Defect-induced melting in nematic liquid crystals

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In this paper we employ a relatively simple theory to show how a nematic disclination line can act as a nucleation site for the growth of the isotropic phase. With this theory we are able to find analytical expressions for the critical temperature of nucleation and the behaviour of the core radius as a function of temperature. We are then able to compare these results with a previous numerical model of this effect.

The structure of defects and defect cores in liquid crystals has long been a subject of interest [1–4]. Previous interest arose due to the disruptive effect of defects in liquid crystal display devices; recently, with the development of the zenithal bistable display (ZBD) [5] in which half-integral disclination lines play an important rôle, there has been increased interest in defects in displays. This paper is concerned with these half-integral disclination lines, which occur in nematic liquid crystals, and the effect they have on the isotropic to nematic phase transition.

The phase transition between the isotropic liquid phase and the anisotropic nematic liquid crystal phase is first order. However, this phase transition is often said to be *weakly* first order. The *weakness* comes from two features in particular: the entropy change at the transition (small as compared with k_B per particle), and the existence of almost critical orientational fluctuations close to the transition. The dependence of the orientational order parameter S on temperature T in thermotropic nematogens is typically as shown in figure 1.

In the isotropic phase $(S = 0)$ the magnitude of fluctuations in the order parameter, and hence the susceptibility to phase change increases dramatically as the temperature approaches $T^* < T_{NI}$. A similar increase occurs in the nematic phase $(S \neq 0)$ at $T^+ > T_{NI}$. Typically the temperature difference $T^+ - T_{NI} \sim 1\,K \ll T_{NI}$, which is another indication of the weakness of the first order phase transition.

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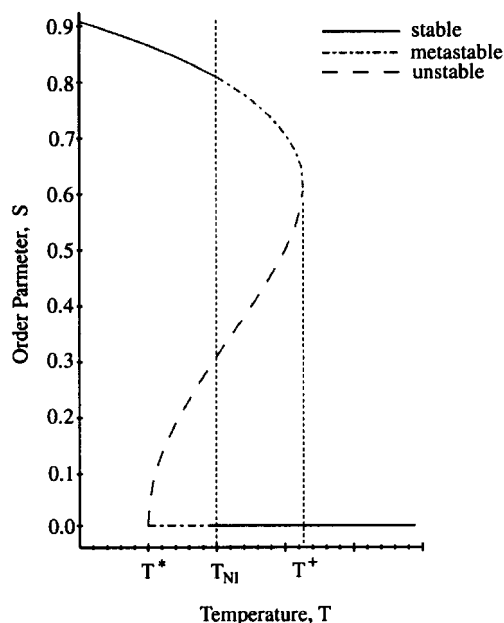
Figure 1. Typical curve of order parameter against temperature, showing the temperatures T_{NI}, T^* and T^+. Full line: global stability branch; dot-dash line: metastable branch; dashed line: unstable branch.

The temperatures T^* and T^+ represent *spinodal* points of the isotropic and nematic phases, respectively. In principle, supercooling of the isotropic state or superheating of the nematic state can occur at temperatures $T^* < T < T^{NI}$ and $T^{NI} < T < T^+$, respectively. In the case of nematic superheating, the isotropic state is the minimum energy state and the nematic state is a metastable, high energy state. However, beyond the spinodal

