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Statics and kinetics at the nematic-isotropic interface in porous media

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Abstract. We extend the random anisotropy nematic spin model to study nematic-isotropic transitions in porous media. A complete phase diagram is obtained. In the limit of relative low randomness the existence of a triple point is predicted. For relatively large randomness we have found a depression in temperature at the transition, together with a first order transition which ends at a tricritical point, beyond which the transition becomes continuous. We use this model to investigate the motion of the nematic-isotropic interface. We assume the system to be isothermal and initially quenched into the metastable *régime* of the isotropic phase. Using an appropriate form of the free energy density we obtain the domain wall solutions of the time-dependent Ginzburg-Landau equation. We find that including a random field leads to smaller velocity of the interface and to larger interface width.

PACS. 64.70.Md Transitions in liquid crystals – 68.10.Jy Kinetics (evaporation, adsorption, condensation, catalysis, etc.)

1 Introduction

Recently many studies have been devoted to liquid crystals confined to randomly interconnected networks of pores (for review see [1–5]). Liquid crystals immersed in such matrices exhibit many interesting physical phenomena such as modification of phase transitions, orientational order, elastic properties, and a director field.

The isotropic-nematic phase transition of thermotropic liquid crystals embedded in various kinds of porous media (Anopore and Nuclepore membranes, aerogels, sintered silica glasses, Vycor glass, and control porous glass are commonly used) has been experimentally investigated using various techniques: calorimetry [6–10], dynamic light scattering [11–13], static light scattering [6,14], magnetic birefringence [15], NMR [7,16], and dielectric spectroscopy [17]. The most important results inferred from these studies are the following. (i) Even at temperatures far above the bulk isotropic-nematic phase transition temperature there exists a weak residual nematic ordering at the enclosed surface. Consequently, it is more appropriate to call the corresponding phase paranematic rather then isotropic. (ii) The nematic order is replaced by a *quasi-long-range* nematic order having continuous but random distorsions of the director. Usually this phase is called the distorted nematic phase or speronematic phase. (iii) The weakly first order isotropic-nematic phase transition temperatures are shifted down a few degrees and the local orientational nematic order gradually increases for porous matrices with characteristic cavity sizes below 0.1μm.

Some of the recent theoretical investigations of confined liquid crystals [7,16] emphasize finite size and surface effects always present in porous media. Stimulated by de Gennes' idea [19,20] (results of the experiments on the phase separation of binary fluids in porous media could be interpreted in terms of a random field Ising model) a number of authors [21–23] have suggested that similar random field-type-models may provide a useful context within which to understand the physical properties of confined liquid crystals. A Monte-Carlo study performed by Bellini *et al.* [6] suggests that the isotropic-nematic phase transition temperature shift of 8CB confined in silica aerogel emerges from a rather complicated coupling between the surface phenomena and randomness.

The random-field-type models [21–23] assume that the porous medium imposes a local field which has a randomizing effect on the nematic director. Such a randomizing field depending neither on temperature nor on the phase structure of liquid crystal, is generally referred to as *quenched disorder*. The structure of the confined liquid crystal is the consequence of the competition between the quenched disorder provided by the porous medium and the elastic force which tends to minimize the distorsions of the nematic director.

Maritan *et al.* [22] have carried out mean field analysis of both the discrete three-state Potts model and the Lebwohl-Lasher model [24]. In both cases they consider an infinitely strong field oriented randomly on a fraction p of the lattice sites, where p may be interpreted

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as the fraction of liquid crystal molecules directly affected by the randomness of the pore geometry. Their analysis predicts a first order isotropic-nematic phase transition at a nonzero temperature for all $p \neq 1$, but the transition temperature decreases with increasing p. Chakrabarti [18] has carried out Monte-Carlo simulations for the Lebwohl-Lasher model for different values of p in a finite random field. The analysis brings out the fact that very low strength of the random orienting field cannot destroy nematic order, resulting in a first order isotropic-nematic phase transition for all values of p, including $p = 1$. For large strength, the nematic order is replaced by a quasi-long-range nematic order (speronematic) phase. The isotropic-speronematic phase transition is first order for low p and second order for large p indicating the presence of a tricritical point on the transition line. Cleaver *et al.* [21] have carried out a Landau-de Gennes-type of mean field analysis, incorporating the effect of a random orienting field, which shows that the isotropic-nematic transition remains first order for low strength of the random field, but becomes second order for high field strength. A tricritical point is also predicted.

The first purpose of the present paper is to investigate the influence of a random orienting field on the isotropic-nematic phase transition. We extend the random anisotropy nematic model (RAN) of Cleaver *et al.* [21] to include the competition between the quenched disorder and the elastic force.

