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KINETICS OF PHASE TRANSFORMATION IN SOME CHOLESTERIC LIQUID CRYSTALS

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Résumé. — La propagation de l'interface entre la phase cholestérique et la phase bleue des esters de cholestéryl a été mesurée comme fonction de température. Les résultats sont interprétés comme consistants avec l'idée physique d'un profil d'interface qui ne change pas sa forme en propageant avec une vitesse déterminée par la relaxation orientationnelle des molécules près de l'interface. Cette méthode d'investigation dispose d'un outil complémentaire aux investigations dynamiques ou en équilibre pour la compréhension supplémentaire des transitions de phases en cristaux liquides.

Abstract. — The time evolution of the interface between the cholesteric and the blue phase of the cholesteryl esters has been measured as a function of supercooling. The results are interpreted as consistent with the physical picture of a shape-preserving interface profile propagating with a rate that is determined by the orientational relaxation of the molecules near the interface. This method of investigation provides a complementary tool to the more often pursued equilibrium and dynamic investigations for the further understanding of phase transformations in liquid crystals.

1. **Introduction.** — Many liquid crystals undergo classic first order phase transformations. By supercooling, a new phase may nucleate from the parent phase with a sharp interface separating them. If the contour of the interface boundary is sufficiently regular, its movement can be monitored providing a measure for the kinetics of the phase transformation. In an early attempt [1], such kind of experiment was carried out for the isotropic/nematic transformation in PAA to find out if the kinetics might yield information on the orientational relaxation of the individual molecules near the interface. It turned out to be negative as the kinetics was dominated by the rate at which latent heat emitted at the interface was being conducted through the parent phase to the outside. Since then further attempts have been made with other systems.

In this communication, we present results for some cholesteric esters. These esters transform as the temperature is lowered from the uniform isotropic phase to the cholesteric phase via two stages [2]. The isotropic phase first transforms very rapidly into a turbid blue phase and then at a somewhat lower temperature slowly into a more macroscopically ordered cholesteric phase. We have chosen the cholesteric/blue phase transformation for our kinetic study because of the small latent heat involved and of the large supercooling possible. By comparison with a recent theory [3] for the kinetics of diffusionless first order phase transformation, we have found that the experimental data are consistent with the

physical picture of a shape-preserving interface profile propagating with a rate that is determined by the local orientational relaxation of the molecules near the interface. The implication of this is that such kinetic investigation constitutes a complementary tool to the more often pursued equilibrium and dynamic investigations for the further understanding of phase transformations in liquid crystals.

2. **Experimental procedure and results.** — Samples of cholesteryl esters nonanoate, decanoate, undecanoate and myristate were introduced between parallel glass slides mounted into a hot stage microscope. The upper slide was simply allowed to float on the film of liquid crystal material. The microscope had a magnification of about 100 and the hot stage (Mettler FP52) was connected to a programmer (Mettler FP5) that produced well defined temperatures. Each specimen was heated to the isotropic state for several minutes. It was then quenched to such a temperature that the cholesteric phase would nucleate within the parent blue phase. After allowing a sufficient number of centres to nucleate, the temperature was raised to the desired temperature and then maintained constant during each run. The growth of the regions of the cholesteric phase was then observed between crossed polarization filters. Because of the geometry of the setup, the growth was strictly two dimensional. Figure 1 shows a typical micrograph taken. To monitor the growth of the circular regions, pictures were taken at the rate of two per second or

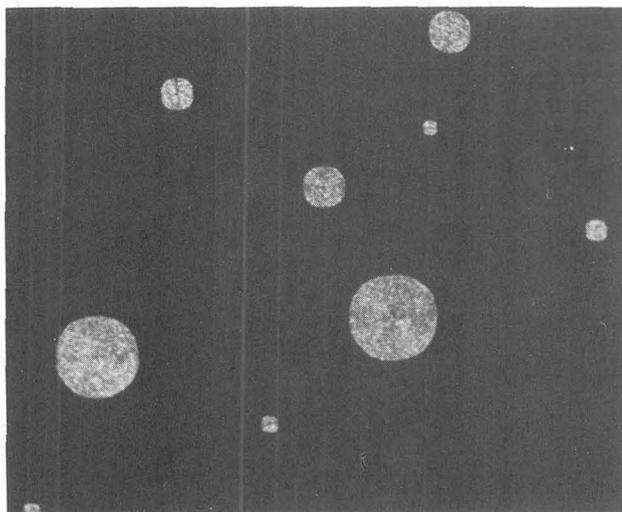


FIG. 1. — Cholesteric regions produced within the blue phase by nucleation and growth.

slower and the radii of the individual circles measured from picture to picture by suitable projection of the negative on a screen.

