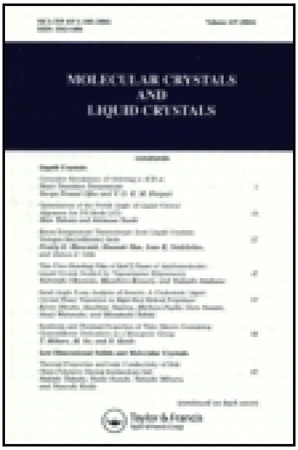

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Non-Equilibrium Phase Transitions in Nematic Liquid Crystals under Shear Flow†

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We discuss the impact of shear flow on the isotropic-nematic transition in crystalline liquids, paying particular attention to the notion of a non-equilibrium coexistence line. We establish a non-equilibrium phase diagram spanned by temperature and externally applied shear stress, by interpreting the locally stable solutions to the equations of motion for the entire nematic order parameter and fluid velocity, in the case of planar Couette flow. This system displays several characteristics reminiscent of homogeneous equilibrium phenomena: a region in the phase diagram in which two states are locally stable; a critical point at which this two-state region vanishes; and singularities associated with this non-equilibrium critical point. By analyzing inhomogeneous solutions of the equations of motion we address the issue of whether a particular state is selected within the two state region. We find state selection throughout the two-state region, except on a coexistence line interpolating between the equilibrium transition point and the non-equilibrium critical point. We mention the singular nature of the interface width and the order parameter discontinuity in the neighborhood of the critical point.

1. INTRODUCTION

The isotropic-nematic (*IN*) transition in the presence of macroscopic fluid flow provides a rich environment in which to explore the physics of non-equilibrium systems. As we shall see, this system displays certain features which are non-equilibrium analogues of equilibrium phase transitions and critical phenomena. In particular, while weak flow mildly perturbs the location of the transition, stronger flow can have significant qualitative effects, including raising the transition temperature and, at a non-equilibrium critical point, suppressing the transition altogether.

This paper is organized in the following way. In Section 2 we briefly review the equilibrium *IN* transition and describe the equations of motion for the nematic order parameter and fluid velocity. In Section 3 we present the conclusions of a numerical investigation of the homogeneous, locally stable, steady state solutions

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§ e-mail address: paul@paul.physics.uiuc.edu to these equations, and discuss the resulting non-equilibrium phase diagram. The results in this section were first discovered by Hess,[1] and more recently discussed in References 2–4. Here, we shall also mention certain formal analogies with equilibrium systems. Conclusions from the numerical investigation of inhomogeneous solutions to the equations of motion are presented in Section 4. These indicate that, in the absence of fluctuations, there is a coexistence line in the non-equilibrium phase diagram spanned by external stress and temperature, interpolating between *the equilibrium IN transition and the non-equilibrium critical point.* Across this coexistence line the steady state nematic order parameter and fluid velocity gradient (i.e., strain rate) vary discontinuously. We conclude in Section 5 with a summary, and indicate directions for future work.

2. PHENOMENOLOGICAL EQUATIONS OF MOTION

In this section we summarize the equilibrium *IN* transition and the equations of motion which govern the time-evolution of the system (given the assumptions of local equilibrium and linear irreversible thermodynamics).[5] At the semi-macroscopic level, the state of molecular alignment of a nematic liquid crystal can be described by a traceless-symmetric second-rank tensor order parameter $Q_{\alpha\beta}(\mathbf{r})$.[6] *The equilibrium transition between isotropic and nematic phases is weakly first-order*, and may therefore be described by the Landau-de Gennes free energy,[7] $F = \int_V \{f_L + f_F\}\, dV$, where

$$f_L = \frac{1}{2}A(T - T^{\dagger})\, Q_{\alpha\beta}Q_{\beta\alpha} + \frac{1}{3}BQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \frac{1}{4}C\,(Q_{\alpha\beta}Q_{\beta\alpha})^2,$$

$$f_F = \frac{1}{2}L_1\,(\partial_\alpha Q_{\beta\gamma})^2 + \frac{1}{2}L_2\,(\partial_\alpha Q_{\alpha\beta})^2. \tag{2.1}$$

The cubic term in f_L ensures a first order transition at a temperature $T_{IN} > T^{\dagger}$ (a negative value for B giving the conventional uniaxial nematic equilibrium phase), and order parameter distortions are accounted for by the Frank free energy density f_F.

