

## Hydrodynamics of three-dimensional stacked hexatic liquid crystals

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The hydrodynamic equations for three-dimensional stacked hexatic liquid crystals, i.e., for hexatic-*B* and its tilted analogs, smectic-*F* and smectic-*I*, are presented. Differences and similarities to the hydrodynamics of smectic-*A* and smectic-*C* are discussed and the role of the additional variable characterizing the bond orientational order is elucidated.

### I. INTRODUCTION

The smectic phases studied so far in thermotropic liquid crystals can be divided into three classes: (i) smectic-*A* and -*C* which are fluid inside the layers<sup>1</sup> (short-range order); (ii) smectic-*B* (crystal), -*E*, -*G*, -*H*, -*J*, and -*K* which are isomorphic<sup>2,3</sup> to a crystal inside the hydrodynamic regime,<sup>4</sup> since the center of mass of the molecules is ordered in three dimensions; and (iii) hexatic-*B*, smectic-*F*, and -*I* (Refs. 5–9). Class (iii) is believed to show short-range positional order inside the layers, although it is considerably longer in range when compared to smectic-*A* and -*C*. In addition, hexatic-*B* and smectic-*I* and -*F* show a certain degree of fluidity inside the layers. Thus, it seems to be very interesting to study these phases, which are intermediate between in-plane fluidity and in-plane crystalline order.

In the present note we give a hydrodynamic description of these three-dimensional stacked phases. They are distinguished from smectic-*A* and -*C* by the existence of long-range bond-orientational order inside the layers, i.e., there exists a hexagonal pattern of the bond directions between neighboring molecules.<sup>10,11</sup> Thus, we have broken rotational invariance but translational invariance is still guaranteed. Since the bond structure is hexagonal the viscosities and static susceptibilities are still isotropic inside the layers. The hexatic-*B* phase<sup>12</sup> can be viewed as a smectic-*A* liquid crystal with additional bond-orientational order inside the layers which gives rise to one additional hydrodynamic variable; smectic-*F* and -*I* are tilted versions of hexatic-*B* and therefore resemble closely smectic-*C* with additional bond-orientational order in the layer planes. On a macroscopic level, smectic-*F* and -*I* are isomorphic but are distinguished microscopically (e.g., by x ray) by a director pointing to the corner (*F* phase) or to the apex (*I* phase) of the unit cell. An extended discussion of the structures (including drawings) of hexatic-*B* and smectic-*F* and -*I* can be found in Refs. 9 and 7, respectively. Like smectic-*C*, smectic-*F* and -*I* are biaxial. In analogy to smectic-*C* it is also possible to chiralize *F* and *I* thus obtaining *F*\* (Ref. 13) and *I*\* (Ref. 14) which are uniaxial.

In Sec. II we give the linearized hydrodynamic equations for hexatic-*B* and in Sec. III those for *I* and *F*. The

role played by a relative rotation between tilt of the molecules and bond-orientational order will also be discussed in Sec. III.

### II. HYDRODYNAMICS OF HEXATIC SMECTIC-*B* PHASE

In hexatics, the two broken continuous symmetries, translational order parallel to the layer normal and bond-orientational order in the layer plane give rise to two additional hydrodynamic variables: The displacement  $\delta R$  (or sometimes called  $u$ ) along the layer normal (characterized by the constant unit vector  $\hat{p}^0$ ) and the rotation angle  $\delta\theta$  describing rotations of the hexagonal bond order within the planes.<sup>15</sup>  $\delta R$  is one component of the (polar) displacement vector  $\vec{R}(\delta R = \vec{R} \cdot \hat{p}^0)$  and  $\delta\theta$  is one component of the (axial) angle vector  $\vec{\theta}(\delta\theta = \vec{\theta} \cdot \hat{p}^0)$ . In equilibrium, i.e., in the undisturbed structure,  $\delta\theta = 0$  and  $\delta R = 0$ . Since homogeneous displacements  $\delta R$  or rotations  $\delta\theta$  lead generally to different states without changing the energy density  $\epsilon$ , only gradients of  $\delta R$  or of  $\delta\theta$  enter the Gibbs relation<sup>16</sup>

$$T d\sigma = d\epsilon - \mu d\rho - \vec{v} \cdot d\vec{g} - \phi_j d(\nabla_j R) - \Psi_{ij} d(\nabla_i \nabla_j R) - \chi_i d(\nabla_i \theta). \quad (2.1)$$

