# Dynamics of transient pattern formation in nematic liquid crystals

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We analyze the dynamics of a transient pattern formation in the Fréedericksz transition corresponding to a twist geometry. We present a calculation of the time-dependent structure factor based on a dynamical model which incorporates consistently the coupling of the director field with the velocity flow and also the effect of fluctuations. The appearance and development of a characteristic periodicity is described in terms of the time dependence of the maximum of the structure factor. We find a well-defined time for the appearance of the pattern and a subsequent stage of pattern development in which the characteristic periodicity tends to an asymptotic value.

#### I. INTRODUCTION

Pattern formation is an important problem which appears in a variety of nonequilibrium systems. An intriguing question regarding this problem is to determine the selected wave number which characterizes a periodicity in the pattern, and also the dynamics of the selection process. Different processes and selection mechanisms have been studied.<sup>1</sup> Most of these studies refer to the formation of a nonequilibrium but stationary pattern. A different problem concerns the formation of transient patterns which appear in the decay of unstable states. An interesting case in this context is the occurrence of transient spatial structures in the Fréedericksz transition in nematic liquid crystals. There is now broad experimental evidence of this phenomenon<sup>2-6</sup> which occurs when applying a magnetic field larger than a critical one to an initially homogeneous nematic sample. In this situation the director field is dynamically coupled to a velocity flow. Such coupling gives rise, during the transient process, to spatial domains with a well-defined periodicity. In these domains the director field reorientates in different but equivalent directions. The selection of a wave number is then associated with the dynamics of a symmetry breaking. This phenomenon has been observed both in thermo-tropics<sup>2,3,5</sup> and lyotropics<sup>3-6</sup> and in different geometries (twist,<sup>3,4</sup> splay,<sup>2,5</sup> and homeotropic to planar<sup>6</sup>). In the simplest cases the pattern consists in a collection of stripes perpendicular to the initial director.<sup>2-4</sup> Oblique<sup>5</sup> and two-dimensional<sup>6</sup> structures have also been observed.

The characteristic periodicity of a transient pattern has been described in terms of a most unstable mode:<sup>2-6</sup> A linear analysis of the equations of nematodynamics<sup>7,8</sup> around the initial configuration identifies one mode of fastest growth. It is assumed that this mode dominates the transient dynamics. Its characteristic wavelength is associated with the observed periodicity. The dependence of this wavelength with respect to the applied magnetic field seems to be in agreement with experimental observations. No theoretical description of the time scales associated with this process has been presented so far.

The analogy of this description with the Cahn-Hilliard theory of spinodal decomposition<sup>9</sup> has been noted:<sup>2,3</sup> During the early stages of a phase separation process, a transient interconnected spatial structure appears. A characteristic length of such structure is also associated, in the Cahn-Hilliard theory, with a most unstable mode. In the context of spinodal decomposition the fact that the most unstable mode is not the homogeneous one is due to the existence of a conservation law. In the Fréedericksz transition this is due to the coupling of the nonconserved director field with the velocity flow. The Cahn-Hilliard theory has several well-known shortcomings.9 Two related issues regarding this theory are the range of validity of such a linear theory, 10-12 and the need for including the effect of thermal fluctuations. In addition, the Cahn-Hilliard theory gives a time-independent characteristic wavelength. Therefore, it does not inform on the time dependence of the pattern formation process. These issues deserve attention also in the context of pattern formation in the Fréedericksz transition. A first step in this direction was the study in the twist geometry of transient orientational fluctuations for low magnetic field such that hydrodynamic effects can be neglected.<sup>13,14</sup>

The decay of an unstable state is triggered by initial fluctuations which are subsequently amplified. When this essential effect of fluctuations is taken into account, the range of validity of a linear theory can be estimated by an onset time which is mathematically defined as a mean first-passage time to leave the vicinity of an unstable state. Its magnitude is determined by the strength of fluctuations. This time is known to be too short to be accessible to experimentation in the case of spinodal decomposition of systems with short-range forces.<sup>9-12</sup> However, our previous calculation in the absence of hydrodynamic effects<sup>13,14</sup> indicates that this is not the case for the Fréedericksz transition. In addition, the calculation<sup>13</sup> of a time-dependent structure factor based on a dynamical model including fluctuations indicates the existence of well-separated stages of evolution. In this paper we use

these ideas in the case of pattern formation due to hydrodynamic coupling. Our aim is to describe the dynamical process of pattern formation identifying the different stages of evolution and, in particular, the time dependence of the characteristic periodicity starting from the homogeneous sample at the initial time.

Our study is based on the equations of stochastic nematodynamics. These are the equations of nematodynamics<sup>7,8</sup> supplemented consistently with thermal fluctuations which satisfy the appropriate fluctuation-dissipation relations. These equations are here presented with whole generality including the random term in a fully nonlinear situation. They provide a starting point for dynamical studies in different configurations and approximations. Our description of the dynamics of pattern formation is given in terms of the time-dependent structure factor for the orientation of the director. The position of the maximum is associated with the characteristic wavelength and its growth with pattern development. In this paper we restrict ourselves to the analysis of a twist geometry. The general equations of stochastic nematodynamics are specialized to this situation in a minimal coupling approximation. Our final results for the structure factor are obtained in a linear approximation which is seen to be reliable during the stages in which the pattern is formed. Our main result concerns the evolution of the position of the maximum of the structure factor. Initially the maximum is at a wave number  $Q_{\text{max}} = 0$ . At a well-defined time it moves rapidly to  $Q_{\max} \neq 0$ . This time is associated with the time of appearance of the pattern. In a subsequent stage of evolution, associated with the pattern development,  $Q_{\text{max}}$  tends slowly to an asymptotic value which is the most unstable mode of deterministic theories.<sup>2-6</sup> However, this asymptotic value is reached beyond the limit of validity of the linear theory.

The paper is organized as follows. In Sec. II the equations of stochastic nematodynamics are presented and discussed. Details of the construction of the dynamical model are given in the Appendix. Section III contains the specialization of these equations to the twist geometry. The effect of hydrodynamic coupling is seen to be accounted for by an effective wave-number-dependent viscosity which enters consistently in a fluctuationdissipation relation. In Sec. IV we present our calculation and discussion of results for the structure factor. Concluding remarks and an outlook are given in Sec. V.

