Influence of undercooling on phase-ordering kinetics in nematic liquid crystals

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The undercooling effect on the phase-ordering dynamics of nematic liquid crystals is considered. We assume the nematic liquid crystal to have a scalar order parameter, and also suppose the system to be isothermal and initially temperature-quenched into the metastable regime of the isotropic phase. Based on planar domain wall solutions of the time-dependent Ginzburg-Landau equation, Bray and Humayun's theory of phase-ordering dynamics is generalized to include the undercooling effect on the late stage of growth.
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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 régime 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 $L(t)$ [1]. Very recently, there have been considerable theoretical [2], experimental [3] and computational [4] efforts to understand the phase-ordering kinetics of nematic liquid crystals. So far, however, little effort has been devoted to the role of a volume driving force (external fields or undercooling), or a symmetry-breaking bias in the initial conditions [5]. The purpose of this Brief Report is to investigate the phase-ordering dynamics of a nematic liquid crystal 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) ($T^*<T<T_{\rm NI}$, where $T_{\rm NI}$ is the first order nematic-isotropic transition temperature, and T^* is the supercooling limit). When $T=T_{\rm NI}$ (i.e., when the well depths of the bulk free energy density are equal) and for a nonconserved scalar order parameter, the motion of the interface (domain wall) is purely determined by its local curvature [6] that generates a domain scale $L(t)\sim t^{1/2}$. In particular, the detailed shape of the bulk free energy density is not important [7]; the main role of the double-well free energy is to establish and maintain well-defined domain walls. For $T^*<T<T_{\rm NI}$ (when the well depths of the bulk free energy density are not equal) the motion of the interface is determined not only by its local curvature but also by a volume driving force [8]. Our purpose is to investigate the effect of this volume driving force (in fact, the undercooling $\Delta T=T_{\rm NI}-T$) on the phase-ordering kinetics.

The order parameter for a nematic liquid crystal is a traceless symmetric second-rank tensor [9] $Q_{ij}(\mathbf{r},t)=\phi(\mathbf{r},t)(3n_in_j/2-\delta_{ij}/2)$ where the unit vector $\mathbf{n}$ is the nematic director, and $\phi(\mathbf{r},t)$ is the scalar order parameter. In the problem we consider, we shall suppose $\mathbf{n}$ to be fixed in space and time, so that the relevant physics is given by $\phi(\mathbf{r},t)$. Within the equal-constant approximation the appropriate Landau–de Gennes free energy functional is

$$F[Q]=\int d^dx[\tfrac{1}{2}K\mathrm{Tr}|\nabla Q|^2+f_b(Q)], \tag{1}$$

$$f_b(Q)=a(T-T^*)\mathrm{Tr}Q^2-B\mathrm{Tr}Q^3+C(TrQ^2)^2. \tag{2}$$

We take the dynamics to be given by the time-dependent Ginzburg-Landau (TDGL) equation $\beta\partial_tQ=-(\delta/\delta Q)F[Q]$ where the transport coefficient β is related to the rotational viscosity of the nematic. Scaling the variables in the following way [10]: $\overline{\phi}=6C\phi/B$, $\tau=24a(T-T^*)C/B^2$, and $\overline{f}_b=24^2C^3f_b/B^4$, and eliminating overbars, the corresponding dimensionless form of the TDGL equation is given by

$$\frac{\partial\phi}{\partial t}-\nabla^2\phi=-f_b'(\phi)=-2\tau\phi+6\phi^2-4\phi^3. \tag{3}$$

In this system of units the distances are scaled with $\xi=(24CK/B^2)^{1/2}$, and times with $t^*=16C\beta/B^2$. The isotropic-nematic transition now takes place at $\tau=1$ to a nematic phase in which the order parameter $\phi=1$.

In the temperature region $0<\tau<1$, the time- and space-independent solutions of Eq. (3) occur at $\phi_1=0$, $\phi_2=3(1-\tau^*)/4$, and $\phi_3=3(1+\tau^*)/4$, where $\tau^*=(1-8\tau/9)^{1/2}$. The solutions ϕ_1 and ϕ_3 correspond, respectively, to the isotropic and nematic minima of f_b, with $f_b(\text{nematic})<f_b(\text{isotrop})$; or, equivalently, the isotropic phase is metastable, whereas the nematic phase is stable.

Considering that ϕ depends on one spatial variable only (flat domain walls), and supposing that the front advances with velocity v, we look for solutions of the form $\phi(g,t)=\phi(g-vt)=\phi(g')$, where g is a coordinate normal to the interface. Equation (3) yields $\phi''+v\phi'=f_b'(\phi)$, subject to the boundary conditions $\phi(-\infty)=\phi_3$ and

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$\phi(\infty)=\phi_1$. This ordinary differential equation has the solution $\phi(g')=\phi_3(1-\tanh g'/w_0)/2$, with the characteristic thickness of the interface $w_0=\sqrt{2}/\phi_3$ and its velocity $v=3(3\tau^*-1)/2^{3/2}$. In the flat domain wall case the driving force for the nematic growth is the difference between isotropic and nematic minima of f_b, generated by the undercooling $\Delta\tau=1-\tau$.