The other hydrodynamic variables are the conserved quantities density  $\rho$ , momentum density  $\vec{g}$ , and the entropy density  $\sigma$ . The thermodynamic quantities  $T$ ,  $\mu$ ,  $\vec{v}$ ,  $\vec{\phi}$ ,  $\psi_{ij}$ , and  $\vec{\chi}$  are defined by Eq. (2.1) as partial derivatives of the energy density  $\epsilon$ . Expressing the thermodynamic quantities by the variables constitutes the statics of the hexatic phase. This is done by pure symmetry arguments: the only quantities, which are odd under time reversal, are  $\vec{v}$  and  $\vec{g}$ . The vector  $\hat{p}^0$  defines an axis (layer normal) without specifying up and down direction. Thus, we can treat  $\hat{p}^0$  as a polar vector and make use of the additional symmetry  $\hat{p}^0 \leftrightarrow -\hat{p}^0$ , which implies  $\delta\theta \leftrightarrow -\delta\theta$  and  $\delta R \leftrightarrow -\delta R$  and  $\phi_i \leftrightarrow -\phi_i$ ,  $\Psi_{ij} \leftrightarrow -\Psi_{ij}$ , and  $\chi_i \leftrightarrow -\chi_i$ , since  $\epsilon$  is invariant under this additional symmetry. The other possibility is to treat  $\hat{p}^0$  as an axial vector, which implies  $\delta\theta$  to be a scalar and  $\delta R$  to be a pseudoscalar quantity (in addition,  $\phi_j$  is an axial vector,  $\Psi_{ij}$  is a tensor odd under parity, and  $\chi_i$  a polar vector since  $\epsilon$  is a scalar and  $\nabla_i$  a

polar vector). In any case, we find the linear relations

$$\begin{aligned}
\rho_0 v_i &= g_i, \\
\delta T &= T_0 C_v^{-1} \delta \sigma + \gamma \delta \rho + \gamma_2 \hat{p}_i^0 \nabla_i R, \\
\delta \mu &= \lambda \delta \rho + \gamma \delta \sigma + \gamma_1 \hat{p}_i^0 \nabla_i R, \\
\phi_i &= \hat{p}_i^0 \hat{p}_j^0 \chi_{||} \nabla_j R + \gamma_1 \hat{p}_i^0 \delta \rho + \gamma_2 \hat{p}_i^0 \delta \sigma, \\
\Psi_{ij} &= K_{ijlm} \nabla_l \nabla_m R, \\
\chi_i &= M_{ij} \nabla_j \theta.
\end{aligned} \tag{2.2}$$

Thereby,  $C_v$ ,  $\gamma$ , and  $\lambda$  are a representation of the usual three susceptibilities of a simple liquid;  $\chi_{||}$  is the stiffness constant of the layers (sometimes called  $B$ ) and  $\gamma_1$  ( $\gamma_2$ ) describe static cross couplings between layer displacement and density (entropy) (or pressure and temperature) and vice versa. The tensor

$$M_{ij} = M_{||} \hat{p}_i^0 \hat{p}_j^0 + M_{\perp} (\delta_{ij} - \hat{p}_i^0 \hat{p}_j^0)$$

contains a longitudinal ( $M_{||}$ ) and a transverse ( $M_{\perp}$ ) stiffness constant of the bond structure. If the layers are only weakly coupled, one can assume that the bond structures in different layers are also only weakly coupled, which implies that  $M_{||}$  is a small quantity compared to  $M_{\perp}$  which describes the stiffness of the bond structure within a layer. The tensor  $K_{ijlm}$  describes fluctuations  $\delta p_i$  of the preferred direction  $\hat{p}_i^0$ ; in linear order they are described by transverse gradients of  $\delta R$ , i.e.,  $\delta p_i = -(\delta_{ij} - \hat{p}_i^0 \hat{p}_j^0) \nabla_j R$  and  $K_{ijlm}$  takes the form

$$K_{ijlm} = (\delta_{jm} - \hat{p}_j^0 \hat{p}_m^0) [K_1 (\delta_{il} - \hat{p}_i^0 \hat{p}_l^0) + K_3 \hat{p}_i^0 \hat{p}_l^0].$$