Little work has been done to characterize the influence of confinement on the different aspects of dynamical behavior of confined liquid crystals. The confinement influences the ordering and changes viscosity, which can lead to a modification of the dynamics of the order parameter. The second aim of this paper is to study the influence of the random orienting field on the dynamics of formation of the nematic phase when the isotropic fluid is cooled quickly, or quenched, to a temperature at which the nematic is thermodynamically stable and the isotropic is metastable. The kinetics of nematic-isotropic phase transition is governed by two dynamical processes: nucleation and growth. Nucleation corresponds to the first appearance of the nematic phase as a fluctuation in the original isotropic phase; if the cost in free energy to create the critical nucleus of nematic is large enough, the rate can be quite small and the isotropic phase can persist in a metastable state for a considerable period of time. The growth process involves the propagation of the stable nematic phase into the metastable isotropic phase.

A full theory of the kinetics of growth in a nematic-isotropic phase transition would involve the variation in space and time of two quantities: an order parameter that distinguishes the two phases, and the temperature, which affects the local driving force for the formation of the new nematic phase. The sharp-interface (or Stefan-type model) of solidification [25,26] assumes that the phase boundary is infinitely narrow, so that the order parameter changes discontinuously across it. It is treated as a delta-function source of heat, and the equation to be solved is the heat flow equation with an explicit front-tracking of the nematic-isotropic interface position [27]. The simplest approaches in this direction do not give velocity selection, but rather permit steady-state solutions over a range of velocities. The phase-field model, which has been fruitfully used in studies of solidification [28–30], provides an alternative approach according to which the nematic-isotropic interface is modelled by a smooth transition region of finite width in the phase-field variable (or order parameter) $Q(\mathbf{r}, t)$. The two phases correspond to regions in which the values of Q are those pertaining to the isotropic and nematic phases (local minima in Q of the bulk free energy). The (nonconserved) order parameter is governed by a nonlinear reaction-diffusion equation of Ginzburg-Landau-type, which can be solved without explicitly tracking the free boundary. The time-dependent Ginzburg-Landau (TDGL) equation leads to definite predictions of dependence of velocity on the degree of undercooling [31,32]. Under normal circumstances, the TDGL equation is combined with the corresponding equations for other field variables (*e.g.*, temperature). However, for the case of growth of a nematic liquid crystal into a undercooled isotropic phase, the thermal field exhibits a characteristic boundary-layer thickness K_T/c (where K_T is the thermal diffusivity and c is the interface velocity) which is a factor 10^3 times greater than the thickness of the interface, so that the isothermal condition remains valid, and the equation may be solved isothermally at a temperature specified in the formulation of the problem.

This paper is organized as follows. In Section 2 we extend the RAN model of Cleaver *et al.* [21] to include the competition between the quenched disorder and the elastic force. The results obtained for nematic-isotropic phase transition are presented in Section 3. In Section 4 we present the solution of TDGL equation which describe the moving interface. Finally in Section 5 we make some concluding remarks.

2 Random anisotropy nematic model

Magnetic properties of a crystalline ferromagnet are defined by two major factors: exchange interaction, which leads to the parallel orientation of the neighbour spins, and magnetic anisotropy, which aligns spins along some preferable direction created by long-range crystalline order (the easy axis).

There are two general models for amorphous magnetism which assume either random space distribution of exchange [33] or random distribution of anisotropy axes [34]. The later model, known as the random anisotropy magnet (RAM) is described by the Hamiltonian

$$H = -J \sum \mathbf{s}_i \mathbf{s}_j - D \sum (\mathbf{s}_i \mathbf{n}_i)^2 \qquad (1)$$

where the exchange constant is J, and the first sum is taken over nearest neighbour pairs. The unit magnetic spins $\mathbf{s}_i$ are placed at site i of a lattice, the quantity $\mathbf{n}_i$ is a unit vector in a random direction marking the local easy axis, and the degree of disorder (anisotropy) is given by the parameter D. The RAM model has been much studied in the literature on magnetism [35,36].

A porous medium acts on the liquid crystal in two ways [22]. First, it provides excluded volume and second, chemical affinity effects introduce a preferential molecular orientation at the pore wall. The first effect should be equivalent to the presence of a random exchange and is considered to be of secondary importance. By analogy with the RAM model, the second effect should be represented by the Hamiltonian

$$H = -J \sum P_2(\mathbf{S}_i \mathbf{S}_j) - D \sum P_2(\mathbf{S}_i \mathbf{n}_i) \tag{2}$$

where P_2 is the second Legendre polynomial and $\mathbf{S}_i$ is a unit three-dimensional vector describing the orientation of a rod-like molecule of the liquid crystal. The $D = 0$ case is the familiar Lebwohl-Lasher lattice model of the liquid crystal [24]. It has been argued that the phase transition described by the Hamiltonian (2) may be in the spin glass universality class.