Figure 2. Director (*a*) and order parameter (*b*) configurations of a disclination line of strength 1/2 [6]. In (*b*) the order parameter S reduces close to the centre of the defect ($r = 0$) whilst there exists a small amount of biaxiality α in this region. The bulk order parameter S_b is defined as the asymptotic value of S as $r \to \infty$ and the core radius R is defined as the radius at which $\mathrm{d}^2 S/\mathrm{d}r^2$ is a maximum.
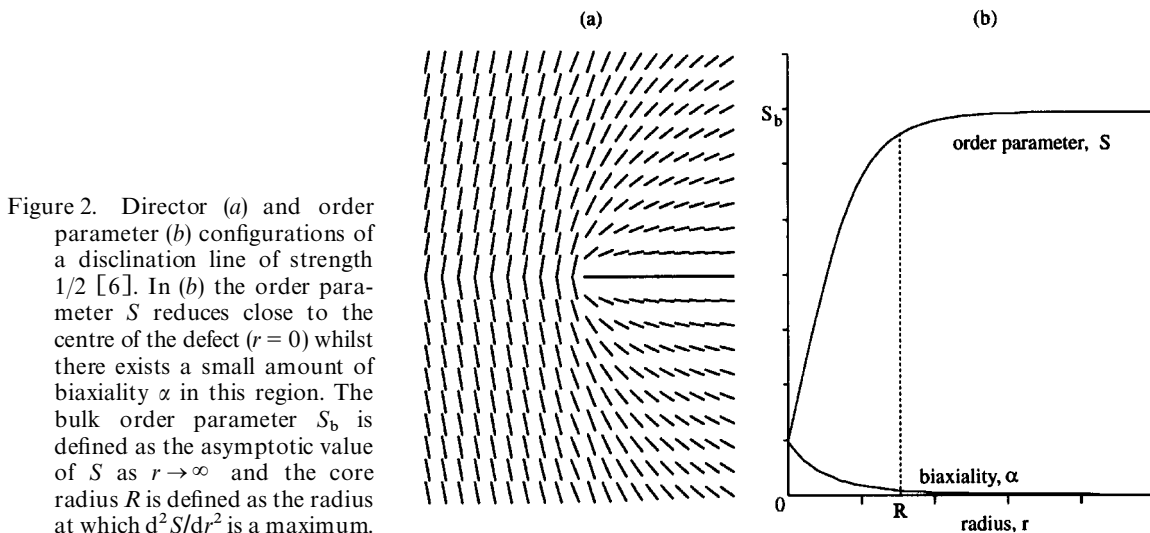
point $T = T^+$ the metastable nematic phase becomes unstable with respect to orientational fluctuations and the isotropic state is the only stable configuration. Thus the nematic phase cannot be superheated above T^+. In practice, however, even this modest amount of superheating is not observed.

Mottram and Hogan [6] have carried out a detailed investigation into the structure of the core of a line disclination within a model closely related to the classic Landau–de Gennes model. Related calculations have also been carried out by other authors [7–11]. The model describes the free energy of the disclination line, at a specific temperature, as the sum of the energy resulting from the difference between the local and equilibrium order parameters and the energy of spatial distortions of both the order parameter and director. In the presence of a defect, a change in the order parameter is inevitable. In circumnavigating a strength 1/2 defect, the director must rotate through π radians, and thus at the centre of the defect there exists a singularity in the director configuration and a corresponding reduction in order.

The director and order parameter solutions from [6] are shown in figure 2. The order parameter in the core of the defect is reduced, and there is also some biaxiality, α. The presence of biaxiality, which is associated with a non-zero amount of ordering about a second molecular axis, perpendicular to the director, was also found by Schopohl and Sluckin [7]. The radius $R(T)$ of the core region can be defined, uniquely if somewhat arbitrarily, as the radius at which $\mathrm{d}^2 S/\mathrm{d}r^2$ is a maximum. Using the numerical package AUTO [12], it was possible to follow the solution structure carefully as temperature was increased above T_{NI}. It was found that stable solutions $R(T)$ exist up to, but not beyond, a temperature $T_c < T^+$.

There also exists a second, unstable, branch $R_u(T)$ in this régime. The radii of the unstable and stable solutions as a function of temperature for typical parameter values are shown in figure 3. This plot can be fitted to the parametric form

$$T(R) = T_{NI} + \frac{a}{R} - \frac{b}{R^2} \qquad (1)$$

where a and b are constants that depend on the parameters used in the calculation. From figure 3 we see that the unstable and stable branches of the curve annihilate at T_c and for temperatures above T_c there is no solution with a finite value of R. Thus the only solution is an infinitely large defect or equivalently the stable isotropic phase.
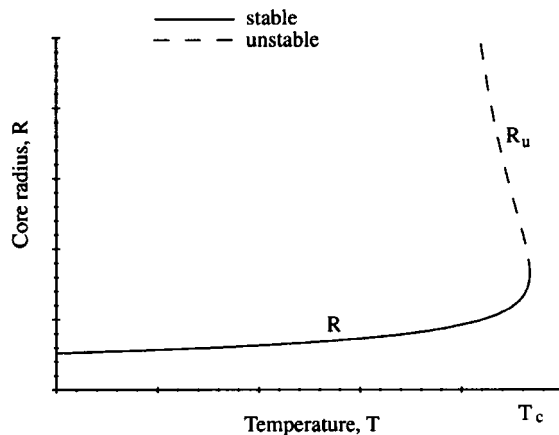

Figure 3. The temperature dependence of the defect core radius. From the numerical results of [6]. The stable core radius R and the unstable core radius R_u annihilate at the critical temperature T_c.

