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Shear induced melting of smectic-*A* liquid crystals

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An analysis of shear induced melting of homogeneously aligned smectic-*A* liquid-crystal material is presented. The solution is based on a Landau expansion of the complex smectic order parameter and its spatial derivative. Two solution branches are obtained and it is suggested that, in practice, shear induced melting involves a transition from one branch to the melt state. [S1063-651X(98)01906-0]

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INTRODUCTION

Smectic-*A* liquid crystals have both orientational and positional molecular order [1]. The uniaxial orientational order parameter can be expressed in the form

$$s=\tfrac{1}{2}\langle(3\cos^2\theta-1)\rangle, \tag{1}$$

where θ is the local molecular tilt fluctuation away from the mean orientation. The positional order in the smectic-*A* phase consists of a density modulation along the average molecular axis. Within the layers there is only very-short-range ordering and the behavior is liquidlike. If the local-density modulation amplitude is represented by ρ and the local layer phase angle by Φ, then to first order the smectic behavior can be expressed through the complex order parameter

$$\psi=\rho\ \exp\ i\Phi(\mathbf{r}), \tag{2}$$

where in the bulk material Φ would have the layer periodicity along the molecular axis and be independent of directions normal to this [2]. In practice both the nematic and smectic order parameters may be modified during shear; here only the latter is considered.

A presentation of order parameter modification through externally imposed deformations on smectic-*A* systems was de Gennes's analogy between smectic-*A* materials and superconductors [3]. It was suggested that a smectic-*A* to nematic phase transition could be induced through a bend deformation, i.e., the smectic-*A* phase could be caused to melt into the nematic phase. Alternatively, edge dislocations could form to take up the smectic layer thickness changes. Which occurs would depend critically on the Landau-Ginsburg parameter [3]. In the case of shear considered here smooth deformations and continuum behavior are assumed; melting is then the only option. Marignan and co-workers have considered the case of instabilities in smectic-*A* layers [4,5] induced by oscillating shear. The instabilities observed were therefore due to dynamic effects and while melting may have been involved in the defect formation it was not the fundamental mechanism investigated.

Quasistatic shear induced melting of smectic-*A* liquid crystals has been investigated experimentally by Cagnon and Durand [6]. In their work a thin layer of homogeneously aligned smectic-*A* liquid crystal was subjected to a slow oscillatory shear. Simultaneously they measured the shear stress transferred between the plates forming the liquid-crystal cell, i.e., through the liquid-crystal smectic layers. The key observation is that this shows a periodicity that is spatially equal to the smectic layer pitch for this material, as independently measured by x-ray diffraction. This was explained as being due to the smectic layering melting and reforming periodically during the shearing process. Cagnon and Durand gave a mathematical description based on a simple algebraic order parameter. Here we present an analysis based on a Landau expansion of the complex order parameter [Eq. (2)]. Smectic order parameter melting effects have also been observed at grain boundaries in bent smectic-*A* liquid crystals [7].

MODEL

We consider the nematic order parameter s to be a fixed quantity and examine how shear modifies the complex smectic order parameter ψ. The coupling between the parameters has been discussed by Linhananta and Sullivan [8]. We set up a coordinate system with the smectic layers in the y-z plane, the layer normal and molecular axis being in the x direction. Cell surfaces are in the x-y plane and shear then takes place in the x-z plane, along the x axis. In order to simplify the Landau energy expansion [9] we assume that the molecular axis remains in the x direction during shear. This is reasonable as it equates to the assumption that the smectic layer thickness is proportional to the cosine of any molecular tilt relative to the local smectic layer normal. Making this assumption also removes the need to include any nematiclike orientational elastic distortion terms in the expression. We can then write

$$f=A|\psi|^2+\frac{B}{2}\,|\psi|^4+C\left|\frac{d\psi}{dz}\right|^2, \tag{3}$$

where the third term has been simplified from that presented by de Gennes and Prost [9] by the above assumptions.

