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# Kinetics of the Nematic-Isotropic Interface

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**Abstract.** — We investigate the motion of an interface between a nematic liquid crystal phase and the isotropic phase of the same fluid. In this simplified model we assume the nematic liquid crystal to have one order parameter only and also suppose the system to be isothermal and initially quenched into the metastable régime of the isotropic phase ( $T_{\text{NI}} > T > T^*$ ). What results is the time-dependent Ginzburg-Landau equation, with domain wall solutions, corresponding to phase interfaces, which interpolate between static isotropic and nematic minima. These domain walls move with a unique velocity which depends more or less linearly on the degree of undercooling. For real liquid crystals this velocity is of the order of  $\text{cm s}^{-1}$ . We also examine the relaxation mode solutions of the Ginzburg-Landau equation, and present a complete phase-diagram of these solutions.

## 1. Introduction

This paper investigates aspects of the dynamics of formation of a nematic liquid crystal phase when the isotropic fluid is cooled quickly, or quenched, to a temperature at which the nematic phase is thermodynamically stable and the isotropic phase is not. In fact this particular problem is one of many analogous problems in which a disordered phase is cooled through a first order phase transition to a region where an ordered phase is more stable thermodynamically. There has been much work in this general area, and where possible we shall call on relevant analogies from similar physical systems [1–5].

The process whereby the new ordered, nematic, phase replaces the disordered, isotropic, phase is extremely complex. First it is important whether the quench is to a region where the disordered phase is thermodynamically metastable, or rather into an unstable régime. In the context of liquid crystals, where the phase transition is at temperature  $T_{\text{NI}}$ , the crucial temperature is  $T^*$ , the temperature at which the susceptibility to nematic fields would diverge if only the isotropic fluid could be cooled so far. For  $T < T^*$  the isotropic phase is thermodynamically unstable. Nucleation of the nematic phase takes place through a ‘phase-ordering’ kinetic process [6, 7], in which the ordering takes place quickly locally, although the system retains topological defects which it gradually expels. By contrast, for  $T_{\text{NI}} > T > T^*$  the isotropic phase is metastable. This is the region on which we concentrate in this paper. Let

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us discuss qualitatively the process whereby the nematic phase replaces the isotropic phase. Thermodynamic fluctuations drive small regions of the system, ‘droplets’, into a nematic phase. In general these droplets are small, and the free energy price of putting in a nematic-isotropic interface is sufficiently large that the nematic droplet is unfavorable from a free energy point of view, and disappears. The relative cost of the droplet surface decreases, however, and eventually, a sufficiently large droplet is thermodynamically favored. Occasionally a sufficiently large droplet is ‘nucleated’. The important, and rather difficult, physics, concerns the nucleation rate.

With droplet nucleation the first stage of phase transformation is over. In the second stage of phase transformation the droplets grow, because larger droplets have lower free energy. The speed of growth depends on the degree of undercooling, or equivalently, the difference in free energy between the nematic and isotropic phases. This speed is the subject of this paper. If one looks at one part of the surface of the droplet it looks more or less flat, and we study the movement of this flat interface. In fact the growth of the droplets is complex, because the latent heat released as the interface moves actually heats up the system, rendering the assumption of constant undercooling inexact.

A third (‘late’) stage of phase transformation occurs when the droplets coalesce, making larger droplets, which in turn coalesce... A complication particular to nematic liquid crystals, which we shall not discuss further here, involves the free energy price paid when the droplets join together, because the directors in adjacent droplets point in different directions.

Many features of the static nematic-isotropic interface can be understood in terms of the phenomenological Landau-de Gennes theory [8]. This theory is a tensor theory. Once the free energy is minimized with respect to the director orientation at the interface, however, a scalar theory more or less suffices. In order to discuss a moving interface we use the dynamic analogue of the Landau-de Gennes theory [9]. In the one order parameter limit, which we justify in more detail below, this becomes the well-known time-dependent Ginzburg-Landau theory (TDGL), which has found wide application in the kinetic theory of phase transitions [10, 11], the propagation of signals in electric circuits [12] and theoretical population biology [13]. A solution to the resulting equations describes a moving nematic-isotropic interface.

