Kinetics of phase ordering of nematic liquid crystals confined in porous media

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Employing a time-dependent Ginzburg-Landau model, we investigate the influence of a random field on the phase ordering kinetics of nematic liquid crystals. We find that in the scaling regime the effect of random field (slowing down the growth of nematic) dominates over initial conditions for spatial dimensionality $d \leqslant 2$, whereas for $d > 2$ the random field has all its effect in the ''initial-growth'' regime. In this last case the mere confinement of liquid crystals is insufficient to produce slow growth of the nematic order.
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Recently many studies have been devoted to liquid crystals confined to randomly interconnected networks of pores (for review see Refs. [1–5]). Such systems raise fundamental issues, such as the effect of finite size and quenched disorder on phase transitions, orientational order, elastic properties, and director field. The simplest liquid crystal state is the nematic phase where the molecules exhibit only orientational long-range order and no translational long-range order. The isotropic (with neither orientational nor translational long-range order) to nematic transition of thermotropic liquid crystals embedded in various kinds of porous media (aerogels, Vycor glass, controlled porous glass, Anapore and Nucleopore membranes 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) The bulk isotropic-nematic phase transition temperatures are shifted down a few degrees and in some cases the character of transition changes. (ii) Even at temperatures far above the bulk isotropic-nematic phase transition temperature there exists a weak residual nematic ordering. Consequently, the corresponding phase is often called paranematic rather than isotropic. (iii) Monte Carlo simulations [18] show that in some cases the nematic order is replaced by a quasi-long-range nematic (usually called speronematic) phase. (iv) The random preferential orientation of liquid crystals along the pore surface (whose normal changes direction randomly over a persistent length) influences the dynamics of the isotropic to nematic phase transition only in the ''initial-growth'' regime. In the late stage of the dynamics, mere confinement of the liquid crystals is insufficient to produce slow growth of the nematic domains [19].

Following de Gennes' ideas [20], the theoretical approaches [21,22] used for the explanation of properties and behavior of confined liquid crystals are based on random-field-type models. In a previous paper [23], which we denote henceforth as paper I, we have extended the random anisotropy nematic spin model [21] to consider the effect of competition between the strength of the random orienting field and the elastic constant on the isotropic-nematic phase transition. In the limit of relative low randomness the existence of a triple point was predicted. For relatively large randomness we have found a reduced temperature at the transition, together with a first order phase transition which ends at a tricritical point, beyond which the transition becomes continuous. We have used this model to obtain the domain wall solutions of the time-dependent Ginzburg-Landau (TDGL) equation. The random orienting field leads to smaller velocity of the interface and to larger interface width.

When a system is quenched from a high-temperature disordered phase to a lower temperature where its ordered phase is thermodynamically favored, it evolves in time toward the latter (phase-ordering process). It has been well established that in the late stages of ordering a scaling regime is entered, characterized by a single time-dependent length scale $L(t)$, such that the domain structure is independent of time when lengths are scaled by $L(t)$ [24]. In this paper, following Filipe *et al.* [25], we study the random field effect on the phase-ordering dynamics of a nematic liquid crystal in a porous medium when its isotropic liquid precursor is cooled quickly to a temperature where the nematic phase is thermodynamically stable and the isotropic one is metastable (supercooled).

The order parameter for a nematic liquid crystal is a traceless symmetric second-rank tensor [26] $Q_{ij}(\vec{r},t) = Q(\vec{r},t)(3n_i n_j - \delta_{ij})/2$ where the unit vector $\vec{n}$ is the nematic director. In the problem we consider, we shall suppose $\vec{n}$ to be fixed in space and time, so that the relevant physics is given by the scalar (nonconserved) order parameter $Q(\vec{r},t)$. The Landau–de Gennes free energy functional appropriate to random anisotropy nematic model is given by $F[Q] = \int (f_b + f_r + f_e) dV$ where f_b, f_r, and f_e are the bulk, random, and elastic parts of the energy density, respectively. The symmetry-allowed expression for f_b is given by $f_b = a(T - T^*)\mathrm{Tr}(Q^2) - B\mathrm{Tr}(Q^3) + C[\mathrm{Tr}(Q^2)]^2$ where T^* is the bulk undercooled temperature limit. The element of randomness comes in when one permits the director axis $\vec{n}$ to point in arbitrary directions and to change significantly over a spacial scale R_a. Using Imry-Ma real-space domain arguments [27] (see also paper I), f_r is given by $f_r = -D(R_Q/R_a)^{-3/2}Q$ where R_Q is the characteristic scale of change of the order parameter. The final term f_e comes from the elastic free energy density $f_e = L_1(\partial_i Q_{jk})^2/2 + L_2(\partial_i Q_{ij})^2/2 = 3LQ^2R_Q^{-2}/4$, where L_1 and L_2 are elastic constants and $L = 3L_1/2 + L_2/4$. This term must be included because the random anisotropy is

