

## Theory of the nonequilibrium phase transition for nematic liquid crystals under shear flow

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We consider the impact of shear flow on the isotropic-nematic transition in crystalline liquids by generalizing Leslie-Ericksen dynamics of nematic systems to include amplitude and biaxial degrees of freedom. Neglecting fluctuations, we find steady-state solutions to the equations of motion for the nematic order parameter and fluid velocity and interpret them in terms of nonequilibrium steady states. We predict a transition temperature increasing with shear rate up to a nonequilibrium critical point, and discuss the singular behavior of the order parameter and external stress near this point.

The purpose of this Rapid Communication is to describe the impact of shear flow on the first-order isotropic-nematic ( $I$ - $N$ ) equilibrium phase transition in crystalline liquids. Shear flow induces alignment above the equilibrium phase transition and, below it, selects a particular alignment from the degenerate collection of orientations that the equilibrium nematic liquid crystal can adopt. (For general reviews, see Refs. 1-4.) Our aim will be to show that shear flow has the following effects: (i) the discontinuity in the degree of nematic order which exists between high- and low-temperature states in the *absence* of shear flow persists up to a finite critical shear rate; (ii) as the shear rate is increased, this discontinuity occurs at higher temperatures and decreases continuously, vanishing at a nonequilibrium critical point; and (iii) for higher shear rates the system exhibits a single state.

Nematic systems in shear flow provide a simple example of phase transitions under nonequilibrium, nonpotential conditions.<sup>5</sup> The effects of shear flow on critical fluctuations in the binary fluid have been discussed by Onuki and Kawasaki<sup>6</sup> using renormalization-group methods. The binary fluid possesses an equilibrium critical point and shear flow suppresses fluctuations. In contrast, the equilibrium  $I$ - $N$  transition is first order, and the suppression of orientation fluctuations by the shear flow makes possible a nonequilibrium critical point associated with amplitude fluctuations.

Imagine the cavity of a cylindrical Couette cell filled with a thermotropic nematic liquid-crystal-mesophase-forming substance (nematogen).<sup>7</sup> The outer cylinder is rotated at a constant rate while the inner cylinder is fixed, and both are maintained at a common constant temperature. In steady state (which we call a nonequilibrium phase) one monitors (i) torque, (ii) nematic alignment, and (iii) nematic correlations. The nonequilibrium phase diagram is then spanned by temperature  $T$  and shear rate  $D$ .

To describe qualitatively this phase diagram we develop a closed set of coupled deterministic dynamical equations<sup>8</sup> which describe phenomenologically the local evolution of

the fluid velocity  $\mathbf{v}(\mathbf{r}, t)$  and the nematic order parameter  $Q_{\alpha\beta}(\mathbf{r}, t)$ .<sup>9</sup> We neglect temporal and spatial temperature variations and restrict attention to a planar Couette geometry, assuming the boundary stress necessary to produce steady, uniform shear flow  $\mathbf{v}(\mathbf{r}, t) = Dye_x$ . These conditions ensure that the order parameter can be spatially uniform in steady state. Among the stationary solutions to the equation of motion for  $Q_{\alpha\beta}(\mathbf{r}, t)$ , given  $D$  and  $T$ , the linearly stable subset comprises candidates for the physically selected state. Since the present method does not resolve questions of metastability, we shall not address the issue of selection here. However, if only one linearly stable solution exists, then we assume that it describes the physical steady state.<sup>10</sup> Using this scheme we construct the nonequilibrium phase diagram.

