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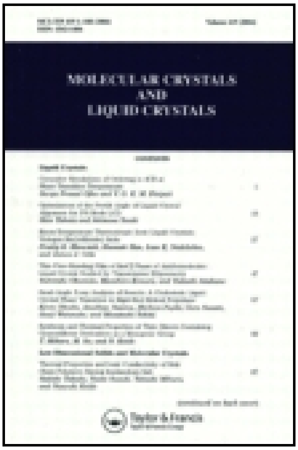

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Waves at the Nematic-Isotropic Interface

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Waves at the Nematic-Isotropic Interface

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We examine surface modes at the nematic-isotropic interface in polymer-liquid-crystal mixtures using the dynamical Landau-de Gennes model for the orientational (non-conserved) order parameter coupled with Cahn-Hilliard equation for concentration (conserved order parameter) and with hydrodynamic degrees of freedom. The generalized dispersion relation is obtained and analyzed in particular cases. Orientational order parameter relaxation dominates in the short wavelength limit, while in the long wavelength limit viscous damping becomes important. The effect of polymer is to increase the surface tension and as a consequence the relaxation rate in the hydrodynamic limit. Finally, we discuss how to measure experimentally the dispersion relation.

1. INTRODUCTION

Inhomogeneous materials that have a conserved order parameter (concentration) and a non-conserved one (orientational order), such as polymer-liquid crystal mixtures are important not only from a fundamental point of view but also for technological applications in electro-optical devices and high modulus fibres [1]. In such systems [2–4], a biphasic region between the isotropic and the nematic phases appear below the nematic-isotropic transition temperature of the pure nematogen. When the system is thermally quenched from the stable isotropic

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phase into the biphasic region, the fluctuations of concentration and of orientational order take place and isotropic or nematic droplets can appear. By whatever early stage process (nucleation or spinodal decomposition), domain walls (interfaces) soon form.

In this paper, we analyze the problem of damping of capillary waves at these interfaces. In the case of a "pure" nematogen, very different dispersion relations for waves at the nematic-isotropic interface can be obtained depending on the way the calculations are done: more precisely, the diffuse interface model, solved by assuming that the order parameter and velocity fields do not interact, leads to purely diffusive surface waves whose mode structure is identical to that of the bulk diffusive modes found in the time-dependent Ginzburg-Landau (TDGL) equation [5]. On the other hand, the sharp interface model yields modified capillary waves, with a large propagating component.

In the two previous papers [6,7], these two points of view have been reconciled by analyzing the surface eigenmodes of the nematic-isotropic interface within the Hess-Olmsted-Goldbart-Qian-Sheng model [8–10]. In the first one [6], it was assumed that the nematic director is fixed in space and time, so that the relevant physics was only described by a scalar order parameter. It turns out that this assumption is only valid if the surface tension is isotropic, (*i.e.* does not depend on the director orientation at the interface) and, less obvious, if the coupling between the flow and the director (and possible 'backflow' effects) can be neglected. A general dispersion relation was then obtained, having as particular cases the (scalar) order parameter relaxation regime in the short wavelength limit and the viscous damping regime valid in the long wavelength limit. The transition between these two regimes takes place at $\lambda_c = 5.2\,\mu\text{m}$, which should be visible experimentally. In the second paper, we have reconsidered this problem in a more general way, by taking into account both the hydrodynamic coupling with the director and the surface tension anisotropy, which we know to be as large as 20% at the nematic-isotropic interface. As a result, interface oscillations couple with the director field via hydrodynamic flow and backflow effects. In the general dispersion relation three distinct regions can be distinguished: (i) at very large values of λ ($\lambda > 6.3\,\text{cm}$) the dissipation due to shear flow dominates and the nematic behaves as a viscous isotropic fluid, (ii) at intermediate values of $\lambda (1.3 \cdot 10^{-4}\,\text{cm} < \lambda < 6.3\,\text{cm})$ curvature elasticity and backflow effects become important, and finally (iii) at low values of λ ($\lambda < 1.3 \cdot 10^{-4}\,\text{cm}$) the relaxation of the order parameter governs the physics. The influence of the anisotropy of the surface tension and of the hydrodynamic coupling between the flow and the director has a fairly small effect ($\simeq$–20%) on the relaxation rate; in contrast,

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this influence on the phase velocity is very important in the second region in which a new propagating mode is observed. The effect of the rotational viscosity and associated backflow effect is much more important than that of the anchoring energy.

In what follows we extend the analysis presented in [6,7] to nematic-isotropic interface in polymer-liquid crystal mixture (the coupling of TDGL equation and Cahn-Hilliard (CH) Eq. [11] with hydrodynamic degrees of freedom). A similar model has been used to analyze the behavior of a suspension of rigid rod particles in shear flow [12]. We consider that the base state of the system is a planar nematic-isotropic interface in equilibrium. This condition fixes its temperature. To simplify, we further assume that the temperature is uniform (no temperature gradient perpendicular to the interface). Due to thermal fluctuations, small amplitude monochromatic waves develop at the interface. A linear stability analysis of the equations is used to obtain their dispersion relation.

The paper is organized as follows. In Sec. 2 we describe the basic model and give the governing equations. We then present in Sec. 3 the dispersion relations corresponding to the two regions defined by the typical lengths in the problem. The general dispersion relation and numerical results are presented in Sec. 4. In Sec. 5 we make some suggestions for measuring the dispersion relation. Finally, in Sec. 6, we draw some conclusions and present directions for future work.

