

Domain growth laws for the phase ordering of chiral liquid crystals

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In liquid crystalline mixed systems domain growth dynamics of the cholesteric and blue phase I was studied in cases of conserved and nonconserved order parameter fields. The experimentally determined exponents agree with the predictions of multiscaling growth kinetics.

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The ordering kinetics of systems with a nonscalar order parameter field recently called for considerable interest [1–5]. After a quench from the isotropic liquid the structure factor during the process of phase ordering can be described generally [1] in terms of dynamic scaling, where the order parameter is an exponential function of the domain size and the wave vector, and the scaling law depends on the number of the components of the order parameter and the dimensionality of space. The other kinds of theoretical predictions, which can be tested experimentally, are domain growth laws [2,6–8]. Generally the domain size L is described by an exponential function of time: $L \sim t^n$. One has to distinguish the growth laws in the case of conserved from that of nonconserved order parameter fields. Let us imagine a domain of a phase X in a coexistence region, which is surrounded by a phase Y . For simplicity let us assume that after the transition the order parameter is changed from $S = 0$ in Y to some equilibrium value S_0 in X . Each domain of the phase X has a boundary region of thickness ξ , where the order parameter varies from some value in the middle of the domain (not obligatory S_0) to zero. (i) If $\xi \ll L$, the director field is characterized by a large amplitude of variations of the order parameter in space and the phase transition takes place in a *nonconserved* in space order parameter field. (ii) The case $\xi \gg L$, when the amplitude of the spatial variation of the order parameter is small, corresponds to phase transitions in a *conserved* order parameter field. The experimental example of the growth of domains in the nonconserved order parameter is the nucleation of an ordered phase from the isotropic liquid. Such a process can be described by a microscopic diffusion theory [7, 9] which predicts $n = 1/2$. The growth process in the case of conserved order parameter can be illustrated by the coarsening at the late stage of the spinodal decomposition [6, 8] with $n = 1/3$. Both the above mentioned laws correspond to the case of a scalar order parameter. If a physical system is described by a multicomponent order parameter the growth law for the nonconserved field remains unchanged ($n = 1/2$) [2]. In the

case of conserved multicomponent order parameter the growth process is characterized by time dependence of two lengths [2]: a rapid changing length as to the domain size is described by the exponential law with $n = 1/4$. Spatial periodicity of the system $d(t)$ is a slow growing length with a time dependence: $d(t) - d_0 \sim (\frac{t}{\ln(t)})^{1/4}$, where d_0 is an initial value of the lattice constant before the quench. Liquid crystals display a rich variety of different types of order parameter fields and are an ideal object for testing theoretical predictions resulting from theories of domain growth kinetics. In the first experimental works about the phase ordering in liquid crystals the formation of nematic phases [3, 4] and of smectic phases (in free standing films) [5] has been investigated.

In this paper we present a study of the ordering dynamics of the cholesteric and blue phase I under several experimental conditions. Molecules of chiral materials have no center of symmetry, which results in the formation of a macroscopic spiral structure with spatial periods of about the wavelength of visible light or more. The structure of the cholesteric phase can be described by a one-dimensional plane spiral where the director is perpendicular to the spiral axis. The structure of the blue phases can be imagined as a three-dimensional periodical array of the double twist cylinders [10]. The order parameter of the cholesteric and blue phases is a tensorial quantity—the anisotropic part of the tensor of the dielectric permittivity [10]. In several theories a simplified nematiclike three component vector order parameter was used [11]. In [12] it was shown that some properties of the blue phases and cholesterics can be described with a scalar order parameter which is proportional to the local optical anisotropy.