Leslie-Ericksen (LE) dynamics of nematic systems<sup>11</sup> describes the hydrodynamics of uniaxial nematic liquid crystals in flow, for which the relevant hydrodynamic modes are orientation fluctuations. To address the role of shear flow near the  $I$ - $N$  transition, we shall generalize LE dynamics of nematic systems to incorporate biaxial and amplitude fluctuations. Following de Gennes,<sup>2</sup> we derive the equations of motion for  $Q_{\alpha\beta}(\mathbf{r}, t)$  and  $\mathbf{v}(\mathbf{r}, t)$  by (i) deriving the entropy production, (ii) identifying the relevant thermodynamic forces and fluxes, and (iii) expanding the fluxes linearly in the forces in accordance with the Onsager reciprocal relations.<sup>12</sup> Since the equilibrium  $I$ - $N$  transition is *weakly* first order, the critical shear rate is expected to be small and, hence, to lie within the domain of validity of linear nonequilibrium thermodynamics.

For isothermal processes, the local entropy production  $\theta$  follows from the rate of change of the free energy  $\dot{F}$  according to

$$\dot{F} = \dot{E} - T\dot{S} = - \int_{\Sigma} j_{\gamma}^E d\Sigma_{\gamma} + T \int_{\Sigma} j_{\gamma}^S d\Sigma_{\gamma} - T \int_V \theta dV, \quad (1)$$

where  $E$  is the total energy,  $S$  is the total entropy,  $j^E$  is the energy flux,  $j^S$  is the entropy flux, and  $\theta$  is the local entropy production.

The free energy of the system is given by

$$F = \int_V [\frac{1}{2} \rho |\mathbf{v}(\mathbf{r})|^2 + f_L + f_F] dV,$$

where  $\rho$  is the uniform density,  $f_L$  is the Landau-de Gennes free-energy density which describes the equilibrium  $I$ - $N$  transition, and  $f_F$  is the Frank free-energy density associated with order-parameter inhomogeneities. There are two contributions to  $F$ , one due to local changes in the order parameter and one due to material distortion (i.e., fluid motion).

Making a local change in  $Q_{\alpha\beta}(\mathbf{r})$  which preserves tracelessness and symmetry yields the equilibrium condition that the molecular field  $H_{\alpha\beta}^{[s]} = 0$ , where  $H_{\alpha\beta} \equiv -\delta F / \delta Q_{\alpha\beta}$ . We denote the symmetric and traceless part of any second-rank tensor  $J_{\alpha\beta}$  by  $J_{\alpha\beta}^{[s]}$  and the antisymmetric part by  $J_{\alpha\beta}^{[a]}$ .<sup>13</sup> Combining this with an incompressible material distortion  $\mathbf{r} \rightarrow \mathbf{r}' = \mathbf{r} + \mathbf{u}(\mathbf{r})$  for which  $Q'_{\alpha\beta}(\mathbf{r}') = Q_{\alpha\beta}(\mathbf{r})$ , we obtain a total change in free energy

$$\delta F = \int_V [(\sigma_{\alpha\beta}^d - P \delta_{\alpha\beta}) \partial_{\alpha\beta} - H_{\alpha\beta}^{[s]} \delta Q_{\alpha\beta}] dV, \quad (2)$$

where  $\sigma_{\alpha\beta}^d \equiv \pi_{\alpha\mu} \partial_{\beta} Q_{\mu\alpha}$  is the distortion stress tensor,  $\pi_{\gamma\alpha\beta} \equiv -\delta F / \delta \partial_{\gamma} Q_{\alpha\beta}$ , and  $P(\mathbf{r})$  is a Lagrange multiplier enforcing liquid incompressibility.

Using the equation of motion for the fluid velocity,  $\rho dv_{\alpha}/dt = \partial_{\beta} \sigma_{\beta\alpha}$ , our expression for  $\delta F$ , an integration by parts, and Eq. (1), we obtain  $\theta$ , the local entropy production:  $T\theta = \sigma_{\alpha\beta}^i V_{\beta\alpha} + H_{\alpha\beta}^{[s]} \dot{Q}_{\alpha\beta}$ . Here,  $V_{\beta\alpha} \equiv \partial_{\alpha} v_{\beta}$  and  $\sigma_{\alpha\beta} \equiv \sigma_{\alpha\beta}^r + \sigma_{\alpha\beta}^i$  is the total stress tensor.  $\sigma_{\alpha\beta}^r \equiv \sigma_{\alpha\beta}^d - P \delta_{\alpha\beta}$  is the reversible part of  $\sigma_{\alpha\beta}$ , and  $\sigma_{\alpha\beta}^i$  is the irreversible part. The overdot denotes a material derivative,  $d/dt \equiv \partial/\partial t + \mathbf{v} \cdot \nabla$ .