We adopt the standard characterization [37] of the uniaxial nematic order at position $\mathbf{r}$ at time t in terms of the traceless symmetric second rank tensor $Q_{ij}(\mathbf{r}, t)$ (with Cartesian indices $i, j = 1, 2, 3$)

$$Q_{ij} = \frac{1}{2} Q(3 n_i n_j - \delta_{ij}) \tag{3}$$

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

The Landau-de Gennes free energy functional appropriate to the Hamiltonian of equation (2) is given by [37]

$$F[Q] = \int_V (f_\mathrm{b} + f_\mathrm{r} + f_\mathrm{e}) \mathrm{d}V \tag{4}$$

where f_b, f_r, and f_e are the bulk, random, and elastic parts of the free energy density, respectively, and V is the volume of the system under consideration. The symmetry-allowed expression for f_b is given by [38],

$$f_\mathrm{b} = a(T - T^*) \mathrm{Tr}(Q^2) - B \mathrm{Tr}(Q^3) + C[\mathrm{Tr}(Q^2)]^2 \tag{5}$$

where T^* is the bulk undercooled temperature limit, and the variation of the coefficients a, B, and C with temperature T is assumed to be weak and will be neglected.

The random free energy density f_r comes from the random anisotropy term in equation (2). The element of randomness comes in when one permits the director axis $\mathbf{n}$ to point in arbitrary directions and to change significantly over a spatial scale R_a which includes some molecular distances a. The earliest analysis of random systems was the domain argument of Imry and Ma [39]. The main application of their ideas to a random anisotropy nematic spin model was made by Cleaver *et al.* [21]. We briefly review that picture now.

The effect of a random field is averaged over a length scale R_Q, over which the orientation is correlated (the characteristic scale of change of the order parameter). Imagine creating a domain of linear dimension R_Q which contains a large number of sites (domains of linear dimension R_a). By the central limit theorem, the effective random field which couples to the local order parameter is reduced by a factor of $N^{1/2}$, where N is the number of sites in a region of dimension R_Q ($N = (R_Q/R_a)^3$). The effective random field is thus approximately $D(R_Q/R_a)^{-3/2}$ and the corresponding free energy density f_r is given by

$$f_\mathrm{r} = -D \left(\frac{R_Q}{R_a} \right)^{-\frac{3}{2}} Q. \tag{6}$$

According to a recent paper of Weinan and Palffy-Muhoray [40], we emphasize that the expression (6) is valid if the random field is slowly varying in space compared to the coherence length. In this case the domain size is comparable to the correlation length of of the random field. When the field is rapidly varying, the domain size becomes large, and approaches the Imry-Ma length, which diverges as the strength of the random field goes to zero.

The final term f_e comes from the elastic free energy density,

$$f_\mathrm{e} = \frac{1}{2} L_1 \left(\partial_i Q_{jk} \right)^2 + \frac{1}{2} L_2 \left(\partial_i Q_{ij} \right)^2 \tag{7}$$

where L_1 and L_2 are elastic constants, and the Einstein summation convention is assumed. This term represents the contribution to the free energy density given by the surface of the domain. Now because Q is changing on a length scale R_Q, $\mid \bigtriangledown Q \mid \; \simeq Q/R_Q$. Using the representation (3) for Q this term is given by

$$f_\mathrm{e} = \frac{3}{4} L Q^2 R_Q^{-2} \tag{8}$$

where $L = \frac{3}{2} L_1 + \frac{1}{4} L_2$ is the effective elastic constant.

The competition between quenched disorder provided by the random field (6) and the elastic contribution to the free energy density (8) is defined by the non-dimensional parameter $\Lambda = D R_a^2 / L$.

In order to carry out calculations on this model it is useful to introduce a new length scale ξ defined by

$$\xi^2 = R_Q^2 - R_a^2 \tag{9}$$

and to scale the variables in the following way

$$\begin{aligned} &\overline{Q} = \frac{6C}{B} Q; \;\; \tau = \frac{24 a (T - T^*) C}{B^4}; \;\; \overline{L} = \frac{12 C L}{B^2 R_a^2}; \\ &\overline{D} = \frac{96 C^2 D}{B^3}; \;\; \overline{\xi} = \frac{\xi}{R_a}; \;\; \overline{f} = \frac{24^2 C^3}{B^4} f; \\ &\overline{\Lambda} = \frac{8 C \Lambda}{B} = \frac{\overline{D}}{\overline{L}}. \end{aligned} \tag{10}$$

Now, eliminating overbars, we obtain a scaled free energy density

$$f = f_{\mathrm{b}} - \frac{D}{(\xi^2+1)^{3/4}}Q + \frac{L}{\xi^2+1}Q^2 \tag{11}$$

where

$$f_{\mathrm{b}} = \tau Q^2 - 2Q^3 + Q^4 \tag{12}$$

is the bulk free energy density, while the last two terms in equation (11) constitute the free energy density generated by the random field.