Our first investigations [14] have revealed the nontrivial character of the ordering process of the cholesteric phase during the phase transition from the blue phase I (BPI) in systems with a short temperature interval of the cholesteric phase in the vicinity of the smectic- A phase. A complication consists in the appearance of the intermediate metastable blue phase S (BPS) and the dramatic increase of the relaxation time of the cholesteric phase in the supercooled BPI temperature interval under the influence of smectic fluctuations. A qualitative picture of the effect of smectic fluctuations on the blue and cholesteric phase structure and their ordering dynamics can be described as follows. Double twist, characterizing the local structure of the blue phase [10], cannot topo-

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logically fill the whole space without discontinuous lines or points. Therefore the structure of the blue phases (BP's) can be described as a periodical array of defects positioned in space in accordance with cubic symmetry ($I4_132$ for the BPI). If the correlation radius of smectic fluctuations becomes of the order of the disclination core the dynamics of such a system is drastically changed and the system needs more time to reach an equilibrium value of the lattice constant after a quench. For example, the time constants of the formation of the cholesteric phase after a quench into a temperature interval close below the BPI stability interval can be several days. In this paper we study (i) the domain growth laws of the BPI phase ordering after a quench from the isotropic liquid with different supercooling depths and (ii) of the cholesteric phase after a quench from the blue phase.

We have used the three following chiral mixtures (transition temperatures are given in $^{\circ}\text{C}$).

(I) 30 mol % cholesteryl benzoate with the nematogenic compound 8OBE [isotropic (iso) \rightarrow 100.2 \rightarrow BPI+iso \rightarrow 99.7 \rightarrow BPI \rightarrow 99.55 \rightarrow cholesteric (chol) \rightarrow 73 \rightarrow smectic C (Sm- C)] [13].

(II) Chiral-racemic mixture of CE6 (Merck) with 60 mol % of the chiral component (iso 44.8 \rightarrow BPI 44.65 \rightarrow chol 40.7 \rightarrow Sm- A).

(III) Mixture of CE8 (Merck) with 2 wt % of a chiral dopant ZLI 4571 (Merck) (iso 136.1 \rightarrow BPIII 136.0 \rightarrow BPII 135.8 \rightarrow BPI 135.5 \rightarrow chol 130.1 \rightarrow Sm- A) [14].

Summarizing the features of the materials under discussion we have to emphasize that the first two mixtures exhibit the isotropic-BPI-cholesteric phase sequence on cooling. In the second and third mixture the metastable BPS was observed [14].

Phase ordering dynamics was examined by means of optical microscopy and Bragg reflection. The procedure of measurements and sample preparation was described earlier in [14].

The growth dynamics of monodomains of the BPI in an isotropic-BPI coexistence region has been studied in mixture I. In this material the BPI occurs first on cooling directly from the isotropic liquid in a two phase region. The broadness of the phase coexistence region was about 0.5 K. The samples were cooled very slowly starting from the isotropic liquid. The cooling was stopped after the first BPI monodomains were observed (Fig. 1)



FIG. 1. Three-dimensional BPI monodomain shape for mixture I.

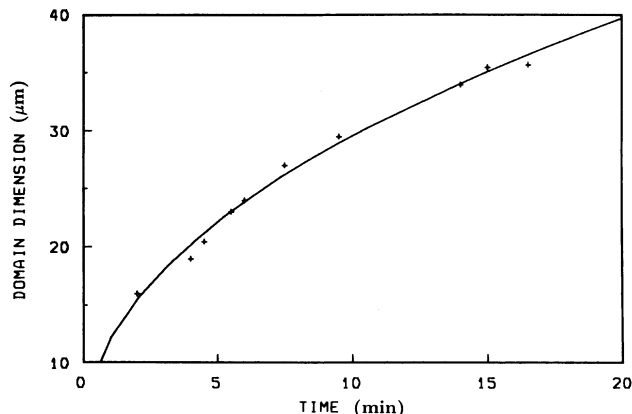


FIG. 2. Time dependence of the BPI monodomain size for mixture I.

and then the domain size along the (110) direction was measured as a function of time. The results of this measurement are shown in Fig. 2. In the same experiment we have measured the growth rate of (211) planes of the BPI monodomains. It is important to note that the growth rate does not depend on the Miller indices of the direction. This fact displays the anomaly of the blue phase structure, which in contrast to the solid state is a lattice of the peculiarities in the orientation with a uniform distribution of the density of molecules. The mass transfer, necessary for the growth of the domains of the blue phases, has to be isotropic. The solid line in Fig. 2 is the best least-square fit with an exponential law which gives $n \approx 0.44 \pm 0.07$. In this case the growth process takes place in the system with a large gradient of the order parameter across the isotropic-BPI boundary. The experimental exponent corresponds within the given accuracy to the predictions of the theory for *nonconserved* order parameter $n = 1/2$ [2, 7]. As is shown by [2] this exponent is not changed in the case of multiscaling behavior.