2. EQUATIONS OF MOTION

We consider a polymer-mesogen mixture described by one conserved parameter (the volume fraction c of mesogen) and a nonconserved order parameter (orientational order parameter $Q_{\alpha\beta}$). The orientational order parameter is a traceless symmetric second rank tensor with the components given by

$$Q_{\alpha\beta} = S(3n_\alpha n_\beta - \delta_{\alpha\beta})/2, \tag{1}$$

where the unit vector $\vec{n}$ is the nematic director, and S the usual scalar order parameter. In this paper, although not in future studies, we shall suppose $\vec{n}$ to be fixed in space and time, and the relevant physics is given by the scalar order parameter $S(\vec{r}, t)$. We note that this is an idealization which is in general not true during the relaxation, and even not true close to the interface. However, previous studies [5] do suggest that the slowest relaxation modes do approximately fulfill this condition when the director anchoring is homeotropic at the interface.

Within the mesoscopic approach, the free energy functional is given by [3,4]

$$F[c, Q_{\alpha\beta}] = \int \Big[f(c, Q_{\alpha\beta}) + \frac{1}{2} K_c (\nabla c)^2 + K_0 (\partial_\alpha c)(\partial_\beta Q_{\alpha\beta}) + \frac{1}{2} L_1 (\partial_\gamma Q_{\alpha\beta}) + \frac{1}{2} L_2 (\partial_\alpha Q_{\alpha\beta})^2 \Big] dV, \tag{2}$$

where

$$f(c, Q_{\alpha\beta}) = \frac{N k_B T}{V} \left[\frac{1-c}{n_p} \ln(1-c) + \frac{c}{n_l} \ln c + \chi c (1-c) + \eta \nu c^2 \left(\frac{1}{3} \left(\frac{1}{3\eta} - 1 \right) Q_{\alpha\beta} Q_{\beta\alpha} - \frac{4}{27} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{2}{27} \eta (Q_{\alpha\beta} Q_{\beta\alpha})^2 \right) \right] \tag{3}$$

is the bulk free energy density [3,4], T the absolute temperature, k_B the Boltzmann constant, n_p the number of segments of the polymer, n_l the axes ratio of the mesogenic molecule, and $\eta = n_l \nu c$. The quantity $\chi = U_0/k_B T$ is the Flory-Huggins interaction parameter related to isotropic interaction between unlike molecular species and $\nu = U_a/k_B T$ parameterizes the orientation-dependent (Maier-Saupe) interactions between the mesogens [13,14]. K_c and K_0 are phenomenological coefficients [4]. The elastic constants L_1 and L_2 are related to the Frank-Oseen elastic constants by the relations $K_1 = K_3 = 9S_n^2(L_1 + L_2/2)/2$ and $K_2 = 9S_n^2 L_1/2$, where S_n is the bulk nematic order parameter. In the so-called "one-constant approximation" ($K_1 = K_2 = K_3 = K_S$) and $S_n = 1, L_1 = 2K_S/9$ and $L_2 = 0$, values which we consider in this paper.

We assume that the heat diffusion is sufficiently rapid in order that the system remains at thermal equilibrium. We therefore ignore the equation for energy conservation and assume an isothermal system at a temperature specified in the formulation of the problem. We further assume the fluid is incompressible. Within these approximations, the equations of motion for the velocity and the order parameters become:

$$\nabla \vec{v} = 0, \tag{4}$$

$$\rho \frac{d\vec{v}}{dt} = -\vec{\nabla} p + \eta \nabla^2 \vec{v} - \vec{\nabla} \left(\frac{\delta F}{\delta \Delta S} \right) \vec{\nabla} S + \frac{\delta F}{\delta c} \vec{\nabla} c, \tag{5}$$

$$\frac{dc}{dt} = \Gamma_c \nabla^2 \left(\frac{\delta F}{\delta c} \right), \tag{6}$$

$$\frac{dS}{dt} = -\Gamma_S \frac{\delta F}{\delta S}, \tag{7}$$

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where ρ is the density, p the pressure, and d/dt is the total time derivative $\partial/\partial t + \vec{v} \cdot \nabla$. The transport coefficients Γ_c and Γ_S are assumed to be constants.

The three typical lengths in the problem are as follows:

(i) The microscopic correlation length $l_S = (K_S/f_0)^{1/2} \simeq 10^{-6}\,\mathrm{cm}$ (where $f_0 = 1.3 \cdot 10^5\ \mathrm{erg/cm^3}$ is the free energy density unit) associated with the nonconserved order parameter changes;
(ii) The second microscopic length $l_c = (K_c/f_0)^{1/2} \simeq 6.6 \cdot 10^{-5}\,\mathrm{cm}$ is related to the conserved order parameter variation;
(iii) The third length is associated to vorticity, *i.e.*, to the flow induced by the motion of the interface. The corresponding physics is described by the generalized Navier-Stokes Eq. (5), which can be considered in the thin interface limit. The important physical parameters are the capillary force, associated to the interfacial tension γ, the viscous dissipation, associated to viscosity coefficient η, and the fluid inertia, governed by the mass density ρ. From these three quantities, we can construct only one length $l_\eta = \eta^2/\rho\gamma \simeq 1\,\mathrm{cm}$, which is the length scale separating the inertial regime from the viscous one. The typical relaxation time of a perturbation of size l_η is given by $t_\eta = \eta^3/\rho\gamma^2 \simeq 10\,\mathrm{s}$.

In the following $\epsilon = l_S/l_\eta = \simeq 10^{-6}$ and $\delta = l_c/l_\eta \simeq 6.6 \cdot 10^{-5}$ constitute the small parameters of the theory.

