Macroscopic dynamics near the nematic-columnar transition in liquid crystals

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We derive the dynamic equations for the macroscopic variables close to the nematic—to—hexagonal-columnar transition in discotic liquid crystals. We discuss especially the physical consequences of a static cross-coupling term between fluctuations of the discotic order parameter and gradients of the nematic director, a term omitted by previous workers. Furthermore, we predict the breakdown of flow alignment in disklike nematics close to the transition to a columnar phase and we discuss the microscopic reasons for this effect and, in general, the same type of behavior for other liquid crystalline phases with positional order such as smectic-A, -B, -C, -G, etc.

After the discovery of thermotropic discotic liquid crystals[1] the investigation of similarities and differences to liquid crystalline phases composed of rodlike molecules has become an important topic in the study of mesophases. The first transition nematic to columnar (positional order in two directions, disorder in one direction—along the columns) was announced[2] in 1979 and since then various phenomena connected with this transition such as an inverted nematic phase[3,4] (the nematic phase is found only below, as a function of temperature, but not above the more ordered columnar phase) and a reentrant nematic discotic phase[5]—the analog of the reentrant nematic phase in compounds made of rodlike molecules[6]—have been found.

Theoretical approaches to understanding the nematic-columnar transition have so far been restricted to writing[7-9] the static free energy for the order parameter and studying—via mode coupling[10]—the influence of order-parameter fluctuations on Frank's elastic constants[8,9] and viscosities.[8] This approach is similar in spirit to the one used[11] to describe fluctuations close to the smectic-A—to—nematic transition.

Here we present a model for the macroscopic dynamics close to the transition, including a new static cross coupling between gradients of the order parameter and gradients of the nematic director. A simple experimental setup to study the influence of this cross coupling is suggested. Furthermore, we predict the breakdown of flow alignment close to the nematic-columnar transition due to fluctuations of the columnar order parameter—a result which is implicitly contained in the mode coupling calculation of Ref. 8. We discuss why the breakdown of flow alignment does not follow from microscopic calculations of the type proposed in Ref. 12 and applied to unaxial nematics[12] and to biaxial nematics and smectics-C.[13] In addition, we investigate where, i.e. for which regime of temperatures, a breakdown of flow alignment can be expected in reentrant nematic phases—a question that has not yet been studied experimentally.

To set up the macroscopic dynamics we complement the hydrodynamic equations for uniaxial nematics[14,15] by the quantities which vary slowly in time and space but the excitation frequencies of which do not vanish in the limit of infinite wavelength. An obvious candidate close to the nematic-columnar transition is the modulus of the columnar order parameter m, if the transition is second order or only weakly first order, as is the case here.[8,9] It will become clear from the discussion on the breakdown of flow alignment below, that the regime for which m is slow might be quite large and extend over most of the regime of existence of the discotic-nematic phase. Before proceeding, we add a word of caution. Since macroscopic dynamics does not have the same degree of rigor as a hydrodynamic approach, one cannot rule out completely that there is an additional "slow" quantity—aside from the order parameter m. But there seems to be no obvious candidate and thus we obtain for the generalized free energy F,

$$F = F_n + F_m + F_{mn} + F_0 , \tag{1}$$

where F_n is the usual Frank free energy for uniaxial nematics,[15] F_m is given by[8]

$$F_m = \int d^3r \left[am^2 + bm^3 + dm^4 - C_{||}(\mathbf{n}\cdot\nabla m)^2 + \frac{C_\perp^2}{4D_\perp}m^2 \right.$$
$$\left. + D_\perp(\nabla_\perp^2 m)^2 + C_\perp \delta_{ij}^{tr}(\nabla_i m)(\nabla_j m) \right] \tag{2}$$

and for F_{mn} we have

$$F_{mn} = \int d^3r\, \xi_{ijk}(\nabla_i m)(\nabla_j n_k) . \tag{3}$$

$F_0(\rho,\sigma,\mathbf{V})$ contains the same contributions as in an isotropic liquid. In writing Eqs. (2) and (3), we have used the abbreviations

$$\delta_{ij}^{tr} = \delta_{ij} - n_i n_j \tag{4}$$

with δ_{ij} the Kronecker symbol and n_i the nematic director ($n_i n_i = 1$), and

$$\xi_{ijk} = \xi(\delta_{ik}^{tr} n_j + \delta_{kj}^{tr} n_i) . \tag{5}$$

The order parameter m is taken to be

$$m = \int_D \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\cdot\mathbf{r}}\rho(k) . \tag{6}$$

