An instability will probably appear when \( \theta(R) \), as given by eq. (1.8), becomes of order unity.

A few words of comment on eq. (1.5) and (1.7), (1.8) might be needed at this point:

a) An attentive reader will have noted that eq. (1.8) gives a plot \( \theta(r) \) which is singular near the center of the capillary: this is unphysical, and is due to our neglect of curvature terms in the elastic energy. When these terms are properly included, the singularity is smoothed out.

b) The boundary conditions at the capillary wall may fix not only the position of the planes, but their orientation, e.g., the planes may have to be locally normal to the wall. This problem is also solved by insertion of the curvature energy [8], and it is found that the adjustment to the correct orientation at the walls takes place in a thickness \( \lambda / \theta_0(R) \) where \( \lambda \) is a length defined in ref. [9], and \( \theta_0(R) \) is the angle which would be estimated from the simplified formula (1.8). For most practical situations the adjustment thickness is small when compared to \( R \), and eq. (1.8) is applicable in a large range of \( r \) values.

Thus permeation in cholesterics is probably observable by direct capillary experiments only if the pressure gradient is very small — in which case the flow is very slow. Other experimental arrangements, where the planes do not have to be anchored, can be imagined; in particular, it should be possible to drive the fluid in a planar cholesteric texture through buoyancy forces, using distributed heat sources. However, the resulting flow velocities remain rather small, and the experiment seems hard [10].

On the other hand, it has recently become apparent that many flow problems in smectics are very sensitive to permeation processes — the latter taking place only in certain thin boundary layers [11]. We shall summarise briefly the relevant arguments in the next section.

2. Smectic boundary layers. — 2.1 Flow near a plate. — Let us first consider the simple flow pattern of figure 2, where the smectic is moving (with a slow velocity \( V \)) towards an infinitely thin plate. The smectic layers are assumed unperturbed and parallel to the plate. Consider a fluid element which was initially at a distant point \( A_0 \), and later reaches point \( A \) (very close to the plate). Its original velocity was \( V \), and its final velocity must be small, since it is so close to a fixed obstacle. Thus the pressure \( p \) at point \( A \) must be higher than the pressure at distant points such as \( A_0 \) (the latter pressure may be chosen equal to 0). The high pressure region will extend up to a distance \( \delta \) from the plate: this distance measures the size of the boundary layer. At larger distances the flow is essentially unperturbed.
The magnitude of $\delta$ can be estimated through the following qualitative argument:

a) The vertical pressure gradient, of order $-p/\delta$, induces a permeation flow

$$v_z \approx \lambda_p p/\delta.$$  \hfill (2.1)

b) The smectic can be treated as incompressible for the slow flows considered here. Then the incoming flux (from the unperturbed flow lines crossing the interval $\delta$), which is of order $V\delta$, must compensate exactly the outgoing permeation flux, leaking through an interval $IA = \delta V x$,

$$V \delta \approx v_z x.$$  \hfill (2.2)

c) Inertial effects are neglected (as allowed for low Reynolds numbers). Then the force balance, along the direction of the plate, is simply

$$-\frac{\partial p}{\partial x} + \eta \nabla^2 v_x = 0.$$  \hfill (2.3)

We shall see in a moment that the steepest variations of $v_z$ take place along $z$, i. e. in a thin layer of thickness $\delta$. Thus we may put

$$\nabla^2 v_x \approx \frac{v_x}{\delta^2} \approx \frac{V}{\delta^2}.$$  \hfill (2.4)

and rewrite (2.3) in the form

$$\frac{p}{x} \sim \eta \frac{V}{\delta^2}.$$  \hfill (2.5)

Eq. (2.1), (2.2), (2.5) are compatible provided that

$$\delta^2 = \kappa^{-1} x.$$  \hfill (2.6)

where $\kappa^{-1}$ (defined by eq. (1.3)) is a molecular length. We are interested in values of $x$ which are much larger than $\kappa^{-1}$. Eq. (2.6) then shows that

$$\frac{\delta}{x} \sim (\kappa x)^{-1/2} \ll 1.$$  \hfill (2.7)

We see that the boundary layer is thin. Typically for $x = 10\mu$ and $\kappa^{-1} = 10\text{Å}$ we expect $\delta = 1000\text{Å}$ — large enough for continuum theories to be meaningful, but too small to be observable optically.

