Time-dependent Landau theory for the smectic-A–nematic phase transition

W. L. McMillan*
Department of Physics, and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
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A time-dependent Landau theory is proposed for the smectic-A–nematic phase transition. It is shown that the nematic viscosity coefficients exhibit a pretransition effect similar to that for the elastic constants.

I. INTRODUCTION

According to the microscopic theory,[1,2] the smectic-A–nematic phase transition is expected to be second order when the temperature range of the nematic phase is large. Second-order transitions have now been observed[3,4] for several materials. deGennes[5] and this author[6] have written down a Landau theory for this transition, and deGennes predicted a pretransition increase in the twist and bend elastic constants of the nematic phase. This effect has been observed[7-9] in a number of laboratories. It has, of course, been known for a long time that the cholesteric helix unwinds at the smectic-A-cholesteric transition as a result of stiffening of the twist elastic constant.

There has been some recent theoretical work on the dynamics of the smectic-A–nematic transition by Brochard[10] and by Kobayashi.[11] Light-scattering experiments are in progress at Orsay and by the author to measure some of the relaxation times. Mieboom[12] has recently observed a pretransition increase in one of the nematic viscosity coefficients (γ_1) using the Tsvetkov method.[13]

In this paper, we examine the pretransition effects on the viscosity coefficients theoretically in order to explain Mieboom's results and to provide a theoretical framework for the interpretation of the light-scattering experiments. We will extend the Landau theory to a time-dependent Landau theory in the usual way by adding a viscous time-dependent term. The smectic-A order parameter is coupled to the nematic director and one must incorporate the Leslie-Erickson nematic hydrodynamics[14-15] to describe the time dependence of the director. Having written down the theory, we can then calculate the effective viscosity coefficients in the nematic phase, taking into account thermal fluctuations of the smectic order parameter. We find pretransition effects in the rotational viscosity (γ_1), the shear alignment viscosity (γ_2), and in one of the anisotropic liquid viscosities (η_1^M).

After this work was completed, I learned of a similar but more sophisticated calculation by Janig and Brochard,[16] who used a linear-response method assuming restricted dynamical scaling[17] for the smectic order parameter. The present work was intended to provide a simple physical explanation of the pretransition effect and was carried out using the mean-field approximation. The present results agree with those of Janig and Brochard if we use the dynamical scaling assumption for the smectic viscosity coefficient.

II. TIME-DEPENDENT LANDAU THEORY

We will assemble the theory from various known parts. We begin with the free energy as a function of the smectic order parameter ψ and the nematic director $\vec{n}$.

$$F = \int d^3r \{A(T)\psi^2 + \tfrac{1}{2}B\psi^4 + C_\parallel |(\vec{n}\cdot\vec{\nabla} - iq_0)\psi|^2 + C_\perp |\vec{n}\times\vec{\nabla}\psi|^2 + \tfrac{1}{2}K_{11}(\vec{\nabla}\cdot\vec{n})^2 + \tfrac{1}{2}K_{22} \times [\vec{n}\cdot(\vec{\nabla}\times\vec{n})]^2 + \tfrac{1}{2}K_{33}[\vec{n}\times(\vec{\nabla}\times\vec{n})]^2 - \chi_a(\vec{n}\cdot\vec{H})^2\} . \quad (1)$$

$\psi(r)$ is a complex scalar order parameter describing the density wave in the smectic-A phase. The particle density is given by

$$\rho(r) = \rho_0\{1 + \mathrm{Re}[\psi(r)]\} . \quad (2)$$

The parameter A is usually assumed to vary linearly with temperature and the other parameters are temperature independent. If one then treats the order-parameter fluctuations as a perturbation, as we will do in this paper, one obtains classical exponents for various physical properties near the critical temperature. In order to obtain the proper critical exponents one must treat the order-parameter fluctuations in a nonperturbative way. However, deGennes has shown that one can assume that

$$A(T) = A_0(T - T_c)^\gamma \quad (3)$$

in the nematic phase and obtain approximate critical exponents perturbatively. Equation (3) will be used in this paper. The director $n(\vec{r})$ is a unit vector pointing in the direction of the local optical

axis. The local torque acting on the director is described by a molecular field[18]

$$\vec{h} = -\frac{\partial F}{\partial \vec{n}} , \tag{4}$$

where the torque is $\vec{n}\times\vec{h}$. The generalized force acting on the smectic order parameter is

$$g = -\frac{\partial F}{\partial \psi} . \tag{5}$$

We now include the Leslie-Erickson hydrodynamics to describe the dynamics of the director. The frictional torque acting on the director is written as