For temperatures well below T_{IN} the coupled time-evolution of the nematic order parameter and the fluid velocity can be described by Leslie-Ericksen nematodynamics, in which it is assumed that the order parameter remains uniaxial, with constant magnitude, regardless of the flow.[8] The resulting coupled equations of motion for the fluid velocity and the director may be considered as generalized Navier-Stokes equations. However, shear flow induces nematic order in the liquid above the equilibrium phase transition temperature and, below it, selects a particular nematic alignment. The flow can therefore be thought of as a nonequilibrium analogue of the applied magnetic field in a ferromagnet. Thus, to address the effect of shear on the transition region itself (rather than at lower temperatures, at which system is well-ordered), we consider the dynamics of the entire order parameter $Q_{\alpha\beta}(\mathbf{r},t)$, rather than the director.[9]

Following the standard prescription of irreversible thermodynamics, the coupled deterministic equations of motion for the order parameter $Q_{\alpha\beta}(\mathbf{r},t)$ and the fluid flow $\mathbf{v}(\mathbf{r},t)$ are found to be[1,2]

$$\partial_t Q_{\alpha\beta} + \mathrm{v}_\gamma \nabla_\gamma Q_{\alpha\beta} = V^{[a]}_{\alpha\gamma} Q_{\gamma\beta} - Q_{\alpha\gamma} V^{[a]}_{\gamma\beta} + \nu_3 V^{[s]}_{\alpha\beta} + \frac{1}{\nu_2} H^{[s]}_{\alpha\beta}, \tag{2.2}$$

$$\partial_t \mathrm{v}_\alpha + \mathrm{v}_\gamma \nabla_\gamma \nu_\alpha = \nabla_\gamma \sigma_{\alpha\gamma}, \tag{2.3}$$

where the stress tensor $\sigma_{\alpha\beta}$ is given by $\sigma_{\alpha\beta} = \sigma^d_{\alpha\beta} + \sigma^{i[s]}_{\alpha\beta} + \sigma^{i[a]}_{\alpha\beta} - p\delta_{\alpha\beta}$, and comprises a distortion part $\sigma^d_{\alpha\beta} \equiv -(\delta F/\delta\partial_\alpha Q_{\rho\mu})\, \partial_\beta Q_{\rho\mu}$, a symmetric-traceless irreversible part $\sigma^{i[s]}_{\alpha\beta} \equiv \nu_1 V^{[s]}_{\alpha\beta} - \nu_3 H^{[s]}_{\alpha\beta}$, an antisymmetric irreversible part (due to bulk torques) $\sigma^{i[a]}_{\alpha\beta} \equiv H^{[s]}_{\alpha\gamma}\, Q_{\gamma\beta} - Q_{\alpha\gamma} H^{[s]}_{\gamma\beta}$, and a pressure part $-p\delta_{\alpha\beta}$. $H^{[s]}_{\alpha\beta}$ is the symmetric-traceless part of the molecular field, $-\delta F/\delta Q_{\alpha\beta}(\mathbf{r})$, and $V^{[s]}_{\alpha\beta}$ and $V^{[a]}_{\alpha\beta}$ are the symmetric-traceless and antisymmetric parts of the velocity gradient tensor $\nabla_\alpha \mathrm{v}_\beta$. Finally, there are two temperature-dependent dissipative Onsager coefficients (with dimensions of viscosity) ν_1 and ν_2, and one dimensionless temperature-dependent kinetic Onsager coefficient ν_3.[10]

Our goal is to determine how shear flow affects the equilibrium *IN* transition and, in particular, to examine selection between locally stable solutions of the equations of motion. Experimentally, one might monitor light scattering from a fluid of nematogens in a cylindrical Couette cell, as a function of temperature and applied stress. However, for convenience, we shall specialize to planar Couette flow, $\mathbf{v}(\mathbf{r}) = Dy\mathbf{e}_x$, as depicted in Figure 1. We shall assume that the significant temperature dependence comes from the Landau-de Gennes coefficient $A(T - T^{\dagger})$, and ignore any temperature dependence in the Onsager coefficients and elsewhere. Note that while we explicitly consider thermotropic liquid crystals,[11] we expect qualitatively similar results for lyotropic systems, with concentration playing