This paper is arranged as follows. In Section 2 we describe the basic model. In Section 3 we present the solutions to the TDGL equations which describe the moving interface. In Section 4 we discuss the implications of this work on the isotropic-nematic surface tension. In Section 5 we discuss some related aspects of nematic domain formation, In Section 6 we present some further ‘relaxation mode’ solutions [14–16] of the TDGL theory. Finally in Section 7 we present some brief conclusions and perspectives for further work.

## 2. Model

Here we briefly recap on the phenomenological Landau-de Gennes theory of nematic liquid crystals [17]. The local state of a nematic liquid crystal at position  $\mathbf{r}$  is described by a traceless symmetric tensor  $Q_{ij}(\mathbf{r})$ . For the conditions we consider,

$$Q_{ij} = \frac{1}{2}S(3n_i n_j - \delta_{ij}), \quad (1)$$

where the unit vector  $\mathbf{n}$  is the usual nematic director, and  $S$  is now a scalar order parameter. In the problems we consider in this paper, we shall suppose  $\mathbf{n}$  to be fixed in space and time, and the relevant physics is given by  $S(\mathbf{r})$ .

The equilibrium statistical mechanics is governed by the free energy functional:

$$\mathcal{F}[\underline{Q}] = \int dr \left( f_b(\underline{Q}) + \frac{L_1}{2} (\partial_k Q_{ij} \partial_k Q_{ij}) + \frac{L_2}{2} (\partial_j Q_{ij} \partial_k Q_{ik}) \right), \quad (2)$$

where  $L_1$  and  $L_2$  are elastic constants, related to the Frank-Oseen elastic constants in the bulk nematic. The bulk free energy  $f_b(\underline{Q})$  is given by:

$$\frac{2}{3} a \tau Q_{ij} Q_{ji} - \frac{4}{3} c Q_{ij} Q_{jk} Q_{ki} + \frac{4}{9} b (Q_{ij} Q_{ij})^2, \quad (3)$$

where  $\tau = T - T^*$  is a temperature unit.

The equilibrium configuration is given by the condition that the symmetric part of the molecular field  $H_{ij}$  be zero, where  $H_{ij}$  is the variable thermodynamically conjugate to  $\underline{Q}$ . Equivalently:

$$\frac{\delta \mathcal{F}}{\delta S} = -H_S = 0. \quad (4)$$

The static isotropic-nematic interface has been much studied, going back all the way to de Gennes [17] in 1971. Normally the elastic constant  $L_2 > 0$ , and this condition ensures that the director aligns in the plane of the interface [17]. The planar anchoring is sufficiently strong that we may suppose that the director to be fixed in the problem. The small amount of biaxiality in the surface region is not important for the surface free energy. The only relevant parameter is then the scalar order parameter  $S(x)$ , where  $x$  is the direction perpendicular to the interface. We suppose in this paper that this remains true, even for an interface moving in the  $x$  direction, and it can be shown that this is a mathematically consistent assumption. In the dynamical version of the theory we shall thus be seeking  $S(x, t) = S(x - vt)$  where  $v$  is the interface velocity.

The dynamical generalization of this theory has been written down by Olmsted and Goldbart [9], and in general involves coupling between the order parameter  $Q$  and the fluid velocity  $\mathbf{u}$ . When no velocities are induced, the time dependent equation for the order parameter  $S(x, t)$  reduces to:

$$\beta \frac{\partial S}{\partial t} - L \frac{\partial^2 S}{\partial x^2} = -\frac{\partial f_b}{\partial S}, \quad (5)$$

where the effective elastic constant  $L = \frac{3}{2} L_1 + \frac{1}{4} L_2$ , and the transport coefficient  $\beta \simeq \gamma_1 / (9S_b^2)$ , where  $\gamma_1 > 0$  is the rotational viscosity of the corresponding nematic liquid crystal and where  $S_b$  is the equilibrium value of the scalar order parameter [18].

This is the time-dependent Ginzburg-Landau equation [10–12]. Hohenberg and Halperin [19] have used this equation with a Gaussian white noise term as ‘model A’ in their classification of dynamical universality classes. TGDL can be regarded as the simplest dissipative dynamics allowed by this statistical mechanics. It can also be derived more directly from a master equation approach as the most probable evolution path of the dynamical variable  $S(x, t)$  from an initial value  $S_0$  into a final value  $S_1$  [10].