## **II. STOCHASTIC NEMATODYNAMICS**

The equations of nematodynamics are based on ideas of nonequilibrium thermodynamics. Its standard formulation<sup>7,8</sup> does not include thermal fluctuations. We have already mentioned that fluctuations are essential to describe the initial stages of the decay of an unstable state. A more recent formulation<sup>5</sup> of linearized nematodynamics in terms of a Lagrangian density and a Rayleigh dissipation function also neglects fluctuations. Thermal fluctuations can be introduced in a linear regime following the ideas of the fluctuating hydrodynamics of Landau-Lifshitz.<sup>15</sup> Fluctuations can be introduced in a nonlinear formulation through a generalized time-dependent Ginzburg-Landau (TDGL) model of the sort used to study critical dynamics<sup>16</sup> and the dynamics of phase transitions.<sup>9,12</sup> These models feature Langevin dynamical equations which incorporate basic reversible and dissipative processes. The equations are such that the stationary distribution of the associated Fokker-Planck equation gives the equilibrium fluctuations in terms of the appropriate coarse-grained free energy. Given a set of relevant variables  $\phi_i(\mathbf{r},t)$  and the free-energy functional  $F[\phi(\mathbf{r})]$ , the Langevin equations have the following general form:<sup>17</sup>

$$\partial_t \phi_i(\mathbf{r}, t) = V_i(\boldsymbol{\phi}) - \mathcal{L}_{ij} \frac{\delta F[\boldsymbol{\phi}]}{\delta \phi_j} + \xi_i(\mathbf{r}, t) . \qquad (2.1)$$

 $V_i(\phi)$  includes nondissipative dynamical contributions. The second term on the rhs of (2.1) accounts for dissipative processes being  $\mathcal{L}_{ij}$  a set of generalized Onsager coefficients. The Gaussian random forces  $\xi_i(\mathbf{r}, t)$  account for thermal noise. The stationary solution of the Fokker-Planck equation associated with (2.1) for the probability density  $P_{st}[\phi]$  is

$$P_{st} = Ne^{-\beta F[\phi]}, \quad \beta = (k_B T)^{-1}$$
(2.2)

provided that the two following conditions are fulfilled: (i) Fluctuation-dissipation relations:

$$\langle \xi_i(\mathbf{r},t)\xi(\mathbf{r}',t')\rangle = 2k_B T \mathcal{L}_{ii}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$
. (2.3)

With this relation the Fokker-Planck equation reads<sup>18</sup>

$$\partial_{t} P[\phi] = -\int d\mathbf{r} \frac{\delta}{\delta\phi_{i}} (V_{i}(\phi) P[\phi]) + \int d\mathbf{r} \frac{\delta}{\delta\phi_{i}} \left[ \mathcal{L}_{ij} \frac{\delta F[\phi]}{\delta\phi_{j}} P[\phi] \right] + 2k_{B}T \int d\mathbf{r} \frac{\delta^{2}}{\delta\phi_{i}\delta\phi_{j}} (\mathcal{L}_{ij} P[\phi]) .$$
(2.4)

(ii) Nondissipative character of  $V_i(\phi)$ :

$$\int d\mathbf{r} \frac{\delta}{\delta \phi_i} (V_i(\boldsymbol{\phi}) e^{-\beta F[\boldsymbol{\phi}]}) = 0 .$$
(2.5a)

Sufficient conditions to fulfill (2.5a) are

$$\int d\mathbf{r} \frac{\delta V_i}{\delta \phi_i} = 0 , \qquad (2.5b)$$

$$\int d\mathbf{r} V_i(\boldsymbol{\phi}) \frac{\delta F[\boldsymbol{\phi}]}{\delta \phi_i} = 0 . \qquad (2.5c)$$

Equation (2.5b) can be interpreted as a generalized Liouville theorem in the sense that the velocity  $V_i(\phi)$  is divergence free in the phase-space spanned by the  $\phi_i$ . Equation (2.5c) indicates that  $V_i(\phi)$  does not contribute to the time derivative of the free energy F.

For the nematic phase the appropriate free energy is

$$F = \frac{1}{2} \int d\mathbf{r} K_{\alpha\beta\gamma\delta} \partial_{\beta} n_{\alpha} \partial_{\delta} n_{\gamma} - \frac{1}{2} \int d\mathbf{r} \chi_{a} (n_{\alpha}H_{\alpha})^{2} + \frac{1}{2} \int d\mathbf{r} \rho \mathbf{v}^{2} - \int d\mathbf{r} p(\mathbf{r}) \partial_{\alpha} u_{\alpha} .$$
(2.6)

The first term gives the Oseen-Frank distortion free energy<sup>7</sup> for the director field  $n_{\alpha}(\mathbf{r})$  with

$$K_{\alpha\beta\gamma\delta} = K_{11}(\delta_{\alpha\delta} - n_{\alpha}n_{\delta})(\delta_{\beta\gamma} - n_{\beta}n_{\gamma}) + K_{22}\epsilon_{\alpha\beta\mu}\epsilon_{\gamma\delta\nu}n_{\mu}n_{\nu} + K_{33}(\delta_{\alpha\gamma} - n_{\alpha}n_{\gamma})n_{\beta}n_{\delta} .$$
(2.7)

 $K_{11}$ ,  $K_{22}$ , and  $K_{33}$  are the elastic constants associated, respectively, with splay, twist, and bend deformations, and  $\epsilon_{\alpha\beta\mu}$  is the totally antisymmetric Levi-Civitta tensor. The second term gives the magnetic contribution,  $H_{\alpha}$ being the magnetic field and  $\chi_a$  the anisotropic part of the magnetic susceptibility. The third term is the hydrodynamic contribution,  $\mathbf{v}(\mathbf{r})$  being the velocity field and  $\rho$ the mass density. The last term introduces the pressure  $p(\mathbf{r})$  as a Lagrange multiplier for the incompressibility condition and the field  $u_{\alpha}(\mathbf{r})$  stands for the position of molecules.

A model of stochastic nematodynamics has to be of the form (2.1) for the independent variables n(r), v(r),

 $L_{\beta\gamma}(\mathbf{n}) = \partial_{\alpha} M_{\alpha\beta\delta\gamma}(\mathbf{n}) \partial_{\delta}$ ,

and  $\mathbf{u}(\mathbf{r})$  with the free energy (2.6). The nonstochastic part of (2.1)  $\partial_i \phi_i - \xi_i$ , has to coincide with the nonlinear deterministic equations of nematodynamics given by De Gennes.<sup>7</sup> The construction of such a stochastic model requires a detailed analysis of the dissipative and nondissipative contributions. This analysis is presented in the Appendix and it leads to the following equations:<sup>20</sup>

$$d_t n_{\beta} = -\frac{1}{\gamma_1} \frac{\delta F}{\delta n_{\beta}} + \Gamma_{\beta\gamma}(\mathbf{n}) \frac{\delta F}{\delta v_{\gamma}} + \xi_{\beta}(\mathbf{r}, t) , \qquad (2.8)$$

$$d_{t}v_{\beta} = L_{\beta\gamma}(\mathbf{n})\frac{\delta F}{\delta v_{\gamma}} - \Gamma^{\dagger}_{\beta\gamma}(\mathbf{n})\frac{\delta F}{\delta n_{\gamma}} - \frac{1}{\rho}\frac{\delta F}{\delta u_{\beta}} + \partial_{\alpha}\Omega_{\alpha\beta}(\mathbf{r},t) , \qquad (2.9)$$

$$d_{\iota}u_{\beta} = \frac{1}{\rho} \frac{\delta F}{\delta v_{\beta}} , \qquad (2.10)$$

where  $d_t$  is the total derivative including convective terms. The operators  $\Gamma_{\beta\gamma}$  and  $L_{\beta\gamma}$  are given by