$$\Gamma = \vec{n}\times\left[\gamma_1^0\left(\frac{d\vec{n}}{dt} - \vec{\omega}\times\vec{n}\right) + \gamma_2^0 \hat{A}\vec{n}\right] , \tag{6}$$

where $\vec{\omega} = \frac{1}{2}\vec{\nabla}\times\vec{v}$ is the local rotational velocity of the fluid, $\hat{A}$ is the shear rate tensor

$$A_{ij} = \frac{1}{2}\left(\frac{\partial v_j}{\partial x_i} + \frac{\partial v_i}{\partial x_j}\right) , \tag{7}$$

and $\vec{v}$ is the local fluid velocity. Neglecting the rotational kinetic energy one sets the frictional torque equal to the elastic torque

$$\vec{\Gamma} = \vec{n}\times\vec{h} . \tag{8}$$

The director motion is coupled to the fluid motion and the Leslie-Erickson expression for the stress tensor is

$$\begin{aligned}\sigma'_{ij} = {} & \alpha_1 n_k n_p A_{kp} n_i n_j + \alpha_2 n_i N_j + \alpha_3 n_j N_i \\ & + \alpha_4 A_{ij} + \alpha_5 n_i n_k A_{kj} + \alpha_6 n_j n_k A_{ki} ,\end{aligned} \tag{9}$$

where

$$\vec{N} = \frac{d\vec{n}}{dt} - \vec{\omega}\times\vec{n}$$

and the equation of motion is

$$\rho\frac{dv_i}{dt} = \frac{\partial}{\partial x_i}(\sigma'_{ji} + p\delta_{ij}) + f_i , \tag{10}$$

where ρ is the fluid density and p is the pressure. The local force density due to the viscous drag of the smectic order parameter on the fluid is

$$\vec{f} = -\tfrac{1}{2}\gamma_3\vec{\nabla}\psi\left(\frac{\partial\psi^*}{\partial t} + \vec{v}\cdot\vec{\nabla}\psi^*\right) + (\text{c.c.}) . \tag{11}$$

Using the local torque

$$\Gamma_z = -\sigma_{xy} + \sigma_{yx} \tag{12}$$

and an Onsager relation, one finds

$$\begin{aligned}\gamma_1 &= \alpha_3 - \alpha_2 , \\ \gamma_2 &= \alpha_6 - \alpha_5 = \alpha_2 + \alpha_3 ,\end{aligned} \tag{13}$$

so that there are five independent viscous parameters in the Leslie-Erickson hydrodynamics. It is convenient to define the Miesowicz[19] viscosities which are the anisotropic liquid viscosities measured with the director held fixed (η_1^M measured with the director parallel to the flow direction, η_2^M measured with the director parallel to the velocity gradient, and η_3^M measured with the director perpendicular to both the flow direction and the velocity gradient). In terms of the α's and γ's, one finds[20]

$$\begin{aligned}\eta_1^M &= \tfrac{1}{2}[\alpha_4 + \alpha_5 - (\gamma_2/\gamma_1)\alpha_2] + (\gamma_1+\gamma_2)^2/4\gamma_1 , \\ \eta_2^M &= \eta_1^M - \gamma_2 , \quad \eta_3^M = \tfrac{1}{2}\alpha_4 .\end{aligned} \tag{14}$$

It is convenient to take γ_1, γ_2, η_1^M, and η_3^M as four independent parameters. The fifth, which enters only in measurements along low-symmetry directions, will not be discussed here.

The above theories have been borrowed from various sources and are all well known. The only addition we wish to make is to include the relaxation of the smectic order parameter by writing down the relevant time-dependent Landau equation:

$$\begin{aligned}\gamma_3\frac{D\psi}{Dt} &\equiv \gamma_3\left(\frac{\partial\psi}{\partial t} + \vec{v}\cdot\vec{\nabla}\psi\right) , \\ &= -\frac{\partial F}{\partial \psi^*} .\end{aligned} \tag{15}$$

The time derivative on the left is taken in the reference frame moving with the liquid. The γ_3 relaxation process describes the motion of the smectic planes relative to the background liquid and this involves diffusion of molecules from one smectic plane to the next. We have inserted the appropriate viscous term in (10).

The parameter γ_3 is a viscosity and is expected to have the magnitude and temperature dependence of an ordinary liquid viscosity outside the critical region. We make contact with Ref. 17 by using dynamical scaling arguments for γ_3 using the analogy to the λ transition. The smectic order-parameter relaxation time $\tau_0 = \gamma_3/4A$ is proportional to $\xi^{3/2}$, where $\xi \sim A^{-1/2}$ is the coherence length. Thus $\gamma_3 \sim \xi^{-1/2}$ in the critical region.