Before discussing the meaning of the terms in Eq. (3) it is useful to substitute from Eq. (2) and write

$$f=A\rho^2+\frac{B}{2}\,\rho^4+C\left[\left(\frac{d\rho}{dz}\right)^2+\rho^2\left(\frac{d\phi}{dz}\right)^2\right], \tag{4}$$

where we have defined

$$\phi(z)=\Phi(\mathbf{r})-\Phi'(x),$$

Φ being independent of the y direction and having constant, shear-independent periodicity in the x direction. The first two Landau terms define the equilibrium bulk smectic order parameter and perturbations away from this value will cost energy. There are additional energy terms associated with gradients in the order parameter amplitude and phase. The latter gradient is equivalent to tilting the director away from the smectic layer normal and the associated energy can equally be considered as the first term in the Landau expansion for induced molecular tilt, commonly used to model the smectic-*A* to smectic-*C* phase transition [10].

Euler-Lagrange equations in ρ and ϕ follow from Eq. (4) as

$$2A\rho+2B\rho^3+2C\rho\left(\frac{d\phi}{dz}\right)^2-2C\,\frac{d^2\rho}{dz^2}=0, \tag{5}$$

$$2C\rho^2\left(\frac{d\phi}{dz}\right)=K', \tag{6}$$

where K' is a constant, the implications of which will be discussed later. Eliminating the $d\phi/dz$ term gives

$$2A\rho+2B\rho^3+\frac{K'^2}{2C\rho^3}-2C\,\frac{d^2\rho}{dz^2}=0 \tag{7}$$

as a single equation in ρ requiring solution. Defining

$$r=\frac{\rho}{\rho_e},$$

$$Z=z\sqrt{\frac{-A}{C}},$$

$$K=\frac{-K'^2B^2}{4A^3C},$$

where $\rho_e=\sqrt{-A/B}$ ($A<0$ in the smectic A phase), allows us to rewrite Eq. (7) as

$$-r+r^3+\frac{K}{r^3}-\frac{d^2r}{dZ^2}=0. \tag{8}$$

Before looking at solutions to this equation it is worth considering qualitatively what might take place during shear. For small amounts of shear we expect a corresponding small tilt to be introduced in the smectic layers, for very large shear molecular tilt becomes $\pi/2$ and no solution is expected, and for intermediate shear we expect melting into the nematic phase to occur. Assuming that this melting is localized (which is expected on energy grounds), it is likely to occur either at the surface or in the center of the cell, which will be dictated by the boundary conditions applied. In this region the smectic order parameter will tend towards zero and the smectic layer phase change will become concentrated at the melt point. If complete melting takes place then a discontinuity in the layer phase can occur and the layers may slide along to a new position. If shearing continues this process could repeat, leading to periodic shear stress: This will be discussed in greater detail later.

SOLUTIONS

We will set up the problem with fixed boundary conditions of $r=1$ at both surfaces. This is equivalent to saying that the surface anchoring is strong and that the smectic order parameter at the surfaces is equal to its bulk equilibrium value and is fixed at this value; also the smectic layer periodicity at the surfaces is fixed at its equilibrium value, i.e., the smectic layer thickness at the surfaces is always equal to its natural size. We believe this to be a reasonable assumption as it should be determined by the phase history of the material and fixed at this value because surface diffusion is quite slow. Setting the surfaces at $Z=\pm d/2$, we then expect melting to occur at the origin (i.e., in the center of the cell) for the boundary conditions we have used. Our constant K is a control parameter in the solution of Eq. (8); once a solution is found the corresponding smectic layer phase angle can be determined through Eq. (6).