In order to carry out further calculations it is convenient to scale variables in the following way [20]:

$$\eta = \frac{2b}{c} S; \quad \bar{\tau} = \frac{4ab}{c^2} \tau; \quad \bar{f}_b = \frac{16b^3}{c^4} f_b. \quad (6)$$

In this system of units,  $\bar{x} = x/\xi$ , with  $\xi^2 = 8b^2 L/c^3$ , and  $\bar{t} = t/t^*$ , with  $t^* = 8\beta b^2/c^3$ ; the natural units of length and time are now  $\xi$  and  $t^*$ . Now eliminating overbars in subsequent calculations, in these units:

$$f_b = \tau \eta^2 - 2\eta^3 + \eta^4. \quad (7)$$

The isotropic-nematic transition now takes place at  $\tau = 1$  to a nematic phase in which the scaled order parameter  $\eta = 1$ . Substituting equation (6) into equation (5), we obtain:

$$\frac{\partial \eta}{\partial t} - \frac{\partial^2 \eta}{\partial x^2} = -\frac{df_b}{d\eta} = -2\tau\eta + 6\eta^2 - 4\eta^3. \quad (8)$$

This is the fundamental equation of the model. In the next section we discuss solutions to this equation.

### 3. Travelling Phase Transformation Waves

Let us briefly discuss the solutions to the TDGL equation (8) in the temperature region  $0 < \tau < 1$ . In this régime both nematic and isotropic phases can exist. Equivalently equation (8) has time and space independent solutions. These occur at:

$$\eta_1 = 0; \eta_2 = \frac{3}{4}(1 - \Phi); \eta_3 = \frac{3}{4}(1 + \Phi), \quad (9)$$

where  $\Phi = (1 - 8\tau/9)^{1/2}$ . The solutions  $\eta_1$  and  $\eta_3$  correspond respectively to the isotropic and nematic minima of  $f_b$ , with  $f_N < f_I$ , or equivalently, the isotropic phase is metastable, whereas the nematic phase is stable. The function  $f_b(\eta)$  possesses only these two minima, with a maximum at  $\eta_2$ . We note that in the region  $1 < \tau < 9/8$ ,  $0 < \Phi < 1/3$ , the nematic phase is superheated and metastable, while the isotropic phase is stable.

The solution which interests us is a *domain wall* solution which interpolates between the isotropic solution, valid for  $x \rightarrow \infty$ , and the nematic solution, valid for  $x \rightarrow -\infty$ . Because for  $0 < \tau < 1$  the nematic solution has lower free energy, the nematic region advances into the isotropic region with velocity  $v$ . These domain wall or travelling wave solutions have the form:

$$\eta(x, t) = \eta(x - vt) = \eta(x'), \quad (10)$$

where  $x'$  is a spatial variable moving in the frame of the domain wall. It is now convenient to transform to this variable, yielding:

$$\frac{d^2 \eta}{dx'^2} + v \frac{d\eta}{dx'} = \frac{df}{d\eta} = 2\tau\eta - 6\eta^2 + 4\eta^3, \quad (11)$$

subject to the boundary conditions  $\eta(-\infty) = \eta_3$  and  $\eta(\infty) = \eta_1$ .

This is now an ordinary differential equation in the variable  $x'$ . The equation has been much studied in the literature [13–15].

The solution is

$$\eta(x') = \frac{3}{8}(1 + \Phi)\left(1 - \tanh \frac{x'}{w_0}\right), \quad (12)$$

with the characteristic thickness of the interface given by:

$$w_0 = \frac{2^{5/2}}{3(1 + \Phi)}, \quad (13)$$

and its velocity given by:

$$v_1 = \frac{3}{2^{3/2}}(3\Phi - 1). \quad (14)$$

We now discuss briefly some notable features of these solutions. Equation (14) yields a *positive* velocity so long as  $\Phi > 1/3$ , or equivalently when  $\tau < 1$ . This confirms that the

$$\sigma_{zz} = \sigma_{[s]} + \sigma_{[a]} + \sigma_p - p \quad (19)$$

This definition allows the surface tension to be calculated even for a moving interface. The total stress tensor  $\sigma_{zz}$  includes an irreversible symmetric part  $\sigma_{[s]}$ , an irreversible antisymmetric part  $\sigma_{[a]}$ , a reversible distortion part  $\sigma_p$ , and an isotropic pressure part  $-p$ . This is given by [9]

$$\sigma = \int_{-\infty}^{\infty} dx (\sigma_{zz} - \sigma_{xx}) \quad (18)$$

This definition can only be used when the phases are strictly in equilibrium. We can also determine the surface tension using its mechanical definition

$$\sigma = \int_{-\infty}^{\infty} dx \left( \frac{dx}{dn} \right) = \int_{n_1}^{n_2} dn \sqrt{2f(n)} = \frac{6}{\sqrt{2}} \quad (17)$$