We now seek a simple thermodynamic model which replicates these results. We do this by regarding the radius of the defect R as the relevant thermodynamic variable, and writing a free energy F as a function of R. Minimization of the free energy will then lead to the stable and unstable solutions, R and R_u.

Let us consider the director structure shown in figure 2(a) contained with a region of radius D, divided into areas as shown in figure 4. These areas, within which we will approximate the behaviour of the liquid crystal, are: an *outer* region C where the order parameter is exactly equal to the bulk equilibrium order parameter, an *inner* region A where the order parameter is zero, and an *intermediate* region B which contains the internal boundary layer, centred at R, of figure 2(b). Thus region A is the *isotropic core* of the defect, C is the distorted nematic liquid crystal and B is a surface between the isotropic fluid inside the defect core, and the nematic fluid outside. It will be assumed that the thickness of this surface region δR is much smaller than the radius of the defect R. It should be noted that the assumption that $S = 0$ within the defect core was made explicitly by Fan [8] whereas in [7], and more recently in [9, 10], the inexactness of the isotropic defect hypothesis was emphasized. However, in this simple model of the free energy we may assume an isotropic defect core. We will now consider the energy contributions (per unit length of the disclination line) of each of these regions.

If the entropic free energy per unit volume of the isotropic phase is f_I then the free energy of region A is simply $f_I \mathscr{A}_A$, where $\mathscr{A}_A = \pi(R - \delta R/2)^2$ is the area of region A.
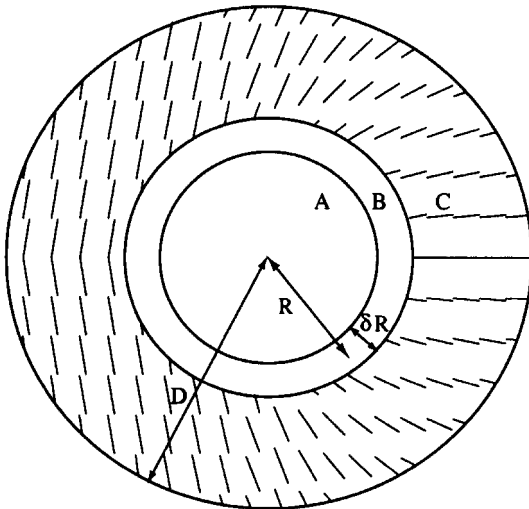

Figure 4. The simplified picture of a disclination line: region A, the inner, isotropic core of the defect; region B, the nematic–isotropic interfacial region; region C, the distorted nematic region.

Region B is associated with a surface free energy σ_{NI} per unit area. Thus the free energy of this region is $\sigma_{NI}\mathscr{L}$, where $\mathscr{L} = 2\pi R$ is the length of the surface.

The free energy of the outer region is the sum of the entropic energy of the nematic phase and the distortional energy of the director configuration. The entropic energy may be written as $f_N \mathscr{A}_C$, where $\mathscr{A}_C = \pi D^2 - \pi(R + \delta R/2)^2$ is the area of region C. The distortional free energy of the director configuration is $K(\nabla\theta)^2/2$ per unit volume, where K is the Frank–Oseen elastic constant and the local director orientation θ takes its asymptotic value $\theta = \phi/2$, where ϕ is the local circular polar coordinate.

The total free energy per unit length of the defect can then be written as

$$F = \pi f_I(R - \delta R/2)^2 + 2\pi\sigma_{NI}R + \pi f_N[D^2 - (R + \delta R/2)^2]$$
$$+ \frac{1}{2}K\int_0^{2\pi}\int_{R+\delta R/2}^{D}(\nabla\theta)^2\,dr\,d\phi. \quad (2)$$

We can simplify the quantities f_I and f_N close to T_{NI} using a Landau expansion of each phase,

$$f_\alpha(T) = f_\alpha(T_{NI}) - S_\alpha(T - T_{NI}) + O(T - T_{NI})^2 \quad (3)$$

where S_α is the entropy per unit volume of the phase α. Letting α be in turn N and I and noting that by definition $f_I(T_{NI}) = f_N(T_{NI})$ we obtain from equation (3):

$$f_I - f_N = -(S_I - S_N)(T - T_{NI}) + \text{higher order terms.} \quad (4)$$

Combining equations (2) and (4), explicitly performing the integration in equation (2) and neglecting higher order terms (in $T - T_{NI}$ and δR) we obtain (to within an irrelevant constant):

$$F(R) = -\pi\Delta S(T - T_{NI})R^2 + 2\pi\sigma_{NI}R - \frac{\pi K}{4}\ln R \quad (5)$$

where $\Delta S = S_I - S_N$.