In mixture II the BPI is formed in the whole sample after the quench from the isotropic liquid very quickly (several seconds). In this case we have studied the BPI grain growth process (coarsening), which takes essentially longer times. The phase coexistence temperature interval in this mixture is negligibly small, the isotropic phase-BPI transition temperature takes place at 44.8 $^{\circ}\text{C}$, the interval of stability of the BPI was 0.2 $^{\circ}\text{C}$. The initial temperature was chosen 0.1 $^{\circ}\text{C}$ above the clearing point. The sample was quenched to 0.1 $^{\circ}\text{C}$ below the isotropic-BPI transition with the cooling rate 1 $^{\circ}\text{C}/\text{min}$. The variation of BPI reflectivity curves during two hours is shown in Fig. 3. The main reflection corresponds to a (110) system of planes. The broadband at the wavelengths shorter than the (110)-Bragg reflection can be ascribed to the scattering from other orientations in analogy with [14]. The intensity of the main band increases and the line broadness decreases. The maximum intensity of the selective reflection from polydomain BPI samples with a thickness 50 μm was smaller than 10% as compared with well oriented thick samples of the cholesteric phase in this material. Therefore we were able to apply the kinematic theory of light diffraction for the description

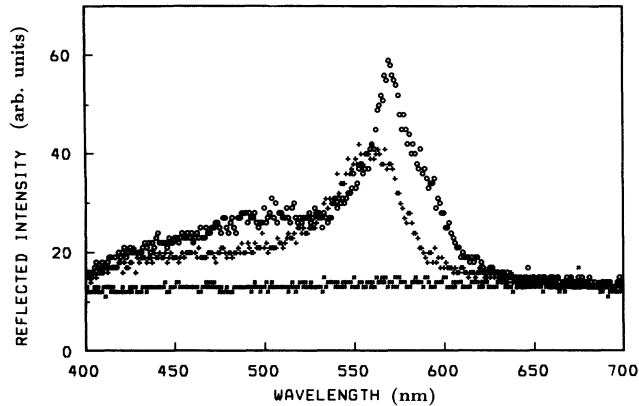


FIG. 3. Time dependence of the Bragg reflection spectra of the BPI polydomain samples of mixture I. (+), 2 min after the quench from the isotropic liquid; (o), 107 min after the quench; (x), isotropic liquid. Supercooling depth 0.1°C below the isotropic liquid-BPI phase transition; sample thickness $d = 50\ \mu\text{m}$.

of the line profiles. In the kinematic theory the line half-width $\Delta\lambda$ is proportional to the reciprocal domain size (L^{-1}) [12]. A $\ln\text{-}\ln$ plot of the time dependence of $\Delta\lambda$ is shown in Fig. 4. We can recognize here two stages of the growth process. The initial stage is very slow and can be described by an exponent of $n \approx 0.04$. The late stage is more rapid and is characterized by the exponent $n \approx 0.18 \pm 0.08$. During the initial stage of this experiment the maximum of Bragg reflection was shifted by a very small value and the time constant for this process was qualitatively of the same order as for the domain growth kinetics. Figure 4 illustrates an important feature of the above cited theories, in which most of the expressions describing kinetic processes are asymptotic results. In our case we were not able to fit the time dependence of the half-width with one exponential function in the whole time interval. The late stage of the growth process can approximately be described by an exponent near $1/4$, which corresponds to multiscaling behavior.

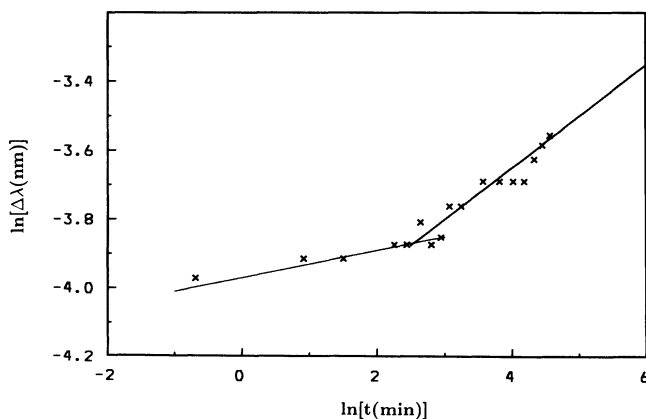


FIG. 4. Time dependence of the half-width of the Bragg peak of the BPI after a quench from the isotropic liquid ($\ln\text{-}\ln$ plot). Solid lines correspond to fit according to exponential law for the initial and late stages of the growth process. Sample as in Fig. 3.

