Growth Dynamics of a Liquid Crystal at the Three- to Two-Dimensional Crossover in a Hele−Shaw Cell

H. K. Chan and I. Dierking*

Schuster Laboratory, School of Physics and Astronomy, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom

Received: June 14, 2007; In Final Form: September 2, 2007

The radial growth of a cholesteric liquid crystal phase was studied experimentally in a thick Hele−Shaw cell. In the experiments, nucleation and growth of the cholesteric phase occurs after a temperature quench from the isotropic liquid. The growth process changes from three- to two-dimensional when the growing phase touches the substrates of the Hele−Shaw cell. It was found that the growth rate generally increases at the dimensional crossover. Also, this increase in growth rate is approximately constant, independent of the depth of the temperature quench. Possible causes for the observed experimental behavior are discussed.

I. Introduction

Understanding the phase ordering of materials after a quench, i.e., the rapid change of an intensive thermodynamic variable of state, such as pressure or temperature, is of fundamental scientific importance.[1−3] This is because phase ordering is involved in the processing of a wide range of materials, from metal alloys, glasses, and polymers to the crystallization of pharmaceutical organic compounds.[1] During a temperature-quench experiment, the temperature T of a system is rapidly decreased across a phase transition temperature $T = T_m$ to $T = T_o < T_m$. Growth of the stable low-temperature phase in the sea of the metastable high-temperature phase occurs, once the nucleating germs exceed a critical radius R_c.[1]

Considering the various states of condensed matter—solids, liquids, and liquid crystals—phase-ordering studies on liquid crystals are comparatively rare, despite the fact that the phase-ordering process can be followed easily via polarizing microscopy and digital image acquisition.[4] In recent years, liquid crystals have been shown to exhibit a variety of different growth behavior, with a range of growth patterns observed.[4,5] These include circular germs,[6−8] bâtonnets,[9,10] dendrites,[11−13] and fractal aggregates.[14−16] For the Euclidean growth of circular germs and bâtonnets, the growth dynamics can generally be described by a growth law $R \sim t^n$, where n is the growth exponent and R is a characteristic linear size of the growing germ.[6−10] R can be the radius of a circular germ[6−8] or the long axis of a bâtonnet.[9,10] It has been reported for both radial and bâtonnet growth that the growth exponent changes from $n = {}^1/_2$ to $n = 1$ for increasing quench depth $T_m - T_o$.[6−10]

For phase-ordering studies, liquid crystals are generally contained within Hele−Shaw cells that have a typical cell gap of a few micrometers.[6−10] In general, the growth process will undergo a three- to two-dimensional crossover when the growing phase touches the cell substrates. A schematic illustration of this dimensional crossover for radial growth is depicted in Figure 1. Experimental measurements are usually performed at the later two-dimensional growth regime, where the linear size R of the growing germs is larger than the cell gap.[6−10] This is because a cell gap of a few micrometers is of the same order of magnitude as the optical resolution of the polarizing microscope, making it difficult to observe the initial three-dimensional growth process.

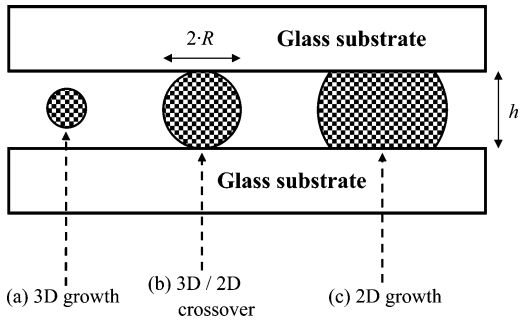

Figure 1. Illustration of the different regimes of radial growth in a Hele−Shaw cell of cell gap h: (a) Initial three-dimensional growth, (b) three- to two-dimensional crossover, and (c) later-stage two-dimensional growth.

In this paper, investigations on the radial growth of a cholesteric liquid crystal phase inside a thick cell of gap 50 μm are presented. The use of such a thick cell allowed the initial three-dimensional growth process to be resolved by optical microscopy and separated from the subsequent two-dimensional growth process. The growth dynamics at the three- to two-dimensional crossover could therefore be studied. It was found that the growth rate dR/dt increases at the dimensional crossover, and this increase in growth rate is approximately constant, independent of the applied quench depths.