We consider a two-dimensional flow with horizontal and vertical velocity components u and v in the x and z directions, respectively. We rewrite Eqs. (4)–(7) in dimensionless forms by measuring length in unit of l_η, time in unit of t_η, and by introducing the dimensionless quantities: $\bar{f} = f/f_0$, $\bar{\rho} = \rho l_\eta^2/t_\eta^2 f_0$, $\bar{p} = p/f_0$, $\bar{\eta} = \eta/f_0 t_\eta$, $\bar{\Gamma}_c = f_0 t_\eta l_c^2 \Gamma_c/l_\eta^4$, $\bar{\Gamma}_S = f_0 t_\eta l_S^2 \Gamma_S/l_\eta^2$. Omitting the bar notation and considering $K_0 = 0$ (in this case the two order parameter interact only indirectly through velocity), the governing Eqs. (4)–(7) can be written as

$$0 = \partial_x u + \partial_z w, \tag{8}$$

$$\begin{aligned}\rho \frac{du}{dt} &= -\partial_x p + \eta \nabla^2 u - \epsilon^2 \nabla^2 S \partial_x S \\ &\quad + \left(\frac{\partial f}{\partial c} - \delta^2 \nabla^2 c \right) \partial_x c,\end{aligned} \tag{9}$$

$$\begin{aligned}\rho \frac{dw}{dt} &= -\partial_z p + \eta \nabla^2 w - \epsilon^2 \nabla^2 S \partial_z S \\ &\quad + \left(\frac{\partial f}{\partial c} - \delta^2 \nabla^2 c \right) \partial_z c,\end{aligned} \tag{10}$$

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$$\delta^2 \frac{dc}{dt} = \Gamma_c \nabla^2 \left(\frac{\partial f}{\partial c} - \delta^2 \nabla^2 c \right), \tag{11}$$

$$\epsilon^2 \frac{dS}{dt} = -\Gamma_S \left(\frac{\partial f}{\partial S} - \epsilon^2 \nabla^2 S \right). \tag{12}$$

In the following we suppose that the stationary planar nematic-isotropic interface (the base state of the system) is situated at $z = 0$, such that the nematic lies in the region $z < 0$ and the isotropic phase in the region $z > 0$. As for x axis, it is taken in the direction of the wave vector $\vec{k}$ of the perturbation along the interface. This is possible without loss of generality, as the system is isotropic in x and y directions (neglecting the biaxiality of the nematic phase). In this way, the wavenumber k represents the modulus of the two-dimensional wavevector in the plane of the interface.

3. ASYMPTOTICS

We seek solution of Eqs. (8)–(12) for $\delta << 1$, in the inner region (of dimension l_c) in which both conserved and nonconserved order parameters varies rapidly and in the outer region (of dimension l_η in which the physics is governed by hydrodynamics (dissipation by shear flow).

3.1. Outer Region

In the outer region S and c are constant in each phase ($(S,c) = (S_{\mathrm{nem}}, c_{\mathrm{nem}})$ for $z < 0$ and $(S,c) = (0, c_{\mathrm{iso}})$ for $z > 0$) and the equations for velocity are the same at all orders in an expansion in δ:

$$0 = \partial_x u + \partial_z w, \tag{13}$$

$$\rho \frac{du}{dt} = -\partial_x p + \eta \nabla^2 u \tag{14}$$

$$\rho \frac{dw}{dt} = -\partial_z p + \eta \nabla^2 w. \tag{15}$$

Thus, the outer problem is equivalent to the Navier-Stokes equation subject to the incompressibility condition [15,16]. We consider that the densities and viscosities of the two phases are equal. The solution corresponding to the stationary planar interface is given by $u_0 = w_0 = 0$, $p_0 = \mathrm{const}$. We now impose a small periodic sinusoidal perturbation to the interface of the form $\xi_I = \xi_k \exp(ikx - \Omega t)$, where ξ_I is the vertical displacement of the interface with respect to its equilibrium position $z = 0$. In our notations, k is the wavevector (real number) and Ω is the angular frequency. The latter quantity is generally a complex

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number whose the real part gives the relaxation time $\tau = 1/\mathrm{Re}(\Omega)$ of the wave, and the imaginary part, the phase velocity $v_p = \mathrm{Im}(\Omega)/k$. We then look for the solution of Eqs. (13)–(15) in the form $u = U_0 \exp(qz + ikx - \Omega t)$, $w = W_0 \exp(qz + ikx - \Omega t)$, $p = p_0 + P_0 \exp(qz + ikx - \Omega t)$. After substitution in Eqs. (13)–(15), we get a system of algebraic equations for the amplitudes:

$$\begin{aligned} ikU_0 + qW_0 &= 0, \\ (\rho\Omega - \eta(k^2 - q^2))U_0 - ikP_0 &= 0, \\ (\rho\Omega - \eta(k^2 - q^2))W_0 - qP_0 &= 0. \end{aligned} \tag{16}$$

Putting the determinant of system (16) equal to zero, we obtain the following bulk characteristic equation, connecting q, k, and Ω:

$$(k^2 - q^2)[\rho\Omega - \eta(k^2 - q^2)] = 0, \tag{17}$$

with solutions:

$$q = \pm k \text{ and } q = \pm l \text{ where } l = k\left(1 - \frac{\rho\Omega}{\eta k^2}\right)^{1/2}. \tag{18}$$

For a nematic of large depth (region $-\infty < z < 0$), the wavelike solutions of Eqs. (13)–(15) are of the form:

$$u = (ikAe^{kz} - Ce^{lz})\exp(ikx - \Omega t), \tag{19}$$

$$w = (kAe^{kz} + ikCe^{lz})\exp(ikx - \Omega t), \tag{20}$$

$$p = p_0 + \rho\Omega Ae^{kz}\exp(ikx - \Omega t). \tag{21}$$

Similarly, in the isotropic phase (region $0 < z < \infty$) (using primed quantities),

$$u' = (ikA'e^{-kz} + lC'e^{-lz})\exp(ikx - \omega t), \tag{22}$$

$$w' = (-kA'e^{-kz} + ikC'e^{-l^z})\exp(ikx - \omega t), \tag{23}$$

$$p = p_0 + \rho\Omega A'e^{-kz}\exp(ikx - \Omega t). \tag{24}$$

In Eqs. (19, 20) and (22, 23) the velocities are determined by two contributions: (i) the potential flow described by the terms with amplitudes A and A', which correspond to the velocity potentials: $\psi = A\exp(kz + ikx - \omega t)$ and $\psi' = A'\exp(-kz + ikx - \omega t)$; (ii) the rotational flow represented by a vector potential with amplitudes $C(k^2 - l^2)$, $C'(k^2 - l^2)$, describing fluids of finite viscosity.

