Shear Alignment and Instability of Smectic Phases

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We consider the shear flow of well-aligned one-component smectic phases, such as thermotropic smectics and lamellar diblock copolymers, below the critical region. We show that, as a result of thermal fluctuations of the layers, parallel (c) alignment is generically unstable and perpendicular (a) alignment is stable against long-wavelength undulations. We also find, surprisingly, that both a and c alignments are stable for a narrow window of values for the anisotropic viscosity.

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In the presence of simple shear flow, smectic phases exhibit a surprising degree of complexity. As shear rate and temperature are changed, a variety of transitions in orientation and morphology have been observed. Although one might expect the liquid layers to simply slide over each other with their normals parallel to the shear gradient, the c orientation (Fig. 1), they often orient with their layer normals pointing in the vorticity (or neutral) direction, the a orientation (Fig. 1). This behavior is seen under some conditions in both thermotropic smectics [1–4] and lamellar phases of diblock copolymers [5–9]. For thermotropics near the nematic-smectic transition, it has been shown that, as a result of nematic fluctuations, a alignment is favored over c [2]. In diblock copolymers, it has been shown that the wave vector dependence of the quartic coupling in the Hamiltonian describing the order-disorder transition favors a alignment [10]. In this paper we consider the steady shear flow of generic one-component smectic phases at temperatures well below the critical regime. We show that well-aligned (i.e., defect free) systems favor the a orientation: the c orientation, as well as orientations intermediate between a and c, suffer an instability from long-wavelength undulations. We also find, surprisingly, that within a small window of values for the anisotropic viscosity, both a and c alignments are stable.

It is clear that smectic phases will align so that the average flow velocity has no component along the layer normals. Otherwise, the layers will be forced to deviate from their preferred spacing, which is energetically costly. For perfectly flat layers, both a and c orientations permit steady shear flows with the layer displacement unperturbed from its equilibrium value. However, thermal fluctuations of the layers are convected differently in the two cases. As we will see below, convection leads to a greater suppression of thermal fluctuations in the c orientation than in the a orientation. Hence, if we adopt a naive picture in which the steady-state dynamics is determined by maximizing layer fluctuations (free energy minimization), the a orientation will be obtained in steady state. Since entropy maximization arguments in nonequilibrium systems are often suspect, we also compute the dynamic response function for small perturbations away from an aligned state and show that the c orientation is indeed unstable towards rotation to a.

Well below the ordering transition, where the amplitude of the order parameter (concentration variations for diblocks or density variations for thermotropics) is fixed, a well-aligned smectic is parametrized by a layer displacement $u(r)$. We take the average layer normals parallel to $\hat{z}$. The Hamiltonian for layer fluctuations is (in Fourier space) [11]

$$\mathcal{H} = \frac{1}{2}\int d^3q u(-q)u(q)\omega(q), \tag{1}$$

$$\omega(q) = Bq_z^2 + Kq_\perp^4,$$

where B and K are, respectively, the layer compression and bending moduli and $q_\perp$ denotes the component of the wave vector $\vec{q}$ in the (x,y) plane. The penetration length $\lambda \equiv \sqrt{K/B}$ is typically of the order of the layer spacing. As a result, modes with $q_z = 0$, which correspond to layer undulations, are much softer than layer compressions, which have $q_\perp = 0$.

Consider now the effect of a steady shear with average flow velocity parallel to $\hat{x}$

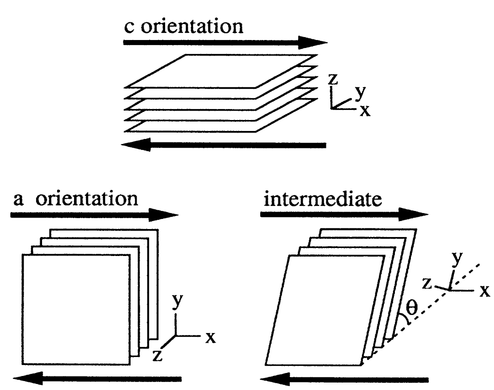

FIG. 1. Schematic of the c, a, and intermediate orientations. We always take the flow velocity to be in the $\hat{x}$ direction and the layer normals to point in the $\hat{z}$ direction. The shear plane is in the plane of the page.