Measurements of the time evolution of the radii for various temperatures were taken for the four esters. The results showed similar behavior for each of the esters. We present here results for the two (nonanoate and decanoate) with the wider temperature range of occurrence of the blue phase for reason of accuracy of the temperature control. Figures 2a and 2b show the time evolution of the radii for various temperatures. For those temperatures shown, all the points fall neatly on straight lines indicating that the growth rate R is independent of the size R . However, the data for still smaller supercooling which are not shown manifest some nonlinear behavior with slightly upward-concaved curvatures. For those data that are strictly linear, a unique growth rate may be obtained from the slope and this is plotted as a function of temperature in figures 3a and 3b for both esters. Above a definite temperature T_0 , the contrast between the cholesteric phase and the blue phase disappeared. Consequently, we were unable to obtain data on how the circular regions might change when the temperature was further raised. So far as we could make out, the growth rate at T_0 was zero. As the temperature was lowered, this growth rate increased faster and faster until it became unmeasurable at a temperature T^* below which the blue phase apparently became absolutely unstable.

3. Theoretical interpretation. — The manner of growth of the individual regions is determined by one or more of the three factors (a) the rate at which latent heat emitted at the interface is transported through the parent phase to the outside, (b) the rate at which secondary nucleation occurs near the

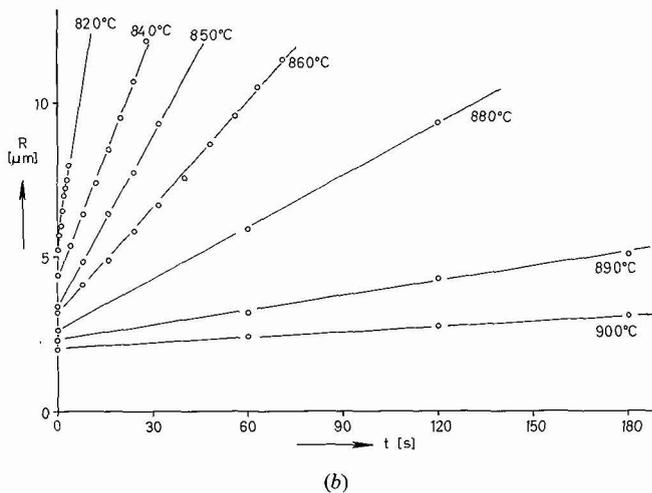
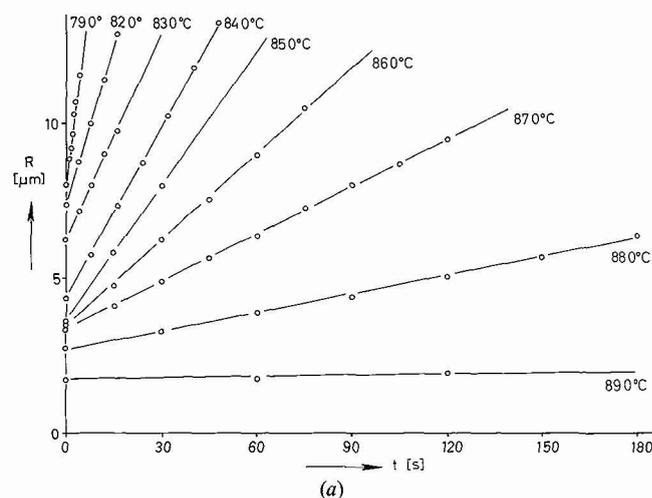


FIG. 2. — Radius of cholesteric region as a function of time at various temperatures for (a) cholesteryl nonanoate and (b) cholesteryl decanoate.

interface and (c) the orientational relaxation of the molecules in the vicinity of the interface.