$$\boldsymbol{M}_{\alpha\beta\gamma\delta}(\mathbf{n}) = \frac{1}{\rho^2} \left[ 2(\boldsymbol{v}_1 + \boldsymbol{v}_2 - 2\boldsymbol{v}_3)\boldsymbol{n}_{\alpha}\boldsymbol{n}_{\beta}\boldsymbol{n}_{\gamma}\boldsymbol{n}_{\delta} + \boldsymbol{v}_2(\delta_{\beta\delta}\delta_{\alpha\gamma} + \delta_{\alpha\delta}\delta_{\beta\gamma}) + (\boldsymbol{v}_3 - \boldsymbol{v}_2)(\boldsymbol{n}_{\alpha}\boldsymbol{n}_{\gamma}\delta_{\delta\beta} + \boldsymbol{n}_{\alpha}\boldsymbol{n}_{\delta}\delta_{\gamma\beta} + \boldsymbol{n}_{\beta}\boldsymbol{n}_{\gamma}\delta_{\delta\alpha} + \boldsymbol{n}_{\beta}\boldsymbol{n}_{\delta}\delta_{\gamma\alpha}) \right],$$
(2.12)

$$\Gamma_{\beta\gamma}(\mathbf{n}) = \frac{1}{2\rho} \left[ (\lambda+1)n_{\alpha}\partial_{\alpha}\delta_{\beta\gamma} + (\lambda-1)n_{\alpha}\partial_{\beta}\delta_{\alpha\gamma} \right] \,. \tag{2.13}$$

 $\lambda = -\gamma_2/\gamma_1$  and  $\gamma_1$ ,  $\gamma_2$ ,  $v_1$ ,  $v_2$ , and  $v_3$  are viscosity coefficients.<sup>7</sup> The adjoint operator  $\Gamma^{\dagger}$  is here in the sense of integration by parts and transposing matrix indexes. The operator L is self-adjoint  $L = L^{\dagger}$ . The noise sources  $\xi_{\beta}$  and  $\partial_{\alpha}\Omega_{\alpha\beta}$  are Gaussian white noise with zero mean and satisfy the following fluctuation-dissipation relations:

$$\langle \xi_{\beta}(\mathbf{r},t)\xi_{\gamma}(\mathbf{r}',t')\rangle = 2\frac{k_BT}{\gamma_1}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')\delta_{\beta\gamma}$$
, (2.14)

$$\langle \Omega_{\alpha,\beta}(\mathbf{r},t)\Omega_{\delta\gamma}(\mathbf{r}',t')\rangle = +2k_B T M_{\alpha\beta\delta\gamma}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t') , \qquad (2.15)$$

$$\langle \partial_{\alpha} \Omega_{\alpha\beta}(\mathbf{r},t) [\partial_{\delta} \Omega_{\delta\gamma}(\mathbf{r}',t')]^{\dagger} \rangle$$
  
=  $-2k_B T L_{\beta\gamma} \delta(\mathbf{r}-\mathbf{r}') \delta(t-t') .$  (2.16

Equations (2.8)-(2.10) exhibit the general structure of (2.1) but both dissipative and nondissipative terms  $(V_i)$  are given in terms of functional derivatives of the free energy F. The dissipative contributions  $-1/\gamma_1 \delta F/\delta n_\beta$  and  $L_{\beta\gamma}(\mathbf{n})\delta F/\delta v_\gamma$  include self-adjoint operators  $[-1/\gamma_1$  and  $L_{\beta\gamma}(\mathbf{n})]$  which are generalized Onsager coefficients. The random forces satisfy the appropriate fluctuation-dissipation relations involving these coefficients. It is important to note that  $L_{\beta\gamma}(\mathbf{n})$  depends on the instantaneous state of the director field so that  $\Omega_{\alpha\beta}$  is a multiplicative noise and the fluctuation-dissipation relation has a non-linear character.

The nondissipative contributions are also written in terms of functional derivatives of the free energy<sup>21</sup> but, as we shall see below, instead of Onsager coefficients they involve, as a whole, an antiadjoint operator. In order to ex-

amine the fulfillment of condition (2.5) for our Eqs. (2.8)-(2.10), we introduce the following self-explanatory notation:

$$V_{n\beta} = \dot{n} \, {}^{R}_{\beta} = \Gamma_{\beta\gamma}(\mathbf{n}) \frac{\delta F}{\delta v_{\gamma}} , \qquad (2.17)$$

$$V_{v_{\beta}} = \dot{v}_{\beta}^{R} + \dot{v}_{\beta}^{E} = -\Gamma_{\beta\gamma}^{\dagger}(\mathbf{n})\frac{\delta F}{\delta n_{\gamma}} - \frac{1}{\rho}\frac{\delta F}{\delta u_{\beta}} , \qquad (2.18)$$

$$V_{u_{\beta}} = \dot{u}_{\beta} = \frac{1}{\rho} \frac{\delta F}{\delta v_{\beta}} , \qquad (2.19)$$

where  $\dot{v}_{\beta}^{E} \equiv -(1/\rho)\delta F/\delta u_{\beta}$  is the term associated with the Ericksen tensor (see Appendix). Condition (2.5b) reads in this case

$$\int d\mathbf{r} \left[ \frac{\delta \dot{n} \frac{R}{\beta}}{\delta n_{\beta}} + \frac{\delta \dot{v} \frac{R}{\beta}}{\delta v_{\beta}} + \frac{\delta \dot{v} \frac{E}{\beta}}{\delta v_{\beta}} + \frac{\delta \dot{u} \frac{R}{\beta}}{\delta u_{\beta}} \right] = 0 . \qquad (2.20)$$

Each term in the bracket of (2.20) vanishes separately:  $\int d\mathbf{r} \delta \dot{n}_{\beta}^{R} / \delta n_{\beta}$  vanishes because of the incompressibility condition  $\partial_{\beta} v_{\beta} = 0$  and the other terms vanish trivially because  $\dot{v}_{\beta}^{R}$ ,  $\dot{v}_{\beta}^{E}$  do not depend on  $v_{\rho}$  and  $\dot{u}_{\beta}$  is independent of  $u_{\beta}$ . On the other hand, condition (2.5c) becomes for (2.8)-(2.10)

$$\int d\mathbf{r} \left[ \dot{n} \,_{\beta}^{R} \frac{\delta F}{\delta n_{\beta}} + \dot{v} \,_{\beta}^{R} \frac{\delta F}{\delta v_{\beta}} + \dot{v} \,_{\beta}^{E} \frac{\delta F}{\delta v_{\beta}} + \dot{u} \,_{\beta} \frac{\delta F}{\delta u_{\beta}} \right] = 0 \;.$$
(2.21)

Substituting the explicit form of the first two terms it is easy to see by a partial integration that they cancel ex-



FIG. 1. Schematic representation of the geometry of the nematic sample. Flows generated by oppositely rotating zones which explain the appearance of transient structures are also schematically displayed.

actly. The last two terms in (2.21) also cancel indentically. It is clear at this point the need for taking into account Eq. (2.10) for the variable u to get a consistent set of closed equations. Otherwise (2.21) would not be satisfied because the term in (2.9) associated with the Ericksen tensor would be unbalanced.