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$$\vec{v}(\vec{r}) = (\vec{r} \cdot \hat{n})\dot{\gamma}\hat{x}, \qquad (2)$$
$$\hat{n} = \cos\theta\hat{z} + \sin\theta\hat{y}.$$

The velocity gradient direction is $\hat{n}$; in the a orientation $\hat{n} = \hat{y}$ and in the c direction $\hat{n} = \hat{z}$ (Fig. 1). A mode with wave vector $\vec{q}$ at time $t = 0$ will be convected by the flow Eq. (2) according to

$$\vec{q}(t) \equiv \vec{q} - \hat{n}\dot{\gamma}q_x t. \qquad (3)$$

In the a orientation, the z component of $\vec{q}$ is unaffected by the shear, $q_z(t) = q_z$; a mode that is a pure undulation ($q_z = 0$) at $t = 0$ remains a pure undulation at later times. In the c orientation, however, $q_z(t) = \dot{\gamma}q_x t$; undulations with $q_x \neq 0$ at $t = 0$ pick up a compressional character ($q_z \neq 0$) at later times. We will see below that the lifetime for a fluctuation with wave vector $\vec{q}$ is given by $1/\omega(q)\beta(q)$, where $\beta(q)$ is a kinetic coefficient. As noted above, layer compressions are much stiffer than undulations, i.e., for fixed $|\vec{q}|$, $\omega(q)$ is larger for compression modes than for undulations. Therefore, the lifetime of modes with $q_x \neq 0$ is much shorter in the c orientation than in the a orientation. (Here we assume an isotropic kinetic coefficient for simplicity.) With a greater suppression of modes in case c, we expect a corresponding increase in the "free energy" and hence an instability towards rotation to a. (It is easy to see that orientations intermediate between a and c suffer from a similar suppression of modes, though to a lesser extent, and thus the free energy should monotonically decrease in passing from c to a.)

In the previous discussion we have invoked free-energy minimization in a nonequilibrium system. One can often determine the steady-state behavior in such cases by minimization of a quasifree energy. However, this usually requires that the equations of motion can be written in the relaxational form $\dot{\phi} = \delta\Gamma/\delta\phi$, where ϕ is the dynamical variable of interest and $\Gamma(\phi)$ is some functional. In our case, one can consider the equation of motion for the angle θ parametrizing orientations between a and c (Fig. 1) after averaging over layer fluctuations. Unfortunately, we have not been able to express the equations of motion in a form that would justify a minimization principle. However, the above picture suggests an alternative course. A long-wavelength undulation in the $\hat{y}$ direction locally looks like a change in θ, i.e., a tilt of the layers in the neutral direction. Therefore, a local driving force for rotating from c to a should appear in the c orientation as an instability towards long-wavelength undulations with $\vec{q} \parallel \hat{y}$.

Below, we first compute a quasifree energy to demonstrate the mode suppression described above. We then compute the dynamic response function (to one loop in perturbation theory) and show that indeed the c orientation, as well as orientations intermediate between a and c, are unstable and the a orientation is stable.

To describe the hydrodynamics of smectics, we follow the treatment of [11,12]. We neglect inertial terms and assume incompressibility. In this limit, the dynamics of u reduces to the relaxational form

$$\frac{\partial u(q)}{\partial t} + \beta(q)\frac{\delta \mathcal{H}}{\delta u} = 0, \qquad (4)$$

$$\beta(q) = b_p + \frac{q_\perp^2}{\eta q^4 + \eta' q_z^2 q_\perp^2}. \qquad (5)$$

η and η' are viscosities [13], and b_p is the permeation constant. Although our results are independent of b_p, we include permeation in order to ensure that subsequent expressions converge for large q_z.

In the presence of steady shear, the time derivative in Eq. (4) is replaced by the convective derivative $\partial/\partial t - \dot{\gamma}q_x\partial/\partial q_n$, $q_n \equiv \vec{q} \cdot \hat{n}$. In order to take into account thermal fluctuations, we add to the right hand side of Eq. (4) a random noise $\zeta(q,t)$ with correlations that ensure for zero shear rate the system relaxes to equilibrium [14]. We thus have

$$\left(\frac{\partial}{\partial t} - \dot{\gamma}q_x\frac{\partial}{\partial q_n}\right)u(q) + \beta(q)\omega(q)u(q) = \zeta(q,t), \qquad (6)$$

$$\langle\zeta(q,t)\zeta(-q,0)\rangle = 2k_BT\beta(q)\delta(t), \qquad (7)$$

where k_B is Boltzmann's constant and T is temperature. From Eq. (6), we find for the equal-time correlation function of u

$$\chi(q) \equiv \langle u(q,0)u(-q,0)\rangle = k_BT\int_{-\infty}^{0} dt\, 2\beta(q(t)) \times \exp\left(-2\int_t^0 dt'\,\beta(q(t'))\omega(q(t'))\right). \qquad (8)$$

Similar expressions are found in [15–18].