For very thick devices (i.e., $d\rightarrow\infty$) some analytic progress can be made in the solution of Eq. (8). Multiplying through by dr/dZ allows the equation to be integrated once with respect to Z, giving

$$-2r^2+r^4-\frac{2K}{r^2}=2\left(\frac{dr}{dZ}\right)^2+D,$$

where the constant D can be eliminated knowing that as $Z\rightarrow\infty$ we have $dr/dZ\rightarrow0$ and $r\rightarrow1$. At $Z=0$ we can also set $dr/dZ=0$ (by symmetry) and $r=r_m$. We can then write

$$K=\frac{2r_m^2-r_m^4-1}{2(1-r_m^{-2})}, \tag{9}$$

which for this case is a relationship between the control parameter K and the minimum normalized smectic order amplitude r_m (at the origin). This relationship is illustrated in Fig. 1 (continuous line). The result is particularly interesting, indicating that, at least for very thick devices, depending on the control parameter K there are three regions of interest. (i) If $K<0.125$ there are two solutions with differing values of the minimum amplitude of smectic ordering (r_m). In the limit of $K\rightarrow0$ these two solutions have $r_m\rightarrow1$ and $r_m\rightarrow0$. The former of these solutions must be $r=1$ everywhere as we have used this as the boundary condition: This assumes that r is not ''enhanced'' by any possible shear process. Substitution of $K\rightarrow0$ back into Eq. (6) shows that if r is finite throughout the device then $d\phi/dz$ is identically zero. Thus, as might be expected, this solution corresponds to the case of no shear. The second solution for $K\rightarrow0$ has $r_m\rightarrow0$ (i.e., $r\rightarrow0$ at the origin). This must correspond to complete melting at this point. Substitution into Eq. (6) now shows that $d\phi/dz$ is identically zero everywhere except at the origin, where it is undefined. Again this is as we might expect: In the melt state the smectic layers are uniform, with any phase shift taken up at the origin where the material is effectively nematic. In this case Eq. (8) has a tanh-like analytic solution, which is shown as a dashed line in Fig. 2. This relates di-

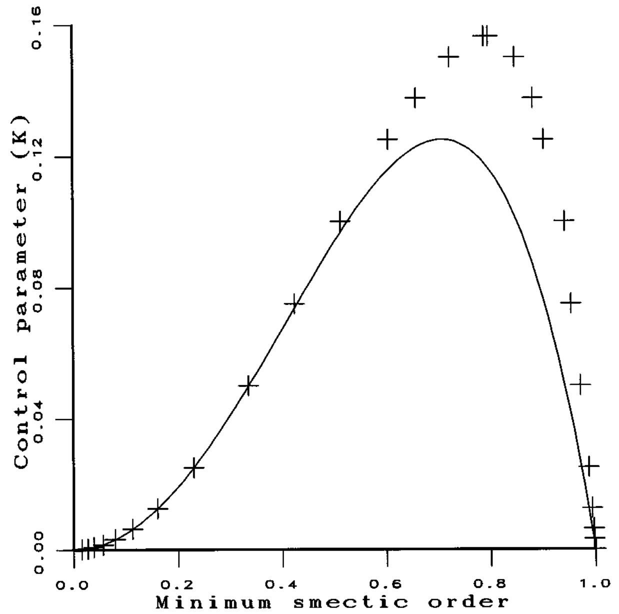

FIG. 1. Plot of the relationship between the control parameter K and the minimum smectic order r_m (located at the origin). The continuous line is the analytic solution for an infinitely thick device and the discrete points are the numerical solution for a device of normalized thickness $\pm 2\sqrt{5}$.