The bulk isotropic-nematic phase transition takes place at $\tau = 1$ to a nematic phase in which the order parameter $Q = 1$. The bulk undercooling limit occurs at $\tau = 0$. The solutions of $\mathrm{d}f_{\mathrm{b}}/\mathrm{d}Q = 0$ occur at

$$Q_{10} = 0;\quad Q_{20} = \frac{3}{4}(1-\Phi);\quad Q_{30} = \frac{3}{4}(1+\Phi) \tag{13}$$

where $\Phi = (1-8\tau/9)^{1/2}$. The solutions Q_{10} and Q_{30} correspond, respectively, to the isotropic and nematic minima. The function $f_{\mathrm{b}}(Q)$ possesses only these two minima, with a maximum at Q_{20}.

Minimizing equation(11) with respect to ξ leads to

$$\xi = 0 \ \text{ when } \ Q < \frac{3}{4}\Lambda \tag{14}$$

and

$$\xi = \left[\left(\frac{4Q}{3\Lambda}\right)^4 - 1\right]^{1/2} \ \text{ when } \ Q > \frac{3}{4}\Lambda. \tag{15}$$

From (11), (14), and (15) the free energy density generated by the random field is given by

$$v_1(Q) = -DQ + \frac{D}{\Lambda}Q^2 \ \text{ when } \ Q < \frac{3}{4}\Lambda \tag{16}$$

and

$$v_2(Q) = -\frac{27}{256}D\Lambda^3 Q^{-2} \ \text{ when } \ Q > \frac{3}{4}\Lambda. \tag{17}$$

We note that the equations (16) and (17) become identical with the corresponding ones obtained in paper [21] in the limit $L = 1$. The existence of two independent parameters generates a completely different phase diagram in the relative low randomness *régime*.

3 The paranematic-speronematic phase transition

For low order parameters Q, the correlation length ξ is zero, and director orientations are correlated only on R_a. The first term $-DQ$ in the corresponding free energy density (16) is as though there were a fixed field on the molecules. The second term $DQ^2/\Lambda = LQ^2$ is the free energy density cost in changing molecular orientation from point to point. When the disorder is comparable to the elastic constant ($\Lambda \geq 1$) this term is negligible, but the two terms become comparable at low values of Λ.

Relaxing the condition $Q < 3\Lambda/4$, the free energy density corresponding to the isotropic phase in our model

$$f_{\mathrm{I}} = -DQ + \left(\tau + \frac{D}{\Lambda}\right)Q^2 - 2Q^3 + Q^4 \tag{18}$$

favours a paranematic-I (less ordered)-paranematic-II (more-ordered) first order phase transition. The equilibrium condition $(\partial f_{\mathrm{I}}/\partial Q) = f_{\mathrm{I}}' = 0$ defines the order parameter profile $Q(\tau, D, \Lambda)$. The paranematic-I-paranematic-II phase transition occurs at $\tau = 1 + D(1 - 1/\Lambda)$. A tricritical point exists for $f_{\mathrm{I}}'' = f_{\mathrm{I}}''' = 0$ which gives $D_{\mathrm{c}} = 0.5$, $Q_{\mathrm{c}} = 0.5$, and $\tau + D_{\mathrm{c}}/\Lambda_{\mathrm{c}} = 1.5$. For $D < D_{\mathrm{c}}$ the $Q(\tau, D, \Lambda)$ curves show a discontinuous (first order) paranematic-I-paranematic-II transition which becomes second order at $D = D_{\mathrm{c}}$. For $D > D_{\mathrm{c}}$ the $Q(\tau, D, \Lambda)$ curves relate continuously the two phases (the order parameter Q will increase smoothly as temperature is decreased). This behaviour is related to that of a nematic placed in a non-random field, *i.e.*, a field in an uniform direction. The uniform external field problem was first studied by Fan and Stephen [41] and there is now an extensive literature, including recent experimental verification [42].

At higher values of Q the cost of changing the orientation from point to point is increased. The system responds by increasing the length scale ξ over which the director orientations are correlated. In the low disorder limit $D \to 0$, the true nematic phase with infinite ξ is recovered.

The free energy density corresponding to higher values of order parameter Q,

$$f_{\mathrm{N}} = -\frac{27}{256}D\Lambda^3 Q^{-2} + \tau Q^2 - 2Q^3 + Q^4 \tag{19}$$

has only one minimum corresponding to the speronematic phase. It is interesting to note that a magnetic ordering field generates two speromagnetic phases [43].