When heat transport is the dominant factor, the resulting growth law has the form $R \propto \sqrt{t}$ usually associated with diffusion-controlled growth as was previously found in the nematic PAA system [1]. However, with our present cholesteryl esters, we did not observe such a behavior so that heat transport was not the rate determining factor. The reason for the difference in behavior is not only that the latent heats are smaller⁽¹⁾ but also the geometry of the setup was such that the interface was in direct contact with the outside so that latent heat could be transported away without building up a temperature gradient within the parent phase.

When secondary nucleation is the mechanism that sustains the growth, the resulting growth law is linear with a negative temperature coefficient. The

⁽¹⁾ The latent heat for the cholesteric/blue phase transformation in cholesteryl nonanoate is 18.5 J mole^{-1} while that for the isotropic/nematic transformation in PAA is 574 J mole^{-1}

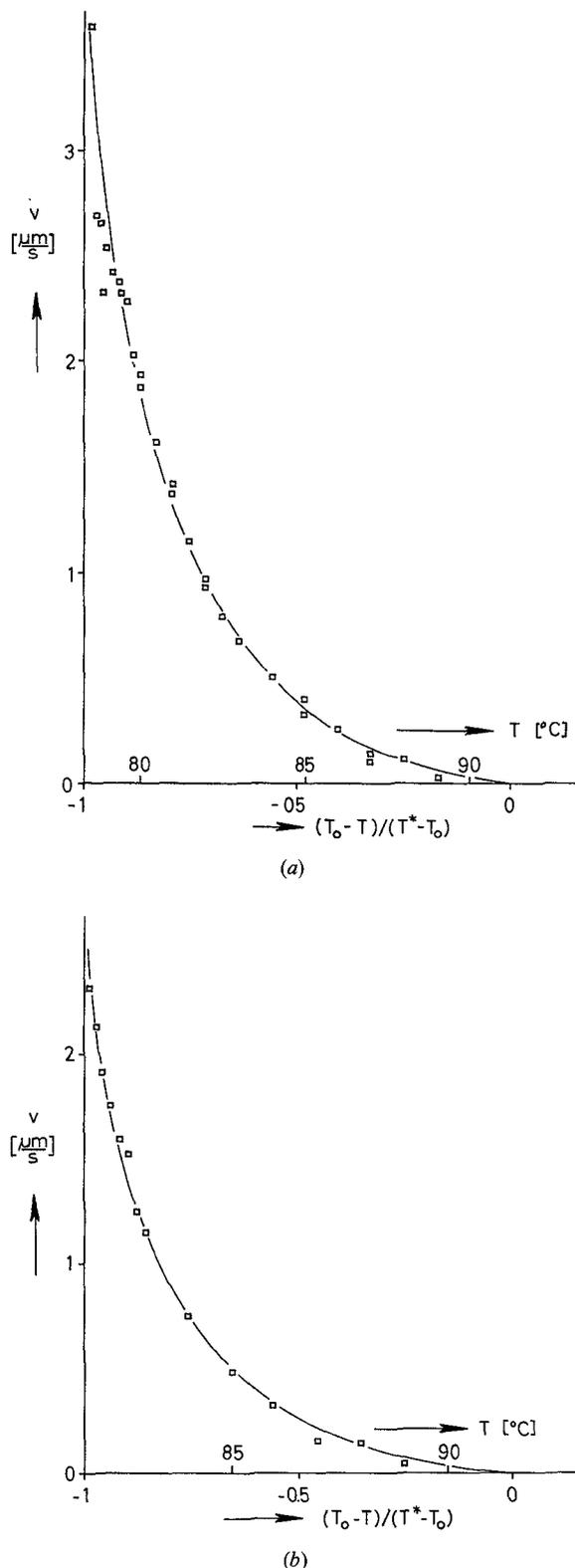


FIG. 3. — Growth rate as a function of supercooling for (a) cholesteryl nonanoate and (b) cholesteryl decanoate.

growth rate \dot{R} for two dimensional circular regions is [2]

$$\ln(\dot{R}) = \alpha + \frac{\beta T_0}{T(T_0 - T)}, \quad (1)$$

where α and β are constants. With our experimental data, we found that $\ln(\dot{R})$ when plotted against $T_0/T(T_0 - T)$ was not a linear function as illustrated in figure 4. This is in contradiction to the conclusion in [2] for cholesteryl myristate.