III. NEMATIC VISCOSITY COEFFICIENTS

In this section, we compute the effective viscosity coefficients in the nematic phase near the smectic-A–nematic phase transition. We will show that there is a pretransition increase in the viscosity coefficients in addition to the pretransition increase in the elastic constants found by deGennes.

We begin by considering the effect of a moving director on the thermal fluctuations of the smectic order parameter. We first write $\psi(\vec{r})$ as a Fourier

series in a box of unit volume:

$$\psi(\mathbf{r}) = \sum_q \psi_q e^{i\vec{q}\cdot\vec{r}} \ . \tag{16}$$

With the fluid at rest and in the nematic phase, the time-dependent Landau equation for ψ_q is

$$\frac{\partial \psi_q}{\partial t} = \frac{-2}{\gamma_3}\left[A + C\ (\vec{n}\cdot\vec{q} - q_0)^2 + C_\perp(\vec{n}\times\vec{q})^2\right]\psi_q + g_q(t) \ , \tag{17}$$

where $g_q(t)$ represents the coupling of the smectic order parameter to a thermal reservoir. The function $g_q(t)$ is a Gaussian distributed random variable which drives the thermal fluctuations of ψ. We consider the case where $\vec{n}$ is uniform in space and rotates with a constant angular velocity Ω. This is the geometry of the Tsvetkov measurement of γ_1 and will enable us to compute γ_1. We write Eq. (17) as

$$\frac{\partial \psi_q}{\partial t} = -\frac{1}{2\tau_q(t)}\psi_q + g_q \ , \tag{18}$$

where

$$1/2\tau_q(t) = (2/\gamma_3)[A + C_\parallel(\vec{n}\cdot\vec{q} - q_0)^2 + C_\perp(\vec{n}\times\vec{q})^2] \ . \tag{19}$$

For fixed q, τ_q is a function of time. The solution of Eq. (18) is

$$\psi_q(t) = \int_{-\infty}^{t} \exp\left(-\int_{t'}^{t} \frac{dt''}{2\tau_q(t'')}\right) g_q(t')\,dt' \ . \tag{20}$$

We now compute the mean-square amplitude at time t averaged over an ensemble of functions $g_q(t)$

$$\langle\psi_q^2(t)\rangle = \int_{-\infty}^{t} dt' \exp\left(-\int_{t'}^{t}\frac{dt''}{2\tau_q(t'')}\right) \times \int_{-\infty}^{t} ds' \exp\left(-\int_{s'}^{t}\frac{ds''}{2\tau_q(s'')}\right)\langle g_q^*(t')g_q(s')\rangle \ . \tag{21}$$

The value of g at time t' is uncorrelated with the value at s' so the correlation function vanishes unless $t' = s'$. We find

$$\langle\psi_q^2(t)\rangle = \langle g_q^2\rangle \int_{-\infty}^{t} dt' \exp\left(-\int_{t'}^{t}\frac{dt''}{\tau_q(t'')}\right) . \tag{22}$$

In the adiabatic limit $\partial\tau/\partial t \ll 1$, we find

$$\langle\psi_q^2(t)\rangle \approx \langle\psi_q^2(t)\rangle_0 \equiv \langle g_q^2\rangle \tau_q(t) \ . \tag{23}$$

In this limit, the time-dependent theory for the mean-square fluctuations should reduce to the value given by equilibrium statistical mechanics, which is

$$\langle\psi_q^2\rangle_{\text{eq}} = \frac{kT}{A + C_\parallel(\vec{n}\cdot\vec{q} - q_0)^2 + C_\perp(\vec{n}\times\vec{q})^2} \ . \tag{24}$$

Comparing Eqs. (23) and (24), we find that we must choose

$$\langle g_q^2\rangle = 4kT/\gamma_3 \ . \tag{25}$$

The time-dependent mean-square fluctuation satisfies

$$\tau_q(t)\frac{\partial\langle\psi_q^2(t)\rangle}{\partial t} = \langle\psi_q^2\rangle_{\text{eq}} - \langle\psi_q^2(t)\rangle \ . \tag{26}$$

Thus $\langle\psi_q^2(t)\rangle$ approaches the equilibrium value with time constant $\tau_q(t)$.