As mentioned above, after a quench to a temperature close below the stability interval of the BPI a mixture of BPS and cholesteric domains is formed which does not relax to the stable cholesteric phase during several days. To investigate the phase ordering of the cholesteric phase after a quench from the BPI we used mixture III, in which this process is more rapid. Oriented samples of the BPI (see [14]) have been quenched by 0.8°C from a temperature 0.1°C below the clearing point to the interval of the metastable BPI (0.5°C below the temperature of the BPI stability interval). The cooling rate was $1^\circ\text{C}/\text{min}$. We used thin samples without spacer (thickness about $3\text{--}5\ \mu\text{m}$) to get a low intensity of the Bragg reflection in the cholesteric phase. The Bragg wavelength is combined with the spatial period of the blue phases with the relation $\lambda_{B,hkl} = nd_{hkl}$, where h, k, l are the Miller indices of a system of planes and n is the refractive index. The time dependence of the Bragg wavelength $\lambda_{B,110}$ is shown in Fig. 5. The Bragg wavelength first increases, then jumps to the lower wavelengths 70 min after the quench, which indicates the phase transition to the metastable intermediate BPS. The solid curve is the best fit function with the law $\lambda(t) - \lambda_0 = 37\left(\frac{t}{\ln(t)}\right)^{0.27}$, where $\lambda_0 = 570\ \text{nm}$ is the value of the Bragg wavelength of the BPI before the supercooling.

Figure 6 shows the time dependence of the half-width $\Delta\lambda$ and maximum intensity of the Bragg peak for the cholesteric phase ordering process. The intensity of the cholesteric peak increases and the half-width decreases. From the fitting of the $\Delta\lambda(t)$ we can find an exponent of $n \approx 0.17 \pm 0.08$ for the late stage of the domain growth process in the cholesteric phase.

The cholesteric Bragg reflection occurs at $t \approx 10$ min after the quench. After this time our system consists of BPI and cholesteric domains. It is interesting to note that both curves in Fig. 6 reveal no peculiarity at the time when the BPS occurs (70 min after quench, see Fig. 5). This is evidence that the phase transition BPI-BPS takes place inside the BPI domains independently from the cholesteric domains. The monodomains of the BPI start to break mechanically in the supercooled region

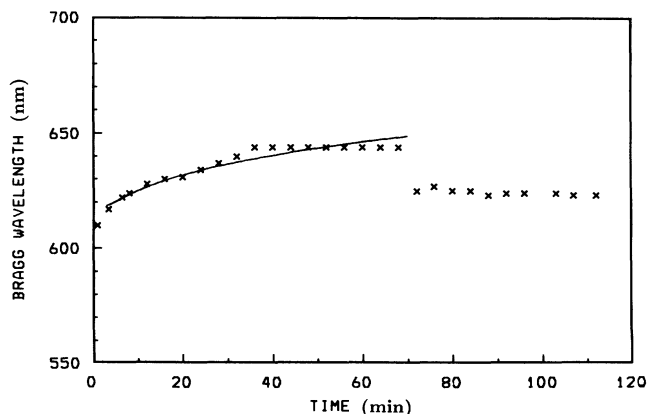


FIG. 5. Time dependence of the Bragg reflection wavelength of the supercooled BPI after quenching from the temperature interval of stability. Sample of mixture III (without spacer). Solid curve: least-square fit with $d(t)$ function of the BPI data.