Considering the constraints given by conditions (16) and (17) it is immediately clear that there are two completely different phase diagrams, one for $0 < D < D_{\mathrm{c}}$ and another for $D > D_{\mathrm{c}}$. In Figure 1 we show the (Λ, τ) phase diagram for $D = 0.2$. For low values of Λ ($\Lambda < \Lambda_{\mathrm{t}} = 1.183$) there is a discontinuous paranematic-I-speronematic phase transition (the paranematic-II minimum does not fulfill the condition $Q < 3\Lambda/4$). At $\Lambda_{\mathrm{t}} = 1.183$ all three phases are in equilibrium so that it can be considered as a triple point. At higher values

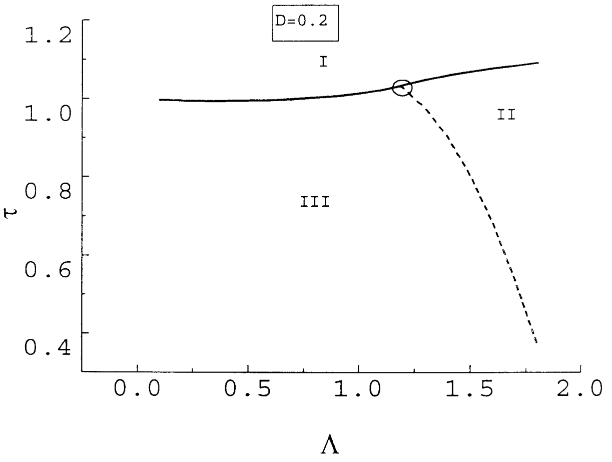

Fig. 1. The (τ, Λ) phase diagram for $D = 0.2$ showing first-order phase transition (full line), triple point ◯, and continuous phase transition (dashed line). Region *I*: *paranematic-I* phase is thermodynamically stable; region *II*: *paranematic-II* phase is stable; region *III*; *speronematic* phase is stable.

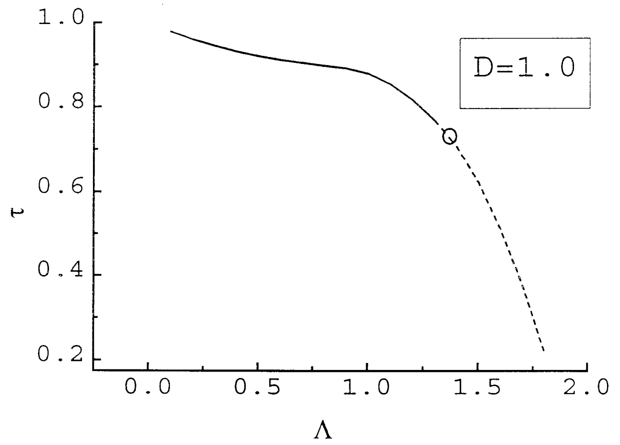

Fig. 2. Plot of the *paranematic-speronematic* phase diagram for $D = 1.0$. The full line denotes the first order phase transition, the dashed line the continuous transition and the circle the critical point.

of Λ ($\Lambda > \Lambda_t$) there are two phase transitions, a discontinuous one between the paranematic-I and paranematic-II phases at higher temperatures, and a continuous one between the paranematic-II and speronematic phases at lower temperatures.

For $D > D_c$ the transition paranematic-I-paranematic-II becomes continuous. The (Λ, τ) phase diagram for $D = 1.0$ is shown in Figure 2. The results confirm the experimental predictions. The first order transition temperature is reduced from $\tau = 0.98$ at $\Lambda = 0.1$ to $\tau = 0.805$ at $\Lambda = 1.2$. At $\Lambda_c \simeq 1.25$ there is a tricritical point beyond which the transition becomes continuous. The continuous transitions paranematic-II-speronematic, in Figure 1, and paranematic-speronematic for $\Lambda > \Lambda_c$, in Figure 2, could be an unphysical consequence of the procedure which consider ξ as a variational parameter. Thus, the procedure induces the constraint $Q < 3\Lambda/4$ for the paranematic phase as well as $Q > 3\Lambda/4$ for the speronematic phase. In the case $D = 0.2$ (see Fig. 1), for $\Lambda < \Lambda_t$, the paranematic-II minimum disappears because it does not fulfil the constraint $Q > 3\Lambda/4$. In the second case ($D = 1$; see Fig. 2), for $\Lambda > \Lambda_c$ the paranematic minimum disappears due to the same condition. This type of phase diagram is perfectly equivalent with that obtained in [21].