We separate  $\sigma_{\alpha\beta}^i$  and  $V_{\alpha\beta}$  into their symmetric-traceless and antisymmetric parts,<sup>13</sup> and parametrize  $\sigma_{\alpha\beta}^{[a]}$  by the vector  $\mathbf{I}$  via  $\sigma_{\alpha\beta}^{[a]} \equiv \frac{1}{2} \epsilon_{\alpha\beta\gamma} I_{\gamma}$ .  $\mathbf{I}$  is the bulk torque density due to distortion of the nematic from its equilibrium value and is given by  $I_{\lambda} = H_{\alpha\beta}^{[s]} (\epsilon_{\lambda\alpha\mu} Q_{\mu\beta} + \epsilon_{\lambda\beta\mu} Q_{\alpha\mu})$ . Consequently, the entropy production acquires the compact form

$$T\theta = \sigma_{\alpha\beta}^{[s]} V_{\alpha\beta}^{[s]} + H_{\alpha\beta}^{[s]} K_{\alpha\beta}, \quad (3)$$

where  $K_{\alpha\beta} \equiv \dot{Q}_{\alpha\beta} - (V_{\alpha\gamma}^{[a]} Q_{\gamma\beta} - Q_{\alpha\gamma} V_{\gamma\beta}^{[a]})$ . We identify the dissipative forces ( $V_{\alpha\beta}^{[s]}$  and  $H_{\alpha\beta}^{[s]}$ ) and fluxes ( $K_{\alpha\beta}$  and  $\sigma_{\alpha\beta}^{[s]}$ ) from Eq. (3) and expand the fluxes to linear order in the forces, obtaining

$$\sigma_{\alpha\beta}^{[s]} = \Gamma_{\alpha\beta\lambda\rho}^{[1]} V_{\lambda\rho}^{[s]} + M_{\alpha\beta\lambda\rho}^{[1]} H_{\lambda\rho}^{[s]}, \quad (4)$$

$$K_{\alpha\beta} = M_{\alpha\beta\lambda\rho}^{[2]} V_{\lambda\rho}^{[s]} + \Gamma_{\alpha\beta\lambda\rho}^{[2]} H_{\lambda\rho}^{[s]}.$$

By virtue of the time-reversal properties of  $\sigma_{\alpha\beta}^{[s]}$  and  $K_{\alpha\beta}$ , the matrices  $\Gamma_{\alpha\beta\lambda\rho}^{[i]}$  and  $M_{\alpha\beta\lambda\rho}^{[i]}$  satisfy the Onsager reciprocal relations,  $M_{\alpha\beta\lambda\rho}^{[1]} = -M_{\lambda\rho\alpha\beta}^{[2]}$  and  $\Gamma_{\alpha\beta\lambda\rho}^{[1]} = \Gamma_{\lambda\rho\alpha\beta}^{[2]}$ . From the tracelessness and symmetry of the forces and fluxes, they also satisfy  $M_{\alpha\alpha\lambda\rho}^{[i]} = \Gamma_{\alpha\alpha\lambda\rho}^{[i]} = 0$ ,  $M_{\alpha\beta\lambda\rho}^{[1]} = M_{\beta\alpha\lambda\rho}^{[1]} = M_{\alpha\beta\rho\lambda}^{[1]}$ , and  $\Gamma_{\alpha\beta\gamma\rho}^{[1]} = \Gamma_{\beta\alpha\gamma\rho}^{[1]} = \Gamma_{\alpha\beta\rho\gamma}^{[1]}$ . The equations of motion for  $\mathbf{v}(\mathbf{r}, t)$  and  $Q_{\alpha\beta}(\mathbf{r}, t)$  follow from Eq. (4).