causing the local orientation to wander in space on R_Q. We note that the ratio of disorder to elastic constant is defined by the nondimensional parameter $\Lambda = DR_a^2/L$. Introducing a new length scale $\xi = (R_Q^2 - R_a^2)^{1/2}$ and scaling the variables in the following way $\bar{Q} = 6CQ/B, \tau = 24a(T-T^*)C/B^2$, $\bar{L} = 12CL/B^2R_a^2, \bar{\xi} = \xi/R_a, \bar{D} = 96C^2D/B^3, \bar{f} = 24^2C^3f/B^4, \bar{\Lambda} = 8C\Lambda/B$, eliminating overbars, and minimizing the free energy density with respect to ξ, we obtain

$$f_P = -DQ + \left(\tau + \frac{D}{\Lambda}\right)Q^2 - 2Q^3 + Q^4 \quad \text{when} \quad Q < 3\Lambda/4, \tag{1}$$

the free energy density corresponding to the paranematic phase and

$$f_S = -\frac{27}{256}D\Lambda^3 Q^{-2} + \tau Q^2 - 2Q^3 + Q^4 \quad \text{when} \quad Q > 3\Lambda/4, \tag{2}$$

the free energy density corresponding to the speronematic phase.

We take the dynamics to be given by TDGL equation with the dimensionless form $\partial Q/\partial t - \nabla^2 Q = -f'(Q)$. We choose an appropriate form of the free energy density which interpolates between f_P valid for $z \to \infty$ and f_S valid for $z \to -\infty$ (see paper I),

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

where $v_1 = -DQ + DQ^2/\Lambda$ is the free energy density generated by the random field for the paranematic phase, $v_2 = 27D\Lambda^3 Q^{-2}/256$ is the corresponding form for the speronematic phase, and w is the characteristic thickness of the interface.

Considering that the system allows an isothermal base state in which the speronematic and paranematic phases are separated by a planar interface of finite width which propagates with velocity c into the paranematic phase, we look for solutions of the form $Q(g,t) = Q(g - ct) = Q(g')$, where g is a coordinate normal to the interface. The TDGL equation yields $Q'' + cQ' = f'(Q)$, subject to boundary conditions $Q(-\infty) = Q_S$ and $Q(\infty) = Q_P$. This ordinary differential equation has the solutionn $Q(g') = [Q_S + Q_P - (Q_S - Q_P)\tanh g'/w]/2$ with the characteristic thickness of the interface $w = \sqrt{2}/(Q_S - Q_P)$ and its velocity $c = 3\sqrt{2}(Q_S + Q_P - 1) - \sqrt{2}D/\Lambda(Q_S - Q_P)$ (see paper I). Thus the kinetics of nematic domain growth is slowed down by the random field.

In the ''Gaussian closure'' schemes a new field $m(\vec{r},t)$ is introduced, which varies smoothly on the domain scale and whose zeros defines the positions of the walls. Generalizing Mazenko approximation [28] (see also Ref. [25]), the transformation $Q(m)$ is defined by the flat moving interface profile function which satisfies $Q''(m) + cQ'(m) = f'(Q)$ with boundary conditions $Q(-\infty) = Q_S$ and $Q(\infty) = Q_P$. With this choice, rewriting TDGL equation in terms of m, gives [29]

$$\frac{\partial m}{\partial t} = \nabla^2 m - \frac{Q''(m)}{Q'(m)}(1 - |\nabla m|^2) - c. \tag{4}$$

The principal role of the double-well ''potential'' $f(Q)$ is to establish and maintain well-defined interfaces. It follows that the detailed form of $f(Q)$ is irrelevant to the large-scale structure. Following Bray and Humayun [30], we choose $Q(m)$ to satisfy $Q''(m) = -mQ'(m)$ which is equivalent to a particular form of the potential [25]. Locating the center of the wall at $m = 0$, we obtain the wall profile function $Q(m) = [Q_S + Q_P - (Q_S - Q_P)\mathrm{erf}(m/\sqrt{2})]/2$. After Fourier transformation, Eq. (4) becomes

$$\frac{\partial m_{\vec{k}}(t)}{\partial t} = [-k^2 + a(t)]m_{\vec{k}}(t) - c\,\delta_{\vec{k},\vec{0}}, \tag{5}$$

where $a(t) = 1 - \langle |\nabla m|^2 \rangle$. Considering the initial conditions for m to be Gaussian distributed, with zero mean and correlator (in Fourier space) $\langle m_{\vec{k}}(0) m_{\vec{k}'}(0) \rangle = \Delta(2\pi)^d \delta(\vec{k} + \vec{k}')$ (d is spatial dimensionality) and solving Eq. (5) for $\vec{k} \neq \vec{0}$ components of m, one finds $m_{\vec{k}}(t) = m_{\vec{k}}(0)(t/t_0)^{(d+2)/4}\exp(-k^2 t)$ where $t_0^{(d+2)/2} = d\Delta/4(8\pi)^{d/2}$ [25] from which the two-time correlator in real space follows immediately