Since the equation of motion Eq. (6) is linear, χ determines the probability distribution of u. We thus define a free energy density by

$$\mathcal{F} \equiv -\frac{k_BT}{2}\int d^3q\,\ln\chi(q). \qquad (9)$$

Equation (9) is a complicated function of $\dot{\gamma}$ and θ, however, we can extract the leading asymptotic behavior as $\dot{\bar{\gamma}} \to 0$, where $\dot{\bar{\gamma}} \equiv \dot{\gamma}\eta/B$. For thermotropics, with typical values of $B = 10^8$ ergs/cm^3 and $\eta = 1$ P [11], small $\dot{\bar{\gamma}}$ implies shear rates $\dot{\gamma} < 10^8$ s^{-1}, which easily encompass the range studied experimentally. For block copolymers, however, B can be much smaller and η much larger by many orders of magnitude. For example, for $B = 10^6$ ergs/cm^3 [19] and $\eta = 10^6$ P [5] we must take $\dot{\gamma} < 1$ s^{-1}. We find for small $\dot{\bar{\gamma}}$

$$\mathcal{F} = \mathcal{F}|_{\dot{\bar{\gamma}}=0} + c_1\frac{k_BT}{\lambda^3}(\dot{\bar{\gamma}}\cos\theta)^{4/3} + \cdots, \qquad (10)$$

where $c_1 \approx 0.25$ is a constant determined numerically. $\mathcal{F}$ will therefore be minimized for $\theta = \pi/2$, which is the a orientation.

While the above analysis is intuitively appealing in its treatment of thermal fluctuations, as we have discussed in the introduction, it is not well justified. We therefore turn to a computation of the dynamic response function.

We can model a time-dependent disturbance to the system by shifting the noise in Eq. (6) $\zeta(q,t) \to \zeta(q,t) + f(q,t)$. The response of the system to $f(q,t)$ is given by

$$\langle u(q,t)\rangle = \int_{-\infty}^{t} dt'\, C(q,t,t') f(q(t'-t),t'), \tag{11}$$

$$C(q,t,t') = \exp\left(-\int_{t'-t}^{0} dt''\, \beta(q(t''))\omega(q(t''))\right). \tag{12}$$

For all orientations θ, disturbances created by f relax exponentially with a decay rate that depends on the convected value of $\vec{q}$. In order to search for an instability, we must go beyond the linear equation (6). The smectic Hamiltonian with the leading anharmonic corrections is given by [20]

$$\mathcal{H} = \int d^3 r\left[\frac{B}{2}\left(\partial_z u + \frac{1}{2}(\nabla_\perp u)^2\right)^2 + \frac{K}{2}(\nabla_\perp^2 u)^2 + C\left(\partial_z u + \frac{1}{2}(\nabla_\perp u)^2\right)\right]. \tag{13}$$

The last term in Eq. (13) is a counterterm that is used to enforce the condition [20]

$$\left\langle \frac{\partial u}{\partial z}\right\rangle\bigg|_{f=0} = 0, \tag{14}$$

which ensures that u describes deviations from the average layer spacing.

Although we have had to include nonlinear corrections in $\mathcal{H}$, this does not mean that the physics underlying the response function differs from the physics presented in the introduction and contained in $\mathcal{F}$, which was only computed for the quadratic Hamiltonian Eq. (1). The nonlinear terms in Eq. (13) are not arbitrary: they are determined by requiring that rotating the layers (in the absence of shear) does not cost any energy [20]. Since $\mathcal{F}$ has been calculated for arbitrary tilt θ within the harmonic theory, it, in principle, contains the same information as the anharmonic terms to one loop.

The equations of motion are now nonlinear,

$$\left(\frac{\partial}{\partial t} - \dot{\gamma} q_x \frac{\partial}{\partial q_n}\right)u(q) + \beta(q)\frac{\delta\mathcal{H}}{\delta u} = \zeta(q,t) + f(q,t), \tag{15}$$

but we are free to choose $f(q,t)$ arbitrarily small so that linear response is still correct. For zero shear $\dot{\gamma} = 0$, the response function, to one loop order, takes the form

$$C(q,t,t') = \exp\left(-\int_{t'-t}^{0} dt''\, \beta(q(t''))[\omega(q(t'')) + \delta\omega(q(t''))]\right). \tag{16}$$

The shift $\delta\omega(q)$ corresponds to a renormalization of B and K; rotation invariance forbids a term proportional to $q_\perp^2$ from appearing [20]. In the presence of shear, however, we can no longer invoke rotation invariance and we expect terms quadratic in q_x and q_y to appear. For sufficiently long times, the q_x-dependent terms will be small compared with the Bq_z^2 and $Kq_\perp^4$ terms in $\omega(q(t))$. [q_z and q_y pick up q_x dependence through convection, Eq. (3).] A contribution to $\delta\omega$ that is proportional to q_y^2 and negative, on the other hand, will be destabilizing. As discussed in the introduction, this is in accord with the intuition that a local tilt of the smectic layers in the neutral direction, i.e., a local change in θ, corresponds to a mode with $\vec{q} \parallel \hat{y}$.

