Role of Shear in the Isotropic-to-Lamellar Transition

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In the isotropic-to-lamellar transition, nonlinear fluctuation terms lower the transition temperature τ_c and drive the transition first order. Here we show that steady shear, by suppressing the fluctuations, raises τ_c; in a certain temperature range the lamellar phase can be induced by applying shear. A study of the effective potential indicates that the transition remains first order, though becoming very weak at high shear rate. We argue heuristically that the lamellar ordering first occurs with wave vector normal to both the velocity and the velocity gradient.

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In many systems, such as lyotropic liquid crystals,[1,2] microemulsions,[3] and block copolymers,[4,5] a transition is observed from a uniform isotropic state to a lamellar (striped) phase upon lowering of temperature. In this Letter we consider how such a transition is influenced by the imposition of a shear flow. Preliminary experimental studies of the isotropic-lamellar (I-L) transition in bilayer-forming surfactant solutions (such as sodium-dodecyl-sulfate–water–pentanol bilayers in dodecane[1]) indicate a strong effect of shear. In some cases, even gentle shaking of a test tube containing an isotropic phase induces a birefringent state, presumably lamellar, which persists for several seconds.[1,2]

Our starting point for discussing these phenomena is the following Landau-Ginzburg Hamiltonian, which describes the ordering of a scalar field ϕ with reflection symmetry, at finite wave number k_0 (with $k_BT\equiv 1$):

$$H(\phi)=\tfrac{1}{2}\sum_{\mathbf{k}}[\tau+(k-k_0)^2]\phi(\mathbf{k})\phi(-\mathbf{k}) + (\lambda/4!)\sum_{\mathbf{k}+\mathbf{k}'+\mathbf{k}''=-\mathbf{k}'''}\phi(\mathbf{k})\phi(\mathbf{k}')\phi(\mathbf{k}'')\phi(\mathbf{k}'''), \quad (1)$$

where $\mathbf{k}$, $\mathbf{k}'$, etc., denote wave vectors; $k\equiv|\mathbf{k}|$; and τ is a temperaturelike control parameter. At the level of mean-field theory (whereby a single configuration of the order parameter ϕ is chosen so as to minimize H), this model exhibits a second-order I-L transition at $\tau=0$. However,[6] mean-field theory is inadequate because of large fluctuation effects associated with the degeneracy in the possible orientations of the ordered state; this gives a large phase volume (the spherical shell $k\simeq k_0$ in $\mathbf{k}$ space) for fluctuations in the isotropic phase. Brazovskii[6] studied the nonlinear coupling to fluctuations, using a self-consistent (Hartree) approach. Introducing the effective potential Φ (the Legendre transform of the free energy), he found Eqs. (2)–(4) for the field variable $2h\equiv\partial\Phi/\partial a$ conjugate to a lamellar state $\phi=2a\cos(\mathbf{q}\cdot\mathbf{r})$ of amplitude $2a$ and wave vector $\mathbf{q}$ on the critical shell:

$$h=r(a)a-\tfrac{1}{2}\lambda a^3,\quad r(a)=\tau+\sigma+\lambda a^2, \quad (2)$$

$$\sigma(r)=(\lambda/2)\int\chi(\mathbf{k})d^3k/(2\pi)^3, \quad (3)$$

$$\chi(\mathbf{k})^{-1}=r+(k-k_0)^2. \quad (4)$$

Here $\chi(\mathbf{k})\equiv\langle\phi(\mathbf{k})\phi(-\mathbf{k})\rangle$ is the two-point correlation function for fluctuations; its behavior in the isotropic phase ($a=0$) is found self-consistently from Eqs. (3) and (4). This gives $r(0)=\tau+\alpha\lambda r(0)^{-1/2}$, where $\alpha\equiv k_0^2/4\pi$; hence $r(0)\geq 0$ for all finite τ and the spinodal point $[r(0)=0]$ is suppressed to $\tau=-\infty$. Correspondingly, the transition must be first order; analysis[6] of Eqs. (2)–(4) shows it to occur at $\tau=\tau_c\simeq-(\alpha\lambda)^{2/3}$, with an amplitude $a_c\simeq\alpha^{1/3}\lambda^{-1/6}$. For weak nonlinearity ($\lambda\ll\alpha^{1/2}$) the Hartree theory is self-consistent near the transition, failing only at lower temperatures ($\tau\lesssim\tau_H\simeq-\lambda^{1/2}\alpha^{3/4}\ll\tau_c$).