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The Eqs. (19)–(24) correspond to the classical sharp-interface approach, where it is assumed that the thickness of the inner region is zero. In this limit, the dispersion relation is determined by the boundary conditions at the nematic-isotropic interface which can be taken at $z = 0$ due to the smallness of the amplitude of the oscillations [15,16]. These conditions are as follows:

(i) and (ii): The x- and z-components of the velocity must be continuous;

(iii) The tangential components of the stress tensor must also be continuous, which gives: $\sigma_{xz} = \sigma'_{xz}$, where $\sigma_{xz} = \eta(\partial_x w + \partial_z u)$ and $\sigma'_{xz} = \eta(\partial_x w' + \partial_z u')$ are the xz-components of the stress tensor in the nematic phase and the isotropic liquid, respectively.

(iv) As for the jump of the normal component of the stress tensor, it is given by the Laplace law,

$$\sigma_{zz} - \sigma'_{zz} = \gamma \frac{\partial^2 \xi_I}{\partial x^2}, \tag{25}$$

where $\sigma_{zz} = -p + 2\eta\partial_z w$ and $\sigma'_{zz} = -p' + 2\eta\partial_z w'$ are the normal component of the stress at the interface in the nematic phase and in the isotropic liquid, respectively. In this equation, $\xi_I = \frac{-1}{\Omega} w \mid_{z=0}$ correspond to the displacement of the interface at point x with respect to the plane $z = 0$ (with $< \xi_I >= 0$). After substituting solutions (19)–(24) into the boundary conditions, we obtain a homogeneous system of equations for the four amplitudes A, A', C, and C'. Equating to zero its determinant gives the dispersion relation in the form:

$$\Omega_\eta^2 = \frac{l - k}{l} \Omega_0^2, \tag{26}$$

where $\Omega_0^2 = -\frac{\gamma k^3}{2\rho}$ is the capillary wave dispersion relation for ideal (inviscid) fluids and $\gamma = \gamma_S + \gamma_c$ (see next section).

3.2. Inner Region

At small scale, hydrodynamics are negligible. By using inner variables $\zeta = x/\delta$ and $\xi = z/\delta$, Eqs. (8)–(12) write as follows:

$$\partial_\zeta p = -\tilde{\epsilon}^2 \nabla^2 S \partial_\zeta S + \left(\frac{\partial f}{\partial c} - \nabla^2 c\right)\partial_\zeta c, \tag{27}$$

$$\partial_\xi p = -\tilde{\epsilon}^2 \nabla^2 S \partial_\xi S + \left(\frac{\partial f}{\partial c} - \nabla^2 c\right)\partial_\xi c, \tag{28}$$

$$\frac{\partial c}{\partial t} = \tilde{\Gamma}_c \nabla^2 \left(\frac{\partial f}{\partial c} - \nabla^2 c \right), \tag{29}$$

$$\tilde{\epsilon}^2 \frac{\partial S}{\partial t} = -\tilde{\Gamma}_S \left(\frac{\partial f}{\partial S} - \tilde{\epsilon}^2 \nabla^2 S \right), \tag{30}$$

where $\tilde{\epsilon} = \epsilon/\delta \simeq 0.015$, $\tilde{\Gamma}_c = f_0 t_\eta \Gamma_c / l_\eta^2 l_c^2$, $\tilde{\Gamma}_S = f_0 t_\eta l_S^2 \Gamma_S / l_\eta^2 l_c^2$.

We consider first an equilibrium planar nematic-isotropic interface perpendicular to the ξ axis. The horizontal momentum Eq. (27) is satisfied identically and the remaining equations give (omitting the tilde signs):

$$d_\xi p_0 = -\epsilon^2 d_\xi^2 S_0 d_\xi S_0 + \left(\frac{\partial f}{\partial c}(S_0, c_0) - d_\xi^2 c_0 \right) d_\xi c_0, \tag{31}$$

$$d_\xi^2 c_0 = \frac{\partial f}{\partial c}(S_0, c_0) - \mu, \tag{32}$$

$$\epsilon^2 d_\xi^2 S_0 = \frac{\partial f}{\partial S}(S_0, c_0), \tag{33}$$

where the subscript 0 refers to the equilibrium interface. Note that we have integrated the CH Eq. (29) twice and employed the far field condition that c is bounded (the chemical potential μ is the Lagrange multiplier that ensures the conservation of the nematic). The boundary conditions are

$$(S, c) = \begin{cases} (S_{\text{nem}}, c_{\text{nem}}) & \text{as } z \to -\infty, \\ (0, c_{\text{iso}}) & \text{as } z \to \infty. \end{cases} \tag{34}$$

In the far field (the spatial gradients vanish) Eq. (31) gives $p_0 = p_\infty$, where p_∞ is the common value of the pressure in the bulk phases and Eqs. (32) and (33) are equivalent to the following equilibrium conditions:

$$\Delta f(S_0, c_0) = 0; \ \frac{\partial \Delta f}{\partial c}(S_0, c_0) = 0; \ \frac{\partial \Delta f}{\partial S}(S_0, c_0) = 0, \tag{35}$$

where $\Delta f(S_0, c_0) = f(S_0, c_0) - f(0, c_{\text{iso}}) - \mu(c_0 - c_{\text{iso}})$ and $\mu = \frac{\partial f}{\partial c}(0, c_{\text{iso}})$ is the chemical potential [11]. The corresponding phase diagram for $n_p = 10$, $n_l = 2$, and $\nu/\chi = 5$ is plotted in Figure 1. In what follows we use the following values: $\tau = 0.875$ (the reduced temperature $\tau = T/T_{NI}$ is normalized by the nematic-isotropic phase transition temperature T_{NI} of the pure nematogen), $c_{\text{iso}} = 0.756$, $c_{\text{nem}} = 0.982$, and $S_{\text{nem}} = 0.509$.