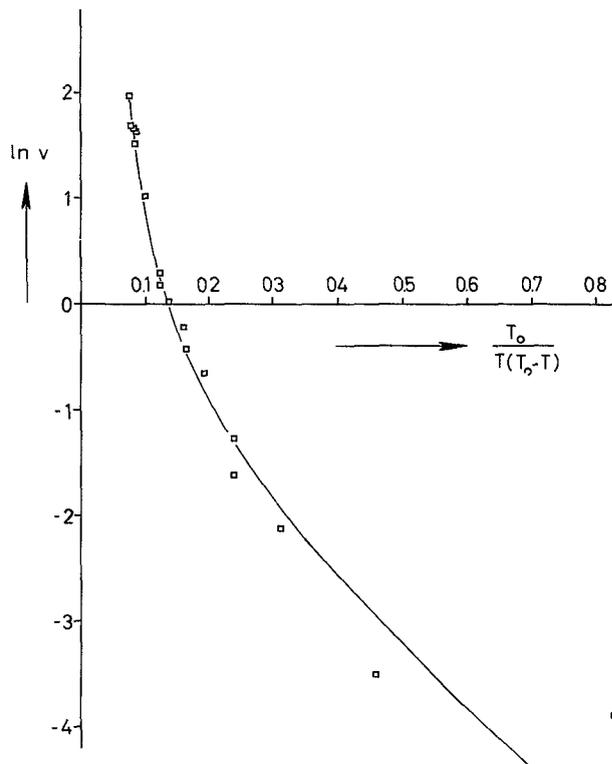


FIG. 4. — The logarithm of the growth rate of cholesteryl nonanoate plotted against $T_0/T(T_0 - T)$ illustrating the nonlinear behavior.

The remaining alternative is that the kinetics of transformation is determined by the orientational relaxation of the individual molecules in the vicinity of the interface. A theory for such diffusionless kinetics has recently been developed [3]. It is appropriate to paraphrase its essential points in the context of the present problem. In essence, if a new phase is related to the parent phase from which it has nucleated by an order parameter $n(r, t)$, then the relaxation of this order parameter which is a measure of the kinetics of transformation is given by the time-dependent Landau-Ginzburg equation

$$\gamma \dot{n} = - \frac{\delta F}{\delta n}, \quad (2)$$

where γ is a frictional coefficient and $\delta F/\delta n$ is the thermodynamic force conjugate to the flux \dot{n} . The free energy functional F has the Landau-Ginzburg (or Cahn-Hilliard) form

$$F = \int d^3r \{ f_0(n) + \kappa(\nabla n)^2 \}, \quad (3)$$

where the free energy density $f_0(n)$ may be expressed

as a power series expansion about the value $n = 0$ that corresponds to the higher symmetry phase, i.e.

$$f_0(n) = An^2 + Bn^3 + Cn^4 + \dots \quad (4)$$

Substituting (3) into (2), we have

$$\gamma \dot{n} = 2\kappa \nabla^2 n - \frac{\partial f_0}{\partial n} \quad (5)$$

The exact nature of the blue phase is at present obscure. A theory for the stable phases of the cholesteric liquid crystals has been put forward [4]. It was concluded that over a broad range of parameters, the isotropic phase transforms first into a phase which has substantially lower symmetry than the cholesteric phase and then into the normal cholesteric phase as the temperature is further lowered. The situation is reminiscent of order-disorder transformations in some binary alloys (e.g. CuAu) in which the disordered phase transforms as the temperature is lowered not directly to the ordered phase but via an intermediate phase of lower symmetry which is stable only over a narrow temperature range.

As an attempt to interpret the experimental results, we assign a scalar order parameter n which takes the value $n = 0$ for the cholesteric phase and $n \neq 0$ for the blue phase which has lower symmetry. For a single circular region of radius R inside of which $n = 0$ while outside $n \neq 0$, the order parameter distribution should look schematically as in figure 5. The abrupt change of n in the vicinity of $r = R$ corresponds to the interface separating the two phases on opposite sides of it.