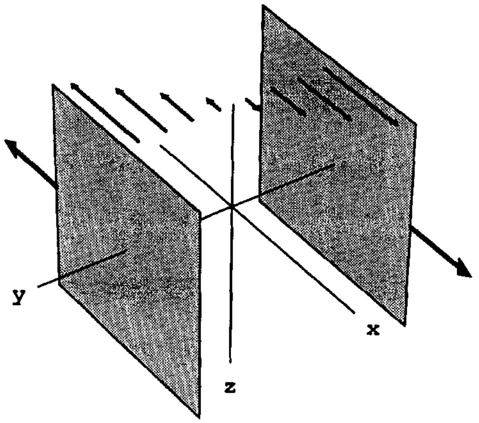

FIGURE 1 Coordinate system for planar Couette flow showing boundary plates and velocity field for a homogeneous phase.

the role of temperature. Moreover, we treat the system deterministically, neglecting thermal fluctuations. In this sense the treatment is a mean field approximation.

3. HOMOGENEOUS STATES: PHASE DIAGRAM

Our first objective is to determine the homogeneous non-equilibrium states of the system. We do this by assuming spatial homogeneity and finding the stationary solutions of the equations of motion. Candidate physical states are those which are linearly stable with respect to fluctuations. We control the system by specifying the temperature, and the stress applied to the plates at $y = \pm L/2$ which maintains the non-equilibrium state, as depicted in Figure 1. The control parameters are therefore the applied stress (rather than the strain rate)[12] and temperature, in contrast with Reference 2. In fact, it is convenient to use the dimensionless parameters $s \equiv \sigma_{xy}/C$ and $\tau \equiv A(T - T^{\dagger})/C$. Spatial gradients in Equations (2.2) and (2.3) vanish for a uniform system and, consequently, the stress tensor is given algebraically in terms of D and $Q_{\alpha\beta}$. The symmetry of the imposed stress[1] allows one to consider only the diagonal and xy-components of the equation of motion for $Q_{\alpha\beta}$, Equation (2.2), which reduces the problem to three coupled algebraic equations, which we solve numerically.

Using the values $B = -1.2\ C$, $\nu_3 = 0.9$, and $\nu_1 = 0.1\ \nu_2$, consistent with low molecular weight thermotropic nematogens, we obtain the homogeneous steady states as a function of temperature and shear stress, as shown schematically in Figure 2. The inset shows the largest eigenvalue $q^{>}$ for all stationary states as a function of the reduced temperature τ and for a particular reduced shear stress s.

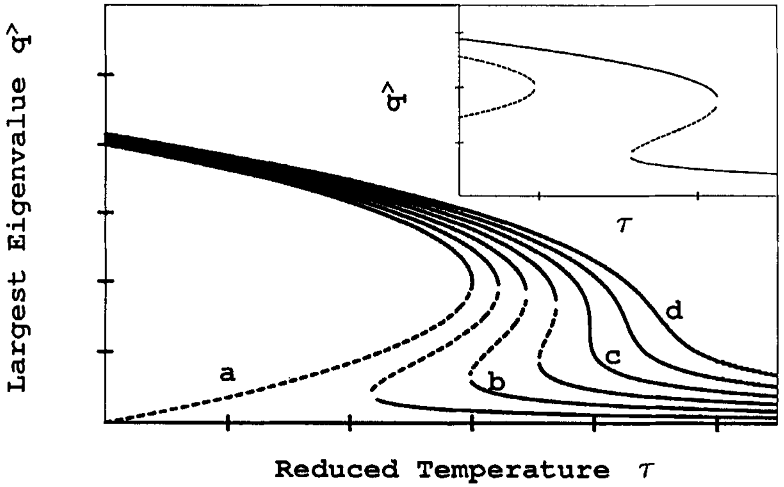

FIGURE 2 Schematic representation of branches containing the largest eigenvalue $q^{>}$ of the stable roots $Q_{\alpha\beta}$, as a function of the reduced temperature τ, for a selection of values of the reduced shear stress s: (a) $s = 0$, (b) $|s| < s^*$, (c) $|s| = s^*$, and (d) $|s| > s^*$. Unbroken lines correspond to linearly stable steady states, while broken lines represent unstable states. The inset shows $q^{>}$ for all stationary points for a typical shear stress $|s| < s^*$.

For a selection of shear stresses, the body of Figure 2 shows those branches of $q^>$ which contain stable roots.