II. Experimental Section

The material investigated was cholesteryl pelargonate (also known as cholesteryl nonanoate), a commercially available liquid crystal supplied by Sigma-Aldrich (Figure 2). The compound exhibits a stable cholesteric phase below a phase transition temperature of $T_m = 93$ °C. Above this temperature, there exists a narrow temperature range ≤1 K where Blue Phases[8,17] are observed. The liquid crystal was contained within a homemade Hele−Shaw cell of cell gap $h = 50$ μm, which is thick enough for the initial three-dimensional growth process to be studied. In the experiments, no surface treatment was

* To whom correspondence should be addressed. E-mail: Ingo.Dierking@manchester.ac.uk.

10.1021/jp074613a CCC: $37.00
Published on Web 11/03/2007

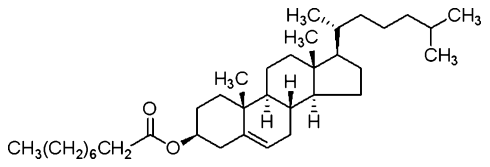

Figure 2. Structural formula of cholesteryl pelargonate, also known as cholesteryl nonanoate.

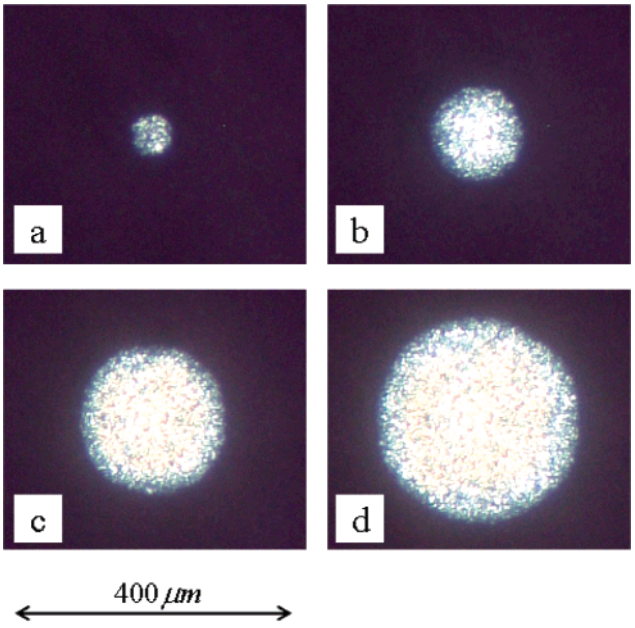

Figure 3. Exemplary time series of radial growth of the cholesteric phase (bright) of cholesteryl pelargonate from the Blue Phase. The time interval between successive images, a−d, is 50 s.

employed for the plain glass substrates of the Hele−Shaw cell. It is worthwhile noting that the study of much thinner as well as much thicker cells bears certain problems. In the former case, due to limits in the microscope's resolution, growth already occurs in two dimensions when measurements start, so that the crossover from three-dimensional to two-dimensional growth cannot be studied. In the latter case, the thickness of the cell implies temperature gradients through the cell and nonuniform growth.

In the temperature-quench experiments, a Linkam TMS91 hot stage was employed for relative temperature control to 0.1 K. A quench rate of 3 K·(min)$^{-1}$ was applied for the best compromise between maximum achievable quench depths and electronic temperature regulation. The hot stage, which contains the Hele−Shaw cell inside, was put on the rotation stage of a polarizing microscope (Nikon Optiphot-Pol) for observation of liquid crystal growth. After each temperature quench, a Blue Phase emerged homogeneously across the sample, followed by nucleation and radial growth of the cholesteric phase. An exemplary time series of the growth of one individual cholesteric germ is shown in Figure 3. This growth process was captured by a digital camera (JVC KY-F1030U), with digital images recorded at a frame rate of 1 Hz and at a resolution of 1280 × 960 pixels. Growth data were obtained by measuring the radius R of a growing cholesteric germ as a function of time t, via the software "ImageTool 3.0", developed at the University of Texas Health Science Center, San Antonio.