### 2.2 Motions of floating bodies and of defects

— Let us now describe some (more or less) practical applications of the boundary layer concept. One first question is to find what is the analog of Stokes' law for the mobility of a sphere (radius $R$) floating in the smectic medium. Reference [11] contains a discussion of this problem, restricted to one rather artificial case: namely it is assumed that the smectic planes remain ideally flat all around the sphere. It is there found that if the sphere moves with a velocity $V$ parallel to the planes, the friction force $F$ is still of the Stokes type — except for a small difference in coefficients:

$$F/V = 8\pi\eta R.$$  \hfill (2.8)

This is essentially due to the fact that the flow lines can avoid the sphere without crossing the smectic planes — no permeation is involved. On the other hand, if the sphere moves normal to the planes, the friction becomes enormous

$$F/V \sim \eta (\kappa R)^2 \gg \eta.$$  \hfill (2.9)

Thus, in spite of its artificial character, this example does illustrate the protean behavior of smectics.

A more realistic example of a moving object is a dislocation. The theoretical structure of edge dislocations (far from the core) has been analysed [12]. Dislocations were the Burgers vector $b$ is much larger than $d$ are more easily observed by optical means, and have indeed been found recently [13]. They are probably of the type shown on figure 3. Their mobility has been estimated first by R. B. Meyer and N. A. Clark [4] using a picture of flow of the layer ending at the dislocation, coupled to diffusion (permeation) of material from the neighbouring layers. But the mobility can also be derived from the boundary layer equations. On figure 3 is shown the case where the line moves parallel to the smectic planes, or conversely where a flow of
velocity \( V \) (along \( x \)) encounters a fixed line. When the flow arrives from the left in the vicinity of the line, it remains confined to the layers, and is thus diverted off the symmetry axis: there is essentially no flow in the core region \( L_1 \), \( L_2 \). Then two boundary layers open up, and finally merge at a distant point \( P \). The distance \( L_1 \), \( P = x_1 \) is of order

\[ x_1 \sim kb^2. \tag{2.9} \]

This ensures that \( \delta(x_1) \sim b \). Using arguments similar in spirit to eq. (2.1), (2.5) one can then show that the friction force \( F \) (per unit length of line) should be of order

\[ F \cong \eta kbV. \tag{2.10} \]

This is proportional to the Burgers vector — in agreement with the Meyer and Clark calculation.

At this stage, we may come back to the problem of the floating sphere and make it slightly more realistic: assume for instance that the smectic planes must constantly be parallel to the surface of the sphere. Then, if the sphere radius \( R \) is not too large (1), we may have the arrangement shown on figure 4, with an equatorial dislocation loop of radius \( R_L \) slightly larger than \( R \).

![Figure 4 - Arrangement of smectic layers around a floating sphere](image)

The layers inside a sphere of radius \( R_L \) form an onion which is practically impermeable. Since \( R_L \) is not very different from \( R \), the mobility of the onion should still be qualitatively given by eq. (2.7), (2.8): the realistic model does not differ widely in its predictions from the original model of reference [11].

2.3 THE UNDULATION MODE IN RESTRICTED GEOMETRIES. — The undulation mode of smectics corresponds to a wave like deformation of the layers with a wave vector \( q \) parallel to their unperturbed planes [2]. In an infinite medium, this deformation leaves the layer thickness unaltered: the restoring force is entirely due to curvature elasticity, and is very weak. Thus this mode has a) a very large thermal amplitude, b) a long relaxation time \( \tau_q \)

\[ 1 \quad \tau_q = \frac{Kq^2}{\eta} \quad (q \text{ parallel to planes}) \tag{2.11} \]

where \( K \) is the splay constant. Also, the very weak restoring forces are not able to induce a significant permeation: the constant \( \lambda_p \) does not show up in eq. (2.11). Inertial forces are constantly negligible for this slow undulation.

The search for this mode has been long. It is easily hidden by static defects [14]. Finally, with carefully prepared planar samples, it has been observed and the relaxation time \( \tau_p \) has been measured [15]. For such restricted geometries, eq. (2.11) does not hold: since the layer displacement \( u \) must vanish on both plates, the interlayer thickness cannot remain quite constant inside the sample. The restoring force is thus increased. Always assuming that permeation is negligible, imposing \( u = 0 \) on both plates, and ignoring any other effect of the plates, one can construct a simple generalization of eq. (2.11). The result is [15]:

\[ \frac{1}{\tau_q} = \eta^{-1}(Kq^2 + Bq^4 q^{-2}) \tag{2.12} \]

where \( q_i = \pi D^{-1} \), \( D \) being the sample thickness. Eq. (2.12) provides a good fit to the data. This came out as a surprise, since the derivation ignores one apparently important boundary condition: namely that the tangential velocity \( v_x \) should vanish on both plates (the normal velocity \( v_n \) vanishes correctly).

