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Dynamic properties near the columnar-crystalline phase transition

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Résumé. — Des quantités dynamiques sont calculées près de la transition entre phase en colonnes et phase cristalline. L'augmentation des viscosités ν_1 et ν_3 due aux fluctuations du paramètre d'ordre se trouve être proportionnelle à la première puissance de la longueur de corrélation. Nous décrivons brièvement comment la divergence en $\omega^{-1/2}$ des viscosités prédite par Ramaswamy et Toner dans la phase en colonnes est supprimée près de la transition vers la phase cristalline.

Abstract. — Dynamic quantities are computed near the transition from the columnar to the crystalline phase. The enhancement from order parameter fluctuations of the viscosities ν_1 and ν_3 is found to be proportional to the first power of the correlation length. We briefly describe how the $\omega^{-1/2}$ divergence of viscosities predicted in the columnar phase by Ramaswamy and Toner is suppressed near the transition to the crystalline phase.

A columnar phase with D_{6h} symmetry [1] was experimentally found by Chandrasekhar, Sadashiva, and Suresh [2]. Early work on the general properties of this phase and the transitions to other phases was due to Kats [3]. Based on the expression for the elastic energy given by Prost and Clark [4], a model which included coupling of the order parameter to elastic degrees was recently presented by the authors, and its static properties near the columnar-crystalline phase transition were discussed [5]. The hydrodynamics in the columnar phase was obtained by Prost and Clark [4]. Since the transition from the columnar to the crystalline phase is predicted to be second order [5], it is of particular interest to examine the dynamics near this transition. We focus on dynamic behaviour in this report.

Compared with the columnar phase, the crystalline phase corresponds to the appearance of a density wave parallel to the C_6 axis, with wave vector $q_{0\parallel} = \frac{2\pi}{d}$, where d is the lattice constant along C_6 axis. Near the columnar-crystalline transition, fluctuations of the density with wave vectors $\mathbf{q}$ near $\pm \mathbf{q}_0 = (0, 0, \pm q_{\|})$ become important and thus their coupling to the other variables should be taken into account. We will take the part of the density with wave vectors near $\pm \mathbf{q}_0$ as our order parameter, m,

$$m(\mathbf{r}, t) = \int_{\mathrm{D}} \frac{\mathrm{d}^3 k}{(2\pi)^3} \mathrm{e}^{i\mathbf{k}.\mathbf{r}} m(\mathbf{k}, t) \tag{1}$$

where $m(\mathbf{k}, t)$ is the Fourier transform of the density, and the integral domain D is taken to be two small separated spheres centred at $\pm \mathbf{q}_0$ respectively. The total free energy of the system can then be written as

$$F = F_m + F_{\mathrm{e}} + F_{\mathrm{v}} \tag{2}$$

where

$$F_m = \frac{1}{2} \int \mathrm{d}^3 r \left(a m^2 + D_{\|} [(\mathbf{n}.\nabla)^2 m]^2 - C_{\|} (\mathbf{n}.\nabla m)^2 + \frac{C_{\|}^2}{4 D_{\|}} m^2 + C_{\perp} \delta_{ij}^{\mathrm{T}} \nabla_i m \nabla_j m + \bar{u} m^4 \right), \tag{3}$$

$$F_{\mathrm{e}} = \frac{1}{2} \int \mathrm{d}^3 r \{ B^0 (\partial_x u_x + \partial_y u_y)^2 + D^0 [(\partial_x u_x - \partial_y u_y)^2 + (\partial_x u_y + \partial_y u_x)^2] + $$
$$+ K_{33}^0 [(\partial_{zz}^2 u_x)^2 + (\partial_{zz}^2 u_y)^2] \}, \tag{4}$$

and

$$F_{\mathrm{v}} = \frac{1}{2} \int \mathrm{d}^3 r \, v^2 . \tag{5}$$

In equations (3) through (5), u_x, u_y are the displacements, in the plane perpendicular to C_6 axis, of a local volume element from its equilibrium position. Also, $\mathbf{n}$ is a unit vector, the director, which indicates the orientations of the local optical axis. For small u_x and u_y in columnar phase $n_x = \frac{\partial u_x}{\partial z}$ and $r_y = \frac{\partial u_y}{\partial z}$. Further, $\mathbf{v}$ is the velocity-field of the material, the spatial average density is taken to be unity, $\delta_{ij}^{\mathrm{T}} = \delta_{ij} - n_i n_j$ with i and j being Cartesian indices, B^0, D^0, and K_{33}^0 are the bare elastic constants, $a = a'(T - T_{\mathrm{c}})$ where T_{c} is the mean field transition temperature, and a', together with $D_{\|}$, $C_{\|}$, $C_{\perp}$, and $\bar{u}$, are positive constants. A sum over repeated Cartesian indices is implied.