For the transition nematic-hexagonal discotic (D_{hd}), the wave-vector integration is over a torus,[8] whereas for a rectangular discotic (D_{rd}) the underlying symmetry requires a corresponding change in the domain of integration. (To include the transition rectangular discotic-nematic is important because many of the nematic-columnar transitions observed are of that type; cf., e.g., Refs. 2—5 and 16.) In Ref. 8 it is implicitly assumed that the domain of integration in k space is very small and that the distribution $\rho(k)$ is sharply peaked; in the following we will assume that— especially far away from the nematic-columnar transition—the domain of integration in k space is large with a distribution $\rho(k)$ which is broad and also contains small, but finite values of the wave vector. The term proportional to ξ [Eq. (3)] has not been considered before.[8,9] It couples gradients of the nematic director to gradients of m where the two gradients are parallel and perpendicular to the nematic director, respectively. By enforcing the director field n to have no spatial variations in the bulk of the sample the influence of the cross-coupling term can be removed (e.g., by a sufficiently strong external magnetic field). It seems worthwhile to note that a similar type of cross coupling (between gradients of an order parameter and gradients of the nematic director) has been discussed before for the uniaxial-to-biaxial phase transition in nematic liquid crystals.[17-19] In contrast to the present case where the order parameter is a scalar, it is an antisymmetric, traceless tensor for the uniaxial-to-biaxial transition.

A possible experimental detection of the effects of ξ can proceed along the lines outlined for that transition.[17] An even simpler way, however, to achieve the same type of effect experimentally seems to be the use of a wedge-shaped sample instead of an inhomogeneous magnetic field. This way one naturally imposes on the director field a certain degree of deformation and as the nematic-columnar transition is approached the ensuing pattern to be observed in the polarizing microscope is expected to change. The estimate of the magnitude of the change, however, is beyond the scope of a continuum-type approach. We also mention that the same technique can obviously also be applied to the uniaxial-to-biaxial phase transition in nematics. The investigation of the nematic-columnar transition offers one advantage: it is known to occur in pure compounds[2-5,16] so that one need not be concerned about multicomponent effects, as it has always been the case so far, for the uniaxial-biaxial transition in lyotropic systems.

Assuming local thermodynamic equilibrium we have the Gibbs relation

$$d\epsilon = \mu \, d\rho + T \, d\sigma + \mathbf{V} \cdot d\mathbf{g} + \phi_{ij} \, d\nabla_i n_j + h_i \, dn_i + \mu_m \, dm \; ,$$
(7)

where ρ, σ, and $\mathbf{g}$ are the conserved densities of particle density, entropy, and linear momentum and μ, T, $\mathbf{V}$, ϕ_{ij}, h_i, and μ_m are thermodynamic conjugate quantities defined via Eq. (7). For the dynamic equations we have—as in uniaxial nematics—conservation and quasiconservation laws for $\rho, \sigma, \mathbf{g}$ and the transverse director fluctuations δn_i with $n_i \delta n_i = 0$,

$$\frac{\partial \rho}{\partial t} + \nabla_i g_i = 0 \; ,$$

$$\frac{\partial \sigma}{\partial t} + \nabla_i \left[\sigma V_i + \frac{q_i}{T} \right] = \frac{R}{T} \; ,$$

$$\frac{\partial g_i}{\partial t} + \nabla_j (g_j V_i + p\delta_{ij}) + \nabla_j \sigma_{ij} = 0 \; ,$$

$$\frac{dn_i}{dt} + Z_i = 0 \; ,$$
(8)

with R the entropy production. For m we have

$$\frac{dm}{dt} + X_m = 0 \; .$$
(9)

To close the system of macroscopic equations we have to relate the currents g_i, q_i, σ_{ij}, Z_i, and X_m in Eqs. (8) and (9) to the thermodynamic conjugate quantities defined via Eq. (7), and then in turn we must express those in terms of the macroscopic variables. Making use of general symmetry arguments we have the following:

