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Phase ordering kinetics of liquid crystalline twist grain boundary TGBA* phases

I Dierking

Institut für Physikalische Chemie, Technische Universität Darmstadt, Petersenstrasse 20,
D-64287 Darmstadt, Germany

E-mail: dierking@hrz2.hrz.tu-darmstadt.de

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Abstract. The phase ordering kinetics of an ordered twist grain boundary (TGBA*) liquid crystalline phase from the disordered isotropic melt was investigated experimentally after a temperature quench with respect to quench rate, quench depth and sample geometry. Nucleus growth was followed *in situ* by polarizing microscopy and image analysis, as spherical germs nucleate and grow, with the germ diameter chosen as a characteristic length L for the growth process. The data are well described by a universal growth law $L(t) \sim t^n$, with a growth exponent $n \approx 1$.

1. Introduction

A quench is a process where a variable of state of a system is changed rapidly across a phase transition, such that the order parameter immediately after the change is the same as before it. This creates a non-equilibrium situation, because the curve of the free energy has changed and eventually, due to thermal fluctuations, leads to the formation of germs of the lower free energy equilibrium phase within the metastable phase of higher free energy (nucleation). Above a critical dimension this nucleus spontaneously grows in a process called coarsening. A suitable way to follow the phase ordering kinetics is the determination of the variation of a characteristic length L with time, which can be the nucleus radius or diameter, as chosen here. This is often described by a universal growth law of the form:

$$L(t) \sim t^n \quad (1)$$

where t is the time after the (temperature) quench and n a growth exponent. Depending on the system under consideration, different exponents are predicted [1]. For systems with a non-conserved order parameter (NCOP), Allen and Cahn [2] described a curvature driven growth law for spherical shaped domains at the transition temperature with a growth exponent of $n = 1/2$, which was also confirmed by other authors [3–6]. For systems with a conserved order parameter (COP), smaller growth exponents are obtained, $x = 1/3$ [6] or $x = 1/4$ [1, 7]. The COP case though does not apply to liquid crystalline systems.

In a report [8] on the Iso.–BPI transition a growth exponent close to $n = 1/2$ was obtained. Diekmann *et al* [9] have pointed out that for the growth of nematic (N) droplets from the isotropic phase, as well as smectic phases (SmA, SmB) from the nematic and blue phases (BP) from the isotropic melt, strong deviations from the $n = 1/2$ growth exponent are observed for increasing quench depth, thus larger super-cooling. This was attributed to the fact that here a volume driving force $\beta \sim \Delta F$ has to be taken into account, which describes the difference in the free energy ΔF of both phases. As the volume driving force (becomes the dominating

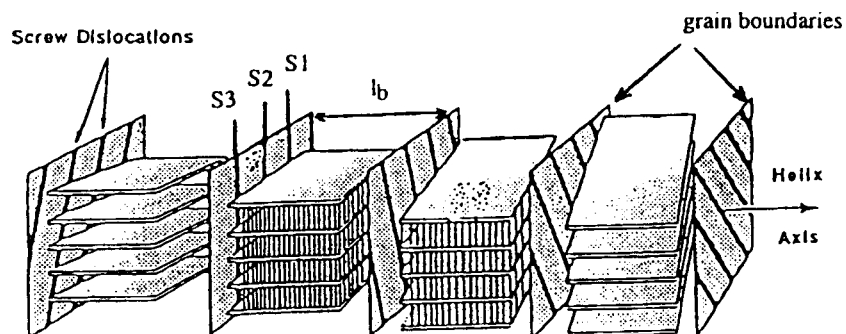


Figure 1. Schematic structural model of the liquid crystalline twist grain boundary TGBA* phase.

factor, the growth exponent varies from $n = 1/2$ (curvature driven nucleus growth) to $n = 1$ (volume driven nucleus growth).

In the present study the phase ordering kinetics of liquid crystalline twist grain boundary (TGB) phases is investigated. TGB phases are frustrated smectic phases, which result from a competition between chirality, i.e. the formation of macroscopically helical superstructures, and thermodynamics, i.e. the formation of smectic layers as the temperature is lowered. Both structural elements are not compatible with each other and defects are introduced, which in the case of TGBA* are regular arrays of screw dislocations mediating blocks with a local SmA* structure. A schematic picture of the TGBA* phase is depicted in figure 1. TGBA* phases are usually observed in a small temperature interval of a few tenths of a kelvin between the cholesteric N* and the SmA* phase. Their occurrence and stability is generally quite sensitive to the sample geometry (cell gap). In the present case we study a rather unusual material with the TGBA* phase being stable over several kelvin and forming from the isotropic melt.