At high temperatures, there is a unique root which we interpret as a non-equilibrium phase. As the temperature is reduced at non-zero shear stress this phase acquires more order, an effect known as pretransitional ordering and discussed by de Gennes.[13] For shear stresses greater than a critical value s^* there is a unique phase whose properties vary smoothly with temperature, while for smaller shear stresses 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. Hence, for $0 < |s| < s^*$, the physical state varies discontinuously with temperature. This range of temperatures shifts upwards and shrinks as the shear stress is increased, vanishing at the point (τ^*, s^*). For the chosen parameters we find $(\tau^*, s^*) \approx (0.0816, 0.00379)$.

Ignoring, for the moment, the broken line, Figure 3 shows the non-equilibrium phase diagram obtained by considering the homogeneous states. The shaded region identifies points for which there are two locally stable states, while a single state prevails outside. The points $(\tau^*, \pm s^*)$ are non-equilibrium critical points at which there are singularities, e.g., $\partial q^>/\partial\tau \to \infty$ as $|\tau - \tau^*| \to 0$. The figure closely resembles the isobars on the density-temperature $(\rho_{lg} - T_{lg})$ phase diagram for the VdW fluid, with the correspondences $(Q_{\alpha\beta}, \tau, s) \Leftrightarrow (\rho_{lg}, T_{lg}, P_{lg})$, where ρ_{lg}, T_{lg} and P_{lg} are, respectively, the density, temperature and pressure of the VdW fluid.[14] The singularities are reminiscent of those (e.g., in the compressibility) in the van der Waals (VdW) fluid at its critical point. We shall mention these singularities further below. The phase diagram presented in this section is identical, in form, to that obtained by Hess,[1] and others.[2-4]

4. INHOMOGENEOUS STATES: COEXISTENCE AND MEAN FIELD CRITICAL BEHAVIOR

For a range of temperatures and for sufficiently small shear stresses there are two locally stable, homogeneous, stationary solutions to the equations of motion, as

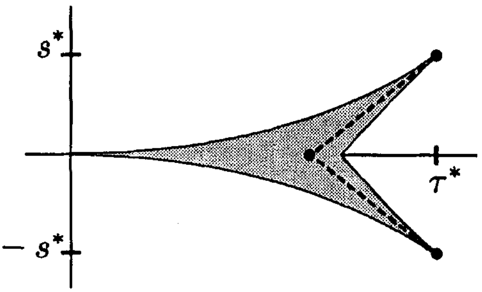

FIGURE 3 Complete stress-temperature (s-τ) phase diagram for $B = -1.2\ C$, $\nu_3 = 0.9$, $\nu_1 = 0.1\ \nu_2$, and $L_1/C = L_2/C = 10^4$ Å^2. Exhibited are the two-state region (shaded), the coexistence line (broken), and stability limits of the two states (solid lines). The central dot marks the equilibrium transition, and the outer dots locate the non-equilibrium critical points at $(\tau^*, s^*) \approx (0.0816, 0.00379)$.

shown schematically in Figure 2. If this were an equilibrium system then there would be a temperature $\tau_c(s)$, determined by the equality of the chemical potentials of the two phases (i.e., the Maxwell construction), at which the two phases could coexist, while at other temperatures within this range one phase would be stable and the other metastable.

To determine whether a coexistence temperature exists for the liquid of nematogens in shear flow we have examined numerically the interface profile interpolating between boundaries fixed at the two stable phases. Recall that we specify the reduced temperature τ and the reduced boundary stress s. We further assume that spatial variations occur only along $\mathbf{e}_y$ and specify the boundary values through $Q_{\alpha\beta}(s, \tau; y = \pm L/2) = Q^{\pm}_{\alpha\beta}(s, \tau)$, where $Q^{+/-}_{\alpha\beta}(s, \tau)$ corresponds to the upper/lower stable branch of Figure 2. Subject to these constraints, the system will adopt an inhomogeneous stationary state in which the velocity field $\mathbf{v}$ and order parameter $Q_{\alpha\beta}$ vary across the width of the system. The interface has a finite width W (except at the critical point) and, for convenience, we define its location to be that of the maximum of the Frank free energy density.