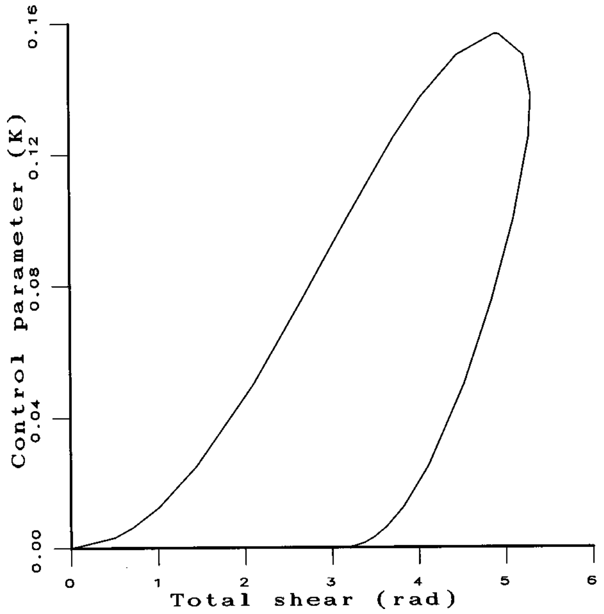

FIG. 3. Plot showing the relationship between $\Delta\phi$ (the total shear) and the control parameter K. The direction traveled around the loop as r_m decreases from 1 to 0 is clockwise. This curve is analogous to that shown in Fig. 1.

rectly to thick cells, i.e., those where d is much greater than the width of the melt region. (ii) If $K=0.125$ there is identically one solution. (iii) If $K>0.125$ there are no solutions to Eq. (8).

In order to investigate the solutions further we use a numerical approach to solving Eq. (8). Here we use a finite thickness of device, $d/2=2\sqrt{5}$, chosen to show a ''nice'' melting solution. The chosen illustrative thickness is of the order of the in-layer smectic coherence length (i.e., around 100 Å), allowing the melt region to take up a significant portion of the solution space. Results are, however, also representative of the central region of a thicker cell, as can be seen from the analytic limit discussed in the preceding paragraph. Although the boundary conditions considered here dictate that the melt always occurs in the center of the cell, we would expect that in practice small perturbations in the boundary conditions may shift the melting point towards one surface. A shooting method is used in the analysis, where the initial slope (at $Z=-d/2$) is adjusted until $r=1$ at the opposite surface. This process is undertaken for a range of values of the control parameter K in order to find a complete solution set. The relationship between K and r_m in this case is also illustrated in Fig. 1 (by the discrete points). Although the change to a finite thickness has perturbed the relationship, the form is as before, and again for K smaller than some critical value the solutions are paired. The corresponding set of solutions to Eq. (8) (r as a function of Z) is shown in Fig. 2. We see that as r_m decreases the region becomes narrower, being concentrated around the origin. For completeness we also wish to consider the corresponding solution to Eq. (6), which is available directly by substitution and numerical integration. In our normalized form Eq. (6) becomes

$$r^2\left(\frac{d\phi}{dZ}\right)=\sqrt{K}. \tag{10}$$

This has a solution $\phi=\phi(Z)$ and we also define the total shear $\Delta\phi$ by integrating this over the normalized thickness of $\pm d/2$. The $\Delta\phi$ relationship to the control parameter K is illustrated in Fig. 3, which is analogous to the result shown in Fig. 1. The set of solutions for ϕ as a function of Z is shown in Fig. 4.

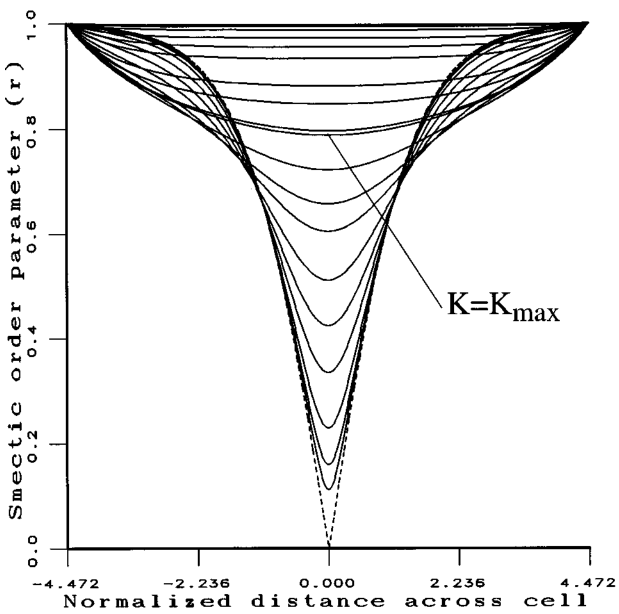

FIG. 2. Set of numerically determined curves for r. As the minimum value of r decreases the melting is concentrated around the origin. The point corresponding to the maximum value of K is indicated. The dashed line shows the analytic (tanh-like) solution for $K=0$ in a very thick device.