(a) for the reversible currents

$$X_i^R = \lambda_{ijk} \nabla_j V_k \; ,$$

$$q_i^R \equiv 0 \; ,$$

$$X_m = \beta_{ij} \nabla_i V_j \; ,$$
(10)

$$\sigma_{ij}^R = \lambda [n_i (h_j - \nabla_l \phi_{jl}) + (i \leftrightarrow j)]$$
$$+ \tfrac{1}{2} [n_i (h_j - \nabla_l \phi_{jl}) - (i \leftrightarrow j)] + \beta_{ij} \mu_m + \phi_{kj} \nabla_i n_k \; ,$$

(b) and for the irreversible currents

$$j_m^D = \zeta \mu_m \; ,$$

$$q_i^D = -\kappa_{ij} \nabla_j T \; ,$$

$$X_i^D = -(1/\gamma_1) h_i \; ,$$
(11)

$$\sigma_{ij}^D = -\nu_{ijkl} \nabla_k v_l \; ,$$

where

$$\lambda_{ijk} = \tfrac{1}{2}(1-\lambda)\delta_{ij}^{tr} n_k - \tfrac{1}{2}(1+\lambda)\delta_{ik}^{tr} n_j$$

and
(12)

$$\beta_{ij} = \beta_{\|} n_i n_j + \beta_\perp \delta_{ij}^{tr} \; .$$

The term proportional to ζ in Eq. (11) just expresses the fact that slow spatial temporal variations of m are non-conserved. A term of the same structure as β_{ij} has been discussed before for the nematic—smectic-A transition.[20] In the present case, the meaning of β_{ij} is quite intuitive; it gives the degree to which columnar order is induced in the nematic phase under the action of an external flow field, especially a shear flow. In Ref. 8 this term has been omitted due to the different assumption about the domain of integration in k space for the order parameter.

It seems worth noting that the existence of an expression similar to β_{ij} in Eqs. (10) is not restricted to phase

transitions from a nematic to a columnar or smectic-A phase. Symmetry allows for the same type of cross coupling close to a columnar-crystal transition which can be of second order,[21] i.e., the dynamic equations given in Ref. 22 should be supplemented by such a term. In the case of the columnar-crystal transition the intuitive physical meaning would be the following: applying a flow, especially a shear flow, to the system leads to a growing degree of solidification as the transition to the crystal is approached in temperature, a phenomenon which one could call shear flow induced solidification, a feature not studied in liquid crystals so far. The effect predicted here is a pretransitional effect and different from the shear flow induced melting which has been studied in colloidal crystals.[23]

To express the thermodynamic conjugate quantities which appear in Eqs. (11) and (12) we can just take variational derivatives of the generalized free energy with respect to one macroscopic variable while keeping all the other ones fixed. We have, e.g.,

$$\mu_m = \frac{\delta F}{\delta m}, \quad H_i \equiv h_i - \nabla_j \phi_{ij} = \frac{\delta F}{\delta n_i} \ . \tag{13}$$

From the fact that under an external shear flow a finite amount of smectic or discotic order is introduced (via β_{ij}), immediately the question arises whether this will have any consequences for flow alignment—a phenomenon characteristic for nematic liquid crystals.[15] By flow alignment we mean here a stationary configuration in which the nematic director encloses with the external shear velocity an angle which is different from 45° (characteristic of an isotropic liquid[15]). In Ref. 13, Pleiner and I discussed flow alignment in nematic discotics using the microscopic model introduced by Forster.[12] On the other hand, we have seen above that approaching the nematic-discotic transition we pick up some degree of columnar ordering in an external shear flow, the magnitude of which is proportional to the β's. Also, it is not clear how these transient columnar areas in the nematic background could be aligned, thus leading to a breakdown of flow alignment as the fraction of these columnar pieces increases. To phrase it in a more formal way, the flow parameter λ assumes a value $0 > \lambda > -1$. This is a result which is implicitly contained in the mode coupling calculations of Swift and Andereck[8] if typical values are inserted into their expression.