$$C_0(1,2) \equiv \langle m(1)m(2) \rangle = \frac{4\sqrt{t_1 t_2}}{d}\left(\frac{4t_1 t_2}{(t_1 + t_2)^2}\right)^{d/4} \times \exp\left(-\frac{r^2}{4(t_1 + t_2)}\right), \tag{6}$$

where 1 and 2 are usual shorthand for space-time points $(\vec{r}_1, t_1)$ and $(\vec{r}_2, t_2)$, and $r = |\vec{r}_1 - \vec{r}_2|$. In the scaling regime $(t \to \infty)$, the correlation function of the field Q is obtained as $C(1,2) = [(Q_S + Q_P)^2 + (Q_S - Q_P)^2 \sin^{-1}\gamma]/4$ where γ is the normalized correlator

$$\gamma(1,2) \equiv \frac{C_0(1,2)}{\sqrt{C_0(0,t_1)C_0(0,t_2)}} = \left(\frac{4t_1 t_2}{(t_1 + t_2)^2}\right)^{d/4} \times \exp\left(-\frac{r^2}{4(t_1 + t_2)}\right), \tag{7}$$

which for equal times $(t_1 = t_2 = t)$ simplifies to $\gamma(1,2) = \exp(-r^2/8t)$.

Thus, the $\vec{k} \neq \vec{0}$ components of m are unchanged by the velocity or equivalently by the random field. In this case the well depths of the ''potential'' $f(Q)$ are equal, the only driving force is interface curvature which generates the well-known $t^{1/2}$ growth law [24].

To solve Eq. (5) for $\vec{k} = \vec{0}$ components of m, we allow for a uniform bias in the initial state, taking Gaussian initial conditions for m with nonzero mean $\langle m(\vec{r},0) \rangle = m_0$ and only short-ranged correlations $\langle m(\vec{r},0)m(\vec{0},0) \rangle_c = \langle m(\vec{r},0)m(\vec{0},0) \rangle - \langle m(\vec{r},0) \rangle^2 = \Delta\,\delta(\vec{r})$. Solving Eq. (5), we obtain the average value of $m(\vec{r},t)$

$$\langle m(\vec{r},t)\rangle = m_0\left(\frac{t}{t_0}\right)^{(d+2)/4} - c\int_{t_0}^{t} t'^{-(d+2)/4}dt' \qquad (8)$$

and also the previous expressions (6) and (7) for the connected pair correlator $C_0(1,2)$ and normalized correlator γ, respectively.

The average (expectation) value and the relative fluctuation of the order parameter Q are given by

$$\langle Q\rangle = \frac{1}{2}(Q_S+Q_P) - \frac{1}{2}(Q_S-Q_P)\,\mathrm{erf}\left(\frac{\langle m\rangle}{\sqrt{2[C_0(0,t)+1]}}\right) \qquad (9)$$

and

$$\frac{(\langle Q^2\rangle - \langle Q\rangle^2)^{1/2}}{\langle Q\rangle} = \frac{[1-\mathrm{erf}^2(\langle m\rangle/\sqrt{2[C_0(0,t)+1]})]^{1/2}}{(Q_S+Q_P)/(Q_S-Q_P) - \mathrm{erf}(\langle m\rangle/\sqrt{2[C_0(0,t)+1]})}, \qquad (10)$$

where $C_0(0,t)=\langle m^2\rangle_c=\langle m^2\rangle-\langle m\rangle^2=4t/d$. In the scaling regime the argument of the error function is given by $\langle m\rangle/\sqrt{2C_0(0,t)}$. The bias m_0 in the initial Gaussian conditions gives a contribution of order $t^{d/4}$ for any d, but the contribution from velocity (or equivalently from the random field) is $t^{1/2}$ for $d<2$, $t^{1/2}\ln t/t_0$ for $d=2$, and $t^{d/4}$ for $d>2$. Thus, for large t, the velocity (random field) dominates over m_0 for $d\leqslant 2$ (continues to have an effect at late times), whereas for $d>2$ the random field has all its effect in the ''initial-growth'' regime (times of order t_0). These results are similar with those obtained in Ref. [19] and [25]. The two main approximations used in this paper involve the consideration of a scalar order parameter and the decoupling of the temperature field. Nematic liquid crystals are described by a nonconserved traceless symmetric tensor field. The presence of the inversion symmetry ($\vec{n}\rightarrow -\vec{n}$) means that, in addition to the monopole defects of the O(3) model, the nematic also possesses stable $\frac{1}{2}$ string defects in which the director rotates through π on encircling the string. The presence of such defects generates a k^{-5} structure factor tail at large $kL(t)$ [24]. The thermal coupling (including the effect of latent heat emission at the interface) can have profound consequences [31].

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