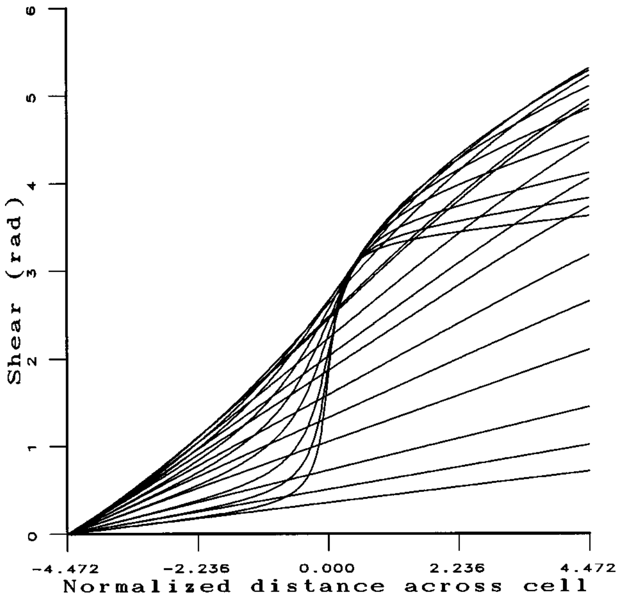

FIG. 4. Set of curves for the local shear of the smectic layers (phase angle ϕ) across a device. The increasing steepness in the center of the device corresponds to the decreasing minimum smectic ordering in this region. Note that this does not correspond to a monotonically increasing total shear.

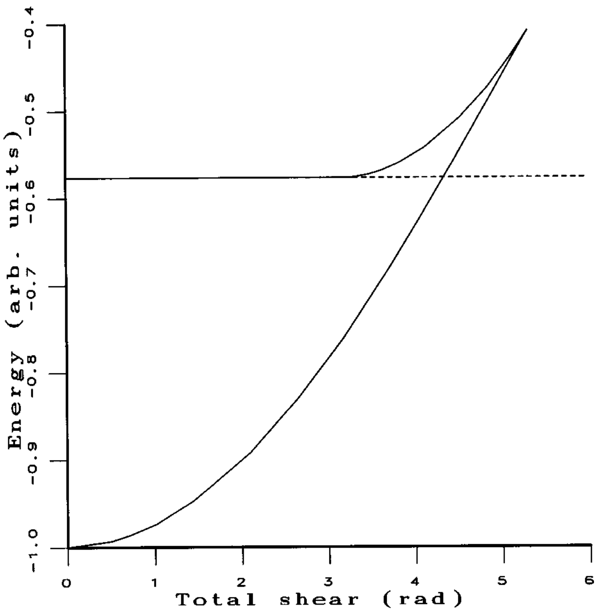

FIG. 5. Dependence of normalized energy on total shear. The dashed line indicates the energy corresponding to the melt state, where $\Delta\phi$ is not defined. Where the solution crosses the melt state energy (at $\Delta\phi \sim 4.34$) a branch jump may take place, leading to melting of the smectic layers.