III. Results and Discussion

As discussed above, a spherical cholesteric germ growing between the cell substrates is forced to change growth from three to two dimensions when its diameter $2R$ surpasses the cell gap $h = 50\ \mu$m, i.e., when $R \approx h/2 = 25\ \mu$m (Figure 1). In the experiments, radial growth of the cholesteric phase with a very low density of nucleating germs was studied at comparatively large quench depths of 2−4 K below $T_m = 93$ °C. For different quench depths, it was found that growth of the cholesteric phase is always faster in two dimensions ($25\ \mu$m < R < $50\ \mu$m) than in three dimensions ($0\ \mu$m < R < $25\ \mu$m), as observed from a distinct difference in slope of the $R(t)$ curves in the two growth regimes (Figure 4). Figure 4 also provides indirect evidence for the nucleation of germs in the bulk of the cell as opposed to nucleation on the substrates, because the crossover in growth rate occurs at a germ radius of half the cell gap, i.e., $25\ \mu$m. For a growing hemisphere, nucleated at one of the substrates, one would expect this crossover at a germ radius of $50\ \mu$m. The average growth rates v_{3D} and v_{2D} in the three- and two-dimensional growth regimes were characterized by linear fits to the growth data within the ranges of $0\ \mu$m < R < $25\ \mu$m and $25\ \mu$m < R < $50\ \mu$m, respectively. For each linear fit, the range of data points was chosen to minimize the root-mean-square deviation from the fitted curve. It was found that the relation between v_{3D} and v_{2D} could be described by a

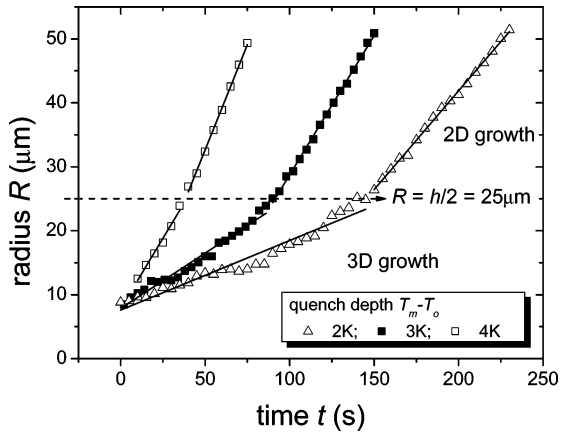

Figure 4. Typical growth data $R(t)$ of a cholesteric germ of cholesteryl pelargonate at the three- to two-dimensional crossover for quench depths of 2, 3, and 4 K, showing an increase in growth rate when the germ radius R surpasses the half cell gap $h/2 = 25\ \mu$m. The solid lines are linear fits for the three- and two-dimensional growth regimes, respectively.

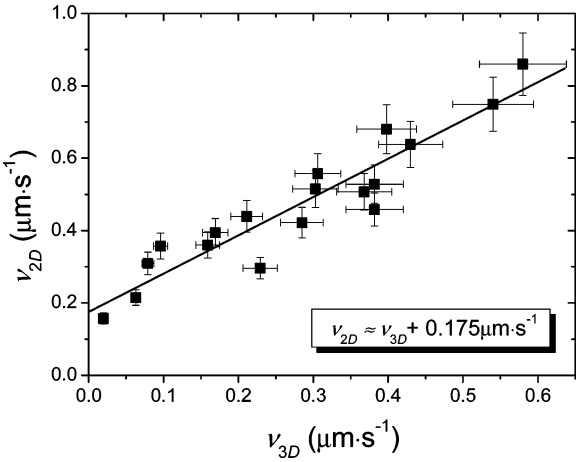

Figure 5. Plot of the later-stage two-dimensional growth rate v_{2D} against the initial three-dimensional growth rate v_{3D} for the radial cholesteric growth of cholesteryl pelargonate. A linear fit of $v_{2D} \approx v_{3D} + 0.175\ \mu$m·s^{-1} (solid line) well describes the relation between the two growth rates. The error bars denote an error estimate of ±10% for both v_{2D} and v_{3D}.

linear relation $v_{2D} \approx a v_{3D} + b$, where $a = 1.058 \pm 0.098$ and $b = (0.175 \pm 0.031)\ \mu m \cdot s^{-1}$ (Figure 5). That is, the change in growth rate upon the dimensional crossover is approximately constant at $v_{2D} - v_{3D} \approx 0.175\ \mu m \cdot s^{-1}$, for $a \approx 1$.