The Landau-Ginzburg Hamiltonian of Eq. (1) is thus appropriate to describe a weakly first-order transition to lamellar order, in systems with no separate tendency towards nematic or cubic order (which permits us to neglect an orientational order parameter and terms of order ϕ^3, respectively). Its application to block copolymers has been well developed.[4,5] Certain lyotropic systems of dilute bilayer-forming surfactants are also characterized[1] by a *weakly* first-order transition between an isotropic (spongelike) and a lamellar phase, with no indication of an intervening "nematic" phase. Thus, we may adopt Eq. (1) for these lyotropics as well.[7]

In what follows, we consider the effect of shear flow on fluctuations, and study the resulting changes to the I-L transition. The methods used here are similar to those of Onuki and Kawasaki[8] and Fredrickson and Larson.[5] Anticipating a self-consistent treatment[6] of the quartic terms in H (as we give below) we may write a linearized convective Fokker-Planck equation[5,8] for the steady-state probability distribution $P[\phi(\mathbf{k})]$,

$$\sum_{\mathbf{k}} \frac{\delta}{\delta\phi(\mathbf{k})}\left\{\mu\left[\frac{\delta}{\delta\phi(-\mathbf{k})}+[r+(k-k_0)^2]\phi(\mathbf{k})\right]-Dk_x\frac{\partial}{\partial k_y}\phi(\mathbf{k})\right\}P[\phi(\mathbf{k})]=0\,, \tag{5a}$$

and take the second moment to obtain an equation for $\chi(\mathbf{k})=\langle\phi(\mathbf{k})\phi(-\mathbf{k})\rangle_P$:

$$[r+(k-k_0)^2]\chi(\mathbf{k})-(D/2\mu)k_x\,\partial\chi(\mathbf{k})/\partial k_y=1\,. \tag{5b}$$

Here the imposed flow velocity in laboratory coordinates (x,y,z) is $(Dy,0,0)$; μ is an Onsager coefficient which can be presumed constant in the vicinity of $k=k_0$. For simplicity we shall also ignore any dependence of μ on shear rate D or temperature.[8] The solution to (5b) is then

$$\chi(\mathbf{k})=\mu\int_0^\infty dt\exp\left(-\mu\int_0^t\{r+[k(t')-k_0]^2\}dt'\right), \tag{6a}$$

$$k(t')^2\equiv k_x^2+(k_y+Dt'k_x/2)^2+k_z^2\,. \tag{6b}$$

Thus, the mean-square amplitude $\chi(\mathbf{k})$ at time zero ("now") arises as a superposition of random Fourier components injected at earlier times $-t$, and convected to the present wave vector $\mathbf{k}$, each convoluted with a memory kernel that causes decay at a rate $\mu\,\partial^2\Phi/\partial\phi(\mathbf{k}')\partial\phi(-\mathbf{k}')$ with $\mathbf{k}'$ the convected wave vector at some intermediate time t'.

The imposition of flow completely changes the fluctuation spectrum. (This fact was noted previously in the block-copolymer context,[5] but without discussion of its possible influence on the I-L transition.) For example, as $r\to 0$, instead of diverging on a shell ($k=k_0$) the fluctuations now diverge only on a circle, where the shell intersects $k_x=0$. To find the nature of the singularity, we study the typical lifetime $\zeta(\mathbf{k})\simeq\chi(\mathbf{k})/\mu$ of a random Fourier component injected at a point $\mathbf{k}$ near the shell. From (6) we see that

$$\int_0^{\zeta(\mathbf{k})}\mu\{r+[k(t')-k_0]^2\}dt'\simeq 1\,. \tag{7}$$

For r small but finite and $D\to 0$, we obtain on expanding (7)

$$\chi(\mathbf{k})/\mu\simeq\zeta(\mathbf{k})\simeq\zeta_0[1-b\mu(k-k_0)f(\mathbf{k})\zeta_0^2 - c\mu f(\mathbf{k})^2\zeta_0^3+\cdots]\,, \tag{8}$$

where $\zeta_0(k)^{-1}=\mu[r+(k-k_0)^2]$, $f(\mathbf{k})=Dk_xk_y/k_0$, and b,c are constants of order unity. Integrating to find the total fluctuation term σ [Eq. (3)], we obtain to leading order in D