The general structure of dissipative and nondissipative terms involved in (2.8)-(2.10) becomes more explicit when these equations are written in the following compact form for a field  $\phi(r) = [\mathbf{n}(\mathbf{r}), \mathbf{v}(\mathbf{r}), \mathbf{u}(\mathbf{r})]$ :

$$d_i\phi_i = A_{ij}(\phi)\frac{\delta F}{\delta\phi_i} + \eta_i, \quad i = 1, 2, \dots, 9 , \qquad (2.22)$$

where

$$\boldsymbol{\eta} \equiv (\boldsymbol{\xi}, \partial_{\alpha} \Omega_{\alpha\beta}, \mathbf{0}) \ . \tag{2.23}$$

The operator A has a dissipative  $A^{D}$  and a nondissipative part  $A^{R}$ :

$$A_{ij}^{D} = -\mathcal{L}_{ij} = \begin{vmatrix} -\frac{1}{\gamma}I & 0 & 0\\ 0 & L & 0\\ 0 & 0 & 0 \end{vmatrix}, \quad (A_{ij}^{D})^{\dagger} = A_{ij}^{D} \qquad (2.24)$$

$$A_{ij}^{R} = \begin{vmatrix} 0 & \Gamma & 0 \\ -\Gamma^{\dagger} & 0 & -\frac{1}{\rho}I \\ 0 & \frac{1}{\rho}I & 0 \end{vmatrix}, \quad (A_{ij}^{R})^{\dagger} = -A_{ij}^{R} .$$
(2.25)

In (2.24) and (2.25) we use a block notation in which each matrix element represents a  $3 \times 3$  matrix and *I* is the identity matrix. Dissipative dynamics is associated with a self-adjoint operator  $A^{D}$  and the nondissipative dynamics with an antiadjoint operator  $A^{R}$ . The noise sources  $\eta_{i}$  satisfy fluctuation-dissipation relations with the dissipative part

$$\langle \eta_i(\mathbf{r},t)\eta_j^{\dagger}(\mathbf{r}',t')\rangle = -2k_B T A_{ij}^D \delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$
. (2.26)

The nondissipative part  $V_i$  of (2.1) is here

$$V_i = A_{ij}^R \frac{\delta F}{\delta \phi_i} , \qquad (2.27)$$

and condition (2.5c) becomes

$$\int d\mathbf{r} \left| A_{ij}^{R} \frac{\delta F}{\delta \phi_{j}} \right| \frac{\delta F}{\delta \phi_{i}} = 0 , \qquad (2.28)$$

which is an immediate consequence of the antiadjoint character of  $A_{ll}^{R}$ .

In summary, Eqs. (2.8)-(2.10) form a closed set of nonlinear equations in which thermal fluctuations are contained consistently and will reproduce the desired stationary distribution. These equations provide us with a starting point to study dynamical questions in different geometries and approximations.

#### III. MINIMAL COUPLING EQUATIONS IN TWIST GEOMETRY. EFFECTIVE VISCOSITY

In this paper we consider the twist geometry described in Fig. 1. The sample is contained between two plates perpendicular to the z axis. The director is initially aligned along the x axis  $[\mathbf{n}^0 = (1,0,0)]$  and the magnetic field is aligned along the y axis. We want to study the transient behavior of the system when the magnetic field is switched at t = 0 from an initial value  $H_i < H_c$  to a final value  $H > H_c$ . The physical picture of the formation of a transient pattern<sup>2-4</sup> is also indicated in Fig. 1. For  $\chi_a > 0$  the director tends to become parallel to the magnetic field. For strong fields the director reorientates locally in opposite but equivalent directions. This local symmetry breaking gives rise to macroscopic flows so that defect walls with a well-defined periodicity along the x axis are developed. Walls separate regions of different but equivalent orientations. The pattern appears then as a consequence of the dynamical coupling between the director and velocity fields.

With the above picture in mind we assume that there only exists macroscopic flow in the y direction so that  $v_x = v_z = 0$ . We also assume homogeneity in the y direction so that **n** and  $v_y$  are independent of the y coordinate. We finally assume that the director reorientates in the x-y plane:

$$n_{x}(x,z) = \cos\phi(x,z) ,$$
  

$$n_{y}(x,z) = \sin\phi(x,z) ,$$
  

$$n_{z} = 0 .$$
  
(3.1)

This assumption seems well suited to study transient be-

havior since the small initial equilibrium fluctuations of  $n_z$  remain stable, while fluctuations of  $n_x$  and  $n_y$  become unstable and they are macroscopically amplified in the transient process. Under the assumption of homogeneity in the y direction and velocity flows only in the same direction, the term associated with the Ericksen tensor in (2.9) vanishes. Even with these simplifications Eqs. (2.8) and (2.9) remain rather complicated. We use here a minimal coupling approximation in which the n dependence of  $\Gamma$  and L in (2.8) and (2.9) is approximated substituting **n** by  $\mathbf{n}^0$ . This procedure retains the initial coupling between  $\mathbf{n}$  and  $\mathbf{v}$  which is essential in the initial stages of evolution. On the other hand, the important nonlinearity associated with the director dynamics is kept through the dissipative term in (2.8). With all these approximations (2.8)-(2.10) convert into the following set of closed equations for  $\phi$  and  $v_{v}$ :

$$d_{t} \begin{bmatrix} \phi \\ v_{y} \end{bmatrix} = \begin{vmatrix} -\frac{1}{\gamma_{1}} & \frac{1}{2\rho} (1+\lambda) \partial_{x} \\ \frac{1}{2\rho} (1+\lambda) \partial_{x} & \frac{1}{\rho^{2}} (v_{2} \partial_{z}^{2} + v_{3} \partial_{x}^{2}) \end{vmatrix} \begin{bmatrix} \frac{\delta F}{\delta \phi} \\ \frac{\delta F}{\delta v_{y}} \end{bmatrix} + \begin{bmatrix} \xi \\ \partial_{x} \Omega_{yx} + \partial_{z} \Omega_{yz} \end{bmatrix}, \qquad (3.2)$$

where

$$\frac{\delta F}{\delta \phi} = -\left[K_{22}\partial_z^2 \phi + K_{33}\partial_x^2 \phi + \chi_a H^2(\phi - \frac{2}{3}\phi^3)\right], \quad (3.3)$$

and the Gaussian random forces satisfy the following fluctuation-dissipation relations: h T

(3.5)

with  $v_x \equiv v_3$ ,  $v_z = v_2$ , and L is the y linear dimension of the sample. [Summation over repeated indexes is not implied in (3.5).]

Equation (3.2) represents a particular and very clear example of utilization of the general scheme of Eqs. (2.22)-(2.25): Diagonal terms in (3.2) are the dissipative contributions given by a self-adjoint operator. Nondiagonal terms in (3.2) are the nondissipative contributions given by an antiadjoint operator. The variables  $\phi$  and  $v_y$ are decoupled in the dissipative dynamics. The dissipative part of the equation for  $\phi$  is the one studied in Ref. 13 describing transient dynamics of orientational fluctuations in the absence of hydrodynamic coupling. The dissipative part of the equation for  $v_y$  is just the Navier-Stokes equation for this particular geometry. The nondiagonal terms in (3.2) give the coupling between  $\phi$  and  $v_y$ needed to obtain a transient pattern. This coupling has a nondissipative character.