The  $K$ 's are the usual Frank constants. Since longitudinal gradients of  $\delta R$  are already present in first order ( $\phi_j$ ), one usually neglects the second-order terms  $\sim K_3 \nabla_{||}^2 R$  against  $\chi_{||} \nabla_{||} R$ . The inclusion of higher gradient order terms  $\nabla_i \nabla_j R$  is justified (and necessary) because first-order terms  $\nabla_i R$  are restricted to longitudinal gradients  $\nabla_{||} R$ . This is a point to be made for all smectic systems. In a nonlinear theory, however, other higher-order gradient terms would also have to be kept.

The constitutive equations (2.2) are equivalent to the free-energy expression

$$\begin{aligned}
f &= f_0 + \frac{1}{2} \chi_{||} (\nabla_{||} R)^2 + \frac{1}{2} K_1 (\nabla_{\perp}^2 R)^2 + \frac{1}{2} M_{||} (\nabla_{||} \theta)^2 \\
&\quad + \frac{1}{2} M_{\perp} (\nabla_{\perp} \theta)^2 + (\nabla_{||} R) (\gamma_1 \delta \sigma + \gamma_2 \delta \rho)
\end{aligned} \tag{2.3}$$

where

$$f_0 = \frac{1}{2} C_v^{-1} T_0 (\delta \sigma)^2 + \frac{1}{2} \lambda (\delta \rho)^2 + \gamma \delta \rho \delta \sigma + \frac{1}{2 \rho} \bar{g}^2$$

is the free energy of a simple liquid. Since  $f$  has to be a positive definite form, we obtain the following restrictions for the susceptibilities:  $C_v$ ,  $\lambda$ ,  $\chi_{||}$ ,  $K_1$ ,  $M_{||}$ , and  $M_{\perp}$  are all positive and  $T_0 C_v^{-1} \lambda > \gamma^2$ ,  $T_0 C_v^{-1} \chi_{||} > \gamma_2^2$ , and  $\lambda \chi_{||} > \gamma_1^2$ . The equations (2.2) were obtained from (2.3) by taking partial derivatives

$$\delta T = \frac{\partial \epsilon}{\partial \sigma}, \quad \delta \mu = \frac{\partial \epsilon}{\partial \rho}, \quad \phi_j = \frac{\partial \epsilon}{\partial (\nabla_j R)},$$

$$\Psi_{ij} = \frac{\partial \epsilon}{\partial (\nabla_i \nabla_j R)}, \quad \chi_i = \frac{\partial \epsilon}{\partial (\nabla_i \theta)},$$

and

$$v_i = \partial \epsilon / \partial g_i.$$

In writing down Eq. (2.3), we have assumed that the bond-orientational order is truly three dimensional. If this is not the case,  $M_{||} \equiv 0$  and one has to keep a term of the form  $\frac{1}{2} K_8 (\nabla_{||}^2 \theta)^2$  in Eq. (2.3) and the corresponding correlation functions [ $\sim (M_{\perp} k_{\perp}^2 + K_8 k_{||}^4)$ ] are of the (columnar) discotic type.<sup>17</sup> Similarly,  $M_{||} k_{||}^2$  must be replaced, in this case, by  $K_8 k_{||}^4$  in all expressions which follow below.

The dynamic equations have the linearized form

$$\begin{aligned}
\dot{\rho} + \nabla_i g_i &= 0, \\
\dot{g}_i + \nabla_i p + \nabla_j \sigma_{ij} &= 0, \quad \nabla_j \sigma_{ij} = \nabla_j \sigma_{ji}, \\
\dot{\epsilon} + \nabla_i (\epsilon_0 + p_0) v_i + \nabla_k j_k^{(\epsilon)} &= 0, \\
\dot{\sigma} + \nabla_i \sigma_0 v_i + \nabla_i j_i^{(\sigma)} &= \frac{D}{T}, \\
\dot{R} + X &= 0, \\
\dot{\theta} + Y &= 0,
\end{aligned} \tag{2.4}$$

where  $\epsilon_0$ ,  $p_0$ , and  $\sigma_0$  are the equilibrium values of the energy density, the pressure, and the entropy density, respectively. The dissipation function  $D$  is zero on the reversible level (i.e.,  $\sigma$  a conserved quantity) and positive for the irreversible contributions. The entropy production is  $\int (D/T) dV$ . The pressure is given by the (linearized) Gibbs-Duhem relation  $\delta p = \rho_0 \delta \mu + T_0 \delta T$ .