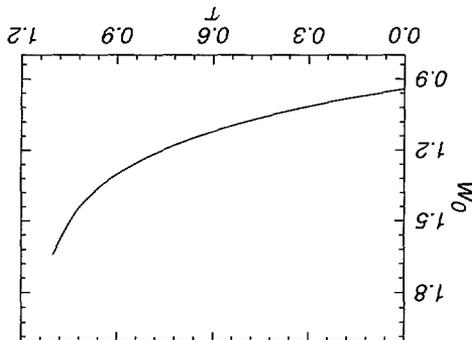
We now calculate the surface tension. In order to avoid complications which appear when the director aligns in the plane of the interface we consider homeotropic orientation at the interface. In equilibrium there are two equivalent definitions of the surface tension. On the one hand one can use the excess surface free energy definition of the surface tension. This yields

#### 4. Surface Tension

A final remark explicitly concerns the nematic orientational degrees of freedom. The length scale, and thus the velocity scale, is set by the effective elastic constant  $L$ . If the interfacial boundary conditions were homeotropic, rather than planar, the effective elastic constant would be  $L' = \frac{2}{3}L_1 + L_2 > L$ . The front velocity would thus paradoxically be increased – paradoxically, because this increase occurs in a region of decreased stability. Let us now suppose an index 1 defect in the front, in such a way that director escape to the third dimension is demanded in the core of the defect. In the core of the defect line the boundary condition is homeotropic, and thus the core should advance more quickly into the isotropic fluid than the surrounding planar region. Presumably the runaway advance of the core will be resisted by surface free energy effects, but nevertheless there seems here a possible new interfacial instability mechanism.

separate the problem into an inner isothermal problem and an outer problem which sets the surface temperature, though we shall return to this question in the final section.

Fig. 2 — The characteristic thickness of the interface  $z_0$  as a function of temperature  $\tau$





$$\sigma_{ij}^{[s]} = -\beta_1 H_{ij}^{[s]} \tag{20}$$

$$\sigma_{ij}^{[a]} = -\frac{\delta \mathcal{F}}{\delta Q_{ik}} Q_{kj} + Q_{ik} \frac{\delta \mathcal{F}}{\delta Q_{kj}} = 0 \tag{21}$$

$$\sigma_{ij}^d = -\frac{\delta \mathcal{F}}{\delta \partial_i Q_{kl}} \partial_j Q_{kl} \tag{22}$$

where  $\beta_1$  is a kinetic coefficient related to the rotational viscosity of the nematic.

The homeotropic boundary condition enforces uniaxial order. We thus have  $Q_1 = Q_{xx} = \eta$ ;  $Q_2 = Q_{yy} = -\eta/2$ ;  $Q_3 = Q_{zz} = -\eta/2$  and  $Q_{ij} = 0$  for  $i \neq j$ . We use the one constant approximation for the elastic free energy ( $L_2 = 0$ ).

The nondimensional forms for the bulk free energy density  $f_b$  and for the elastic free energy density  $f_g$  are now respectively:

$$f_b = \frac{2}{3} \tau \text{Tr} Q^2 - \frac{8}{3} \text{Tr} Q^3 + \frac{4}{9} (\text{Tr} Q^2)^2, \tag{23}$$

and

$$f_g = \frac{1}{3} \text{Tr} (dQ/dx)^2. \tag{24}$$

The mean field  $H_{ij}$  is given by:

$$H_{ij} = -\frac{\delta \mathcal{F}}{\delta Q_{ij}} = -\frac{4}{3} \tau Q_{ij} + 8Q_{ij}^2 - \frac{16}{9} Q_{ij} \text{Tr} Q^2 + \frac{2}{3} \frac{d^2 Q_{ij}}{dx^2}, \tag{25}$$

with symmetric part

$$H_{ij}^{[s]} = -\frac{4}{3} \tau Q_{ij} + 8(Q_{ij}^2 - \frac{1}{3} \delta_{ij} \text{Tr} Q^2) - \frac{16}{9} Q_{ij} \text{Tr} Q^2 + \frac{2}{3} \frac{d^2 Q_{ij}}{dx^2} \tag{26}$$