To proceed further we make the approximation of negligible inertia which is common in the literature.<sup>2-4</sup> In this approximation the director field is considered the

slow variable and the velocity field is assumed to follow the director instantaneously. This approximation enables us to obtain a closed equation for the deformation angle  $\phi$ . Setting  $\rho d_t v_y = 0$ , the equation for  $v_y$  in (3.2) can be written as

$$\eta_a \partial_z^2 v_y + \partial_x [\alpha_2 d_t \phi - \alpha_2 \xi(\mathbf{r}, t) + \eta_c \partial_x v_y] = -\rho (\partial_x \Omega_{yx} + \partial_z \Omega_{yz}), \quad (3.6)$$

where we have introduced Leslie and Meiscowitz coefficients according to their usual definition

$$\alpha_2 = -\frac{1}{2}\gamma_1(1+\lambda) , \qquad (3.7)$$

$$\eta_a = v_2 , \qquad (3.8)$$

$$\eta_c = v_3 + \frac{1}{4}\gamma_1(1+\lambda)^2 . \tag{3.9}$$

The closed equation for  $\phi$  is obtained solving (3.6) for  $v_y$ and substituting in the equation for  $\phi$  in (3.2). This elimination is more easily done introducing a Fourier transform. Assuming strong anchoring boundary conditions at  $z = \pm d/2$ , we take

$$\phi(x,z;t) = \sum_{m} \sum_{q_x} \theta_{m,q_x}(t) \cos(2m+1) \frac{\pi z}{d} e^{iq_x x} , \qquad (3.10)$$

$$\xi(x,z;t) = \sum_{m} \sum_{q_x} \xi_{m,q_x}(t) \cos(2m+1) \frac{\pi z}{d} e^{iq_x x} , \qquad (3.11)$$

$$\Omega_{y\alpha}(x,z;t) = \sum_{m} \sum_{q_x} \Omega^{\alpha}_{m,q_x}(t) \cos(2m+1) \frac{\pi z}{d} e^{iq_x x} ,$$
  
$$\alpha = x, z , \qquad (3.12)$$

The fluctuation-dissipation relations become

$$\langle \xi_{m,q_x}(t)\xi_{n,q'_x}(t')\rangle = 2\frac{2k_BT}{\gamma_1 V}\delta_{m,n}\delta_{q_x,-q'_x}\delta(t-t'), \quad (3.13)$$

$$\langle \Omega^{\alpha}_{m,q_x}(t)\Omega^{\alpha}_{n,q'_x}(t')\rangle = 2\frac{2k_BT}{\rho^2 V}v_{\alpha}\delta_{m,n}\delta_{q_x,-q'_x}\delta(t-t'),$$

$$\alpha = x,z, \quad (3.14)$$

where V is the volume of the sample:  $V = L^2 d$ .

The resulting equation for the amplitude  $\theta_{m,q_x}(t)$  can be written in the linear approximation for  $\delta F / \delta \phi$  as

$$\partial_t \theta_{m,q_x}(t) = \frac{1}{\overline{\gamma}_1} \left[ \chi_a H^2 - K_{22} (2m+1)^2 \frac{\pi^2}{d^2} - K_{33} q_x^2 \right] \\ \times \theta_{m,q_x}(t) + \eta_{m,q_x}(t) , \qquad (3.15)$$

where

$$\overline{\gamma}_1 = \gamma_1 - \frac{\alpha_2^2}{\eta_c + \eta_a Q^{-2}} , \qquad (3.16)$$

$$Q = \frac{q_x}{(2m+1)\frac{\pi}{d}} , \qquad (3.17)$$

 $\eta_{m,q_x}(t) \!=\! \xi_{m,q_x}(t)$ 

$$+\frac{\alpha_{2}\rho}{\gamma_{1}(\eta_{c}+\eta_{a}Q^{-1})-\alpha_{2}^{2}}[\Omega_{m,q_{x}}^{x}(t) -iQ^{-2}\Omega_{m,q_{x}}^{z}(t)].$$
(3.18)

 $\overline{\gamma}_1$  is an effective viscosity which depends on the wave number Q. The coupling of the director and velocity fields produces a reduction of the viscosity for all modes  $q_x \neq 0$ . This permits modes  $q_x \neq 0$  to grow faster than the homogeneous mode, giving rise to pattern formation. The complex random force  $\eta_{m,q_x}(t)$  is a linear combination of  $\xi_{m,q_x}(t)$  and  $\Omega^{\alpha}_{m,q_x}(t)$ . Therefore it is still Gaussian, of zero mean, and completely characterized by its correlation  $\langle \eta_{m,q_x}(t)\eta_{n,q'_x}(t') \rangle$ . It is easy to see from (3.13),(3.14), and (3.18) that this correlation function establishes a fluctuation-dissipation relation with the effective viscosity  $\overline{\gamma}_1$ 

$$\langle \eta_{m,q_x}(t)\eta_{n,q'_x}^*(t')\rangle = 2\frac{2k_BT}{\overline{\gamma}_1 V}\delta_{m,n}\delta_{q_x,q'_x}\delta(t-t')$$
. (3.19)

This relation makes clear the consistency of a description in terms of an effective viscosity. It would not be obtained if noise terms were forgotten in the equation for the velocity field. Actually (3.15) is the same than in the absence of hydrodynamic coupling but with an effective viscosity. The whole effect of the coupling between the director and velocity fields is then, under this approximation, the change of  $\gamma_1$  by  $\overline{\gamma}_1$ . This modification occurs both in the deterministic dynamics and also in the fluctuation-dissipation relations which characterizes thermal fluctuations [compare (3.13) and (3.19)]. The inclusion of nonlinear terms in (3.15) does not change the conclusion of a consistent description in terms of  $\overline{\gamma}_1$ . Here we restrict ourselves to the initial stages of pattern formation which, as discussed below, are well described by (3.15).

### IV. DYNAMICS OF PATTERN FORMATION: TIME-DEPENDENT STRUCTURE FACTOR

We describe the formation of transient periodic structures through the study of the dynamical evolution of the time-dependent structure factor  $C_{q_x,m}(t)$  $= \langle \theta_{m,q_x}(t)\theta_{m,-q_x}(t) \rangle$ . Starting with Eq. (3.15) for the amplitude  $\theta_{m,q_x}(t)$ , and using the fluctuation-dissipation relations (3.19), standard methods lead to the evolution equation for  $C_{q_x,m}(t)$ :

$$\partial_t C_{q_x,m}(t) = \frac{2}{\overline{\gamma}_1} \left[ \chi_a H^2 - K_{22} \left[ \frac{(2m+1)\pi}{d} \right]^2 - K_{33} q_x^2 \right] \\ \times C_{q_x,m}(t) + \frac{2}{\overline{\gamma}_1} \frac{2k_B T}{V} .$$
(4.1)