In the limit $\epsilon \to 0$ there are two regions inside the inner region. One is the inner-inner region (of dimension l_S) in which the orientational

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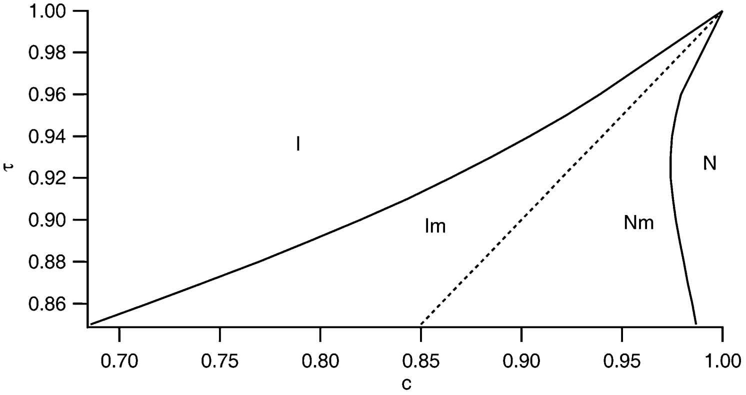

FIGURE 1 Phase diagram for $n_p = 10$, $n_l = 2$, and $\nu/\chi = 5$. The solid curve refers to the binodal and dotted line shows the hidden first-order nematic-isotropic phase transition.

order parameter varies and the conserved one is constant and the inner-outer region (of dimension l_c) in which the conserved order parameter varies and the orientational one is constant.

In the inner-outer region, S is constant in each phase ($S = S_{\text{nem}}$ for $z < 0$ and $S = S_{\text{iso}}$ for $z > 0$) and Eqs. (31), (32) are the same at all orders in an expansion in ϵ:

$$d_\xi p_0 = \frac{\partial \Delta f}{\partial c}(c_0) d_\xi c_0, \tag{36}$$

$$d_\xi^2 c_0 = \frac{\partial \Delta f}{\partial c}(c_0), \tag{37}$$

where $\Delta f(c_0) = \Delta f(S_{\text{nem}}, c_0) = \Delta f(S_{\text{iso}}, c_0)$. Eq. (36) allows us to calculate the pressure field: $p_0 = p_\infty + (d_\xi c_0)^2/2$.

The corresponding solution of Eq. (37) with boundary condition $c_0(-\infty) = c_{\text{nem}}$ and $c_0(\infty) = c_{\text{iso}}$ is given by

$$c_0(\xi) = \frac{1}{2}(c_{\text{nem}} + c_{\text{iso}}) - \frac{1}{2}(c_{\text{nem}} - c_{\text{iso}}) \tan h \frac{\xi}{\sqrt{2}}, \tag{38}$$

where we have fixed the center of the interface (defined by $c_0 = (c_{\text{nem}} + c_{\text{iso}})/2$) at $\xi = 0$. Correspondingly, the surface tension (in real variables) is given by

$$\gamma_c = (f_0 K_c)^{1/2} \int_{-\infty}^{\infty} (d_\xi c_0)^2 d\xi. \tag{39}$$

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Fitting Eq. (39) with the experimental value $\gamma_c = 0.1\,\mathrm{erg/cm^2}$ [17] we find $K_c = 5.5 \cdot 10^{-4}\,\mathrm{dyn}$ and $l_c = 6.6 \cdot 10^{-5}\,\mathrm{cm}$.

To obtain the CH dispersion relation [18,19] (valid in the inner-outer region) we conveniently rewrite Eq. (29) in the form (omitting the tilde sign):

$$\frac{\partial \Delta f}{\partial c} - \nabla^2 c - \frac{1}{\Gamma_c}(\nabla^2)^{-1}\partial_t c = 0. \tag{40}$$

Substituting a small periodic perturbation of the form $c(\zeta, \xi, t) = c_0(\xi) + \mathcal{C}(\xi)\exp(ik\zeta - \Omega t)$ (the relaxation rate Ω defines the time scale, $\tau = 1/\Omega$, for the relaxation of a perturbation with characteristic length scale $2\pi/k$) in Eq. (40) leads to the eigenvalue equation:

$$\frac{d^2\Delta f}{dc^2}(c_0)\mathcal{C} - (d_\xi^2 - k^2)\mathcal{C} - \frac{1}{\Gamma_c}(\nabla^2)^{-1}\Omega\mathcal{C}, \tag{41}$$

which gives

$$\Omega_c = \Gamma_c k^2 \frac{\int_{-\infty}^{\infty}(d_\xi c_0)\mathcal{C} d\xi}{\int_{-\infty}^{\infty} d\xi \int_{-\infty}^{\infty} G_k(\xi - \xi')(d_\xi c_0)\mathcal{C}(\xi')d\xi'}, \tag{42}$$

where

$$G_k(\xi - \xi') = \int_{-\infty}^{\infty}\frac{dq}{2\pi}\frac{\exp[iq(\xi - \xi')]}{k^2 + q^2} = \frac{\exp(-k \mid \xi - \xi' \mid)}{2k} \tag{43}$$

is the Green function for the operator $(k^2 - d_\xi^2)$. Since $k = 0$ corresponds to a uniform translation of the interface, we know that $\Omega_{k=0} = 0$ is the eigenvalue with the eigenfunction $d_\xi c_0$. For $k \neq 0$, higher eigenvalues are separated by a gap for the ground state, so any component of the corresponding eigenfunctions, in the initial displacement of the interface, relaxes quickly to zero. For this reason, we can consider (at least in the limit of $k \to 0$) that the ground state ("slow mode") eigenfunction $d_\xi c_0$ is the eigenfunction for any value of k. In the same limit, $G_k = 1/2k$, so that the dispersion relation becomes:

$$\Omega_c = \frac{2\Gamma_c\gamma_c}{(c_{\mathrm{nem}} - c_{\mathrm{iso}})^2}k^2. \tag{44}$$