The paradox has been clarified by the introduction of the boundary layer concept [11]. Near each plate we have a boundary layer. The characteristic length associated with it, in the direction of the planes (i. e.: the analogy of \( x \) in eq. (2.6)) is the undulation wavelength \( 2\pi/q \). The thickness of the boundary layer is then

\[ \delta \equiv (q\varepsilon)^{-1/2}. \tag{2.13} \]

Just below the plates, in a region of thickness \( \delta \), permeation is important and the velocity profile adjusts to the condition \( v_x = 0 \) (Fig. 5). But this region is very thin (\( \delta \sim 1000 \AA \)) and, in all the remaining parts of

![Figure 5 - Undulation mode of smectics. The wavelength is \( 2\pi/q \). The transverse velocity vanishes in a boundary layer of thickness \( \delta \).](image)

(1) At very large values of \( Rld \), the dislocation ring is expected to become unstable with respect to a set of focal conics.
the sample, the permeationless motion described by eq. (2.12) does occur: the simple analysis is correct in practice.

2.4 SURFACE WAVES. — In nematic fluids, the capillary waves have been carefully studied by light scattering [16]: they are not very different from surface waves in isotropic liquids, except for an anisotropy in the damping. In smectics, the surface waves represent a much more delicate problem, both for the theorist and the experimentalist.

One first non trivial requirement is to have a really flat free surface, without any Grandjean Terrace [1]. Assuming that this is achieved, will the thermal amplitudes of the capillary waves be large enough for light scattering studies? (a smectic is intermediate between a liquid and a solid; the scattering by thermal waves at a liquid surface is visible, but the corresponding effect in a solid is very small).

The answer to this question depends very much on the sample thickness $D$. For $D \to \infty$ the scattering intensity should be of the liquid type, as can be shown by a purely static calculation (static properties control the intensity of the light scattering): the only effect of the smectic elasticity is to renormalise the surface tension $\gamma$ [9]:

$$A \to \tilde{A} = A + (BK)^{1/2} = A + B\lambda. \quad (2.14)$$

Eq. (2.14) holds only for thick samples

$$D > q^{-2} \lambda^{-1} \quad (2.15)$$

where $q$ is the wave vector of the capillary mode, and $\lambda = (K/B)^{1/2} \cong 20 \lambda$. The total intensity scattered by mode $q$ is then proportional to

$$< | z_q |^2 > = \frac{T}{\tilde{A}q^2} \quad (2.16)$$

where $z$ represents the displacement of the interface. Because of the inequality (2.15), this is at most equal to $TAD/\tilde{A}$: the large factor $D$ may help to get measurable intensities.

The frequency spectrum of the scattered light (for a given $q$) has been calculated recently by A. Rapini [17]; the results do depend significantly on the physical boundary conditions at the interface. Here we shall only consider the case of smectics proper, where it is plausible to assume that no new layers are created (or destroyed) during the oscillation (2). Then, for a fixed $q$, there is one dominant mode, with amplitudes varying like $e^{i\omega t} e^{i\omega t}$ (where $z$ is the normal to the interface). The dominant mode has the following features:

a) Inertial effects are negligible (This differs strongly from isotropic liquids).

b) Permeation is negligible.

c) The pressure gradients are small, and the main restoring force $g$ is derived from the elastic energy. It is parallel to $(z)$ and given by [2]

$$g = B \frac{\partial^2 u}{\partial z^2} - K \frac{\partial^4 u}{\partial x^4} = B(s^2 - \lambda^2 q^2) u. \quad (2.17)$$