Equation (4.1) is analogous to the Cahn-Hilliard-Cook equation for studying spinodal decomposition.<sup>9,12</sup> The second term on the rhs of (4.1) accounts for thermal fluctuations disregarded in the Cahn-Hilliard theory. The stable and unstable modes are easily identified from (4.1). Unstable modes are those for which

$$\omega(q_x,m) = \frac{1}{\overline{\gamma}_1} \left[ \chi_a H^2 - K_{22} \left[ \frac{(2m+1)\pi}{d} \right]^2 - K_{33} q_x^2 \right] > 0.$$
(4.2)

Using (3.16) and the literature values<sup>22</sup> for MBBA at

room temperatures  $(\alpha_2^2/\gamma_1\eta_c = 0.74, \eta_a/\eta_c = 0.40)$  it is easy to see that  $\overline{\gamma}_1$  is always positive, with a maximum value  $\overline{\gamma}_1 = \gamma_1$  when  $q_x = 0$  and a minimum  $\overline{\gamma}_1 = 0.26\gamma_1$ for  $q_x \to \infty$ . This implies that the stability range of the different modes  $(q_x, m)$  remains unmodified with respect to the case without hydrodynamic coupling: For  $H > H_c = (K_{22}\pi^2/\chi_a d^2)^{1/2}$  we can have unstable modes in the z direction, more m modes becoming unstable the larger H is (For  $H_c < H < 3H_c$  only the m = 0 mode becomes unstable). In addition linear instability of the  $q_x$ modes is predicted whenever

$$\frac{\chi_a H_c^2}{K_{22}} \left[ \frac{H^2}{H_c^2} - (2m+1)^2 \right] > \frac{K_{33}}{K_{22}} q_x^2 .$$
(4.3)

Let us note from (4.2) that  $\omega(q_x,m)$  decreases monotonously with m, and as a consequence m = 0 is the most unstable z mode. However, due to the dependence of  $\overline{\gamma}_1$ on  $q_x$ ,  $\omega(q_x,m)$  is no longer a monotonously decreasing function of  $q_x$ . This is the crucial hydrodynamic effect here considered. As a direct consequence we will see that the maximum of the transient structure factor is not always associated with the homogeneous mode  $q_x = 0$ . To show this in more detail we rewrite the amplification factor  $\omega(q_x,m)$  as

$$\omega(q_x,m) = \frac{1}{\gamma_1 f(Q)} K_{22} \frac{(2m+1)^2 \pi^2}{d^2} \times \left[ h^2(m) - 1 - \frac{K_{33}}{K_{22}} Q^2 \right], \qquad (4.4)$$

where  $h^2(m)$  is the reduced magnetic field:  $h^2(m) = H^2/[(2m+1)^2H_c^2]$  and the lowering factor for the effective viscosity is

$$f(Q) = 1 - \frac{\overline{\alpha}}{1 + \overline{\eta}Q^{-2}} \tag{4.5}$$

with

$$\overline{\alpha} = \alpha_2^2 / \gamma_1 \eta_c, \quad \overline{\eta} = \eta_a / \eta_c \quad . \tag{4.6}$$

The mode of fastest response is obtained as a solution of  $d\omega/dQ=0$ . Physically acceptable solutions  $Q\neq 0$  exist if

$$h^{2}(m) > 1 + \frac{K_{33}}{K_{22}} \frac{\bar{\eta}}{\bar{\alpha}}$$
, (4.7)

with the chosen material parameters  $(K_{33}/K_{22}=2.5)$  it results in  $h^2(m) > 2.35$ .

Accepting that the fastest mode slaves other modes during the transient response one predicts the appearance of a periodic pattern for magnetic fields satisfying (4.7). This occurs for fields not much larger than the critical one  $h^2=1$ , although there still exists a range of fields for which the homogeneous response dominates.

Studying the time-dependent structure factor we can follow the emergence of those transient patterns starting with initial conditions corresponding to undistorted samples ( $H_i < H_c$ ). With the previous identifications and introducing a dimensionless time  $s = t / \tau_0(m)$ ,

$$\tau_0(m) = \frac{\gamma_1}{K_{22}} \frac{d^2}{\pi^2} \frac{1}{(2m+1)^2} = \frac{\gamma_1}{\chi_a H_c^2 (2m+1)^2} , \qquad (4.8)$$

Eq. (4.1) becomes

$$\frac{d}{ds}C_{q_x,m}(s) = \frac{2}{f(Q)} \left[ h^2(m) - 1 - \frac{K_{33}}{K_{22}}Q^2 \right] C_{q_x,m}(s) + \frac{2}{f(Q)}\epsilon(m) , \qquad (4.9)$$

where

$$\epsilon(m) = 2 \frac{k_B T}{V} \frac{1}{\chi_a H_c^2 (2m+1)^2} .$$
(4.10)

Solving for  $C_{q_x,m}(s)$  we obtain

$$C_{q_{x},m}(s) = C_{q_{x},m}(0)e^{2/f(Q)[h^{2}(m)-1-K_{33}/K_{22}Q^{2}]s} + \frac{\epsilon(m)}{(h^{2}(m)-1-\frac{K_{33}}{K_{22}}Q^{2})} \times (e^{2/f(Q)[h^{2}(m)-1-K_{33}/K_{22}Q^{2}]s} - 1), \quad (4.11)$$

where the initial conditions for  $H_i < H_c$  are consistently obtained as a stationary solution of (4.1),

$$C_{q_x,m}(0) = \frac{\epsilon(m)}{1 + \frac{K_{33}}{K_{22}}Q^2 - \frac{H_i^2}{(2m+1)^2 H_c^2}} .$$
 (4.12)

Equation (4.11) describes the growth of the unstable modes responsible for the Fréedericksz transition. A consistent treatment of fluctuations is essential in the study of the initial growth right after the time the system begins to feel the instability. Fluctuations appear in (4.11) through the consistent initial conditions and also through the effects of thermal noise during the evolution. These are taken into account by the last term on the rhs of (4.9). At s = 0 initial conditions dominate and the homogeneous mode  $q_x = 0$  is preponderant. During an initial stage, initial conditions and the constant noise term in (4.11) are important, but, as time goes on, the growth of the structure factor will be largely dominated by the exponential factor. In this way the structure factor will be eventually dominated by the mode of fastest growth. The analysis of (4.11) enables us to elucidate the way this is accomplished and also to calculate the time scales associated with pattern formation. This is seen in Figs. 2-5 where we have plotted  $C_{q_{\chi},m}$  versus  $Q^2 = [q_x/(2m+1)\pi/d]^2$  at different times for the most unstable z mode m = 0. We observe an initial condition peaked at Q = 0 which grows. At a well-defined time a maximum at a  $Q_{\max} \neq 0$  appears. This maximum grows and moves to the right tending to the asymptotic value which maximizes  $\omega(q_x, 0)$ . The value  $Q_{\text{max}}$  of the maximum characterizes the spatial periodicity. The displacement of  $Q_{\text{max}}$  describes the dynamical emergence of the pattern from the initially homogeneous sample. The growth of the peak describes the development of the pattern. The effect of varying initial and final magnetic fields is seen in Figs. 4 and 5. When decreasing the initial magnetic field, the growth of the peak of the structure factor is faster but less intense. On the other hand, when the final field increases, the development of a maximum at a  $Q \neq 0$  occurs earlier, in our case by an order of magnitude. In addition the peak is much more pronounced when comparing same values of  $C_{q_x,m}$  and it also affects a larger range of values of Q.