$$\sigma(r,D)-\sigma(r,0)\sim(|\tau_c|/r)^{7/2}(D/D^*)^2\tau_c\,, \tag{9}$$

where $D^*=\lambda\mu\alpha^{1/2}$ and τ_c denotes the transition temperature in the absence of shear. A second interesting limit is for $r\to 0$ at finite D; in this case we find from (7) (for $k\simeq k_0$ with k_x small)

$$\mu\{r+[bDk_xk_y\zeta/k_0+c(Dk_x\zeta)^2/k_0 - d(Dk_xk_y\zeta)^2/k_0^3]^2\}\zeta\simeq 1\,, \tag{10}$$

with b,c,d of order unity. For all but a very small region near $k_y=0$, which does not affect the calculations below, we may (for D finite and $r\to 0$) represent $\chi(\mathbf{k})$ in the approximate form[9]

$$\chi(\mathbf{k})^{-1}\simeq r+(k-k_0)^2+\text{const}\times(Dk_xk_y/\mu\alpha^{1/2})^{2/3}\,. \tag{11}$$

Crucially, the fluctuation integral σ is now *finite* as $r\to 0$: We find the leading behavior (omitting coefficients)

$$\sigma(r,D)\simeq(D/D^*)^{-1/3}|\tau_c|-(D/D^*)^{-1}r[\ln\beta r]^2\,, \tag{12}$$

where $\beta\simeq|\tau_c|^{-1}(D/D^*)^{2/3}$. As shown below, the existence of a finite limit $\sigma(0,D)$ as $r\to 0$ means that under shear a local (spinodal) instability of the isotropic phase can occur, in contrast to the static case.

We now use the results (8)–(12) to study the effect of flow on the I-L transition. To do this, we should in principle solve self-consistently the Fokker-Planck equation (5a). However, since our estimates (8) and (11) involve writing $\chi(\mathbf{k})\simeq\mu\zeta(\mathbf{k})$, with $\zeta(\mathbf{k})$ a mode lifetime, their use amounts to replacing the convective term in (5a) by a purely dissipative term. Subject to this, it may be shown that for states with $q_x=0$ (those in which order may develop) the stability of steady-state solutions is exactly as given by minimizing the effective potential Φ obtained by substituting our results (9) and (12) for $\sigma(r,D)$ into Eq. (2) for $h=\frac{1}{2}\,\partial\Phi/\partial a$. Note that this procedure would not be valid for describing the instability of states with $q_x\neq 0$. When $q_x=0$ (only), the direct convective term in Eq. (5) vanishes, and the sole effect of shear is to alter the fluctuation contribution to r. It is this which enables us to find stable steady-state solutions to Eq. (5) by minimizing Φ. In addition, we have checked that under shear, non-Hartree corrections to Φ are negligible under the same conditions as in the static case ($\tau\gtrsim\tau_H$).

On substitution of Eq. (9), valid for $D\ll D^*$, into Eq. (2) we obtain perturbatively a shift in the transition temperature

$$\tau_c(D)-\tau_c\simeq(D/D^*)^2|\tau_c|\,, \tag{13}$$

where $\tau_c\equiv\tau_c(0)\simeq-(\alpha\lambda)^{2/3}$ is Brazovskii's value.[6] We find a similar perturbative reduction in the amplitude a_c of the lamellar phase at onset. Thus, when shear is applied, the transition is raised to higher temperature and becomes more weakly first order. The spinodal locus $\tau_s(D)$, which identifies the onset of an absolute instability of the isotropic state [$r(0)=0$], may be identified for all D using Eq. (12) as

$$\tau_s(D)=-\sigma(0,D)\sim(D/D^*)^{-1/3}\tau_c\,. \tag{14}$$

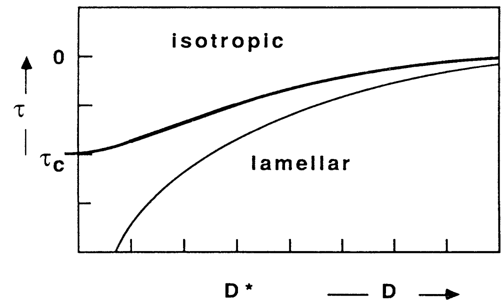

FIG. 1. Schematic plot of the dependence on shear rate D of critical temperature (upper curve) and spinodal (lower curve).