With the sole assumption that the interface profile maintains an invariant shape during propagation, it was shown [3] that eq. (5) leads to the growth law

$$\dot{R} + \frac{2\kappa}{\gamma R} = v, \quad (6)$$

where the asymptotic growth rate v which may depend on temperature T is related to the interface profile n by

$$2\kappa \frac{d^2 n}{dX^2} + \gamma v \frac{dn}{dX} - \frac{\partial f_0}{\partial n} = 0, \quad (7)$$

in which $X = r - R$.

First we examine the implications of (6) in relation to our experimental results. For systems with small κ (i.e. small interface energy) or large γ (i.e. large resistance to orientational change), the asymptotic growth rate v may be reached at very small size provided that v is not too small. One would find that R is essentially a linear function of t for all observable sizes. However, when the temperature is such that v becomes very small, some departure from linearity may show up. These features of eq. (6) are consistent with our experimental findings.

Next, we examine the temperature dependence of the asymptotic growth rate v . Eq. (7) is in general insolvable. However, it was observed in [3] that if the power series (4) was truncated after the fourth power, then eq. (7) has the solution

$$v = \frac{3}{4\gamma} \sqrt{\frac{\kappa}{C}} \{ \sqrt{9B^2 - 32AC} - B \}. \quad (8)$$

Corresponding to this truncation, the free energy density $f_0(n)$ has the form as shown in figure 6 in which T_c is the upper critical temperature at which the cholesteric phase becomes absolutely unstable, T^* is the lower critical temperature at which the blue phase becomes absolutely unstable and T_0 is the temperature at which the two phases may be at equilibrium with each other.

As a first approximation, one may assume that of the coefficients A , B and C in the expansion (4),

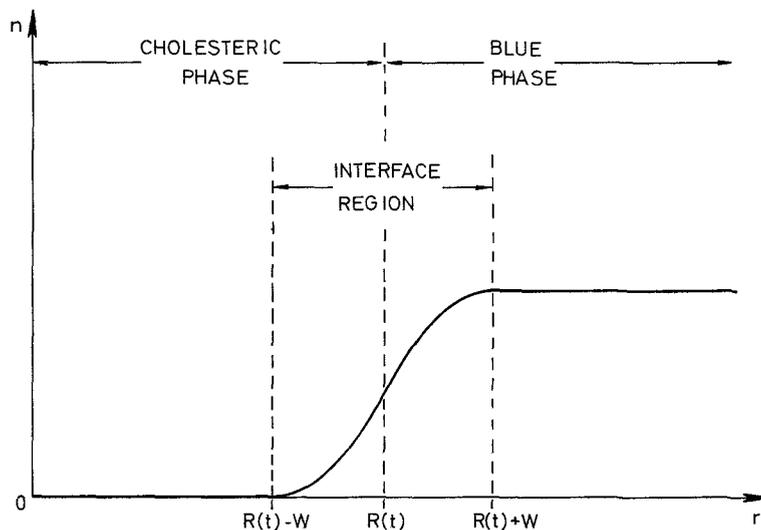


FIG. 5. — Schematic illustration of the order parameter distribution and the interface profile.

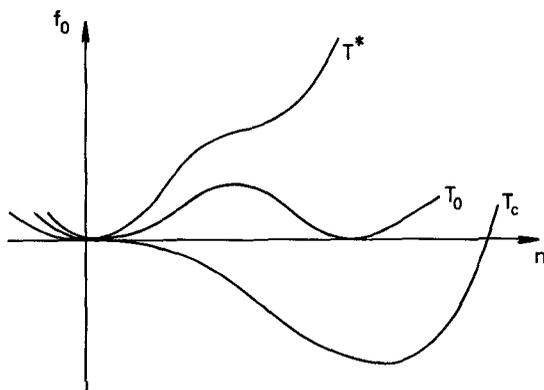


FIG. 6. — Behaviour of the free energy density f_0 as a function of n showing the three characteristic temperatures.