One way to understand the above experimental observations is via the Gibbs−Thomson effect and a kinetic equation for growth processes. For *d*-dimensional radial growth, the Gibbs−Thomson relation[1] for a curvature-dependent transition temperature is

$$T_m \approx T_m' - \frac{(d-1)\Gamma}{R} \tag{1}$$

where T_m' is the zero-curvature equilibrium temperature and Γ the Gibbs−Thomson coefficient. On the other hand, the growth rate of the cholesteric phase should be an increasing function of quench depth.[18] The growth rate can therefore be written as

$$\frac{dR}{dt} \approx \gamma(T_m - T_o) \tag{2}$$

where $\gamma > 0$ is known as the kinetic coefficient, taken to be constant for a first-order approximation. Combining eqs 1 and 2, one obtains

$$\frac{dR}{dt} \approx \gamma(T_m' - T_o) - \frac{\gamma(d-1)\Gamma}{R} \tag{3}$$

According to eq 3, one can approximate the growth rates in the three- and two-dimensional regimes as

$$v_{3D} \approx \gamma(T_m' - T_o) - \frac{2\gamma\Gamma}{R_{3D}} \tag{4}$$

$$v_{2D} \approx \gamma(T_m' - T_o) - \frac{\gamma\Gamma}{R_{2D}} \tag{5}$$

where $R_{3D} \approx h/4 = 12.5\ \mu m$ and $R_{2D} \approx 3h/4 = 37.5\ \mu m$. Subtracting eq 4 from eq 5 results in a quench-depth independent change in growth rate,

$$v_{2D} - v_{3D} \approx \frac{20\gamma\Gamma}{3h} \approx 0.13\gamma\Gamma \approx \text{constant} \tag{6}$$

for a cell gap of $h = 50\ \mu m$. This matches the experimentally observed linear relation between v_{2D} and v_{3D} discussed above, i.e., $v_{2D} - v_{3D} \approx 0.175\ \mu m \cdot s^{-1} \approx$ constant. Nevertheless, this simple model has neglected the interactions between the liquid crystal and the glass substrates, which could also have possible effects on T_m and hence on the growth rate. Also, the growth process after the dimensional crossover has been approximated as a real two-dimensional process, so that the detailed geometry of the curved phase boundary within the finite cell gap was neglected.

IV. Conclusions

Experimental investigations on the three- to two-dimensional crossover of the radial growth of a cholesteric liquid crystal phase in a Hele−Shaw cell were presented. It was found that the growth rate increases at the dimensional crossover and that this increase in growth rate is approximately constant, independent of the applied quench depths. The experimental observations are consistent with a simple explanation based on the Gibbs−Thompson relation and a kinetic equation.

References and Notes

(1) Ratke, L.; Voorhees, P. W. *Growth and Coarsening*; Springer: Berlin, 2002.

(2) Bray, A. J. *Adv. Phys.* **1994**, *43*, 357.

(3) Hohenberg, P. C.; Halperin, B. I. *Rev. Mod. Phys.* **1977**, *49*, 435.

(4) Dierking, I. *Textures of Liquid Crystals*; Wiley-VCH: Weinheim, Germany, 2003.

(5) Oswald, P.; Pieranski, P. *Nematic and Cholesteric Liquid Crystals: Concepts and Physical Properties Illustrated by Experiments*; CRC Press: Boca Raton, FL, 2005.

(6) Diekmann, K.; Schumacher, M.; Stegemeyer, H. *Liq. Cryst.* **1998**, *25*, 349.

(7) Dierking, I. *J. Phys. Chem. B* **2000**, *104*, 10642.

(8) Dierking, I. *Appl. Phys. A* **2001**, *72*, 307.

(9) Dierking, I.; Russell, C. *Physica B* **2003**, *325*, 281.

(10) Chan, H. K.; Dierking, I. *Phys. Rev. E* **2004**, *70*, 021703.

(11) Oswald, P.; Baudry, J.; Rondepierre, T. *Phys. Rev. E* **2004**, *70*, 041702.

(12) Melo, F.; Oswald, P. *Phys. Rev. E* **1993**, *47*, 2654.

(13) Bechhoefer, J.; Oswald, P.; Libchaber, A.; Germain, C. *Phys. Rev. A* **1988**, *37*, 1691.

(14) Baehr, C.; Ebert, M.; Frick, G.; Wendorff, J. H. *Liq. Cryst.* **1990**, *7*, 601.

(15) Dierking, I. *J. Phys.: Condens. Matter* **2001**, *13*, 1353.

(16) Dierking, I.; Chan, H. K.; Culfaz, F.; McQuire, S. *Phys. Rev. E* **2004**, *70*, 051701.

(17) Thoen, J. *Phys. Rev. A* **1988**, *37*, 1754.

(18) Schaefer, R. J.; Glicksman, M. E. *J. Cryst. Growth* **1969**, *5*, 44.