The dynamical emergence of the pattern is better depicted plotting  $Q_{max}$  versus time as we do in Figs. 6 and 7. Different and well-separated time scales can be distinguished in these figures. A first well-defined time corresponds to the sharp increase of  $Q_{\max}$  when the system takes off from the initial conditions and  $C_{q_x,m}$  starts to grow exponentially. This time is associated with the characteristic time at which the periodic pattern appears. It is seen in Fig. 7 that pattern appearance occurs earlier when increasing  $h^2$  by an order of magnitude for the chosen parameters. A second time scale can be identified in Figs. 6 and 7 corresponding to the slow growth of  $Q_{max}$ . In this stage of evolution, after the initial sharp growth,  $Q_{\text{max}}$  tends asymptotically to the value which maximizes  $\omega(q_x, m=0)$ . It seems reasonable to associate this time scale with the formation and development of the spatial pattern after its nearly instantaneous appearance. From our analysis we conclude that this time scale elapses for one order of magnitude after the emergence of the pattern. It is important to note that the asymptotic value of  $Q_{\max}$  is the one characterizing the periodic structure in a deterministic



FIG. 2. Structure factor  $C_{q_x,m=0}$  vs  $Q^2$  at different times. Parameter values correspond to 4-methoxybenzyledene-4-(n-butyl)aniline (MBBA) at room temperatures (see text) with  $h_i^2=0.5$  and  $h^2=5$ . Times are measured in units of  $\tau_0 \sim 10$  sec. The asymptotic value of  $Q^2$  which maximizes  $\omega(q_x,m=0)$  is depicted.



FIG. 3. Same as Fig. 2.



FIG. 4. Structure factor  $C_{q_x,m=0}$  vs  $Q^2$  at different times for different initial conditions  $(h_i^2=0)$  than in Figs. 2 and 3.

analysis.<sup>2-6</sup> In our approach the periodicity is characterized by the maximum of the structure factor which is time dependent in a nontrivial manner. This time dependence has been obtained through a consistent dynamical analysis of the role of fluctuations. The periodicity predicted in a deterministic analysis is only

reached after very long times which are, as we will discuss below, beyond the range of validity of the linear approximation. Indeed, during the last part of the second time scale referred above, nonlinear contributions may become important. In our stochastic analysis we can use the mean first-passage time (MFPT) T to estimate the or-



FIG. 5. Structure factor  $C_{q_x,m=0}$  vs  $Q^2$  at different times under a stronger magnetic field  $(h^2 = 40)$  than in Figs. 2 and 3.

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der of magnitude of the limit of validity of a linear approximation. This criterion was analyzed in some detail in Refs. 13 and 14. Physically T measures the time taken by the system to leave the vicinity of the unstable state. In the dimensionless time scale of s we have for m = 0

 $T \simeq \frac{1}{\frac{2}{f(Q)} \left[h^2 - 1 - \frac{K_{33}}{K_{22}}Q^2\right]} \ln\left[\frac{1}{2\epsilon}\right].$  (4.13)

For a typical sample  $(S = 1 \text{ cm}^2, d = 10^{-2} \text{ cm})$ ,



FIG. 7 Maximum of the structure factor corresponding to Fig. 5 vs time.

 $\tau_0 \sim 10_{\rm sec}$ , so that in the laboratory time units we find  $T \simeq 25$  sec. for  $h^2 = 5.^{23}$  According to Fig. 6 one can see that a periodic pattern appears at time  $t \simeq 4$  sec., and develops continuously being well structured at time  $T \simeq 25$ sec. From then on, linear theory is not reliable but according to our analysis the linear approximation should give a good description of practically the whole process of formation of the structure. However, and we would like to stress this point, the asymptotic  $Q_{max}$ , this is the deterministic predicted value, is not reached within this time domain. For t > T more complicated effects responsible for the mobility and recombination of defect walls should eventually be considered to account for the final destruction of these transient patterns. A theory based on defect dynamics seems better suited to study this final stage of evolution.

We conclude by noting that the existence of wellseparated stages of evolution corresponding to appearance, formation, and decay of transient patterns, which we have found, is in agreement with experimental observation.<sup>4</sup> Our estimates for the time scales involved are also consistent with experimental values<sup>3</sup> but detailed data on these time scales do not seem to be available yet in the literature.

#### V. CONCLUSIONS AND OUTLOOK

We have seen how the consistent introduction of fluctuations permits us to describe dynamical aspects of the process of pattern formation. In particular we have found the time scale associated with the emergence of the pattern and a subsequent stage of pattern development. These time scales are of experimental relevance and seem to be well described within a linearized theory which in other related situations have a range of validity not accessible to experimentation. We hope that our results will encourage more precise measurements of the time development of those transient patterns. It is clear that the same methods used here can be applied to other experimental situations with more complicated patterns than those considered here.<sup>5,6</sup> A different question is the description of the decay of these structures which probably requires a modeling based on defect dynamics.

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#### APPENDIX

In this appendix we give some details of the construction of the dynamical model (2.8)-(2.10). Following the presentation by De Gennes<sup>7</sup> and starting from the free energy (2.6), the dissipation for an isothermal process is written as

$$T d_{\iota} S = \int d\mathbf{r} [(\sigma_{\alpha\beta} - \sigma^{E}_{\alpha\beta})\partial_{\alpha}v_{\beta} + h_{\alpha}\dot{n}_{\alpha}], \qquad (A1)$$

where the molecular field  $h_{\alpha}$  is

$$h_{\alpha} = -\frac{\delta F}{\delta n_{\alpha}} \quad . \tag{A2}$$

 $\sigma_{\alpha\beta}$  is the total stress tensor and  $\sigma_{\alpha\beta}^E$  is the Ericksen stress tensor associated with variations of the free energy caused by displacements of molecules in which the director field is kept fixed (see Ref. 7, Sec. 3.5). One obtains

$$\sigma^{E}_{\alpha\beta} = -\frac{\partial F_d}{\partial(\partial_{\alpha}n_{\gamma})}\partial_{\beta}n_{\gamma} - p\delta_{\alpha\beta} , \qquad (A3)$$

where  $\overline{F}_d$  is the free-energy density in (2.6) associated with distortions. Also

$$-\partial_{\alpha}\sigma^{E}_{\alpha\beta} = \frac{\delta F}{\delta u_{\beta}} . \tag{A4}$$