After the Fourier transform, equations (3) through (5) can be further written as

$$F_m = \frac{1}{2} \int_{\mathbf{q}} U(\mathbf{q}) \, m(\mathbf{q}, t) \, m(-\mathbf{q}, t) - \sum_{i=1}^{2} \int_{\mathbf{q}} \int_{\mathbf{k}} i k_3 \, \Gamma_i(\mathbf{q}, \mathbf{k}) \, u_i(-\mathbf{k}, t) \, m(-\mathbf{q}, t) \, m(\mathbf{q} + \mathbf{k}, t) - $$
$$- \sum_{i,j=1}^{2} \int_{\mathbf{q}} \int_{\mathbf{k}} \int_{\mathbf{k}'} k_3 k'_3 \, \Gamma_{ij}(\mathbf{k}, \mathbf{k}', \mathbf{q}) \, u_i(-\mathbf{k}, t) \, u_j(-\mathbf{k}', t) \, m(-\mathbf{q}, t) \, m(\mathbf{q} + \mathbf{k} + \mathbf{k}', t) , \tag{6}$$

$$F_{\mathrm{e}} = \frac{1}{2} \int_{\mathbf{k}} [E_1^0(\mathbf{k}) \, u_1(\mathbf{k}, t) \, u_1(-\mathbf{k}, t) + E_2^0(\mathbf{k}) \, u_2(\mathbf{k}, t) \, u_2(-\mathbf{k}, t)] , \tag{7}$$

and

$$F_{\mathrm{v}} = \sum_{i=1}^{3} \int_{\mathbf{k}} \frac{1}{2} v_i(\mathbf{k}, t) \, v_i(-\mathbf{k}, t) \tag{8}$$

where $\int_{\mathbf{k}} \equiv \int \frac{\mathrm{d}^3 k}{(2\pi)^3}$,

$$U(\mathbf{q}) = a + D_{11}(q_{\|}^2 - q_{0\|}^2)^2 + C_{\perp} q_{\perp}^2 , \tag{9}$$

with $q_{0\parallel}^2 = \frac{C_\parallel}{2 D_\parallel}$, and

$$E_1^0(\mathbf{k}) = (B^0 + D^0)\, k_1^2 + K_{33}^0\, k_3^4 \quad (10a)$$

$$E_2^0(\mathbf{k}) = D^0\, k_1^2 + K_{33}^0\, k_3^4 . \quad (10b)$$

In the above, $\Gamma_i(\mathbf{q}, \mathbf{k})$ and $\Gamma_{ij}(\mathbf{k}, \mathbf{k}', \mathbf{q})$ are vertex functions which have exactly the same form as that in N-A-C model system with $D_\perp = 0$. The explicit form of $\Gamma_{ij}(\mathbf{k}, \mathbf{k}', \mathbf{q})$ is not needed because of the Ward identity [6]. The subscripts 1, 2, and 3 for k_i, u_i, and v_i indicate their three Cartesian components in a special coordinate system. Here and hereafter, when working in reciprocal space, we will always choose the x_3 axis in the direction parallel to C_6 axis, the x_1 axis is parallel to the projection of $\mathbf{q}$ in the plane perpendicular to the C_6 axis, and the x_2 axis perpendicular to both x_1 and x_3 axes. (See Fig. 1 in Ref. [5].)

The Langevin equations which describe the dynamics in columnar phase near the columnar-crystalline transition point are :

$$\frac{\partial m(\mathbf{r}, t)}{\partial t} + \nabla .(m(\mathbf{r}, t)\, \mathbf{v}) = - \Gamma \frac{\delta F}{\delta m} + N^m(\mathbf{r}, t) \quad (11a)$$

$$\frac{\partial u_i(\mathbf{r}, t)}{\partial t} = v_i(\mathbf{r}, t) - \zeta \frac{\delta F}{\delta u_i} + N_i^u(\mathbf{r}, t) , \quad (i = 1, 2) \quad (11b)$$

and

$$\frac{\partial v_i(\mathbf{r}, t)}{\partial t} = - \frac{\partial P}{\partial x_i} - \sum \delta_{ij}^{0T} \frac{\delta F}{\delta u_j} + \frac{\partial m(\mathbf{r}, t)}{\partial x_i} \frac{\delta F}{\delta m(\mathbf{r}, t)} - \sum_j \frac{\partial}{\partial x_j} \sigma_{ij}^{D} + N_i^v(\mathbf{r}, t) \quad (i = 1, 2, 3) , \quad (11c)$$