We now express the unknown currents  $\sigma_{ij}$ ,  $j_k^{(\epsilon)}$ , and  $j_k^{(\sigma)}$  and quasicharges  $X$  and  $Y$  by the thermodynamic conjugates. These currents are not independent but are related by Eq. (2.1). For the reversible parts of the currents (superscript  $R$ ) this means that the sum

$$j_i^{\sigma R} \nabla_i T + \sigma_{ij}^R \nabla_j v_i + X^R (\nabla_j \phi_j - \nabla_i \nabla_j \Psi_{ij}) + Y^R \nabla_i \chi_i$$

must be zero or a pure divergence ( $j_i^{(\epsilon)} = T_0 j_i^{(\sigma)}$  in the linearized theory) while for the dissipative parts (superscript  $D$ ) we have

$$j_i^{\sigma D} \nabla_i T + \sigma_{ij}^D \nabla_j v_i + X^D (\nabla_j \phi_j - \nabla_i \nabla_j \Psi_{ij}) + Y^D \nabla_i \chi_i = D > 0.$$

In the present case, the reversible parts of the currents

$$\begin{aligned}
Y^R &= -\frac{1}{2} \hat{p}_i^0 \epsilon_{ijk} \nabla_j v_k, \\
X^R &= -\hat{p}_i^0 v_i, \\
\sigma_{ij}^R &= -\hat{p}_i^0 (\phi_j - \nabla_l \Psi_{lj}) - \frac{1}{2} \hat{p}_k^0 \epsilon_{kij} \nabla_p \chi_p, \\
j_i^{\sigma R} &= 0,
\end{aligned} \tag{2.5}$$

are pinned down completely by the nature of the broken symmetries: Since the momentum is the generator of translations,  $\delta R$ , which describes the breaking of the translation symmetry (along  $\hat{p}^0$ ), is canonical conjugate to

$\vec{g} \cdot \hat{p}^0$  and  $\vec{R} = \vec{v} \cdot \hat{p}^0$ . In the same way,  $\delta\theta$  is canonical conjugate to the angular momentum  $\vec{J} \cdot \hat{p}^0$  and  $\dot{\theta} = \vec{\omega} \cdot \hat{p}^0$  where  $\omega_i = (1/2)\epsilon_{ijn}\nabla_j v_n$  is the vorticity. Other reversible contributions to the currents, e.g., flow alignment terms<sup>1,3,18,19</sup> like in uniaxial and biaxial nematics, are ruled out by symmetry (isotropy in the layer plane). For the irreversible parts of the currents symmetry allows for

$$\begin{aligned} Y^D &= -\mu \nabla_i \chi_i, \\ X^D &= -\zeta (\nabla_i \phi_i - \nabla_i \nabla_j \Psi_{ij}) - \xi \hat{p}_i^0 \nabla_i T, \\ \sigma_{ij} &= -v_{ijkl} \nabla_l v_k, \\ j_i^{(\sigma)} &= \frac{-1}{T_0} \kappa_{ij} \nabla_j T - \xi \hat{p}_i^0 (\nabla_k \phi_k - \nabla_k \nabla_j \Psi_{kj}). \end{aligned} \quad (2.6)$$

The heat conduction tensor  $\kappa_{ij}$  and the viscosity tensor are of uniaxial form and contain two and five independent (irreversible) transport parameters, respectively. There are three further transport parameters present, i.e.,  $\mu$ ,  $\zeta$ , and  $\xi$ , the latter describing a dynamical cross coupling between layer displacement and entropy (temperature) fluctuations. The positivity of entropy production requires the constraints  $\mu$ ,  $\zeta$ ,  $\kappa_{||}$  and  $\kappa_{\perp}$  to be positive and  $\kappa_{||}\zeta > \xi^2$ .