Using equation (22) the distortion stress tensor is now given by:

$$\begin{aligned} \sigma_{xx}^d &= -\frac{2}{3} \text{Tr} \left( \frac{dQ}{dx} \right)^2 = -\left( \frac{d\eta}{dx} \right)^2 \\ \sigma_{zz}^d &= 0. \end{aligned} \tag{27}$$

Hence

$$\begin{aligned} \sigma_{xx} &= -\beta_1 H_{xx}^{[s]} + \sigma_{xx}^d - p \\ &= \beta_1 \left( \frac{4}{3} \tau \eta - 4\eta^2 + \frac{8}{3} \eta^3 - \frac{2}{3} \frac{d^2 \eta}{dx^2} \right) - \left( \frac{d\eta}{dx} \right)^2 - p; \end{aligned} \tag{28}$$

$$\sigma_{zz} = -\beta_1 H_{zz}^{[s]} - p = \beta_1 \left( -\frac{2}{3} \tau \eta + 2\eta^2 - \frac{4}{3} \eta^3 + \frac{1}{3} \frac{d^2 \eta}{dx^2} \right) - p; \tag{29}$$

and

$$\sigma_{zz} - \sigma_{xx} = \beta_1 \left( -\frac{df_b}{d\eta} + \frac{d^2 \eta}{dx^2} \right) + \left( \frac{d\eta}{dx} \right)^2 = \beta_1 \frac{\partial \eta}{\partial t} + \left( \frac{d\eta}{dx} \right)^2. \tag{30}$$

The surface tension is now:

$$\sigma = \int_{-\infty}^{\infty} (\sigma_{zz} - \sigma_{xx}) dx = \beta_1 \int_{-\infty}^{\infty} \frac{\partial \eta}{\partial t} dx + \int_{-\infty}^{\infty} \left( \frac{d\eta}{dx} \right)^2 dx. \tag{31}$$

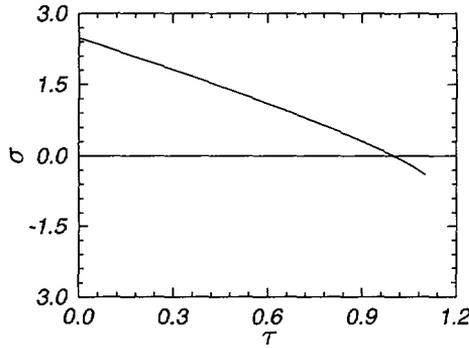


Fig. 3. — The dimensionless surface tension  $\sigma$  as a function of temperature  $\tau$ .

Changing the variable to  $x' = x - vt$  we obtain

$$\sigma = -\beta_1 v [\eta(\infty) - \eta(-\infty)] + \frac{\sqrt{2}}{6} = \beta_1 v \eta_3 + \frac{\sqrt{2}}{6} \quad (32)$$

It is clear from equations (31,32) that the surface tension is *increased* from its equilibrium value if  $\eta$  is increasing with time,  $v > 0$ ,  $\tau < 1$  and  $T < T_{\text{NI}}$  whereas it *decreases* for  $T > T_{\text{NI}}$ .

Using the relations  $\eta_3 = 3(1 + \Phi)/4$  and  $v = 3(3\Phi - 1)/2^{3/2}$ , we obtain:

$$\sigma = \frac{\sqrt{2}}{6} \left[ \frac{27\beta_1}{8} (1 + \Phi)(3\Phi - 1) + 1 \right] \quad (33)$$

This formula shows explicitly that the surface tension decreases below its equilibrium value above  $T_{\text{NI}}$ , in the region where the isotropic phase advances into the nematic. The nematic phase loses its stability at  $\tau = 9/8 = 1.125$ . What happens to the behavior of the surface tension in this limit? This depends on the numerical value of  $\beta_1$ . Letting  $\tau = 1 - \Delta\tau$ , we can linearise the surface tension, yielding:

$$\sigma = \frac{\sqrt{2}}{6} \left( \frac{27}{2} \Delta\tau \beta_1 + 1 \right) \quad (34)$$

The surface tension goes negative for  $-\Delta\tau > 2\beta_1/27$ . We can estimate the value of the dimensionless parameter  $\beta_1$  in a plausible nematic from the relation  $\beta_1 = 3\eta_3\lambda/2$  (Eq.(4.9a) in [9]), with  $\lambda = 1.04$ , yielding  $\beta_1 \approx 0.78$ . In Figure 3 we plot the surface tension as a function of temperature with this value of  $\beta_1$ . There is strong temperature dependence of  $\sigma$ . The surface tension goes to zero at  $\tau = 1.057$ , about half way to the point where the bulk nematic phase loses its stability. Conversely, it increases dramatically at temperature is decreased toward the isotropic spinodal point.