For the Landau-de Gennes free energy  $f_L$  we take<sup>2</sup>

$$f_L = \frac{1}{2} A (T - T^+) Q_{\alpha\beta} Q_{\beta\alpha} + \frac{1}{3} B Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{1}{4} C (Q_{\alpha\beta} Q_{\beta\alpha})^2. \quad (5)$$

Since we shall be considering homogeneous steady states, the explicit form of the Frank term  $f_F$  is irrelevant, provided it stabilizes the homogeneous equilibrium nematic phase. We close the system of equations by assuming explicit forms for  $\Gamma_{\alpha\beta\lambda\rho}^{[i]}$  and  $M_{\alpha\beta\lambda\rho}^{[i]}$ . An expansion of  $\Gamma_{\alpha\beta\lambda\rho}^{[i]}$  and  $M_{\alpha\beta\lambda\rho}^{[i]}$  in powers of  $Q_{\alpha\beta}$  does not terminate, in contrast with the LE theory. However, as  $Q_{\alpha\beta}$  is small near the first-order equilibrium transition, and we find it to be small throughout the two-phase region, it is consistent to neglect the dependence of  $\Gamma_{\alpha\beta\lambda\rho}^{[i]}$  and  $M_{\alpha\beta\lambda\rho}^{[i]}$  on  $Q_{\alpha\beta}$ .<sup>14</sup> Within this approximation we find

$$\sigma_{\alpha\beta}^{[s]} = v_1 V_{\alpha\beta}^{[s]} - v_3 H_{\alpha\beta}^{[s]}, \quad (6)$$

$$\dot{Q}_{\alpha\beta} = v_{\alpha\gamma}^{[a]} Q_{\gamma\beta} - Q_{\alpha\gamma} v_{\gamma\beta}^{[a]} + v_2 V_{\alpha\beta}^{[s]} + \frac{1}{v_2} H_{\alpha\beta}^{[s]},$$

where we have introduced two temperature-dependent dissipative coefficients (with dimensions of viscosity)  $v_1$  and  $v_2$ , and one dimensionless temperature-dependent kinetic coefficient  $v_3$ . The required positivity of the entropy production is ensured if  $v_1$  and  $v_2$  are positive.

The stationary values of  $Q_{\alpha\beta}$  satisfy a set of five coupled third-order algebraic equations which we are unable to solve analytically; hence, we proceed numerically. We choose  $B = -1.2C$  and  $v_3 = 0.9$ , consistent with typical nematics.<sup>3</sup> The inset in Fig. 1 shows the largest eigenvalue  $q^>$  of all stationary points as a function of the reduced temperature  $\tau \equiv A(T - T^+)/C$ , for a particular reduced shear rate  $\delta \equiv Dv_2/C = 0.005$ . Figure 1 shows branches of  $q^>$  containing stable roots for a range of shear rates. For large temperatures there is a unique root and thus a single phase. As the temperature is reduced in nonzero shear, this phase acquires more order; this pretransitional ordering has been discussed by Zvetkov<sup>15</sup> and de Gennes.<sup>16</sup> As the temperature is reduced further, there are two possibilities. For shear rates above a critical value  $\delta^*$  the phase varies smoothly with temperature. Alternatively, for shear rates smaller than  $\delta^*$ , the physical state must vary