The physical impact of linearized hydrodynamics is best discussed by looking at the normal modes. In linear order in  $k$  ( $\omega \sim k$ ) hexatics behave like smectic-*A* liquid crystals.<sup>3</sup> There are two soundlike excitations ( $\omega = \pm ck$ ) coupled together (first- and second-sound or ondulation mode) mainly built up by  $\delta\rho$ ,  $\vec{k} \cdot \vec{g}$ ,  $\delta R$ , and  $\hat{p}^0 \cdot \vec{g}$ . Both sound velocities  $c_{1,2}$  depend on the direction of  $\vec{k}$  relative to  $\hat{p}^0$ . (For the special cases  $k_{\perp} = 0$  or  $k_{||} = 0$  one of the sound modes decays into two diffusion modes.) In the next  $k$  order ( $\omega \sim k^2$ ), the sound modes acquire diffusive contributions to  $\omega$  ( $\sim ik^2$ ), again direction dependent, which involve  $\delta\sigma$  (or  $\delta T$ ) additionally. The heat conduction mode  $\omega \sim iEk^2$  with direction dependent  $E$ , besides  $\delta\sigma$  (or  $\delta T$ ), also involves  $\delta R$  and  $\delta\rho$ . The motion of  $\delta\theta$ , which discriminates hexatic-*B* from smectic-*A*, is generally coupled with that component of  $\vec{g}$ , which is perpendicular to both  $\vec{k}$  and  $\hat{p}^0$ ,  $\vec{g} \cdot \vec{k} = 0 = \vec{g} \cdot \hat{p}^0$  but decoupled from the rest. The mode structure is

$$\begin{aligned} \omega &= -\frac{i}{2} \left[ \mu \hat{M}^2 + \frac{1}{\rho_0} \hat{v}^2 \right] \\ &\pm \frac{i}{2} \left[ \left[ \mu \hat{M}^2 - \frac{1}{\rho_0} \hat{v}^2 \right]^2 - \frac{1}{\rho_0} k_{\perp}^2 \hat{M}^2 \right]^{1/2} \end{aligned} \quad (2.7)$$

with

$$\begin{aligned} \hat{M}^2 &= M_{||} k_{||}^2 + M_{\perp} k_{\perp}^2, \\ \hat{v}^2 &= 3v_2 k_{\perp}^2 + v_3 k_{||}^2. \end{aligned}$$

For  $k_{\perp} = 0$ , there are two decoupled diffusions  $\omega = -i\mu M_{||} k_{||}^2$  and  $\omega = -i\rho_0^{-1} v_3 k_{||}^2$  of  $\delta\theta$  and  $\vec{g} \cdot (\hat{p}^0 \times \vec{k})$ , respectively. For  $k_{\perp} \neq 0$ ,  $\delta\theta$  and  $\omega_{||}$  exhibit a coupled diffusion as long as

$$\frac{1}{\rho_0} k_{\perp}^2 \hat{M}^2 < \left[ \mu \hat{M}^2 - \frac{1}{\rho_0} \hat{v}^2 \right]^2;$$

in the reversed case, Eq. (2.7) describes a strongly damped propagating wave with dispersion  $[\omega \sim k^2(\alpha + i\beta)]$ , which can be called a ‘‘bond-vorticity’’ wave. The structure of (2.7) strongly resembles the director-shear modes of nematics<sup>18</sup> (there are two of them in nematics) or the orbit ‘‘waves’’ in <sup>3</sup>He-*A*.<sup>20</sup> From the experience with the latter systems it would be, however, a surprise, if this ‘‘bond-vorticity wave’’ would not be overdamped (purely dissipative).

In experiments, these modes can be excited by an externally-imposed inhomogeneous rotation along  $\hat{p}^0$  (or an inhomogeneous shear stress within the layers). If the inhomogeneity is parallel to  $\hat{p}^0$  ( $k_{||} \neq 0, k_{\perp} = 0$ ) one can measure the two diffusion constants  $\mu M_{||}$  and  $(1/\rho_0)v_3$ . If the inhomogeneity is perpendicular to  $\hat{p}^0$  ( $k_{||} = 0, k_{\perp} \neq 0$ ), one finds either the bond-vorticity wave or the coupled diffusion described above. If a propagating wave is found, then

$$|2\rho_0\mu^2 M_{\perp} - 6v_2\mu - 1| < (1 + 12v_2\mu)^{1/2}$$

limits the possible values for  $M_{\perp}$ ; if  $\mu v_2 \ll 1$  this implies

$$M_{\perp} > \frac{3}{4} \frac{v_2^2}{\rho_0}$$

and  $M_{\perp} < (1/\rho_0\mu^2)$ . If  $v_2$  is known from other experiments,  $\mu$  and  $M_{\perp}$  can be obtained from Eq. (2.7) for  $k_{\perp} \neq 0, k_{||} = 0$ .