In approximate treatments (''Gaussian closure'' schemes) of Eq. (3) for the general case, a new field $m(\mathbf{x},t)$ is introduced, which varies smoothly on the domain scale, and whose zeros define the positions of the walls. Generalizing the Mazenko approximation [11] (see also [5]), the transformation $\phi(m)$ is defined by the flat moving interface profile function which satisfies $\phi''(m)+v\phi'(m)=f_b'(\phi)$ with boundary conditions $\phi(-\infty)=\phi_3$ and $\phi(\infty)=\phi_1$. With this choice for $\phi(m)$, rewriting Eq. (3) in terms of m, gives

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

The principal role of the double-well ''potential'' $f_b(\phi)$ is to establish and maintain well-defined interfaces. It follows that the detailed form of $f_b(\phi)$ is irrelevant to the large-scale structure. Following Bray and Humayun [7], we choose $\phi(m)$ to satisfy $\phi''(m)=-m\phi'(m)$, which is equivalent to a particular form of the potential (for a discussion of this approximation, see [5]). Locating the center of the wall at $m=0$, i.e., $\phi(0)=\phi_3/2$, we obtain the wall profile function $\phi(m)=\phi_3\mathrm{erfc}(m/\sqrt{2})/2$, where erfc is the complementary error function. After Fourier transformation, Eq. (4) becomes

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

where $a(t)=1-\langle|\nabla m|^2\rangle$. Solving Eq. (5) for $\mathbf{k}\neq\mathbf{0}$ components of m, one finds the equal-time pair correlation function in the scaling régime $C(12)=\arcsin(\gamma_0)/2\pi$, where 1 and 2 are usual shorthand for space-time points $(\vec{x}_1,t)$ and $(\vec{x}_2,t)$, and γ_0 is the normalized correlator $\gamma_0=\exp(-r^2/8t)$. Thus, the $\mathbf{k}\neq\mathbf{0}$ components of m are unchanged by the velocity or equivalently by the undercooling. In this case the well-depths of the ''potential'' $f_b(\phi)$ are equal, the only driving force is the interface curvature which generates the well-known $t^{1/2}$ growth law [1].

In the scaling régime, solving Eq. (5) for $\mathbf{k}=\mathbf{0}$ components of m, we obtain the expectation value of ϕ;

$$\langle\phi\rangle=\frac{\phi_3}{2}\mathrm{erfc}\left(\frac{\langle m\rangle}{(2C_0(0,t))^{1/2}}\right), \tag{6}$$

and the relative fluctuation,

$$\frac{(\langle\phi^2\rangle-\langle\phi\rangle^2)^{1/2}}{\langle\phi\rangle}=\left(\mathrm{erfc}\left(-\frac{\langle m\rangle}{(2C_0(0,t))^{1/2}}\right)\right)^{1/2}\times\left(\mathrm{erfc}\left(\frac{\langle m\rangle}{(2C_0(0,t))^{1/2}}\right)\right)^{-1/2}, \tag{7}$$

where the argument of the complementary error function is given by

$$\frac{\langle m\rangle}{(2C_0(0,t))^{1/2}}=\frac{m_0(0)}{(2\Delta)^{1/2}}(8\pi t)^{d/4}-v\left(\frac{d}{8}\right)^{1/2}t^{d/4}\int_{t_0}^{t}dt'\,t'^{-(d+2)/4}, \tag{8}$$

with d the spatial dimensionality and $t_0\sim(\Delta d)^{2/(d+2)}$ a short-time cutoff. The bias $m_0(0)$ in the initial Gaussian conditions gives a contribution of order $t^{d/4}$ for any d, but the contribution from the velocity (or equivalently from the undercooling) is $t^{1/2}$ for $d<2$ (when times of order t dominate the integral in Eq. (8), $t^{1/2}\ln t/t_0$ for $d=2$, and $t^{d/4}$ for $d>2$ (when times of order t_0 dominate the integral). Thus, for large t, the velocity (or the undercooling) dominates over $m_0(0)$ for $d\leqslant 2$ (continues to have an effect at late times), whereas for $d>2$ both terms are of the same order (the velocity has all its effect at early times of order t_0).

It is to be noted that the introduction of a magnetic field has the same consequence in the sense that the symmetric double-well potential also becomes asymmetric, which generates a volume driving force of the interface. For this reason our results are similar to those obtained in [5]. The two main approximations used in this paper involve the consideration of a scalar order parameter field 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 ($\mathbf{n}\rightarrow-\mathbf{n}$) 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 $kL(t)$ [2]. The thermal coupling (including the effect of the latent heat emission at the interface) can have profound consequences [12]. We shall address this aspect of the problem in a future paper.

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