We have computed the response function $C(q,t,t')$ for Eq. (15) perturbatively to one-loop order. If we assume $f(q,t)$ is nonzero only for $\vec{q} = q_y\hat{y}$, then, in the limit of long times (low frequencies), linear response still takes the form of Eq. (11) with the response function as in Eq. (16). After taking care to maintain Eq. (14), we find, again in the limit of small $\dot{\gamma}$,

$$\delta\omega(q) \approx -c_2 q_y^2\left(2 + \frac{\eta'}{\eta}\right)\frac{k_B T}{\lambda^3}(\dot{\gamma}\cos\theta)^{4/3} + \cdots, \tag{17}$$

where $c_2 \approx 1.4 \times 10^{-3}$ is determined numerically. For $\vec{q}$ along $\hat{y}$, $\omega(q)$ goes as q_y^4 and so for sufficiently small q_y, $\delta\omega \gg \omega$. Hence, for orientations with θ not too close to $\pi/2$ (i.e., away from the a orientation), disturbances with $\vec{q} \parallel \hat{y}$ will grow and the smectic will be unstable. Here we have implicitly assumed $2 + \eta'/\eta > 0$; we will return to this point below.

When θ is sufficiently close to $\pi/2$ such that $\cos\theta \sim \dot{\gamma}\sin\theta$, subleading terms in Eq. (17) will be important and can change the sign of $\delta\omega$. To check the stability of the smectic in this limit, we have computed the response function for $\theta = \pi/2$. In this case we find

$$\delta\omega(q) \approx c_3 q_y^2 \frac{k_B T}{\lambda^3}\dot{\gamma} + \cdots, \tag{18}$$

where $c_3 \approx 4.6 \times 10^{-3}$. Thus for the a orientation, the correction $\delta\omega$ is positive and the smectic is stable.

As was mentioned previously, in concluding that the c orientation is unstable we have assumed $2 + \eta'/\eta > 0$. In fact, there is a small window in which the sign may be reversed. The five viscosities that enter the constitutive relation between stress and strain rate in a uniaxial fluid are constrained by the requirement of non-negative energy dissipation [12]. In our case [13], this requires $\eta \geq 0$ and $\eta' \geq -4\eta$. Thus as η' is lowered into the range $-4\eta \leq \eta' \leq -2\eta$, we find a transition to a regime in which the smectic is stable for all orientations θ. This range of viscosities corresponds to small dissipation for uniaxial extensional flow along $\hat{z}$ compared with the dissipation for shear flow. Unfortunately, we have no simple physical argument for this result.

We have considered the shear flow of well-aligned one-component smectic phases outside of the critical regime. Very close to the nematic-smectic transition, where nematic fluctuations are large, our analysis is inappropriate. However, the appearance of the a orientation in this regime has been accounted for in [2]. Our work is similarly complementary to that in [10], where the role of amplitude fluctuations is considered. Also note that our analysis requires modification for two-component systems (i.e., lyotropic smectics) where there is an additional hydrodynamic variable.

We have argued that, as a result of convection and the higher energetic cost of compressing smectic layers compared with bending, there is a greater suppression of fluctuations in the c orientation. With the naive view that the steady-state behavior is determined by minimization of a "nonequilibrium free energy," the a orientation will be favored over c. To demonstrate the scenario suggested by these arguments, we have computed the dynamic response of the system to a long-wavelength perturbation corresponding to a local tilt of the layers. We find that over most of the range of allowed values for the anisotropic viscosity, the c orientation and orientations intermediate between c and a are indeed unstable and the a orientation is stable. Surprisingly, we have also found that there is a window of values for the viscosity in which all orientations are stable. Our treatment completely neglects the role of defects as well as the possibility of a nonlinear relation between stress and strain rate (non-Newtonian behavior), both of which are likely to play an important role in some ranges of temperature and shear. While our analysis by no means accounts for the entire phase behavior of smectics under shear, we suggest that the mechanism described in this paper may account for the prevalence of the a orientation observed in the shear flow of one-component smectics.

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