In concluding the section on the hydrodynamics of hexatic-*B*, we will briefly discuss the hydrodynamic aspects of a so far hypothetical nematic phase with additional bond-orientational order.<sup>21</sup> In this case, one has a uniaxial phase with three additional variables: The two director deviations  $\delta n_i$  from the preferred direction  $n_i^0$ , characterizing the broken rotational symmetries of a uniaxial nematic and, in addition, the bond angle  $\theta$  (rotations about  $n_i^0$ ). For the statics we refer to Ref. 21, but we only mention in passing that  $K'_4 = K'_6$ , via integration by parts, if the corresponding surface term vanishes (we use the notation of Ref. 21). For the reversible currents one finds a mere superposition of the results for uniaxial nematics<sup>3</sup> and for the bond angle in hexatic-*B*. For the irreversible currents, we get, in addition to the terms present in uniaxial nematics and hexatic-*B* (for the bond angle) a separate cross coupling in the entropy production which reads

$$(n_i \delta_{kj}^{\theta} + n_j \delta_{ik}^{\theta}) (\nabla_i \theta) (\nabla_j n_k).$$

### III. HYDRODYNAMICS OF SMECTIC-*F* AND -*I* LIQUID CRYSTALS

Smectic-*F* and -*I* are similar to hexatic-*B* with respect to the layer structure and the bond-orientational order within the layers. In contrast to hexatic-*B*, however, the molecule axes are, on average, not directed along  $\hat{p}^0$  (the layer normal), but are tilted away from  $\hat{p}^0$  by a tilt angle  $\Psi_0$ , i.e., there is a second preferred direction  $\hat{n}^0$  with  $\hat{n}^0 \cdot \hat{p}^0 = \cos\psi$ . This gives rise to a preferred direction within the layers  $\hat{c}^0$  which reads in normalized form

$$\hat{c}^0 = [\hat{n}^0 - \hat{p}^0 (\hat{p}^0 \cdot \hat{n}^0)] [1 - (\hat{p}^0 \cdot \hat{n}^0)^2]^{-1/2}.$$

$\hat{n}^0$  or  $\hat{c}^0$  break rotational invariance (about  $\hat{p}^0$ ) and  $\delta\vec{c}$

(with  $\hat{c}^0 \cdot \delta \vec{c} = 0 = \hat{p}^0 \cdot \delta \vec{c}$ ) is the appropriate hydrodynamic variable. This is a situation similar to smectic-C.<sup>1,3,16</sup> Alas, things are more complicated in smectic-F and -I. The bond-orientational order *also* breaks rotational invariance about  $\hat{p}^0$ .  $\delta \vec{c}$  and  $\delta \theta$  describe physically distinct operations: The former rotations of the long molecular axes about the centers of mass and the latter rotations of the bonds, i.e., of the centers of mass. In equilibrium, however, the bond-orientational order and the  $\hat{c}^0$  vector are locked together: Either  $\hat{c}^0$  is parallel to one bond orientation (smectic-F) or it is perpendicular to it (smectic-I). Thus, even a homogeneous rotation ( $\hat{p}^0 \times \hat{c}^0 \cdot \delta \vec{c} \neq 0$  with  $\delta \theta = 0$  (or a homogeneous rotation  $\delta \theta \neq 0$  with  $\delta \vec{c} = 0$ ) will produce a (homogeneous) restoring force. Only a combined rotation,  $\delta \theta + (\hat{p}^0 \times \hat{c}^0) \cdot \delta \vec{c}$ , is the true hydrodynamic variable connected with the broken rotational symmetry, while all other linear combinations of  $\delta \theta$  and  $(\hat{p}^0 \times \hat{c}^0) \cdot \delta \vec{c}$  are microscopic variables. If the homogeneous restoring force is weak, however, their motion will be slow and quasihydrodynamic. In the following we will take  $2\delta\theta \equiv \delta\theta + (\hat{p}^0 \times \hat{c}^0) \cdot \delta \vec{c}$  as a hydrodynamic variable and  $2\delta\phi \equiv \delta\theta - (\hat{p}^0 \times \hat{c}^0) \cdot \delta \vec{c}$  as a quasihydrodynamic (macroscopic) variable; in addition, there are, like in smectic-A, the other variables  $\rho$ ,  $\vec{g}$ ,  $\epsilon$  and  $\delta R$ .