We now ask how much credence to attach to this result and what the physical consequences might be. We do not attach very great significance to the detailed numbers primarily because we adopt here a grossly simplified model, in which there is no coupling with the thermal, hydrodynamic, or orientational degrees of freedom. A more sophisticated calculation including these features may rescue a positive surface tension. It does, however, seem likely that the result that the surface tension is strongly temperature dependent is robust against changes in the model; we should not adopt the equilibrium value of the surface tension uncritically as one might expect to do in a continuum calculation.

## 5. The Critical Nucleus

The critical radius of a spherical nucleus of nematic immersed in an infinite bulk of isotropic phase is given by (see [10]),

$$R_c = \frac{2\sigma_1}{f(\eta_1) - f(\eta_3)} \eta_3^2 \quad (35)$$

where we have used dimensionless quantities. In our case, the equation (35) becomes,

$$R_c = \frac{4\sqrt{2}}{3} \frac{1}{3\Phi - 1} \quad (36)$$

If  $T > T_{\text{NI}}$  ( $\Phi < 1/3$ ) for  $R > R_c$  the nucleus will grow and for  $R < R_c$  it will disappear in time. If  $T < T_{\text{NI}}$  ( $\Phi > 1/3$ ) then no positive  $R_c$  exists. Finally, if  $T = T_{\text{NI}}$  ( $\Phi = 1/3$ ) then  $R_c = \infty$ , and nematic and isotropic phases coexist with a planar surface of contact. Thus, in the vicinity of  $T_{\text{NI}}$  (*i.e.* for small supercooled and superheated domains, which is experimentally true for the real nematics) the planar interphase constitutes a good approximation.

This order of magnitude estimate is, however, only indicative. A droplet with planar boundary conditions everywhere is topologically forbidden. Boojum defects must appear at the poles of the droplet, and at these defects planar boundary conditions should obtain. The region around the defect should then – as discussed above – expand more quickly (by a factor of about 2 in our calculation) than the rest of the droplet, causing it to adopt a prolate shape. A naïve estimate, based only on kinetic factors would suggest a stable cylinder with a length roughly twice its diameter; this would be mitigated by energetic effects preferring a smooth (and spherical) surface with a small homeotropic surface region.

## 6. Relaxation Modes

In this section we discuss, for completeness, the relaxation mode solution of equation (11). The relaxation mode solution interpolates between the nematic solution  $\eta_3$ , and the maximum of  $f_b(\eta)$ ,  $\eta_2$ . The physical relevance of these solutions is unclear at this stage, though they may be important in the region where the isotropic phase is thermodynamically unstable. The relaxation modes have a continuum of possible velocities, can be both monotonic and *nonmonotonic* [14–16], and are given by

$$\eta_{\text{rm}}(x') = \frac{3}{4} \left( 1 - \Phi \tanh \frac{x'}{x'_{01}} \right); \quad x'_{01} = \frac{2^{3/2}}{3\Phi}, \quad (37)$$

with the velocity given by  $v_2 = 3/\sqrt{2}$ .

Solutions of equation (11) correspond to the trajectories in the  $(\eta, \psi)$  phase-space of the system,

$$\frac{d\eta}{dx'} = \psi; \quad \frac{d\psi}{dx'} = -v\psi + 2\tau\eta - 6\eta^2 + 4\eta^3. \quad (38)$$