In the inner-inner region ($\bar{\zeta} = x/\epsilon$ and $\bar{\xi} = z/\epsilon$), c is constant in each phase ($c = c_{\mathrm{nem}}$ for $z < 0$ and $c = c_{\mathrm{iso}}$ for $z > 0$) and Eqs. (31), (33)

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become:

$$d_{\bar{\xi}} p_0 = -d_{\bar{\xi}}^2 S_0 d_{\bar{\xi}} S_0, \tag{45}$$

$$d_{\bar{\xi}}^2 S_0 = \frac{\partial \Delta f}{\partial S}(S_0), \tag{46}$$

where $\Delta f(S_0) = \Delta f(S_0, c_{\text{nem}}) = \Delta f(S_0, c_{\text{iso}})$. Eq. (46) allows us to calculate the pressure field: $p_0 = p_\infty - (d_{\bar{\xi}} S_0)^2/2$.

The corresponding solution of Eq. (46) with boundary condition $S_0(-\infty) = S_{\text{nem}}$ and $S_0(\infty) = S_{\text{iso}} = 0$ is given by

$$S_0(\bar{\xi}) = \frac{1}{2} S_{\text{nem}} \left(1 - \tanh \frac{\bar{\xi}}{\sqrt{2}}\right), \tag{47}$$

where we have fixed the center of the interface (defined by $S_0 = S_{\text{nem}}/2$) at $\bar{\xi} = 0$. Correspondingly, the surface tension (in real variables) is given by

$$\gamma_S = (f_0 K_S)^{1/2} \int_{-\infty}^{\infty} (d_{\bar{\xi}} S_0)^2 d\bar{\xi}. \tag{48}$$

Using the experimental value $K_S = 2.1 \cdot 10^{-7}$dyn [14] and fitting Eq. (48) with the experimental value $\gamma_S = 0.01\,\text{erg/cm}^2$ [20] we find $f_0 = 1.3 \cdot 10^5\,\text{erg/cm}^3$ and $l_S = 1.3 \cdot 10^{-6}\,\text{cm}$.

To obtain the TDGL dispersion relation (valid in the inner-inner region), we start with the corresponding form of Eq. (30):

$$\frac{\partial S}{\partial t} = -\Gamma_S \left(\frac{d\Delta f}{dS} - \nabla^2 S\right). \tag{49}$$

We perturb the base state Eq. (27) by $S(\bar{\zeta}, \bar{\xi}, t) = S_0(\bar{\xi}) + \mathcal{S}(\bar{\xi}) \exp(ik\bar{\zeta} - \Omega t)$. Substituting this form into Eq. (49) and linearizing in perturbation, give

$$H\mathcal{S} = \Omega \mathcal{S} \tag{50}$$

where $H = -d_z^2 + k^2 + \frac{d^2 \Delta f}{dS^2}(S_0)$ can be conveniently thought of as a quantum mechanical Hamiltonian operator [21]. Note that $\frac{d^2 f}{dS^2}(S_0)$ is positive at $\bar{\xi} = \pm\infty$ (where $S_0 = 0$ and $S_0 = S_{\text{nem}}$) and negative at $\bar{\xi} = 0$ (where $S_0 = S_{\text{nem}}/2$). It follows that $\frac{d^2 f}{dS^2}(S_0)$ represents a potential well which must have at least one bound state. $\Omega_{k=0} = 0$ is the eigenvalue with the eigenfunction $d_{\bar{\xi}} S_0$ (this can be easily checked by differentiating Eq. (46) with respect to $\bar{\xi}$). Also, since this function has no node, it must be the ground state. Since the k dependence of H is simply the additive constant k^2, it follows that $dS_0/d\bar{\xi}$ is, for all k, the ground state eigenfunction, the so-called ‘slow mode’ of eigenvalue (in “real units”):

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$$\Omega_S = \Gamma_S K_S k^2. \tag{51}$$

In order to obtain the full dispersion relation, we need to match the solutions obtained in the inner-outer and in the inner-inner regions, respectively, at first order in ϵ. A similar matching was already done in Ref. [6] and we refer to that paper for detailed calculations. Using the same procedure, we obtain the inner region dispersion relation

$$\Omega_{Sc} = \frac{\gamma_S + \gamma_c}{\frac{\gamma_S}{\Omega_S} + \frac{\gamma_c}{\Omega_c}}, \tag{52}$$

where Ω_c and Ω_S are given by Eqs. (42) (or in simplified form Eq. (44)) and (51), respectively.