The Gibbs relation takes then the form

$$T d\sigma = d\epsilon - \mu d\rho - \vec{v} \cdot d\vec{g} - \phi_j d(\nabla_j R) - \Psi_{ij} d(\nabla_i \nabla_j R) - \chi_i d(\nabla_i \theta) - h d\phi - \pi_j d(\nabla_j \phi). \quad (3.1)$$

Since the dynamics (and statics) involving the variables  $\epsilon(\sigma)$ ,  $\rho$ ,  $\vec{g}$ , and  $\delta R$  is (in structure) the same as in smectic-A or hexatic-B, we will not repeat the appropriate formulas in Sec. II. The only difference is the biaxiality in smectic-F and -I, which causes the material tensors  $K_{ijlm}$ ,  $\kappa_{ij}$ , and  $\nu_{ijlm}$  to be of a more complicated form.

We will concentrate in the following on the dynamics of  $\delta\theta$  and  $\delta\phi$ . For the statics symmetry allows

$$X_i = M_{ij} \nabla_j \theta + N_{ij} \nabla_j \phi, \quad (3.2)$$

$$h = B \delta \phi,$$

$$\pi_i = P_{ij} \nabla_j \phi + N_{ij} \nabla_j \theta,$$

which is equivalent to the free-energy contributions

$$f = f_A + \frac{1}{2} M_{ij} (\nabla_i \theta) (\nabla_j \theta) + \frac{1}{2} P_{ij} (\nabla_i \phi) (\nabla_j \phi) + N_{ij} (\nabla_i \phi) (\nabla_j \theta) + B (\delta \phi)^2, \quad (3.3)$$

where  $f_A$  is the free-energy part of the other variables and the susceptibility tensors  $M$ ,  $P$ , and  $N$  take the form<sup>22</sup>

$$U_{ij} = U_1 \hat{p}_i^0 \hat{p}_j^0 + U_2 \hat{c}_i^0 \hat{c}_j^0 + U_3 (\delta_{ij} - \hat{p}_i^0 \hat{p}_j^0 - \hat{c}_i^0 \hat{c}_j^0) + U_4 (\hat{c}_i^0 \hat{p}_j^0 + \hat{c}_j^0 \hat{p}_i^0). \quad (3.4)$$

The energy  $B(\delta\phi)^2$  expresses the fact that bond-orientational order and the direction  $\hat{c}^0$  cannot rotate freely against each other even in the limit  $k \rightarrow 0$ .

For the dynamics we find,

$$\begin{aligned} \dot{\theta} + Y &= 0, \\ \dot{\phi} + Z &= 0, \end{aligned} \quad (3.5)$$

with the reversible quasicurrents

$$\begin{aligned} Y^R &= -\hat{p}^0 \cdot \vec{\omega} + \frac{1}{2} (\alpha_1 \hat{c}_i^0 + \alpha_2 \hat{p}_i^0) (\hat{p}^0 \times \hat{c}^0)_k (\nabla_k v_l + \nabla_l v_k), \\ Z^R &= -\frac{1}{2} (\alpha_1 \hat{c}_i^0 + \alpha_2 \hat{p}_i^0) (\hat{p}^0 \times \hat{c}^0)_k (\nabla_k v_l + \nabla_l v_k). \end{aligned} \quad (3.6)$$