Now we consider the case of a uniform director rotating slowly. We take

$$n_x = \sin\Omega t, \quad n_y = 0, \quad n_z = \cos\Omega t \ , \tag{27}$$

so that the director points in the z direction at time $t = 0$. We assume that $\Omega t_0 \ll 1$, where τ_0 is the longest time constant in Eq. (19); That is,

$$\tau_0 \equiv \gamma_3/4A \ . \tag{28}$$

We substitute (27) into (19) to find $\tau_q(t)$ and then use the exact solution (22) to find $\langle\psi_q^2(0)\rangle$. To lowest order in Ω, we find

$$\langle\psi_q^2(0)\rangle = \frac{kT}{D_q} - \frac{C_\perp q_0 q_x \gamma_3 kT\Omega}{8D_q^3} \ , \tag{29}$$

where

$$D_q \equiv A + C_\parallel(q_z - q_0)^2 + C_\perp q_\perp^2 \ , \tag{30}$$

with the director stationary the mean-square fluctuations peak at $\vec{q} = q_0\vec{n}$. With the director moving, the mean-square fluctuations lag behind the director.

We have just solved for the time-dependent behavior of the smectic order-parameter fluctuations with a moving director. We will now examine the effect of these fluctuations on the equation of motion of the director. The molecular field acting on $\vec{n}$ is given by Eq. (4). We take a uniform director and set $\vec{n} = \hat{z}$ after the differentiation and find

$$h_x = \sum_q \left[-2C_\parallel(q_z - q_0)q_x + 2C_\perp q_z q_x\right]\psi_q^2 - 2\chi_a H_z H_x \ . \tag{31}$$

In the nematic phase, we want to integrate out the smectic order-parameter fluctuations and we replace $\psi_q^2(t)$ by its expectation value $\langle\psi_q^2(t)\rangle$. The dominant contribution is from q_z near q_0; setting $q_z = q_0$, we find

$$h_x = 2C_\perp q_0 \sum_q q_x\langle\psi_q^2(t)\rangle - 2\chi_a H_z H_x \ . \tag{32}$$

Finally using expression (29) for $\langle \psi_q^2(0) \rangle$ when the director does point in the z direction, we find

$$h_x = -\frac{C_\perp^2 q_0^2 \gamma_3 kT\Omega}{4} \sum_q \frac{q_x^2}{D_q^3} - 2\chi_a H_z H_x \ ,$$
$$= -\frac{q_0^2 \gamma_3 kT\Omega}{128\pi (AC_\parallel)^{1/2}} - 2\chi_a H_z H_x \ . \tag{33}$$

The direct frictional torque between the director and the background fluid is

$$\Gamma_y = \gamma_1^0 \Omega \ , \tag{34}$$

which is balanced by the elastic torque which we have just computed

$$\Gamma_y = (\vec{n} \times \vec{h})_y = -\frac{q_0^2 \gamma_3 kT\Omega}{128\pi (AC_\parallel)^{1/2}} + \chi_a H^2 \sin 2\theta . \tag{35}$$

The torque exerted by the field is

$$\chi_a H^2 \sin 2\theta = \{\gamma_1^0 + q_0^2 \gamma_3 kT/128\pi (AC_\parallel)^{1/2}\}\Omega$$
$$= \gamma_1 \Omega \ , \tag{36}$$

which defines the effective rotational viscosity γ_1.

$$\gamma_1 = \gamma_1^0 + q_0^2 \gamma_3 kT/128\pi (AC_\parallel)^{1/2} \ . \tag{37}$$

This is our central result. It is in agreement, within a numerical factor, with Eq. (6.6) of Ref. 16.

We now want to discuss a simple physical picture of the pretransition phenomena. In the nematic phase near the smectic-A–nematic phase transition the fluctuations of the smetic-A order parameter are large and important. One can picture regions of the nematic liquid crystal in which the molecules have moved temporarily into a smectic-like configuration. These smectic droplets are characterized by a longitudinal dimension (along the director) of $\xi_\parallel = (C_\parallel/A)^{1/2}$ and a transverse dimension $\xi_\perp = (C_\perp/A)^{1/2}$. The smectic droplets are transient and disappear after a time $\tau_0 = \gamma_3/4A$. The correlation lengths and relaxation times increase as one approaches the transition temperature. What effect will these smectic droplets have on the elastic constants? It is energetically very costly to bend or twist the smectic planes, while a splay distortion costs no energy. A smectic droplet occurring in a distorted region of a nematic will tend to straighten out the bend or twist distortion. This leads to an increase in the bend and twist elastic constants near the phase transition.[5] The effect on the viscosity coefficients has a similar origin. In the Leslie-Erickson hydrodynamics, the rotational viscosity γ_1^0 represents a frictional torque between the director and the fluid. We have introduced a new viscosity γ_3 which represents a frictional force on the smectic planes when the liquid flows normal to the planes. When the director rotates the smectic droplets are forced to rotate by the elastic forces. A frictional torque then develops as the fluid is forced to flow across the planes in the droplet. This torque adds to the Leslie-Erickson torque and is the origin of the pretransition contribution to γ_1. This contribution becomes larger near the phase transition as the smectic droplets become larger and longer lived.