The force $g$ is balanced by viscous friction:

$$\eta \nabla^2 v_z + g = 0. \quad (2.18)$$

Also it will turn out that $| s | < q$, and thus

$$\nabla^2 v_z = (s^2 - q^2) v_z \cong -q^2 v_z. \quad (2.19)$$

In the absence of permeation the molecules flow with the layer velocity:

$$v_z = \frac{\partial u}{\partial t} = i\omega u. \quad (2.20)$$

Combining eq. (2.17), (2.19), (2.20) we arrive at

$$s^2 = q^2(\lambda^2 + i\omega \tau_M) \quad (Re s > 0) \quad (2.21)$$

where $\tau_M$ is a Maxwell relaxation time

$$\tau_M = \frac{\eta}{B} \sim 10^{-9} s. \quad (2.22)$$

Having characterised the dominant mode, we can proceed to discuss the intensity. One useful intermediate (just as in the case of bulk nematics [18]) is a response function $\chi(q,\omega)$, giving the displacement $z_q$ induced by an external pressure distribution $p_{tot}$ proportional to $e^{i\omega t} e^{i\omega t}$. The response function is found to be

$$\chi(q,\omega) \equiv -\frac{1}{p_{tot}} = \frac{1}{\tilde{A}(q,\omega) q^2} \quad (2.23)$$

where $\tilde{A}(q,\omega)$ is an effective surface tension, given explicitly by a natural extension of eq. (2.14)

$$\tilde{A}(q,\omega) = A + B \frac{\tilde{s}(q,\omega)}{q^2}. \quad (2.24)$$

The explicit form of $\tilde{s}(q,\omega)$ is found in eq. (2.21). Note that $s, A$ and $\chi$ are complex numbers. The prescription to derive the light scattering spectrum $I$ from $\chi$ is simply [18]:

$$I(q,\omega) = \frac{T}{\pi} \text{Im} (\chi(q,\omega)) \quad (2.25)$$

This leads to a rather complicated form for the spectrum. The main qualitative conclusions are:

a) The spectrum at fixed $q$ and variable $\omega$ should not show oscillation peaks, but only damped waves (in strong contrast with isotropic or nematic liquids where capillary oscillations are often visible [16]).

b) The linewidth $\Delta \omega$ of the central peak can be roughly estimated by equating real and imaginary parts in the eq. (2.21) for $s^2$. $\Delta \omega$ is then essentially equal to the relaxation rate $1/\tau_q$ for the bulk undulation mode (eq. (2.11)).

We must emphasize that the dominant mode described here does not satisfy all the required boundary conditions at the interface (in particular the condition on tangential stresses). But boundary layers come again to our help, and lead to an adjustment in a very small thickness $(q\lambda)^{-1/2}$. 

(2) This would not be true for cholesterics.
Finally, in connection with surface waves, we should mention briefly the problem of gravitational instabilities: namely, if we put a heavy liquid (e.g., mercury) on top of a smectic, will the system be unstable? The answer for planar samples is that they should be stable — except if their thickness became larger than ~ 1 kilometer! But with cholesterics or twisted nematics, in suitable arrangements, some amusing effects could be expected on the laboratory scale [19].

3. Squeezing a smectic between two plates. —

3.1 The conventional thrust bearing. — Let us start with a drop of an isotropic liquid, squeezed in the gap (of thickness \( D(i) \)) between two solid plates, by a constant force \( F \). This is a classical problem of low Reynolds number hydrodynamics; a complete discussion can be found for instance in reference [20]. We shall first summarize the argument for this simple case. The drop has a large radius \( R(t) \). It is essentially incompressible and thus

\[
R^2 D = W = \text{constant}.
\]  

(3.1)

The pressure \( p \) is of order \( F/R^2 \), and the pressure gradient (between the symmetry axis and the edge of the drop) is of order \( F/R^3 \). This induces a radial Poiseuille flow in the gap, with velocities of order \( dR/dt \). The balance of radial forces is of the form

\[
\eta D^{-1} \frac{dR}{dt} \approx \frac{F}{R^3}.
\]  

(3.2)

Using (3.1) to eliminate \( R \) this can be integrated to give

\[
D(t) = \frac{D(0)}{\left(1 + \frac{C_1 F(t)D^2(0)}{\eta W^2} \right)^{1/4}}.
\]  

(3.3)

where \( C_1 \) is a numerical constant. How does this law extend to smectics? We shall discuss this in two separate cases:

a) for a large sample, in terms of continuum theory,

b) for small objects (in view of applications to the stabilisation of emulsions) in terms of dislocations.