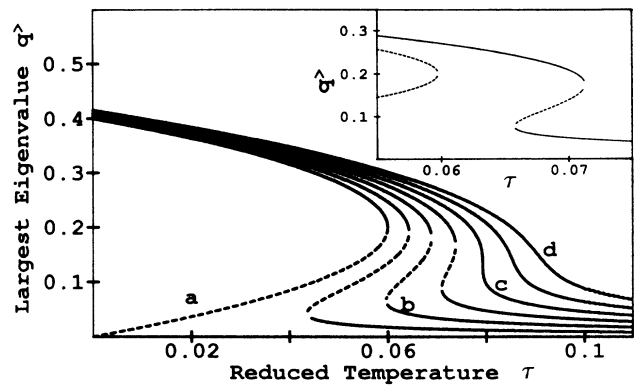


FIG. 1. Branches containing the largest eigenvalue  $q^>$  of the stable roots  $Q_{\alpha\beta}$  as a function of reduced temperature for a range of values of the reduced shear rate and for  $B = -1.2C$  and  $v_3 = 0.9$ : (a)  $\delta = 0$ , (b)  $|\delta| < \delta^*$ , (c)  $|\delta| = \delta^*$ , and (d)  $|\delta| > \delta^*$ . Solid lines correspond to linearly stable steady states, while broken lines represent unstable states. The inset shows  $q^>$  for all stationary points for  $\delta = \pm 0.005$ .

discontinuously with temperature; there is a range of temperatures for which there are *two* distinct linearly stable roots, the more (less) ordered one continuing to the low-(high-) temperature phase. This range shifts to higher temperatures and shrinks as the shear rate is increased, vanishing at the point  $(\tau^*, \delta^*)$ . Upon further reduction of  $\tau$ , with  $|\delta| < \delta^*$ , there is a unique phase.

We find that shear flow induces biaxiality rather strongly in the high-temperature phase, whereas the low-temperature phase remains almost uniaxial. Stable states have an order parameter with one minor axis orthogonal to the shear plane, and the alignment of the major axis with the fluid velocity is greater for better-ordered states. LE theory predicts flow alignment at an angle  $\phi = \frac{1}{2} \cos^{-1}(1/\lambda)$ , where  $\lambda$  is the LE kinetic coefficient.<sup>11</sup> For general  $Q_{\alpha\beta}$ , and alignment in the shear plane, this generalizes to  $v_3 \cos 2\phi = 3x + y$ , where  $x$  and  $y$  are defined in Ref. 9.

Figure 2 shows the nonequilibrium phase diagram. The shaded region identifies the points with two locally stable steady states, while outside it we find a single-phase region. For an equilibrium problem, a Maxwell construction would produce a phase boundary (or line of first-order transitions) within the shaded area. Except on this boundary, such a construction would distinguish the physical equilibrium phase from the metastable state. However, the system is not in equilibrium when  $D \neq 0$ , and an alternative criterion is required to determine whether or not a physical phase is selected. If one steady state is selected, then we have a nonequilibrium analog of a first-order phase transition, with a phase boundary connecting the equilibrium first order and critical points. In the absence of a selection mechanism, neither state is metastable, the exhibited state depends on preparation, and the system is intrinsically hysteretic.<sup>17</sup>

The nonequilibrium critical points  $(\tau^*, \pm \delta^*)$  are analogous to the equilibrium liquid-gas critical point, provided one makes the identifications  $Q_{\alpha\beta} \leftrightarrow \rho_{l-g}$ ,  $T \leftrightarrow T_{l-g}$ , and  $D \leftrightarrow P_{l-g}$  where  $\rho_{l-g}$ ,  $T_{l-g}$ , and  $P_{l-g}$  are the density, temperature, and pressure of the liquid-gas system. Near the liquid-gas critical point  $(P_{l-g}^*, T_{l-g}^*)$  the thermodynamic functions are singular. For example,  $\partial \rho_{l-g} / \partial T_{l-g} \sim |T_{l-g} - T_{l-g}^*|^{\beta-1}$  at  $P_{l-g}^*$ , and  $\partial \rho_{l-g} / \partial P_{l-g} \sim |P_{l-g} - P_{l-g}^*|^{1/\delta-1}$  at  $T_{l-g}^*$ , with  $\beta$  and  $\delta$  taking the approximate values 0.35 and 4.5, respectively, in three dimensions.<sup>18</sup> For the nonequilibrium system, we expect analogous divergences as either nonequilibrium critical point is approached. Preliminary numerical analysis suggests that, within our approximations,  $\partial Q_{\alpha\beta} / \partial \tau \sim |\tau - \tau^*|^{\beta-1}$  at  $\delta^*$ , and  $\partial Q_{\alpha\beta} / \partial \delta \sim |\delta - \delta^*|^{1/\delta-1}$  at  $\tau^*$ , with  $\beta \approx \frac{1}{3}$  and  $\delta \approx 3$ . We expect that when fluctuations are neglected,  $\hat{\beta}$  and  $\hat{\delta}$  are independent of our truncation of the expansion of  $\Gamma_{\alpha\beta\lambda\rho}^{[i]}$  and  $M_{\alpha\beta\lambda\rho}^{[i]}$ . We anticipate that the inclusion of fluctuations will alter their values, and it is also conceivable that couplings set to zero by our truncation of  $\Gamma_{\alpha\beta\lambda\rho}^{[i]}$  and  $M_{\alpha\beta\lambda\rho}^{[i]}$  will produce a variety of universality classes.