We adopt as our criterion for non-equilibrium coexistence the condition that inhomogeneous, stationary states, constrained to interpolate between the two homogeneous states, have the following property: the ratio of the distances from the interface to each boundary should tend to a number of order unity, as the system width tends to infinity. The rationale for this criterion is that if one phase is selected then the interface should relax to a position which, in the wide system limit, leaves only an infinitesimal fraction of the system in the rejected phase. In this planar geometry the convective terms remain zero, since $v_y = 0$, and therefore the stationarity condition on the fluid velocity becomes an equation of constraint which determines $D(y)$ algebraically in terms of s, $Q_{\alpha\beta}(y)$ and $dQ_{\alpha\beta}(y)/dy$. We use this to eliminate $D(y)$ from the stationarity condition for $Q_{\alpha\beta}$, obtaining an ordinary differential equation in y which determines $Q_{\alpha\beta}(y)$ in the inhomogeneous stationary state.

Thus, our algorithm for finding the inhomogeneous stationary state is: (i) fix s and τ; (ii) find the locally stable homogeneous states $Q^{\pm}_{\alpha\beta}$; (iii) eliminate $D(y)$ from the stationarity condition for $Q_{\alpha\beta}$; and (iv) solve the resulting ordinary differential equation for $Q_{\alpha\beta}(y)$ using the relaxation method with an implicit Crank-Nicholson scheme.[15] Applying this algorithm, with the parameters $B = -1.2\ C$, $\nu_3 = 0.9$, $\nu_1 = 0.1\ \nu_2$, and $L_1/C = L_2/C = 10^4$ Å,[2] we adjust the temperature to balance the interface at the midpoint of the sample, for each value of the stress and hence obtain the coexistence line shown in Figure 3. This line interpolates between T_{IN} and the critical point, and lies between the limits of stability of the two states.

Finally, we mention the singular behavior near the non-equilibrium critical point, which is analogous to the singular behavior found near equilibrium critical points. We have considered the temperature dependence of the interface width and the order parameter discontinuity, on the coexistence line. Preliminary data suggest that $W \sim (\tau^* - \tau)^{-\hat{\nu}}$ and $(Q^{+}_{\alpha\beta} - Q^{-}_{\alpha\beta}) \sim (\tau^* - \tau)^{-\hat{\beta}}$, with $\hat{\nu} \approx 0.5$ and $\hat{\beta} \approx 0.5$; such exponents would be consistent with the classical equilibrium exponents ν and β.

5. CONCLUSION

In summary, we have investigated, numerically, homogeneous and inhomogeneous solutions to the equations of motion for nematic liquid crystals in shear flow, in order to establish the non-equilibrium phase diagram. We have neglected important phenomena associated with thermal fluctuations, chaos, tumbling, and spatially modulated states. Furthermore, we have considered spatial gradients only in one dimension. Nevertheless, we hope to have captured the essential features of this system. Assuming the validity of the present description, the phase structure of liquid crystals in shear flow resembles that of the van der Waals gas; it consists of a two-state region, a discontinuous transition at a coexistence line which terminates at a non-equilibrium critical point, and behavior near the critical point which parallels classical equilibrium critical behavior. In the future we plan to address, *inter alia*, the issues of metastability, and fluctuations near the critical point.

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References

1. S. Hess, *Z. Naturforsch*, **31a**, 1507 (1976).
2. P. D. Olmsted and P. M.Goldbart, *Phys. Rev.*, **A41**, 4578 (1990).
3. H. See, M. Doi and R. Larson, *J. Chem. Phys.*, **92**, 792 (1990).
4. S.-Q. Wang and W. Gelbart, *J. Chem. Phys.*, **90**, 597 (1989).
5. S. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962).
6. For a description of the order parameter for a nematic liquid crystal see T. C. Lubensky, *Phys. Rev.*, **A2**, 2497 (1970).
7. P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1975).
8. F. M. Leslie, *Quart. J. Appl. Math.*, **19**, 357 (1966); *Archs. Ration. Mech. Analysis*, **28**, 265 (1968); J. L. Ericksen, *Archs. Ration. Mech. Analysis*, **4**, 231 (1990); *Phys. Fluids*, **9**, 1201 (1966).
9. We note, in passing, that planar Couette flow has biaxial symmetry.
10. As an alternative to the present phenomenological approach, one can develop a picture in terms of molecular distribution functions; see References 3 and 4.
11. G. Vertogen and W. H. de Jeu, *Thermotropic Liquid Crystals, Fundamentals* (Springer, Berlin, 1988).
12. Whether we work at fixed shear stress or fixed shear rate is a matter of convenience, and is analogous to exchanging density for pressure in a liquid-gas system.
13. P.G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12**, 193 (1971).
14. See, for example, L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1980).
15. W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, 1986).