DISCUSSION

This solution set is very interesting. The increasing steepness in the center of the device (at $Z=0$) corresponds to decreasing r_m in Fig. 2. Clearly this does not, however, correspond to monotonically increasing $\Delta\phi$. It is difficult to see directly from this what happens physically and the qualitative understanding outlined above needs refinement. Apparently, increasing the shear from zero to the maximum value observed in Fig. 4 would not cause melting. However, there are no solutions beyond this point, so what happens if further shear is applied? In order to understand what takes place we must consider the energy as a function of the shear distance. This is easily obtained by numerically integrating Eq. (4) using the solutions we have obtained for the smectic order amplitude and phase. We scale the energy to be -1 for the equilibrium state (before shear is applied). A plot of energy against $\Delta\phi$ is shown in Fig. 5. This also shows the energy calculated for the melt state (or branch), which is of course independent of $\Delta\phi$ because ϕ is not defined at the melting point.

What we expect to take place when a device is sheared now becomes clear. Initially we move along the energy-$\Delta\phi$ line, starting at the lower left-hand corner. However, at $\Delta\phi \sim 4.34$ the energy of the melt state is crossed. States above this line (the shaded region in Fig. 5) are therefore not global minima. Physically, there are two possibilities. (i) If a nucleation point or layer structure defect site is present then we may expect local melting to occur in this region as soon as the melt state energy is crossed. This may be expected to seed melting, which then grows throughout the device. (ii) If no nucleation points are present then we may expect to continue to move along the shearing branch, even though this is at a higher energy: We might call this a supersheared state. This would continue until we meet the end of this branch, where we are forced to jump directly to the melt state (simultaneously for the whole cell).

The calculation we have performed is of course quasistatic and in the process of jumping branches there will be some dynamics of liquid-crystal reorientation involved. Thus it is reasonable to expect that at the point where melting occurs (by either of the mechanisms discussed above) the layering will re-form one step back, at some point lower down the energy-$\Delta\phi$ line. If shearing continues this process could repeat, leading to steps in the surface shear stress with period equal to the layer spacing. This process will, however, be highly dependent on device thickness. For a thick (much greater than the smectic coherence length) device a moderate amount of shear will be required before any such process can take place; thus the periodic shear stress will be preceded by a monotonically increasing shear stress. For a thin (much less than the smectic coherence length) device, however, we expect melting to take place much earlier; if the device is sufficiently thin this may occur for shears of less than one-half the smectic layer spacing. In this case the melt state will be formed and will exist for shears up to the point where a state with opposite shear can form, which would show negative shear stress. During the melt state the measured surface shear stress will be dictated by material viscosity. Continued shearing would again lead to periodicity.

It is further interesting to note that with differing boundary conditions the solution set could be somewhat more complex. For values of the control parameter K between zero and its maximum value consideration of Eq. (8) indicates that the solution space for r can be broken into three regions. These regions are defined by the values $r=0$, $r=1$, and the two solutions of $r^4(1-r^2)=K$; in these regions the curvature of r is respectively positive, negative, and positive. For example, if $K=0.05$ then in the region $0<r<0.5098$ the curvature of r is positive, in the region $0.5098<r<0.9715$ the curvature of r is negative, and in the region $0.9715<r<1$

the curvature of r is again positive. With the boundary condition we have used ($r=1$ at the surfaces) this allows two solutions: one in which the curve remains in the region $0.9715<r<1$ and one in which the curve crosses through the region $0.5098<r<0.9715$ and into the region $0<r<0.5098$, this is what we have observed. However, if the launch point of the curve (boundary condition) is such that at the surfaces r is in the region $0.5098<r<0.9715$ then it is possible that the curve could cross between this region and the lower positive curve region one or more times. Interestingly, these solutions are similar to those for Jeffrey-Hamel flows between nonparallel walls [11] and could be worthy of further investigation. Finally, it should also be noted that with ''free'' (Neumann) boundary conditions on r (i.e., $dr/dZ=0$ at the surfaces), melting occurs simultaneously for all Z. This takes place at the point in shear where $d\phi/dZ=1$ or $d\phi/dz=(-A/C)^{1/2}$.

It appears that the mathematics developed here may be able to explain periodic shear stress, but there is a richer solution set than that observed experimentally by Cagnon and Durand.

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