As a consequence of the singular behavior of  $Q_{\alpha\beta}$ , the

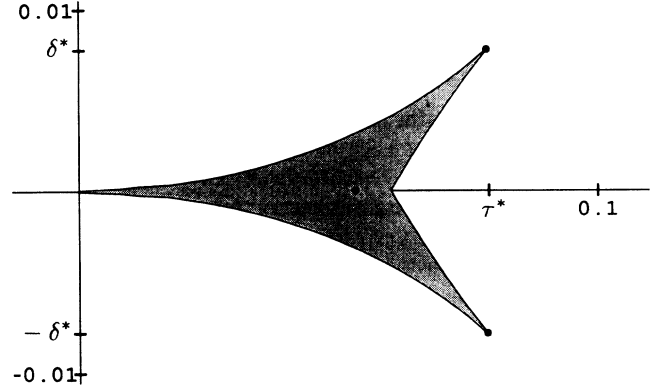


FIG. 2. Nonequilibrium phase diagram spanned by reduced temperature (abscissa) and reduced shear rate (ordinate) for  $B = -1.2C$  and  $v_3 = 0.9$ . The shaded region is the two-phase region. The internal black point locates the equilibrium first-order phase transition. The boundary points at  $(\tau^*, \pm \delta^*) \approx (0.079 \pm 0.0078)$  locate the nonequilibrium critical points.

boundary stress will depend in a singular way on the temperature and shear rate as the critical point is approached. To see this, regard the system as a *black box*. In steady state, the work put into the system by the stress applied at the boundary balances the heat flowing out through the boundary, while the total entropy production is balanced by the entropy flux out of the system. Hence,  $T \int_V \theta dV$  is equal to the work done on the system,  $\int_{\Sigma} d\Sigma_{\alpha} \sigma_{\alpha\beta} v_{\beta}$ . Thus, for the planar Couette geometry and for a homogeneous steady state, we find  $T\theta = \sigma_{xy}D$ . Hence, we see that near the critical point the boundary stress  $\sigma_{xy}$  will be singular through the dependence of  $\theta$  on  $Q_{\alpha\beta}$ . For example,  $\partial \sigma_{xy} / \partial T \sim |T - T^*|^{\beta-1}$  at  $\delta^*$ .

Finally, we illustrate these phenomena by considering physically reasonable parameters for low molecular-weight nematogens:<sup>4</sup>  $A = 50 \text{ kJm}^{-3} \text{K}^{-1}$ ,  $B = -360 \text{ kJm}^{-3}$ , and  $C = 300 \text{ kJm}^{-3}$ ;  $v_3 = 0.9$  and  $v_2 = 0.1 \text{ kgm}^{-1} \text{s}^{-1}$ . We then find  $T^* - T^{\dagger} \approx 0.47 \text{ K}$ , which should be compared with  $T_{l-N} - T^{\dagger} = 0.32 \text{ K}$ , and  $D^* = 23700 \text{ s}^{-1}$ . While low-molecular-weight nematogens are significantly affected only by rather large shear rates, the much larger viscosity of polymeric nematogens enhances their response to shear flow and suggests them as candidate materials in which to observe the effects that we have introduced here.