where Γ determines the bare decay rate of $m(\mathbf{r}, t)$, ζ is associated with permeation [4], and $N^m(\mathbf{r}, t)$, $N_i^u(\mathbf{r}, t)$ and $N_i^v(\mathbf{r}, t)$ represent noise sources. In equation (11c) σ_{ij}^D is the dissipative part of the stress tensor for systems with uniaxial symmetry, which is given in equation (8) of reference [7]. We have already neglected variations in the temperature in the above equations. In (11c) P is the pressure. The introduction of the noise sources is to obtain a self-consistent theory with invariance under time translation unbroken [8]. Finally $\delta_{ij}^{0T} = \delta_{ij} - n_i^0\, n_j^0$, with $\hat{\mathbf{n}}^0 = (0, 0, 1)$.

Starting from (11a) through (11c) and using (6) through (8), we have the motion equations in wave-vector space ; i.e.,

$$\frac{\partial m(\mathbf{q}, t)}{\partial t} + \Gamma U(\mathbf{q})\, m(\mathbf{q}, t) = N^m(\mathbf{q}, t) + f^m(\mathbf{q}, t) \quad (12a)$$

$$\frac{\partial u_2(\mathbf{k}, t)}{\partial t} - v_2(\mathbf{k}, t) + \zeta E_2^0(\mathbf{k})\, u_2(\mathbf{k}, t) = N_2^u(\mathbf{k}, t) + f_2^u(\mathbf{k}, t) \quad (12b)$$

$$\frac{\partial v_2(\mathbf{k}, t)}{\partial t} + ik_2\, P(\mathbf{k}, t) + E_2^0(\mathbf{k})\, u_2(\mathbf{k}, t) + \eta_{22}^0(\hat{\mathbf{k}})\, k^2\, v_2(\mathbf{k}, t) = N_2^u(\mathbf{k}, t) + f_2^u(\mathbf{k}, t) \quad (12c)$$

$$\frac{\partial u_1(\mathbf{k}, t)}{\partial t} - v_1(\mathbf{k}, t) + \zeta E_1^0(\mathbf{k})\, u_1(\mathbf{k}, t) = N_1^u(\mathbf{k}, t) + f_1^u(\mathbf{k}, t) \quad (12d)$$

$$\frac{\partial v_1(\mathbf{k}, t)}{\partial t} + ik_1\, P(\mathbf{k}, t) + E_1^0(\mathbf{k})\, u_1(\mathbf{k}, t) + \eta_{11}^0(\hat{\mathbf{k}})\, k^2\, v_1(\mathbf{k}, t) + \eta_{31}^0(\hat{\mathbf{k}})\, k^2\, v_3(\mathbf{k}, t) = N_1^v(\mathbf{k}, t) + f_1^v(\mathbf{k}, t) \quad (12e)$$

$$\frac{\partial v_3(\mathbf{k}, t)}{\partial t} + ik_3\, P(\mathbf{k}, t) + \eta_{33}^0(\hat{\mathbf{k}})\, k^2\, v_3(\mathbf{k}, t) + \eta_{31}^0(\hat{\mathbf{k}})\, k^2\, v_1(\mathbf{k}, t) = N_3^v(\mathbf{k}, t) + f_3^v(\mathbf{k}, t) \quad (12f)$$

where, η_{11}^0, η_{22}^0, $\eta_{13}^0 = \eta_{31}^0$, and η_{33}^0 are defined by equations (A.11a) through (A.11d) in the Appendix of reference [9] and f_m, f_i'', and f_i^{v} are non-linear terms which appear in the corresponding equations. Five independent viscosity coefficients ν_1^0 through ν_5^0 are included in $\eta_{ij}^0(\mathbf{k})$ [9], and three elastic constants are included in $E_i^0(\mathbf{k})$. The renormalized equations can be obtained by treating the non-linear terms as perturbations. The equations have the form of the linear homogeneous equations corresponding to equations (12a) through (12f) (put the right side of the equations (12a) through (12f) equal to zero) with renormalized viscosity and elastic coefficients. The enhancement of those coefficients can then be obtained. The calculations are tedious, but analogous to those of reference [9]. We will just write down the results :

$$\delta K_{33} = \frac{q_{0\parallel}^2 k_B T}{24 \pi} \xi_\parallel \tag{13}$$

$$\delta \nu_1 = \frac{1}{8 \pi \Gamma} \left(\frac{D_\parallel}{2 C_\parallel} \right)^{1/2} \frac{q_{0\parallel}^3}{C_\perp} \xi_\parallel \tag{14}$$

$$\delta \nu_3 = \frac{1}{32 \pi \Gamma} \frac{q_{0\parallel}}{(2 C_\parallel D_\parallel)^{1/2}} \xi_\parallel \tag{15}$$

where $\xi_\parallel = \left[\frac{2 C_\parallel}{a'(T - T_c)} \right]^{1/2}$ is the correlation length along C_6 axis. All other viscosity and elastic coefficients and the permeation coefficient ζ are not enhanced.