3.2 Squeezing a large sample. — What we call large is a smectic sample, with \( D \sim 100 \mu \) and \( R \sim 1 \text{ mm} \). We assume that this is a single domain (except possibly on the periphery) the smectic planes being parallel to the walls, and that the permeation coefficient \( \lambda_p \) is non vanishing (this probably excludes certain systems such as lipid + water).

Upon squeezing, we expect a boundary layer of thickness \( \delta \) to appear near each plate. According to (2.11) \( \delta \) should be of order \( R^{3/2} \kappa^{-1/2} \sim 1 \mu \). More generally we can think of two regimes:

a) \( \delta > D \). Then permeation is not a serious obstacle to the flow, and eq. (3.2) should hold.

b) \( \delta < D \). Then permeation is the limiting factor. We shall now restrict our attention to this case, treating the smectic as incompressible and neglecting inertial effects. Consider for instance the vicinity of the upper plate: we have a vertical pressure drop of \( F/R^2 \) taking place in a thickness \( \delta \). Thus the permeation velocity is

\[
v_s \approx - \lambda_p \frac{F}{R^3} \frac{1}{\delta} = - \lambda_p F \kappa^{1/2} R^{-5/2}.
\]  

(3.4)

This must be equal to \(- \frac{1}{2} \frac{dD}{dt} \). Eliminating \( R \) by eq. (3.1) in the resulting rate equation one arrives at

\[
D(t) = \frac{D(0)}{\left(1 + \frac{F(t)D^2(0)}{\eta W^5 \kappa^{3/2}} \right)^{1/4}}.
\]  

(3.5)

Comparison with (3.2), (3.3) shows that the rate of decrease of the thickness is much slower — by a factor \((\delta/D)^3 \sim \) than in isotropic fluids. Of course at sufficiently long times \( \delta \) increases, \( D \) decreases, \( \delta \) becomes comparable to \( D \) and eq. (3.2) takes over. But the regime \( \delta < D \) could give an interesting mechanical test of the permeation process. More detailed formulas for this regime are worked out in the appendix.

3.3 Stabilisation of emulsions and foams by smectics. — The remarkable efficiency of certain smectic phases, for the stabilisation of emulsions and foams, has been pointed out by Friberg and coworkers [21]. Here we are dealing with a small number of layers (typically 10) between two smooth surfaces (droplets or bubbles). The two surfaces attract each other by van der Waals forces. In the simplest case (no retardation) the resulting pressure is

\[
p = \frac{A}{12 \pi D^2}
\]  

(3.6)

where \( A \) is the relevant Hamaker constant, and \( D \) is the gap thickness [22].

Thus we are again dealing with a squeezed smectic, but the physics is rather different, for the following reasons:

a) Permeation is probably very weak in the amphiphilic systems of interest.

b) During contraction a certain number of smectic planes must be eliminated.

This elimination should involve edge dislocations as shown on figure 6, located either in the bulk, or most probably near the limiting surfaces of the smectic. For the thick samples of the last section, the glass surfaces limiting the smectic are rather irregular on the scale of say 30 \( \AA \): the irregularities may act as nucleation centers for dislocation loops, and the elimination of smectic planes is probably not a serious bottleneck: thus the continuum picture may have some validity. On the other hand, the thin layers which we are considering now are bounded by very smooth surfaces (liquid or air). Nucleation of dislo-
cations is then a very slow process, and may well control the stability of the system. We shall now describe this nucleation in very simple terms.

\[ E = -b \pi r^2 p + \gamma_L 2 \pi r \]  \hspace{1cm} (3.7)

where \( b \) (\( \sim d \)) is the Burgers vector, and \( \gamma_L \) is a line tension. The exact value of \( \gamma_L \) would depend on whether the line is close to one limiting surface or not. In any case we expect \( \gamma \) to be comparable to a Frank constant \( K \approx 10^{-6} \) dynes. The energy \( E(r) \) is a maximum for

\[ r = r^* = \frac{\gamma_L}{\partial p} \]  \hspace{1cm} (3.8)

and the corresponding energy barrier is

\[ E^* = E(r^*) = \pi \frac{\gamma_L^2}{\partial p}. \]  \hspace{1cm} (3.9)

The relative rate of decrease of the thickness is of the form

\[ -\frac{1}{D} \frac{dD}{dt} = \frac{U}{D} \exp \left( -\frac{E^*}{T} \right). \]  \hspace{1cm} (3.10)

The prefactor \( U \) should be proportional to the size of the nucleation region, but as usual with such problems, the exact value of \( U \) is unimportant, and we may take for \( U/D \) a typical molecular frequency \( 1/\tau_0 \).