Having computed the pretransition contribution to γ_1, we can find the contributions to the other viscosity coefficients by simple physical arguments. We first discuss the flow-alignment viscosity γ_2. Assume the liquid to be flowing in the x direction with a velocity gradient in the z direction and the director lying in the x-z plane at an angle θ with respect to the x axis. The torque on the director is

$$\Gamma_y = (\gamma_1 + \gamma_2 \cos 2\theta)\, \frac{1}{2} \frac{\partial v_x}{\partial z} \ . \tag{38}$$

With $\theta = 90^\circ$ the flow is parallel to the smectic planes and there will be no pretransition effect on the torque (proportional to γ_1-γ_2) in this configuration. Recalling that γ_2^0 is usually negative, we have

$$\gamma_2 = -|\gamma_2^0| + q_0^2 \gamma_3 kT/128\pi (AC_\parallel)^{1/2} \ . \tag{39}$$

The torque vanishes when

$$\cos 2\theta = -\gamma_1/\gamma_2 \tag{40}$$

and in a flow experiment the director takes up a steady-state value provided $\gamma_1 < |\gamma_2|$. If $\gamma_1 > |\gamma_2|$ the director tumbles. Note that the theory predicts a decreasing magnitude of $|\gamma_2|$ as one approaches the phase transition so that the director should destabilize and tumble for a range of temperatures near the transition temperature. In a fluid viscosity measurement, it is clear that η_1^M measured with the director parallel to the flow direction will exhibit the pretransition effect and that η_2^M and η_3^M will not. Since $\eta_2^M = \eta_1^M - \gamma_2$ does not show the effect, we must have

$$\eta_1^M = \eta_1^{M^0} + q_0^2 \gamma_3 kT/128\pi (AC_\parallel)^{1/2} \tag{41}$$

and

$$\eta_2^M = \eta_2^{M^0} \ , \quad \eta_3^M = \eta_3^{M^0} \ . \tag{42}$$

deGennes[5] predicted the following pretransition effect on the Frank elastic constants

$$K_{11} = K_{11}^0 \ ,$$
$$K_{22} = K_{22}^0 + (kTq_0^2/24\pi)(2C_\perp^2/C_\parallel A)^{1/2} \ ,$$
$$K_{33} = K_{33}^0 + (kTq_0^2/24\pi)(2C_\perp/A)^{1/2} \ . \tag{43}$$

This effect has been observed by static measure-

ments of the critical field of the Fredericks transition[7-9] and by light-scattering intensity measurements.[8] With light scattering, one can also measure the relaxation times of the director fluctuations.[18] For the pure twist mode, the relaxation rate is

$$1/\tau_2 = K_{22} q_\perp^2/\gamma_1 , \tag{44}$$

which approaches

$$1/\tau_2 \sim \tfrac{16}{3}\sqrt{2}\,(q_\perp^2/\gamma_3) C_\perp \tag{45}$$

as T approaches T_c. The expression for the relaxation time of the pure bend mode is more complicated, but it approaches

$$\frac{1}{\tau_3} \sim \frac{16\sqrt{2}}{3} \frac{(C_\parallel C_\perp)^{1/2}}{\gamma_3} q_\parallel^2 \tag{46}$$

as T approaches T_c. For both these modes, the elastic constant increases and the scattered-light intensity goes to zero as $T \to T_c$. With the mean-field assumption, $\gamma_3 \sim$ const, the relaxation times approach a constant. With the dynamical scaling assumption, $\gamma_3 \sim \xi^{-1/2}$, the relaxation times go to zero as $\xi^{-1/2}$. For the pure splay mode, the elastic constant and the relevant viscosity remain finite at $T \to T_c$ and we have

$$1/\tau_1 \sim K_{11}^0 q_\perp^2/\gamma_1^0 . \tag{47}$$

Thus the splay mode remains essentially unmodified as one approaches the smectic-A phase.

IV. CONCLUSIONS

The time-dependent Landau theory predicts a pretransition increase in γ_1, γ_2, and η_1^M. The pretransition effect on γ_1 had been observed by Meiboom. The present results are in agreement with those of Janig and Brochard if we use the dynamical scaling assumption for γ_3.

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