The enhancement of K_{33} is exactly the same as equation (10) in reference [5] as it should be. The results for ν_1 through ν_5 have some differences from that in nematic system near the nematic to smectic A (N-A) and the nematic to columnar (N-Col.) transitions. Such differences can be partly explained by some simple geometric considerations. For simplicity, we just consider the system to be incompressible which will be true if all the variables in (12a) through (12f) are slowly varying with respect to space and time compared with the propagation of sound waves, in the considered systems. Then, ν_4 and ν_5 which are associated with bulk dilations and compressions can be neglected [7]. The viscosity which has direct physical meaning among ν_1, ν_2 and ν_3 is $\nu_2 = \eta_a$, where η_a is one of the Miesowitz viscosities. Its geometric configuration is pictured in figure 5.1(a) of reference [11]; i.e., a strong enough constant magnetic field **H** is imposed so that the molecular orientations are firmly aligned along **H**, the laminar flow velocities are perpendicular to **H**, and the gradient of the velocities is perpendicular to both **H** and the velocity. In this case, there are no motions of the director with respect to the background-fluid, so the measured dissipation is determined by only ν_2, which is associated with the shear deformations in the plane perpendicular to **H**. The dissipation may be greatly increased if such a shear deformation is restricted by extra geometric constraints when the system undergoes a transition from one phase to another. For the N-A transition, no extra geometric constraints appear in the plane perpendicular to **H**, so no enhancement of ν_2 can be expected in the nematic phase near N-A transition points. For the N-Col. transition, the additional geometric constraint is the appearance of the hexagonal lattice structure in the columnar phase, so ν_2 gets enhanced. For the columnar-crystalline transition, no extra constraints appear, so there is no enhancement of ν_2.

Now we consider another situation. Suppose there are both the velocities and its gradient along the optical axis (a strong enough **H** is also employed). For an incompressible system, we have $\nabla . \mathbf{v} = 0$, which corresponds to a dilation (or compression) along the optical axis and a compression (or dilation) in the plane perpendicular to the optical axis. In this case, the dissipative force for a small volume encountered in the direction along the optical axis is determined by $\nu_1 \left(\sigma_{33}^D = -2 \nu_1 \frac{\partial v_1}{\partial x_3} \right)$. In nematic phase, this deformation is easy to realize, but in smectic A phase, such a deformation accompanies the increasing of the spacing between two layers and the compressions of the area in the layers. Thus in the smectic A phase, this deformation becomes more difficult than in the nematic phase. Thus, near the N-A transition in the nematic phase, ν_1 is enhanced. Near the N-Col. transition, the given deformation in the columnar phase accompanies the compressions of the hexagonal structures, and ν_1 is also enhanced. For columnar-crystalline transition, the appearance of a periodic structure along the optical axis also leads to an enhancement of ν_1 in the columnar phase near the columnar-crystalline transition. These qualitative discussions coincide with the results obtained in references [9, 10] and this work.

The permeation coefficient ζ has no critical enhancement, in contrast to the twist viscosity γ_1 near the N-A transition, because of the gradient appearing in the relation between the director and the displacements.

Finally we describe how the $\omega^{-1/2}$ divergence of ν_1, ν_2, ν_4, and ν_5, predicted by Ramaswamy and Toner [12] to be present in the columnar phase, is suppressed near the transition to the crystalline phase. These authors considered the influence of anharmonic elastic terms on the hydrodynamics of the columnar phase and found enhancements of the viscosities given by their equation (12). We have computed the contributions to the viscosity ν_3 (called η_3 in Ref. [12]) and K_{33} (called K_1 in Ref. [12]) from order parameter fluctuations. If we insert our renormalized expressions for ν_3 (Eq. (15)) and K_{33} (Eq. (13)) into their equation (12) and keep only the dominant contributions near the transition, we find that the contribution from the anharmonic elastic terms, $\delta\nu_i|_{\text{AET}}$,

$$\delta\nu_i|_{\text{AET}} \propto \frac{1}{\xi_{\parallel}\,\omega^{1/2}} \tag{16}$$

for $i = 1, 2, 4, 5$. Expression (16) gives the suppression of the $\omega^{-1/2}$ divergence near the crystalline transition as the correlation length becomes large. Of course, since our calculation is based on perturbation theory [13] and since one must remain in the hydrodynamic regime, expression (16) cannot hold extremely close to the transition.

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