*Note added.* After this work was submitted for publication we received a copy of a manuscript, subsequently published, from See,<sup>19</sup> in which a number of the results contained in this manuscript were independently derived using quite different methods.

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- <sup>1</sup>M. J. Stephen and J. P. Straley, *Rev. Mod. Phys.* **46**, 617 (1974).
- <sup>2</sup>P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1975).
- <sup>3</sup>E. F. Gramsbergen, L. Longa, and W. H. de Jeu, *Phys. Rep. C* **135**, 195 (1986).
- <sup>4</sup>G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals, Fundamentals* (Springer-Verlag, Berlin, 1988).
- <sup>5</sup>The connection between *elongational* flow (which admits a potential description) and phase transitions in nematic systems has been discussed by several authors, including D. Thirumali, *J. Chem. Phys.* **84**, 5869 (1986); S.-D. Lee, *ibid.* **86**, 6567 (1987); S.-Q. Wang and W. Gelbart, *ibid.* **90**, 597 (1989); and the crossover to a single-phase region for sufficiently large strain rates has been predicted.
- <sup>6</sup>A. Onuki and K. Kawasaki, *Ann. Phys. (N.Y.)* **121**, 456 (1979).
- <sup>7</sup>Nematic crystalline liquids are melts (solutions) of rodlike mesogens which are known as thermotropic (lyotropic) if they exhibit a nematic to isotropic transition upon heating (dilution). Aside from issues of phase separation, we expect corresponding results for lyotropic systems.
- <sup>8</sup>We make a mean-field approximation by neglecting fluctuations.
- <sup>9</sup> $Q_{\alpha\beta}(\mathbf{r}, t)$  is symmetric and traceless and characterizes the distribution of molecular orientations; for a description, see T. C. Lubensky, *Phys. Rev. A* **2**, 2497 (1970). A microscopic definition for a system of  $N$  molecules with positions  $\mathbf{r}^i$  is  $Q_{\alpha\beta}(\mathbf{r}) = \langle \sum_{i=1}^N (v_{\alpha}^i v_{\beta}^i - \frac{1}{3} \delta_{\alpha\beta}) \delta(\mathbf{r} - \mathbf{r}^i) \rangle$ , where  $v^i$  is the unit vector describing the orientation of the  $i$ th molecule. For uniaxial states,  $Q_{\alpha\beta}^u(\mathbf{r}) = \frac{1}{2} x (n_{\alpha} n_{\beta} - \frac{1}{3} \delta_{\alpha\beta})$ , where  $x(\mathbf{r})$  ranges from  $-\frac{1}{3}$  to  $\frac{2}{3}$ , and  $\mathbf{n}(\mathbf{r})$  is a unit vector. For biaxial states,  $Q_{\alpha\beta} = Q_{\alpha\beta}^u + Q_{\alpha\beta}^b$ , where  $Q_{\alpha\beta}^b(\mathbf{r}) = -\frac{1}{3} \delta_{\alpha\beta} - \frac{1}{2} y [m_{\alpha} m_{\beta} - (\mathbf{n} \times \mathbf{m})_{\alpha} (\mathbf{n} \times \mathbf{m})_{\beta}]$ , where  $\mathbf{m}(\mathbf{r})$  is a unit vector orthogonal to  $\mathbf{n}(\mathbf{r})$ . Generally,  $Q_{\alpha\beta}$  has five independent components.
- <sup>10</sup>To determine whether a fixed point  $Q_{\alpha\beta}^{(0)}$  is linearly stable, we set  $Q_{\alpha\beta}(t) = Q_{\alpha\beta}^{(0)} + \delta Q_{\alpha\beta}(t)$  and expand to lowest order in  $\delta Q_{\alpha\beta}(t)$ , obtaining a linear equation of motion for the fluctuation  $\delta Q_{\alpha\beta}(t)$ . Accounting for the constraints, this takes the form  $\dot{Y}_i = W_{ij} Y_j$ , where  $i, j = 1, \dots, 5$  and  $W_{ij}$  is not necessarily symmetric. If the eigenvalues of the matrix  $W_{ij}$  have negative real parts then the uniform stationary state  $Q_{\alpha\beta}^{(0)}$  is linearly stable.
- <sup>11</sup>F. M. Leslie, *Q. J. Appl. Math.* **19**, 357 (1966); *Arch. Ration. Mech. Anal.* **28**, 265 (1968); J. L. Ericksen, *ibid.* **4**, 231 (1960); *Phys. Fluids* **9**, 1201 (1966).
- <sup>12</sup>L. Onsager, *Phys. Rev.* **37**, 405 (1931); **38**, 2265 (1931); S. de Groot and P. Mazur, *Nonequilibrium Thermodynamics* (North-Holland, Amsterdam, 1962). One might obtain the reversible parts of the equations of motion using the formalism of Poisson brackets; see for example I. E. Dzyaloshinskii and G. E. Volovik, *Ann. Phys. (N.Y.)* **125**, 67 (1980).
- <sup>13</sup>Since we are considering an incompressible fluid, we may consistently omit terms proportional to the identity in stress and velocity gradient tensors.
- <sup>14</sup>We have also expanded  $\Gamma_{\alpha\beta\lambda\rho}^{[ij]}$  and  $M_{\alpha\beta\lambda\rho}^{[ij]}$  to cubic order in  $Q_{\alpha\beta}$ . For the small number of choices of expansion coefficients that we have considered, we find results that are quantitatively close to those for our zeroth-order truncation.
- <sup>15</sup>V. Zvetkov, *Acta Physicochim. URSS* **19**, 86 (1944).
- <sup>16</sup>P. G. de Gennes, *Mol. Cryst. Liq. Cryst.* **12**, 193 (1971).
- <sup>17</sup>For a first-order transition, hysteresis is extrinsic in the sense that the hysteresis loop depends on the rate of the cycle. In the absence of selection, hysteresis may be regarded as intrinsic: There is a single hysteresis loop, *independent* of the rate, and it includes all locally stable states.
- <sup>18</sup>See, for example, S.-K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, Reading, MA, 1971).
- <sup>19</sup>H. See, M. Doi, and R. G. Larson, *J. Chem. Phys.* **92**, 792 (1990).