These considerations can only be reconciled with the microscopic calculations for the flow alignment[12,13] (in which alignment is always found) if one takes into account that the mass quadrupole moment R_{ij}, as introduced in Ref. 12, is no longer a "good" order parameter everywhere in space in the nonequilibrium situation considered (external shear), since via β_{ij} some degree of columnar order is being introduced. For example, although the thermal average of the mass quadrupole moment is still a well-defined quantity, this is no longer true for R_{ij}. To cure this formally, one could use as an "effective" order parameter $R_{ij}(1-\epsilon)$ with ϵ being positive and growing as the columnar phase is approached. If this is done, one can get values for the parameter λ characteristic

for the breakdown of flow alignment.

Experiments on this question close to the nematic-columnar transition have not been performed as yet—a situation which is completely different from that at the nematic—smectic-A transition or even the nematic phase above a crystalline phase[24−31] where the breakdown has been observed by different groups using different setups and various compounds. When inspecting the experimental results several interesting features emerge. First of all, only three pure compounds, HBAB [4-(n-hexyloxy)benzylidene-4'-aminobenzonitrile] (Refs. 24—28), CBOOA [N-(4-cyanobenzylidene)-4'-(n-octyloxy)aniline] (Refs. 27—29), and 8CB [4-cyano-4'-(n-octyl)biphenyl] (Refs. 30 and 31) and one mixture[24,25] have been investigated; all of those share one important property: they are all strong polar compounds with a cyano end group. In addition the nematic phases in these compounds are followed at lower temperatures by an A phase made of dimers[32] as is the case for 8CB and CBOOA or they have strong fluctuations (HBAB and its mixtures) in x-ray scattering in the nematic phase at a layer spacing $d \approx 1.3l$, with l the molecular length. That is, the breakdown of flow alignment so far has only been observed in compounds composed of molecules which have a strong tendency to pair. From the general arguments given above, however, one would expect to observe the same behavior also in the vicinity of a nematic—smectic-A transition with the A phase composed of monomers. The fact that so far all experimental investigations have been carried out on polar compounds might have the trivial reason that those are easier available commercially, but it is definitely worthwhile to perform flow alignment in nonpolar compounds to rule out the possibility that the breakdown has anything to do with the polarity of the molecules.

Another noteworthy feature which appears from the analysis of the experimental data is the fact that the temperature range over which the breakdown of alignment occurs is not necessarily restricted to the close vicinity of the transition but can cover as much as 85% of the temperature range of existence of the nematic phase thus leaving only a narrow temperature range close to the nematic-isotropic transition where the conventional behavior of a nematic liquid crystal is found. In 8CB, e.g., this strip can be as narrow as about 1 K (Ref. 31) and the temperature range over which no alignment occurs can be as large as 66 K.[25] Therefore it seems that the range of the validity of macroscopic equations which contain the modulus of the order parameter as a variable can be quite large near liquid-crystal phase transitions which is in sharp contrast to the vicinity of the λ transition in ^{4}He.[33]

We would also like to emphasize that our analysis presented here is not restricted to the "vicinity" of the nematic-columnar discotic or nematic—smectic-A transition, but applies as well to nematic phases above transitions to smectic-A_2, -C, -B, and -G phases or above a transition to a tilted discotic phase, in particular, as long as those are only weakly first order.

For reentrant nematic phases completely new experimental aspects open up; one will be able to observe in a

nematic phase below a columnar phase or a smectic phase a breakdown of flow alignment on heating, i.e., just the opposite behavior from all experiments which have been done so far. This can definitely be expected to be true if one has an isotropic phase below the reentrant or inverted nematic phase, as has been observed recently.[34] On the other hand it seems quite conceivable to find inverted or reentrant nematic phases which show no flow alignment over their whole range of existence. This is to be expected in particular if the range is small and the transition to the phase at lower temperature is strongly first order. Finally, we would like to comment on the vicinity of the biaxial-uniaxial transition in nematics. In this case, we do not expect a breakdown since only orientational order and not positional order, as in all cases investigated above, is

added at the transition. So we would expect to have flow alignment in both the uniaxial and biaxial nematic phases and it will be more interesting to check the predictions made for the biaxial phase.[13,35,36]

In closing, we have proposed a general mechanism for the breakdown of flow alignment in nematic liquid crystals, namely the existence of sufficiently strong fluctuations of density waves in one or two directions, a mechanism which does not require the close vicinity of a phase transition. This does not rule out the possibility of finding other mechanisms not considered so far.

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