The real part of solution of Eq. (52) and its asymptotic limit are drawn in Figure 2. Two regions must be clearly distinguished. In the short wavelength limit (region II in the figure) the relaxation of the orientational order parameter is the dominant process. The dispersion relation is then given by Eq. (51) (dotted curve in Fig. 2). In the large wavelength limit, the interface is sharp with respect to orientational order parameter, the relaxation of the conserved order parameter in the inner-outer region dominates and the corresponding dispersion relation is given by Eq. (44) (dashed curve in Fig. 2). The transition between these two regimes takes place when

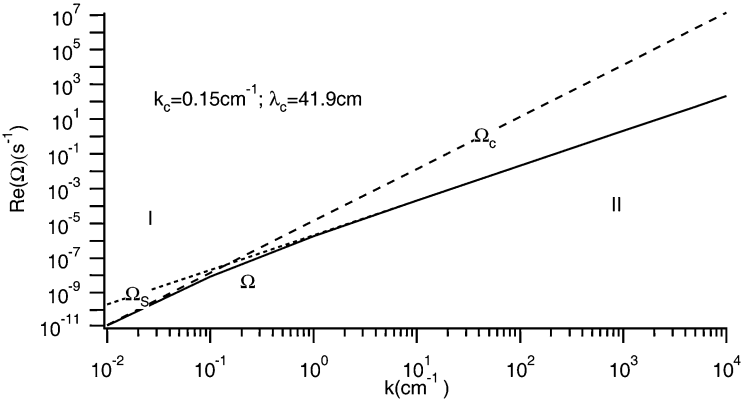

FIGURE 2 The damping rate Re(Ω) in the inner regionas function of the wave vector k in a log-log plot. The complete dispersion relation, Eq. (52) (continuous curve), the conserved order parameter dispersion relation Eq. (44) (dashed line), and non-conserved order parameter dispersion relation Eq. (51) (dotted curve).

$\mathrm{Re}(\Omega_S) = \mathrm{Re}(\Omega_c)$, which gives the critical wave number $k_c = 0.15\,\mathrm{cm}^{-1}$ and the corresponding critical wavelength $\lambda_c = 41.9\,\mathrm{cm}$.

4. GENERAL DISPERSION RELATION

Matching the solution obtained in the outer and in the inner region, respectively, at first order in δ, we obtain the generalized dispersion relation

$$\Omega^2 - \Omega_{Sc}\Omega = \Omega_\eta^2, \tag{53}$$

where Ω_η and Ω_{Sc} are given by Eqs. (26) and (52) respectively. The real part of solution of Eq. (53) and its asymptotic limit are drawn in Figure 3. In the short wavelength limit (region II in the figure) hydrodynamics are negligible and the relaxation of the order parameters is the dominant process. The dispersion relation is then given by Eq. (52) (dotted curve in Fig. 3) (in this limit the relaxation of the orientational order parameter is dominant (see Fig. 2)). In the large wavelength limit (region I in Fig. 3), the interface is sharp and can be considered as a surface of discontinuity. The viscous damping process in the outer region then dominates and the corresponding dispersion relation is given by Eq. (26) (dashed curve in Fig. 3). The transition between these two regimes takes place when $\mathrm{Re}(\Omega_\eta) = \mathrm{Re}(\Omega_{Sc})$, which gives the critical wave number $k_1 = 1.4 \cdot 10^5\,\mathrm{cm}^{-1}$ and the corresponding critical wavelength $\lambda_1 = 0.5\,\mu\mathrm{m}$. Inside the region I (in the

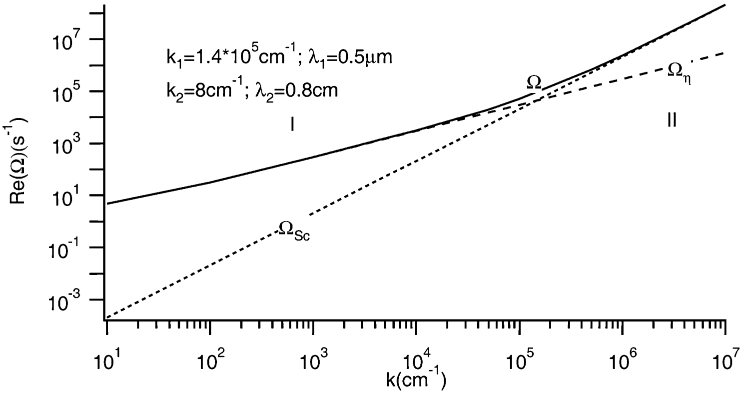

FIGURE 3 The general damping rate $\mathrm{Re}(\Omega)$ as a function of the wave vector k in a log-log plot. The general dispersion relation Eq. (53) (continuous curve), the viscous damping dispersion relation Eq. (26) (dashed curve), and the order-parameters relaxation dispersion relation Eq. (52) (dotted curve).

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hydrodynamic limit) there are two regions corresponding to weak damping ($v_p = \mathrm{Im}(\Omega)/k \neq 0$) and strong damping ($v_p = 0$), respectively. The crossover between these two regimes takes place at $\Omega_0 = -\eta k^2/\rho$, which gives $k_2 = 8\,\mathrm{cm}^{-1}$ and the corresponding $\lambda_2 = 0.8\,\mathrm{cm}$. In the strong damping regime $\Omega = \gamma k/4\eta$ [6], this explains the linear character of the dashed curve in Figure 3.

It is interesting to compare these results with those obtained in a "pure" nematic case, in which the dispersion relation becomes [6]:

$$\Omega^2 - \Omega_S\Omega = \Omega_\eta^2. \tag{54}$$

In Figure 4 we have plotted comparatively the real part of solution of Eqs. (53) and (54), respectively. In the large wavelengths limit (where the hydrodynamics dominate and the relaxation rate is given by Eq. (26)) the relaxation rate is enhanced by the polymer as a consequence of the enhancement of the surface tension due to concentration variation Eq. (39) (see also the experimental results [17].

At small wavelengths, in both cases the physics is governed by the relaxation of the orientational order parameter and the relaxation rates become identical.