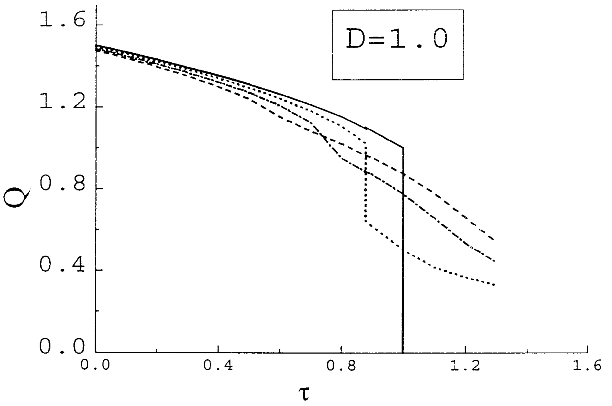

Fig. 3. Plots of $Q(\tau)$ for different Λ at $D = 1.0$. Full line: the bulk $Q(\tau)$ ($D = 0$); dotted line: $\Lambda = 1$; dash-dotted line: $\Lambda_c = 1.3$; and dashed line: $\Lambda = 1.5$.

The general topology of the phase diagram in $D-\Lambda-\tau$ space would be as follows. In the limit of low randomness ($D < D_c$) the region in (Λ, τ) over which the paranematic-II phase occurs shrinks with increasing D. The tricritical point which occurs in the limit of relatively large randomness ($D > D_c$) would shift to large Λ with increasing D.

In Figure 3 we show the profiles of the order parameters as a function of temperature for a few typical values of Λ. For $\Lambda < \Lambda_c$ there is a discontinuity in $Q(\tau)$ at the first order phase transition, whereas for $\Lambda > \Lambda_c$ there is a discontinuity in the slope $\mathrm{d}Q/\mathrm{d}\tau$. The behaviour of $Q(\tau)$ curves confirms the experimental results in the sense that the bulk first order isotropic-nematic phase transition is weakened and eventually suppressed when the randomness increases.

The behaviour of the correlation length ξ as a function of temperature τ for a number of different values of Λ is shown in Figure 4. ξ is a quantity of key importance for understanding of phase transition in the presence of disorder. ξ is in fact a direct measure of the "resistance" or the "stability" of the nematic phase to the presence of quenched disorder. In principle, ξ could be larger than the typical length over which the disordering structure is correlated [12]. As expected, ξ increases as τ decreases, and indeed as Q increases.

We postpone further discussion of the results to the last section. In the next section we discuss the influence of the random field on the dynamics of formation of a speronematic phase when the paranematic fluid is cooled quickly, or quenched, to a temperature at which the speronematic is thermodynamically stable and the paranematic is metastable.

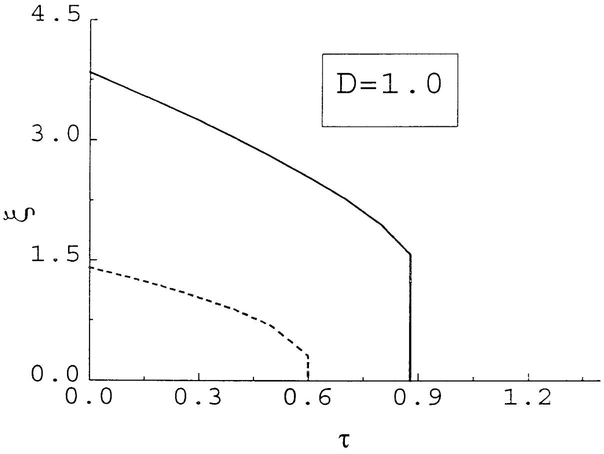

Fig. 4. The variation of the correlation length ξ as a function of temperature τ for $D = 1.0$. Full line: $\Lambda = 1$; dashed line: $\Lambda = 1.5$.

4 Moving interface-phase field model

Modelling the speronematic-paranematic interface by a smooth transition region of finite width in the phase-field variable (or order parameter) we describe the time evolution of the order parameter using the TDGL equation appropriate to non-conserved order parameters,

$$\beta \frac{\partial}{\partial t} Q_{ij}(\mathbf{r}, t) = -\frac{\delta F[Q]}{\delta Q_{ij}} \tag{20}$$

where β is a transport coefficient related to the rotational viscosity of the nematic. In the present work we take β to be constant. The same equation with an additional Langevin noise term is known from the theory of critical dynamics, where it is called model A in the classification of Hohenberg and Halperin [44].

In this paper we consider a system under conditions that allows an isothermal base state, in which the speronematic and paranematic phases are separated by a planar interface of finite width (usually called a domain wall) perpendicular to the z-axis, and which propagates with normal velocity $+c$ into the paranematic phase. Using the equations (3– 5, 7), and the scaling (10), the TDGL equation (20) becomes

$$\frac{\partial Q}{\partial t} - \frac{\partial^2 Q}{\partial z^2} = -\frac{\partial f}{\partial Q} \tag{21}$$

where f is the free energy density given by the equations (18) and (19) for the paranematic and speronematic phases, respectively. Appropriate units for distance and time are respectively $\zeta = (24CL/B^2)^{1/2}$ and $t^* = 16C\beta/B^2$.