If we choose for instance the form (2.6) for the pressure, we have a rate of the form

\[ -\frac{1}{D} \frac{dD}{dt} = \frac{1}{\tau_0} \exp \left( -\frac{(D)}{I^3} \right) \]  \hspace{1cm} (3.11)

where

\[ I = \left( \frac{1}{6 \pi^2} \frac{A T b}{\gamma_L} \right)^{1/3}. \]  \hspace{1cm} (3.12)

Typically with \( A = 2 \times 10^{-13} \) ergs, \( \gamma_L = 10^{-6} \) dynes and \( T = 5 \times 10^{-14} \) ergs, we expect \( I \approx 4 \) Å; thus as soon as \( D \) is larger than \( \approx 3 \) \( I \) the rate of thinning becomes negligible. This may well explain the observed stabilities.

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Appendix

Derivation of the rate equation for the thickness of a finite smectic film under constant external force. — Here we shall be concerned with the case where the permeation is a strong obstacle to the flow. According to section 3, this corresponds to the limit

\[ \delta < D \quad \{ \delta^2(t) = \kappa^{-1} R(t) \} \]  \hspace{1cm} (A.1)

where the boundary layers close to each plate are uncoupled (\(^3\)). The problem is then solved by considering a semi-infinite slab submitted to a constant force \( F \) (for the geometry see Fig. 7). The force balance equations for the fluid, in the limit of low Reynolds number and neglecting inertial terms, are

\[ \rho \dot{v}_z = -\frac{\partial p}{\partial z} - \frac{1}{\kappa_p} v_z \approx 0 \]  \hspace{1cm} (A.2)

\[ \rho \dot{v}_L = -V_L p + \eta \frac{\partial^2 V_L}{\partial z^2} \approx 0 \]  \hspace{1cm} (A.3)

where \( V_L \) and \( v_L \) are respectively the gradient operator and the velocity, in a plane perpendicular to the

\(^3\) A similar boundary layer problem is solved in reference [10].
symmetry axis of the film. The last term in eq. (A.2) indicates that the fluid motion results from permeation and that there is no motion of the layers. This results from elimination of smectics layers by rapid nucleation of dislocations as described in (3.3).

Viscosity terms are not included in eq. (A.2) since reads

\[ F = \int_0^R \rho(r, z = 0) 2 \pi r \, dr \]

reads

\[ F = -\frac{4 \pi}{\sqrt{2}} \frac{\partial D}{\partial t} \sum_{|q|} \frac{1}{(q^2)^{1/2}} \left( \int_0^{R(t)} J_0(q_1 r) r \, dr \right)^2 \]

Using the relation

\[ \left( \int_0^R J_0(q_1 r) r \, dr \right)^2 = \frac{2}{q^2} \]

and the numerical computation of the series

\[ S = \sum_{|q|} \frac{1}{(q_1 R)^{1/2}} = 0.14 \]

one obtains, after integration of eq. (A.7), the rate equation for the thickness of the film:

\[ D(t) = \frac{D(0)}{1 + C_2 \frac{F I}{\eta \kappa^{3/2} W^{5/4}}} \]

for

\[ \delta(t) < D(t) < R(t) \]

where

\[ W = R^2(t) D(t) = Cte \]

and

\[ C_2 = \frac{32 \pi}{\sqrt{2}} \times S \approx 10 \]

Comparing eq. (A.9) with eq. 3.3 (for an isotropic liquid \( C_1 \approx 1 \)) one finds a very different rate of decrease of \( D(t) \) for smectics and isotropic liquids. The ratio of these two rates is, at \( t = 0 \):

\[ \rho = \frac{\partial D}{\partial t} \bigg|_{t=0} = 16 C_2 \left( \frac{\delta(0)}{D(0)} \right)^3 \ll 1 \]

for a typical sample where \( D(0) = 100 \mu \) and \( \delta(0) \approx 1 \mu \).

References

[1] The best review on smectics A is still probably FREIDEL, G., *Annls de Phys.* The classification of smectics is due to SACKMANN, H., DEMUS, D.


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[7] We are indebted to HELFRICH, W., for a fruitful conversation on this point.


[22] See for instance Intermolecular forces (North Holland).