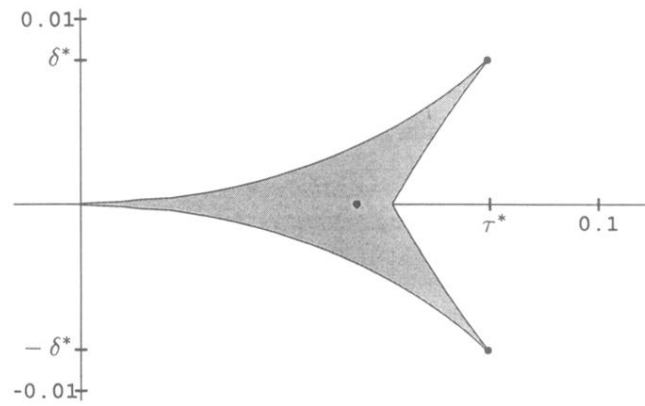


FIG. 2. Nonequilibrium phase diagram spanned by reduced temperature (abscissa) and reduced shear rate (ordinate) for  $B = -1.2C$  and  $v_3 = 0.9$ . The shaded region is the two-phase region. The internal black point locates the equilibrium first-order phase transition. The boundary points at  $(\tau^*, \pm \delta^*) \approx (0.079 \pm 0.0078)$  locate the nonequilibrium critical points.