The domain wall solution of equation (21) interpolates between the paranematic minimum, valid for $z \to \infty$, and speronematic minimum, valid for $z \to -\infty$. This domain wall or travelling wave solution has the form

$$Q(z, t) = Q(z - ct) = Q(z') \tag{22}$$

where z' is a spatial variable in a reference frame moving with the interface velocity c in the positive z direction. Transforming to this variable, we obtain

$$Q'' + cQ' = \frac{\partial f}{\partial Q} \tag{23}$$

where prime denotes differentiation with respect to z'.

An appropriate form of the free energy density is the following

$$f = \tau Q^2 - 2Q^3 + Q^4 + \frac{1}{2}(v_1 + v_2) + \frac{1}{2}(v_1 - v_2) \tanh \frac{z'}{w} \tag{24}$$

where v_1 is the free energy density generated by the random field for the paranematic phase (16), v_2 is the corresponding form for the speronematic phase (17), and w is the characteristic thickness of the interface. In what follows we adopt a linearized form of v_2

$$v_2 = -\frac{81}{256} D\Lambda^3 Q_{30}^{-2} + \frac{27}{128} D\Lambda^3 Q_{30}^{-3} Q \tag{25}$$

where Q_{30} is the bulk nematic minimum (13). We note that the results obtained for paranematic-speronematic phase transition with the equation (25) are almost the same with those obtained with the equation (17) (the difference is less than 1%).

The paranematic minimum Q_1 is the solution of the equation $(\partial f/\partial Q)_{z'=\infty} = 0$ whereas the speronematic minimum Q_3 is the solution of $(\partial f/\partial Q)_{z'=-\infty} = 0$. Using the equations (24) and (25), the solutions of TDGL equation (23) subject to the boundary conditions $Q(-\infty) = Q_3$ and $Q(\infty) = Q_1$ is given by

$$Q(z') = \frac{1}{2}(Q_3 + Q_1) - \frac{1}{2}(Q_3 - Q_1) \tanh \frac{z'}{w} \cdot \tag{26}$$

The characteristic thickness of the interface is

$$w = \frac{\sqrt{2}}{Q_3 - Q_1} \tag{27}$$

and its velocity is given by

$$c = 3\sqrt{2}(Q_3 + Q_1 - 1) - \frac{\sqrt{2}D}{\Lambda(Q_3 - Q_1)} \cdot \tag{28}$$

We note that in the case of a bulk nematic-isotropic moving interface (without random field) the well-known results are obtained [31]

$$Q_0(z') = \frac{1}{2} Q_{30} \left(1 - \tanh \frac{z'}{w_0}\right); \;\; w_0 = \frac{\sqrt{2}}{Q_{30}};$$
$$c_0 = 3\sqrt{2}(Q_{30} - 1). \tag{29}$$

We show in Figure 5 the behaviour of the domain wall velocity as a function of Λ at $D = 1.0$ and $\tau = 0.75$ (this value of temperature is chosen such that for all values of Λ the speronematic phase is thermodynamically stable

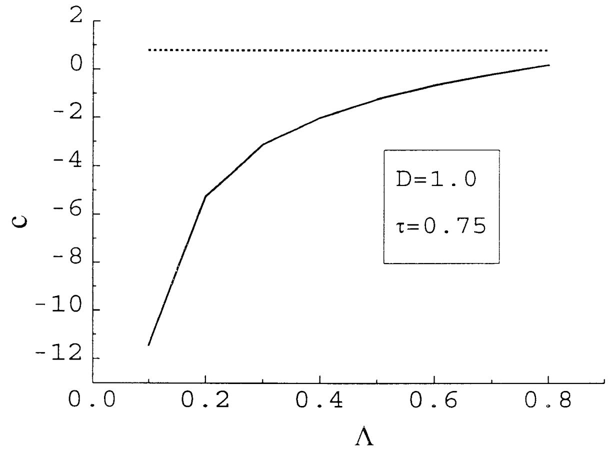

Fig. 5. The domain wall velocity c as a function of Λ at $D = 1$ and $\tau = 0.75$ (full line). Dotted line: the velocity c_0 of the nematic-isotropic moving interface without random field.