$Y^R$  shows the usual coupling to the antisymmetric gradients of  $\vec{v}$  ( $\vec{\omega}$ ), which comes from the physical nature of  $\delta\theta$  describing rotations about  $\hat{p}^0$ . Such a term is absent in  $Z^R$ , because  $\delta\phi$  describes a relative rotation, where such terms cancel. The coupling to the symmetric part of  $\nabla_u v_l$ , characterized by two reversible transport-parameters  $\alpha_1$  and  $\alpha_2$  (in nematics there is only one, usually called  $\lambda$ ), is due to the fact, that  $(\hat{p}^0 \times \hat{c}^0) \cdot \delta \vec{c}$  is the projection onto the component of the director  $\vec{n}$ , which is known to couple to the symmetrized velocity gradients even on the reversible level. The situation is quite similar to that in smectic-C, but different from that in hexatic-B, where  $\delta\theta$  was a pure rotation angle and where no  $\hat{c}^0$  axis was present.

Vanishing entropy production requires the following counter terms in the stress tensor

$$\begin{aligned} \sigma_{ij}^R &= -\frac{1}{2} \hat{p}_k^0 \epsilon_{kji} \nabla_l \chi_l - \frac{1}{2} (h + \nabla_l \chi_l - \nabla_l \pi_l) \\ &\quad \times [(\alpha_1 \hat{c}_i^0 + \alpha_2 \hat{p}_i^0) (\hat{c}^0 \times \hat{p}^0)_j + (i \leftrightarrow j)]. \end{aligned} \quad (3.7)$$

The dissipative parts of the currents are

$$\begin{aligned} Y^D &= -\mu_1 \nabla_i \chi_i + \mu_2 (h - \nabla_i \pi_i), \\ Z^D &= \tau (h - \nabla_i \pi_i) - \mu_2 \nabla_i \chi_i. \end{aligned} \quad (3.8)$$

Again, the term  $\tau h$  shows the nonhydrodynamic character of  $\delta\phi$ . Since  $\delta\theta$  couples not only to  $\vec{\omega} \cdot \hat{p}^0$  but to all components of the velocity and because of the biaxiality, the mode structure is very complicated and all variables are coupled together. Of course, there is one nonhydrodynamic relaxational mode with  $\omega(k \rightarrow 0) = i\tau B$  connected with  $\delta\phi$ . In general, there are two soundlike modes (except for certain directions of  $\vec{k}$ ), a heat-diffusion mode, and two coupled-diffusion modes (vorticity parallel to  $\hat{p}^0$ , and combined bond orientation and  $\vec{c}$  vector); the possibility that the latter can have a propagating part (as in hexatic-B) is suppressed in smectic-F and -I if  $\tau B$  is greater than the  $k$ -dependent hydrodynamic frequencies.

Aside from the analysis of the normal mode structure which can be detected, e.g., by light scattering or sound absorption, another possibility for future experiments emerges immediately from the basic equations for smectic-I and -F. Whereas it is clear from Eq. (2.5) that hexatic-B will not show flow alignment, such a possibility exists in the tilted phases I and F. From Eq. (3.6) we obtain

$$\alpha_1 = \frac{1}{\cos(2\theta)} \quad (3.9)$$

for  $\nabla_1 v_2 \neq 0$ , where  $\hat{p}^0$  has been chosen to be parallel to the three-direction, i.e., the layer normal. However, it is not quite clear whether this flow alignment is observable, since the degree of freedom, which is responsible for the effect (i.e., rotation of the molecules,  $\delta\theta$ ) is coupled to a rotation of the bond-orientational order  $\delta\phi$ . Equation (3.9) can only be obtained if  $\delta\theta$  and  $\delta\phi$  are decoupled. Flow alignment measurements could, therefore, give new

information on that coupling. Of course, if  $|\alpha_1| < 1$ , flow alignment cannot occur but tumbling can occur. The same conclusions follow for the phase discussed in Ref. 21.

It is obvious that the inclusion of the nonhydrodynamic variable  $\delta\phi$  into the set of macroscopic variables is somewhat arbitrary. At least in the vicinity of the phase transition to the hexatic-*B* phase, the tilt angle  $\psi$  (also a nonhydrodynamic variable) is also a good candidate of being a macroscopic variable. Thereby  $\psi$  couples reversibly

to  $(\hat{p}^0 \times \hat{c}^0) \cdot \vec{\omega}$  and has static and dynamic (dissipative) cross couplings with  $\delta\theta$  and  $\delta\phi$ . Such a treatment would go, however, beyond the scope of this paper.

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