The system (38) defines three equilibrium points (steady states):  $(\eta_1, 0)$ ,  $(\eta_2, 0)$  and  $(\eta_3, 0)$ . The roots of the characteristic equation for the first and third steady states are both real but have opposite signs, so these two equilibrium points are always saddle points. For the second steady state, the roots can be (depending on the value of the velocity  $v$ ) either both real and negative or both complex, so that the second steady state can be either a stable node or a stable focus. The critical value of the velocity (*i.e.*, the value  $v_c$  for which the second equilibrium point transforms from a stable focus ( $v < v_c$ ) into a stable node ( $v > v_c$ )) is given by,

$$v_c = 3\sqrt{2\Phi(1 - \Phi)}. \quad (39)$$

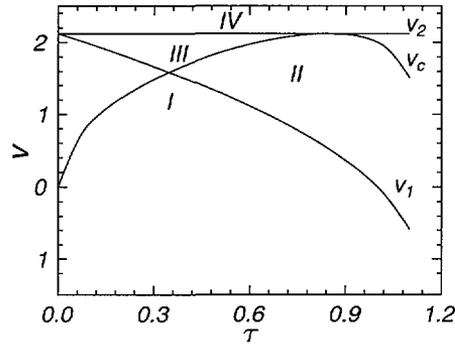


Fig. 4. — The  $(\tau, v)$  phase diagram of the solutions of TDGL equation; region I: unbounded solution; region II: nonmonotonic relaxation mode; region III: monotonic relaxation mode; region IV: unbounded solution.

For  $T = T_{NI}$  ( $\Phi = 1/3$ ) the critical value of the velocity is  $v_c = 2$ , the well-known result [14,15].

The  $(\tau, v)$  phase diagram is presented in Figure 4. For small values of  $v$  ( $v < v_1$ ) the separatrix is an unbounded solution (region I in Fig. 3). There is a unique value of  $v$  ( $v = v_1$ ) for which the separatrix becomes a saddle-saddle connection *i.e.*, the relaxation mode becomes domain wall. For values of  $v$  such that  $v_1 < v < v_c$  the separatrix is a saddle-focus connection, the relaxation mode being nonmonotonic (region II). For  $v_c < v < v_2$  the separatrix connects the saddle point and the stable node, the relaxation mode being monotonic (region III). Thus  $v_c$  is the minimum value of velocity for which relaxation mode is monotonic. For  $v > v_2$  (region IV) the relaxation mode becomes again an unbounded solution.

## 7. Conclusions

Firstly we make some numerical estimates of the quantities we have calculated. We use parameters reasonable for the low molecular weight nematic fluid N-[p-methoxybenzylidene]-p-butylaniline (MBBA). Vertogen and de Jeu [21] cite the following values for the material parameters entering the Landau-de Gennes theory:  $a = 75 \text{ kJ m}^{-3} \text{ K}^{-1}$ ,  $b = 169 \text{ kJ m}^{-3}$ ,  $c = 90 \text{ kJ m}^{-3}$ ,  $L = 9 \times 10^{-15} \text{ kJ m}^{-1}$  and  $\beta = 10^{-4} \text{ kJ s m}^{-3}$ . Using these parameters we find the following values for the units of time, space and velocity, respectively:  $t^* \simeq 10^{-6} \text{ s}$ ;  $\xi \simeq 10^{-8} \text{ m}$  and  $\xi/t^* \simeq 10^{-2} \text{ ms}^{-1}$ . The velocity of the moving front is thus of the order of  $\text{cm s}^{-1}$ , the interface thickness of the order of  $10^{-8} \text{ m}$ . The critical radius of the nematic droplet at  $T = T^*$  is also of this order and remains so for  $\tau \leq 0.5$ ; however it increases as  $T$  approaches  $T_{NI}$ ; by  $\tau = 0.95$ , for example,  $R_c/\xi \sim 10$ .

In this paper we have discussed the growth of nematic droplets in a supercooled isotropic fluid. We have concentrated on the moving nematic-isotropic interface at the surface of these droplets. We have constructed the simplest phase field theory model of this interface. In this simplest theory there is only one relevant order parameter. This is the largest eigenvalue of the liquid crystal ordering matrix. The principal axes of this matrix are not spatially dependent in this simplest model.

We have written down the travelling-wave profiles which move with a constant velocity and conserve their initial shape. These are solutions of the one-dimensional time-dependent Ginzburg-Landau equation for the nematic-isotropic phase transition. When the isothermal system is initially quenched into the metastable régime of the isotropic phase ( $T_{NI} < T < T^*$ )

the time evolution of the order parameter is a domain wall solution of the TDGL equation. Domain walls constitute the simplest form of topological defects and are surfaces - planar in our case - which separate domains of the two equilibrium phases.