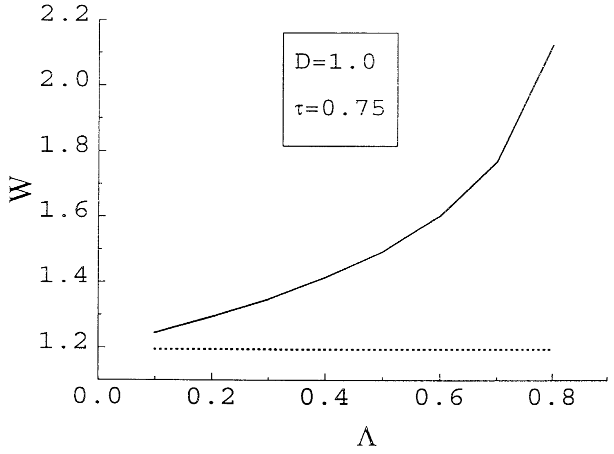

Fig. 6. The characteristic thickness of the interface w as a function of Λ at $D = 1$ and $\tau = 0.75$ (full line). Dotted line: same quantity without random field.

and the paranematic phase is metastable). Due to second term in the r.h.s. of equation (28), the random field slows down the motion of the interface. This result can be explained considering that an extra degree of disorder in the system generates a slowing of the moving interface (similar with the influence of biaxiality discussed in [32]). It is also confirmed by recent simulations [45]. For $\Lambda \leq 0.75$ the velocity goes negative (even if the speronematic phase is stable and the paranematic one is metastable, the paranematic advances into the speronematic). For low values of Λ, the elastic force represented by the effective elastic constant L becomes large and the second term in the r. h. s. of equation (28) becomes important.

Figure 6 shows the dependence of the characteristic thickness of the interface w on Λ at $D = 1$ and $\tau = 0.75$. The interface width is increased by the random field. The typical values of the interface thickness for usual liquid crystals are of the order of 10^{-8}m. In all matrices the characteristic size of voids is typically below the micrometer range (for some matrices even in the nanometer range). Depending on the ratio of the interface thickness to the pore size there are two distinct kinds of first-order phase transition behaviour [46]. If the interface thickness is less than the pore size, intrapore phase coexistence is observed, whereas if the interface thickness is larger than the pore size, speronematic order nucleates on a scale larger than the mean pore size and grows simultaneously in pores of all sizes.

5 Conclusions

In the first part of this paper (Sects. 2 and 3) we have discussed a generalization of the random anisotropy nematic model presented in [21]. Including the competition between the quenched disorder and the elastic force, the results are strongly dependent on two parameters: the degree of disorder (anisotropy) D and the ratio of anisotropy to elastic constant $\Lambda = D/L$. In the limit of low randomness the model predicts the existence of a triple point (for $\Lambda = \Lambda_t$) where the three phases (paranematic-I, paranematic-II, and speronematic) coexist in equilibrium. In the same limit, at low values of Λ ($\Lambda < \Lambda_t$) there exists a first order paranematic-I-speronematic phase transition. At higher values of Λ ($\Lambda > \Lambda_t$) there are two phase transitions, a first order one between paranematic-I and paranematic-II at higher temperatures, and a continuous one between paranematic-II and speronematic at lower temperatures.

At relatively large D we have found a reduced temperature at the transition, together with a first order paranematic-speronematic transition whose strength diminishes as Λ increases. We have obtained that the first order transition ends at a tricritical point, beyond which the transition becomes continuous. The results obtained in this relatively large randomness *régime* are perfectly equivalent with those of paper [21] and are confirmed by experiment. We emphasize that the analysis of Maritan *et al.* [22] predicts only a first order isotropic-nematic phase transition since the competition between quenched disorder and elastic force was not considered.

The second part of the paper (Sect. 4) is devoted to the influence of the random field on the growth of the speronematic phase into an undercooled paranematic phase. We have constructed a phase field model of the speronematic-paranematic moving interface. In this 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 model. Considering that the free energy density generated by the random field acts as an external potential, we have fitted a specific form of this field (see Eq. (24)) which interpolates between the paranematic potential valid for $z' \to \infty$ and speronematic potential valid for $z' \to -\infty$. 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 TDGL equation. When the isothermal system is initially quenched into the metastable *régime* of the paranematic phase 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 on the parameter Λ. We have obtained the result that the random field slows down the motion of the interface and increases the interface width. We have obtained also an unexpected result in the sense that for low Λ the velocity goes negative.

This simplified phase field model omits crucial features of the relevant physics. The thermal coupling (including the effect of the latent heat emission at the interface) can have rather profound consequences [47]. In the same framework it would be very interesting to analyse the interaction between the complex order parameter and hydrodynamic degrees of freedom.

Nevertheless the random anisotropy nematic model correlated with the associated time-dependent Ginzburg-Landau model gives some insight into the behaviour of the paranematic-speronematic phase transition as well as of the moving interface and is a necessary prerequisite for further work.

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