Identifying the symmetric and antisymmetric parts of  $\sigma'_{\alpha\beta} = \sigma_{\alpha\beta} - \sigma^E_{\alpha\beta}$  and  $\partial_{\alpha}v_{\beta}$ , (A1) is rewritten as

$$T d_{t}S = \int d\mathbf{r} (A_{\alpha\beta}\sigma_{\alpha\beta}^{s} + h_{\alpha}N_{\alpha}) , \qquad (A5)$$

where  $\sigma_{\alpha\beta}^s$  is the symmetric part of  $\sigma'_{\alpha\beta}$  and  $A_{\alpha\beta}$  is the symmetric part of the shear flow tensor  $\partial_{\alpha}v_{\beta}$ . The antisymmetric part of  $\sigma'_{\alpha\beta}$  is given by an axial vector  $\Gamma = \mathbf{n} \times \mathbf{h}$ , and the antisymmetric part of  $\partial_{\alpha}v_{\beta}$  is associated with the vorticity  $\boldsymbol{\omega}$ . These antisymmetric parts combine with  $\dot{n}_{\alpha}$  in (A1) to give  $N_{\alpha}$ 

$$N_{\alpha} = d_{t} n_{\alpha} - (\boldsymbol{\omega} \times \mathbf{n})_{\alpha} . \tag{A6}$$

We will now invoke the interpretation of (A5) in terms of a product of fluxes and forces. The basic idea behind the modeling of the dissipative terms in the TDGL models (2.1) is to extend Onsager's procedure beyond the linear domain. Fluxes are still written as a combination of forces, but forces are functional derivatives of a free energy which now, in general, is not quadratic, and the coefficients of the combinations are not constant. Since  $\sigma_{\alpha\beta}^s$  is a flux in the equation for the velocity and  $N_{\alpha}$  is related to  $\dot{n}_{\alpha}$ , we interpret  $\sigma_{\alpha\beta}^s$  and  $N_{\alpha}$  as fluxes. We write the fluxes as combinations of the forces  $A_{\alpha\beta}$  and  $h_{\alpha}$  which are given by functional derivatives of the free energy (2.6)<sup>24</sup>

$$\sigma_{\alpha\beta}^{s} = R_{\alpha\beta\gamma\delta}(\mathbf{n})A_{\gamma\delta} + Q_{\alpha\beta\gamma}(\mathbf{n})h_{\gamma} , \qquad (A7)$$

$$N_{\alpha} = Q'_{\alpha\beta\gamma}(\mathbf{n}) A_{\beta\gamma} + P_{\alpha\beta}(\mathbf{n}) h_{\beta} .$$
 (A8)

The form of the coefficients R, Q, Q', and P is obtained in the usual way<sup>7</sup> imposing symmetry conditions and the requirements for incompressible flows. With these coefficients (A8) gives the evolution equation for the director. The equation for the velocity is obtained from (A7) taking into account the antisymmetric part of  $\sigma'_{\alpha\beta}$ and  $\sigma^{E}_{\alpha\beta}$ . We have

$$d_{I}n_{\beta} = \frac{1}{\gamma_{1}}h_{\beta} + \lambda n_{\alpha} A_{\alpha\beta} + (\boldsymbol{\omega} \times \mathbf{n})_{\beta}$$
$$= \frac{1}{\gamma_{1}}h_{\beta} + \frac{\lambda - 1}{2}n_{\alpha}\partial_{\beta}v_{\alpha} + \frac{\lambda + 1}{2}n_{\alpha}\partial_{\alpha}v_{\beta} , \quad (A9)$$

$$\rho d_t v_\beta = \partial_\alpha (\sigma^s_{\alpha\beta} + \sigma^a_{\alpha\beta} + \sigma^E_{\alpha\beta}) , \qquad (A10)$$

where

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$$\sigma_{\alpha\beta}^{s} = 2v_2 A_{\alpha\beta} + 2(v_1 + v_2 - 2v_3)n_{\alpha}n_{\beta}n_{\mu}n_{\rho} A_{\mu\rho}$$

$$+2(\nu_3-\nu_2)(n_{\alpha}n_{\mu}A_{\mu\beta}+n_{\beta}n_{\mu}A_{\mu\alpha})$$

$$-\frac{\kappa}{2}(n_{\alpha}h_{\beta}+n_{\beta}h_{\alpha}), \qquad (A11)$$

$$\sigma^a_{\alpha\beta} = \frac{1}{2} (n_\beta h_\alpha - n_\alpha h_\beta) , \qquad (A12)$$

$$\sigma^{E}_{\alpha\beta} = -p \delta_{\alpha\beta} - K_{\gamma\alpha\mu\delta} \partial_{\delta} n_{\mu} \partial_{\beta} n_{\gamma} . \qquad (A13)$$

The first term on the rhs of (A9) gives the director dynamics in the absence of hydrodynamic effects. The last two terms arise from coupling of the director and velocity fields. Likewise, the term proportional to  $v_2$  in (A11) and the pressure term in (A13) give the Navier-Stokes equation in (A10). Other terms in (A10) are coupling terms. In order to write our equations in the general form (2.1) it is necessary to identify which of these coupling terms are dissipative and which are not.<sup>25</sup> Random forces will then be included as Gaussian white noise of zero mean satisfying a fluctuation-dissipation relation with the dissipative terms. This identification is more easily done when the rhs of (A9) and (A10) are written in terms of  $\delta F / \delta n_{\beta}$ ,  $\delta F / \delta v_{\beta}$ , and  $\delta F / \delta u_{\beta}$  as in (2.8)–(2.10) Equations (A9) and (A10) are rewritten as the deterministic part of (2.8) and (2.9) using (A2)-(A4) and not-

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ing that

$$\frac{\lambda - 1}{2} n_{\alpha} \partial_{\beta} v_{\alpha} + \frac{\lambda + 1}{2} n_{\alpha} \partial_{\alpha} v_{\beta} = \Gamma_{\beta\gamma}(\mathbf{n}) \frac{\delta F}{\delta v_{\gamma}} , \quad (A14)$$

$$\partial_{\alpha} \left| \sigma_{\alpha\beta}^{s} + \frac{\lambda}{2} (n_{\alpha}h_{\beta} + n_{\beta}h_{\alpha}) \right| = \rho L_{\beta\gamma}(\mathbf{n}) \frac{\delta F}{\delta v_{\gamma}} , \quad (A15)$$

$$\partial_{\alpha} \left[ \sigma^{s}_{\alpha\beta} - \frac{\lambda}{2} (n_{\alpha}h_{\beta} + n_{\beta}h_{\alpha}) \right] = -\rho \Gamma^{\dagger}_{\gamma\rho} \frac{\delta F}{\delta n_{\gamma}} \,. \tag{A16}$$

(A14) contains the coupling terms in (A9). It is shown in Sec. II that (A14) combined with (A16) is nondissipative in the sense that (2.5) is satisfied. (A16) contains  $\sigma_{\alpha\beta}^{a}$  and also the terms proportional to  $\lambda$  of  $\sigma_{\alpha\beta}^{s}$ . Therefore, a term of the symmetric part of the stress tensor does not contribute to dissipation. The term associated with the Ericksen tensor in (A10) is also nondissipative, as shown in Sec. II, taking into account the equation for  $n_{\alpha}$ . In summary, the dissipative terms are  $(1/\gamma_1)h_{\beta}$  in the equation for the director, and the coupling term (A15) in the equation for the velocity. Other coupling terms are nondissipative. It is now an easy matter to include random forces balancing those dissipative terms. These are  $\xi_{\rho}$  and  $\partial_{\alpha}\Omega_{\alpha\beta}$  in (2.8) and (2.9) satisfying the fluctuation-dissipation relations (2.14)-(2.16).

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