5. PROPOSED EXPERIMENTS TO MEASURE THE DISPERSION RELATION

A method to measure the dispersion relation in the strong damping limit of region I (see Fig. 3) would be to look at the mechanically excited deformation modes of a large (size in centimeters) drop placed

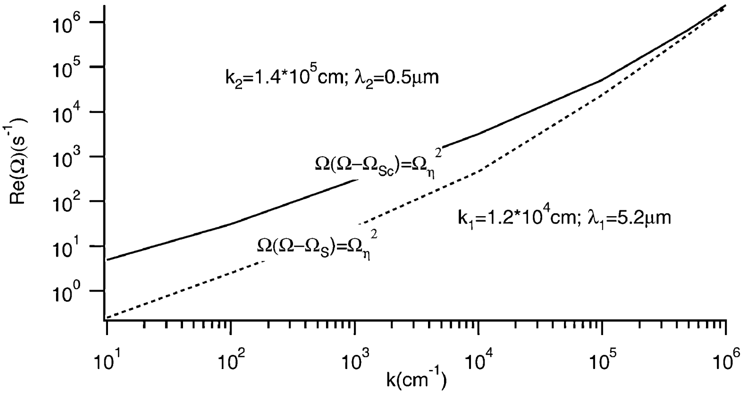

FIGURE 4 Re(Ω) calculated from Eq. (53) (continuous curve) and Eq. (54) (dotted curve).

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on a Teflon plate, itself situated in a transparent recipient filled with the isotropic liquid [22,23].

Another method to probe the strong damping limit of regime I would be to prepare a flat nematic-isotropic interface in a large recipient (many centimeters in size). The experimental procedure would then consist of mechanically (or electrically) exciting 'plane' surface waves at a fixed frequency $f = 2\pi/\omega$. In this case, the wavevector of the waves is complex ($q = \mathrm{Re}(q) + i\mathrm{Im}(q)$). Each component of q can then be measured by observing the deflection of a laser beam with a position sensitive photodiode as a function of the distance to the excitation point. These two components are then compared to the solution (in q at fixed $\Omega = \omega$) of the dispersion relation. Note that this method has already been used for studying capillary waves at the nematic-air interface [24].

To obtain direct information about dynamics of capillary waves, quasi-elastic laser light-scattering can be used. Briefly, the technique consists of measuring the power spectrum $P(k, \omega)$ of the scattered light at different wavevector k by using an heterodyne detection (for more details see [25,26]. To a first approximation, the spectrum is Lorentzian of half-width $\mathrm{Re}(\Omega(k))$ and it is shifted by $\mathrm{Im}(\Omega(k)))$ (Doppler effect due to the wave propagation). Wavevectors accessible experimentally range between $100\,\mathrm{cm}^{-1}$ and $10^4\,\mathrm{cm}^{-1}$, which turn out to be the weak damping limit of region I of the present study. Nevertheless, it must be noted that in this range of wavevector, $\mathrm{Im}(\Omega)$ is typically ten times smaller than $\mathrm{Re}(\Omega)$. For this reason, $\mathrm{Im}(\Omega)$ will be difficult to measure. One way to improve the situation consists of decreasing the viscosity in order to increase the phase velocity of the waves while decreasing their damping.

As for the region of transition between regimes I and II, which is predicted to appear at a wavevector of the order of $1.4 \cdot 10^5\,\mathrm{cm}^{-1}$, it should be accessible by diffuse scattering of X-rays at grazing incidence. In particular, a photon correlation spectroscopy experiment should give valuable information in this region where dynamics of the order parameter become dominant.

Finally, we suggest that the Faraday instability could also be used to study capillary waves at the nematic-isotropic interface in polymer-liquid crystal mixtures. We recall that this method consists of exciting parametrically capillary waves by vibrating a recipient containing the liquid crystal in the direction perpendicular to the interface. This experiment has already been performed at the liquid-vapor interface of the carbon dioxide close to the critical point [27] and we believe it should be feasible also in our system and provide information about capillary waves in regime I.

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6. CONCLUSIONS

In this paper we have examined surface modes at the nematic-isotropic interface in polymer-liquid crystal mixtures. We have assumed an isothermal system characterized by a scalar orientational (nonconserved) order parameter and a conserved order parameter (volume fraction of nematogen), both phases having the same density and viscosity, respectively. We have considered the equilibrium planar nematic-isotropic interface as the base state of the system. The front was then perturbed with a small amplitude monochromatic plane wave and the linear stability of the front was examined to obtain the generalized dispersion relation, Eq. (53). Two distinct regions can be distinguished (see Fig. 3): (i) At low values of k ($k < k_1 = 1.4 \cdot 10^5\,\mathrm{cm}^{-1}$) the dissipation due to shear flow dominates and the polymer-nematic mixture behaves as a viscous isotropic fluid (region I). Inside region there is a crossover between a weak and a strong damping regimes that takes place at $k = k_2 = 8\,\mathrm{cm}^{-1}$. We mention that the transition defined in Figure 2 does not exist anymore being covered by hydrodynamics. (ii) At large values of k ($k < k_1$) the relaxation of the orientational order parameter governs the physics (region II).

We compared these results with those obtained in Ref [6] for a "pure" nematogen (Fig. 4). The variation of concentration (that describes the polymer-nematic mixture) gives a ten time larger surface tension Eq. (39) which enhances ten times the relaxation rate in the hydrodynamic limit (see the low k region in Fig. 4). At the large values of k the effect of concentration disappears and the physics is governed only by the relaxation of the orientational order parameter.

In Sec. 5, based on some experiments already done especially in the static case, we have proposed experiments to examine and study the dynamics of the capillary waves in these two regimes.

Finally, we note that a similar analysis applied to Cahn-Hilliard equation coupled with hydrodynamics gives a wavelength of the transition $\lambda \simeq 400\,\mu\mathrm{m}$ which is of the same order of magnitude as the Mullins-Sekerka threshold wavelength [14]. Thus, it would be very interesting to study the influence of hydrodynamics on the Mullins-Sekerka instability, problem which we want to address in a future study.

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