only the leading one has sensitive temperature dependence and set

$$A = a(T - T_c)^\varepsilon, \quad (9)$$

where $\varepsilon = 1$ in a mean field approximation [5]. Using (9), one obtains [3] for the asymptotic growth rate⁽²⁾

$$v = \frac{3}{\gamma} \sqrt{2\kappa a(T_0 - T^*)} \left\{ 1 - \sqrt{1 - \frac{T_0 - T}{T_0 - T^*}} \right\} \quad (10)$$

Assuming that κ and γ have no temperature dependence over the range of temperature of our experiment, then (10) has essentially one unknown parameter, namely $\frac{3}{\gamma} \sqrt{2\kappa a(T_0 - T^*)}$. Using this as a scaling unit, we have plotted v as a function of temperature in figure 7. Comparing this with figures 3a and 3b, we find that in this first approximation, $v(T)$ behaves similar to what was observed in our experiment. In particular, $dv/dT \rightarrow -\infty$ near T^* and $v \rightarrow 0$ near T_0 . However, the slope dv/dT of approach to T_0 in the theoretical curve is somewhat steeper than in the experimental ones. This discrepancy near to T_0 may be due to the inadequacy of the mean field approximation (9) or of the assumption of a constant frictional coefficient γ over the rather wide temperature range of some ten degrees covered in the experiment.

4. Discussion. — Our analysis of the kinetic data indicates that the rate of propagation of the interface between the cholesteric and the blue phase of the

⁽²⁾ The sign of v here as well as in eq. (8) is opposite to that in eq. (21a) of [3] because the higher symmetry phase is now on the inside of the interface.

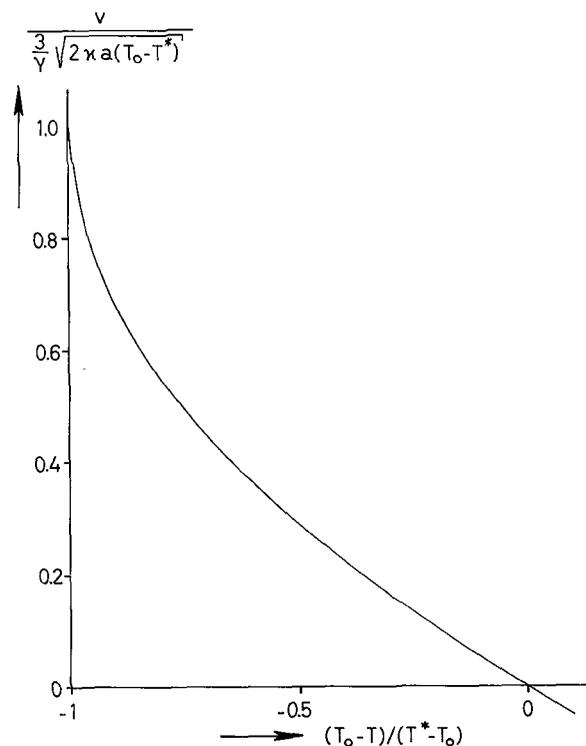


FIG. 7. — Asymptotic growth rate v in reduced units as a function of supercooling.

cholesteryl esters is not, determined by secondary nucleation as has previously been suggested [2] but by the local orientational relaxation of the molecules near the interface. While no new light is shed on the nature of the blue phase, it appears that its structure is rather simply related to that of the cholesteric phase by a scalar order parameter.

Although we have studied only a particular system, the potential of the kind of kinetic investigation reported here should be assessed in broader perspective. Many of the theories [6, 7] on the equilibrium properties of liquid crystals are based on the Landau-Ginzburg type free energy functional (3). Some [5] of the theories on the dynamic properties are based on the linearized form of the time-dependent Landau-Ginzburg eq. (2) for the homogeneous situation (i.e. $\gamma \dot{n} \propto -n$). Consequently, these theories for the equilibrium and dynamic properties involve exactly the same fundamental parameters as we used here for the interpretation of the kinetics. Therefore, the kind of kinetic investigation reported here constitutes a complementary tool to the more often pursued equilibrium and dynamic investigations for the further understanding of phase transformations in liquid crystals.

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