as it was shown in [14]. This process can be observed microscopically and by a broadening of the Bragg reflection bands. The time constant of the decrease of the BPI domain size was about 10 min, whereas the change in λ_B is sufficiently slower. The boundary conditions on the substrates have obviously no strong effect on the domain dynamics in the supercooled region, because the same relation between the characteristic relaxation times for the two lengths was found in the polydomain samples without any treatment of the glass substrates. The ordering of the cholesteric phase in the supercooled BPI region can be subdivided into several stages. In the first stage we can say nothing about the ordering in the cholesteric phase before we get a distinct selective reflection. During this stage the BPI domains break and their Bragg wavelength is shifted to the longer wavelengths. In the later stage the cholesteric phase and the intermediate BPS are formed. The observation of two different time constants for the change of the domain size of the BPI and for the variation of λ_B corresponds to the situation described in [2] for the multiscaling behavior. We have fitted the time dependence of λ_B by $d(t)$ and found $n \approx 0.27$ which correlates with predictions for the multiscaling growth law in a conserved order parameter field. This plot is shown in Fig. 5 by a solid line.

From results of [12] it follows that a change in the average amplitude of the order parameter during the cholesteric-BPI phase transition is smaller than 0.01. Therefore phase ordering of the cholesteric phase from the BPI can be regarded as an example of a transition in a conserved order parameter field. In the blue phases the amplitude of the order parameter is a function of spatial coordinate, whereas in the cholesteric phase this value is constant in space. Hence the transition BPI-cholesteric consists in smoothing out the local inhomogeneities of the amplitude of the order parameter, taking place in an order parameter field with a constant average amplitude. From this point of view this case is similar to the late stage of the spinodal decomposition. The exponent $n \approx 0.17$ of the function $\Delta\lambda(t)$ in Fig. 6 corresponds to the predictions of [2] for the ordering in the conserved multicomponent order parameter field. We have not observed any shift of the position of the maximum of the cholesteric reflection which can take place during the initial stage. We have not tried to determine the number

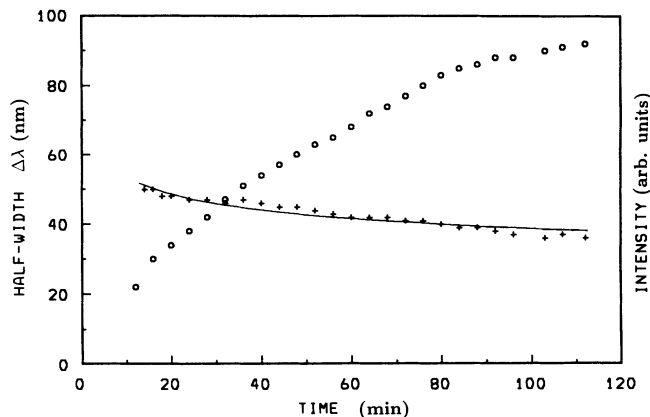


FIG. 6. Time dependence of the maximum intensity and the half-width of the Bragg peak of the cholesteric phase quenched from the BPI in mixture III. (o), maximum intensity; (+), half-width. The solid line fits the experimental data with the exponential law.

of independent components of the order parameter fields: more detailed characterization of the dynamics of the order parameter field shall be the purpose of our future work.

We have tested predictions of theories describing domain growth laws for the phase ordering in conserved and nonconserved multicomponent order parameter in the cholesteric and blue phases. Experiments on the growth of monodomains of the BPI from the isotropic phase correlate well with theoretical predictions for nonconserved order parameter fields, which does not depend on the number of components of the order parameter. Different time constants were found for the domain breaking and lattice constant dynamics of the BPI during the initial stage of the cholesteric phase ordering. The phase ordering of the cholesteric phase from the BPI is a new example of a kinetic process in conserved order parameter field. The experimentally found domain growth laws in the cholesteric and blue phases correspond to multiscaling behavior.

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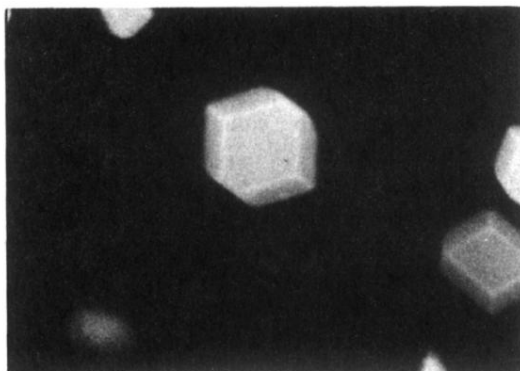


FIG. 1. Three-dimensional BPI monodomain shape for mixture I.