The domain walls propagate with a unique velocity, which depends more or less linearly on the degree of undercooling. The thickness of the interface depends significantly on the temperature. We have also estimated the surface tension for the stationary and mobile nematic-isotropic interfaces. In the latter case we have obtained an unexpected result in the sense that for  $\tau > 1.06$  the surface tension is negative, though the significance of this result is unclear. The velocity is sufficiently slow that the experimental inability to supercool isotropic fluid can be definitively attributed to rapid *nucleation* rather than *invasion* of the nematic phase.

An expression for the critical radius of a spherical nucleus of nematic immersed in an infinite bulk of isotropic phase as function of temperature has also been determined. We have also discussed the shape of the true critical droplet.

We have also discussed the relaxation mode solutions of the time dependent Ginzburg-Landau theory. These have a continuum of possible velocities and can be both monotonic and nonmonotonic. We have obtained the complete temperature-velocity phase diagram for the solutions of TDGL equation.

The two main approximations used in this paper involve the decoupling of the temperature field, and the neglect of all but the very simplest features of the orientational degrees of freedom. Nevertheless this simple time-dependent Ginzburg-Landau model gives some insight into the behavior of the moving interface, and is a necessary prerequisite for further work.

This simplified model, of course, omits crucial features of the relevant physics. The thermal coupling (including the effect of the latent heat emission at the interface) must be correctly treated in all theories of moving interphase regions, and as shown by Schofield and Oxtoby [5] this can have rather profound consequences. Competition between the bulk and surface liquid crystalline textures as a result of the effect of external fields or the thermal gradient, related instabilities of the flat nematic-isotropic interface, and the coupling between a changing nematic tensor order parameter and velocity fields in the medium, are all specific to the moving liquid-crystalline interface. We shall address both these aspects of the problem in future work.

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## References

- [1] Gunton J.D., San Miguel M. and Sahni P.S., in "Phase Transitions and Critical Phenomena", Vol.8, C. Domb and J.L. Lebowitz Eds. (Academic, New York, 1983) p. 267.
- [2] Binder K., *Rep. Prog. Phys.* **50** (1987) 783.
- [3] see *e.g.* "Homogeneous Nucleation Theory", F.F. Abraham Ed. (Academic Press, New York, 1974).
- [4] Collins J.B. and Levene H., *Phys. Rev. B* **31** (1985) 6119.
- [5] Schofield S.A. and Oxtoby D.W., *J. Chem. Phys.* **94** (1991) 2176; Löwen H., Schofield S.A. and Oxtoby D.W., *J. Chem. Phys.* **94** (1991) 5685.
- [6] Bray A.J., *Adv. Phys.* **43** (1994) 357.

- [7] Zapotocky M., Goldbart P.M. and Goldenfeld N., *Phys. Rev.* **51** (1995) 1216.
- [8] de Gennes P.G., "The Physics of Liquid Crystals" (Clarendon, Oxford, 1975).
- [9] Olmsted P.D. and Goldbart P.M., *Phys. Rev.* **46** (1992) 4966.
- [10] Metiu H., Kitahara K. and Ross J., *J. Chem. Phys.* **64** (1976) 292.
- [11] Chan S.K., *J. Chem. Phys.* **67** (1978) 5755.
- [12] Scott A.C., *Rev. Mod. Phys.* **47** (1975) 487.
- [13] Haken H., "Synergetics" (Springer, Berlin, 1983).
- [14] Aronson D.G. and Weinberger H.F., *Adv. Math.* **30** (1978) 33.
- [15] Ben-Jacob E., Brand H., Dee G., Kramer L. and Langer J.S., *Physica* **14D** (1985) 348.
- [16] van Saarloos W., *Phys. Rev.* **37** (1988) 211; **39** (1989) 6367.
- [17] de Gennes P.G., *Mol. Cryst. Liq. Cryst.* **12** (1971) 193.
- [18] Olmsted and Goldbart, *op. cit.* equation (4.9). Note that our transport parameter is related to  $\beta_2$  defined in this paper by the relation  $\beta = \frac{3}{2}\beta_2$
- [19] Hohenberg P.C. and Halperin B.I., *Rev. Mod. Phys.* **49** (1977) 435.
- [20] Sen A.K. and Sullivan D.E., *Phys. Rev.* **35** (1987) 1391.
- [21] Vertogen G. and de Jeu W.H., "Thermotropic Liquid Crystals, Fundamentals" (Springer-Verlag, Berlin, 1988).