Let us examine the significance of the terms in this equation. For $T < T_{NI}$ the first two terms imply that the presence of a region of isotropic fluid or a nematic–isotropic interface leads to an increase in the free energy of the system. Thus these terms favour a small defect. It is only the third term that favours a large defect since, for a small defect, the tightly splayed nematic region close to the nematic–isotropic interface leads to a large free energy contribution. By contrast, for $T > T_{NI}$ the entropic term in equation (5) is now negative and, like the director distortion term, favours a *large* defect. Only the surface term prevents unrestricted growth of the defect core.

Typical free energy curves are shown in figure 5. For $T < T_{NI}$ the balance of energy terms produces a minimum energy configuration at a finite defect radius $R(T)$. For
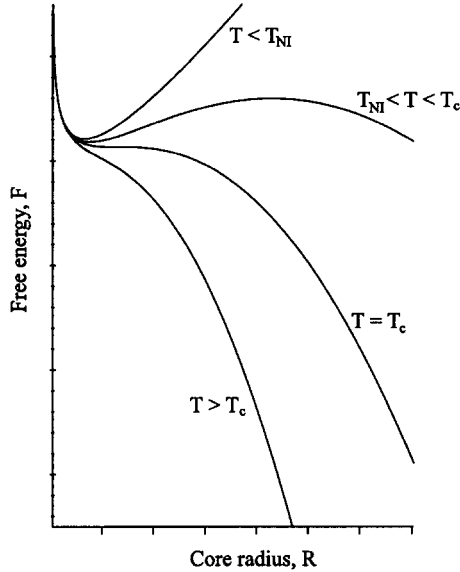
Figure 5. Schematic behaviour of free energy F at various temperatures. For $T < T_{NI}$ there exists only one energy minimum; for $T_{NI} < T < T_c$ there exists a minimum and a maximum; the minimum and maximum coalesce at $T = T_c$; for $T > T_c$ no energy minimum exists.

a small amount of superheating, $T > T_{NI}$, $T \sim T_{NI}$ the asymptotic behaviour of the free energy has changed since $F(R) \to -\infty$ as $R \to \infty$. The free energy $F(R)$ now has a minimum at $R(T)$ *and* a maximum at $R_u(T)$. For a large amount of superheating, the energetic advantage of the isotropic core is so great that it now overwhelms the surface energy-induced maximum. The minimum and the maximum annihilate at a critical temperature T_c, at which there is only a point of inflection. For $T > T_c$ the isotropic defect core grows catastrophically to invade the whole region.

The maximum and minimum solutions can be found analytically by minimizing $F(R)$ in equation (4). The governing equation for R is

$$\frac{\partial F}{\partial R} = 0 \qquad (6)$$

which gives

$$T(R) = T_{NI} + \frac{\sigma_{NI}}{\Delta S R} - \frac{K}{8\Delta S R^2} \qquad (7)$$

which is of identical form to that of equation (1), from the numerical calculations by Mottram and Hogan [6]. In equation (7) we have assumed that the material parameters are independent of temperature. This is equivalent to saying that the first order jump in order parameter in figure 1 is the dominant effect and the change in S along the upper branch of the curve in figure 1 is negligible.

From equation (7) the critical temperature T_c is found to be

$$T_c = T_{NI} + \frac{2\sigma_{NI}^2}{\Delta S K} \qquad (8)$$

and the maximum core radius of the stable solution is

$$R_{max} = \frac{K}{4\sigma_{NI}} \qquad (9)$$

which is *twice* the core radius at the transition temperature T_{NI}.

This defect-induced transition is a form of *heterogeneous nucleation*. During such a nucleation process, the need for thermal fluctuation to serve as a seed for the new phase can be avoided if there are sufficiently large impurities present. For sufficiently large superheating or supercooling, the impurity will be larger than a critical radius $R_c(T)$, and at that point the new phase grows from the surface of the impurity. The macroscopically small, but microscopically large finite size of the impurity provides a surface free energy term which increases with impurity size. It is this energy which must be overcome for nucleation to occur.

In our case the nucleation site is not an impurity but a defect, but broadly speaking the physics of the nucleation remains the same. In an analogous fashion, grain boundaries and dislocations in solids can also serve as nucleation sites for liquid nucleation. Thus heterogeneous nucleation can *always* occur from a pure phase which sustains topological defects.

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