Hence there is a regime of temperature $(0>\tau>\tau_c)$ in which the isotropic state is stable in the absence of flow but becomes locally unstable to lamellar ordering at high enough shear. Similarly at $\tau\leq\tau_c$ the isotropic phase is metastable in the static limit but becomes unstable when sufficient shear is applied.

From (12) we may also identify at $D\simeq D^*$ a crossover to a strong-shear regime. To study the transition for $D\gg D^*$, we substitute Eq. (12) in Eq. (2) with a small. At the spinodal point $[r(0)=0]$ we obtain

$$h(a)=\lambda a^3\{1+D^*[\ln(\beta\lambda a^2)]^2/D\}^{-1}-\lambda a^3/2\,. \quad (15)$$

We see that the first nonvanishing derivative of h is negative for small a. Thus the isotropic state at its spinodal point cannot be a global minimum of the free energy; correspondingly the transition must remain first order even at high shear rates. However, the amplitude of the ordered state $a_c(D)$ becomes extremely small for $D\gg D^*$; from (15) we find

$$a_c(D)\simeq a_c(0)(D/D^*)^{1/3}\exp[-(D/D^*)^{1/2}]\,. \quad (16)$$

Similarly, the transition temperature $\tau_c(D)$ becomes exponentially close to the spinodal [Eq. (14)].

The results (13)-(16) are shown schematically in Fig. 1. We note from Eq. (10) that the divergence in $\zeta(\mathbf{k})$ for $k_x\rightarrow 0$ is strongest near $k_y=0$. Thus, the lamellar fluctuations which appear as the transition is approached have wave vectors concentrated in the $(0,0,k_0)$ direction, transverse to both the flow velocity and its gradient. We therefore suggest that, when the I-L transition is induced by shear, the lamellar phase should occur preferentially with this orientation. We may also estimate the characteristic shear rate D^*, for example in the case of a lyotropic surfactant solution.[1] Here (from the usual hydrodynamic arguments) the Onsager coefficient μ obeys $\mu a\sim k_BT/\eta\xi^3$, with η the viscosity of the isotropic fluid and $\xi\simeq k_0^{-1}$ the interlamellar spacing. An estimate of λ is obtained from measurements of $\chi(k)$ in the isotropic phase: Near the transition point in the static system one has $\chi(k_0)/\chi(0)\simeq 1+a/\tau_c\simeq(a/\lambda^2)^{1/3}$. Experimentally[1] this ratio is of order 2, so that $\lambda\sim a^{1/2}$. For $\xi\sim 1000$ Å and $\eta\simeq 1$ cP, this gives $D^*\sim 10^{3\pm1}$, which is perhaps a rather high value.[10] Recall, however [from Eq. (13)], that the shear-induced I-L transition can occur at shear rates $D\ll D^*$ in systems already close to their static transition temperature τ_c.

In summary, we have shown how steady shear can raise the transition temperature for the I-L transition and make it less strongly first order in character. This is in qualitative agreement with preliminary experiments[1,2] on bilayer-forming surfactant solutions. The effect arises because shear reduces the influence of nonlinear fluctuations, which are the cause of a lowered transition temperature and first-order behavior in the static case. We may contrast these results with that of a mean-field approach in which fluctuations are ignored. In that case the only effect of shear is to restrict the possible directions of the lamellar ordering to those with $k_x=0$. Crudely then, one might argue that when fluctuations are included, the transition under strong flow should resemble a static Brazovskii transition in two space dimensions. This is qualitatively correct in predicting a raised τ_c, but wrongly predicts that the isotropic state is always locally stable. In contrast, our self-consistent treatment shows that for all temperatures $\tau<0$ a local (spinodal-like) instability of the isotropic phase is reached at high shear. This result stems from the integrability of $\chi(\mathbf{k})$ [Eq. (11)] near $k_x=0$ and hence is directly dependent on the nonanalytic flow-rate dependence of the typical decay time $\zeta(\mathbf{k})$ [Eq. (7)] near the critical shell.

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[10]In fact, for these multicomponent systems, the I-L transition involves phase coexistence over a finite temperature range (Refs. 1–3). To describe this in detail one needs a more complicated form than (1) for H (perhaps with several order parameters). We hope to address this issue in future work.