2. Experiment

The compounds under investigation were the $n = 9$ and $n = 18$ homologues of a material abbreviated as FH/FH/HH- n -BTMHC, first reported in [10]. Their phase transition temperatures (in °C) on cooling, as listed in [10], are given by:

$n = 9$: Iso. 71.1 BPIII 67.0 BPII 65.1 TGBA* 53.0 SmC* 30 Cryst.

$n = 18$: Iso. 72.3 BPIII 71.2 BPII 70.6 BPI 70.2 TGBA* 67.7 TGBC* 63 SmC* 44.6 Cryst.

These are in good agreement with transition temperatures observed in this study. It should be noted that the blue phases reported in [10] could not be observed in the geometry used for the investigations presented here, although they do appear in preparations between untreated substrates. Thus here, an isotropic to TGBA* transition is observed on cooling. To perform cell gap dependent measurements, wedge cells were used with a variable cell gap between $d = 0 \mu\text{m}$ and $d = 20 \mu\text{m}$. Cell gap dependent measurements were carried out in order to detect a possible crossover from two-dimensional to three-dimensional nucleus growth. For measurement series not related to the cell gap dependence, a gap of $d = 10 \mu\text{m}$ was used. The substrates were treated with an agent promoting homeotropic boundary conditions (long molecular axis perpendicular to the substrate plane), which gives rise to a basically spherical growth of nuclei. In contrast, planar boundary conditions lead to elongated germs, which make it difficult to define a characteristic length L . Cells were filled by capillary action in

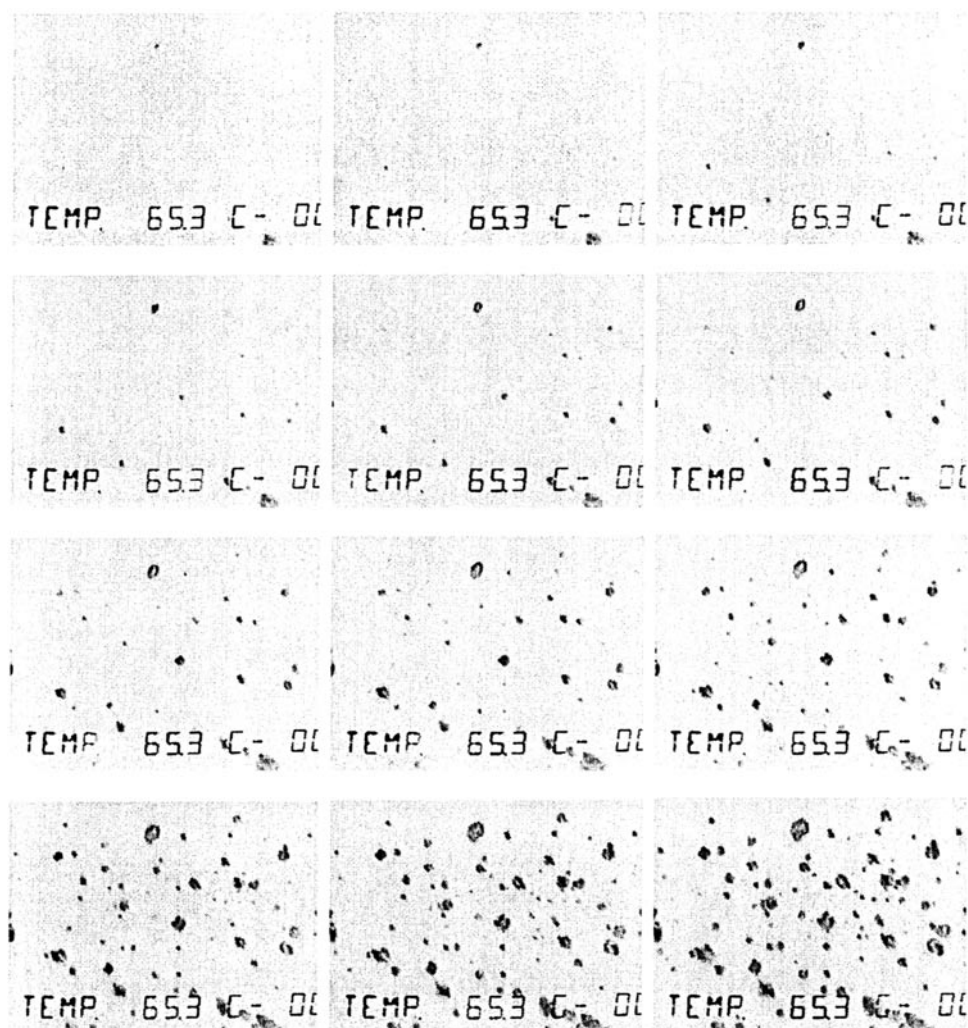


Figure 2. Series of (inverted) polarizing microscopic images showing the evolution of spherical nucleus growth with time for a $10\ \mu\text{m}$ cell with homeotropic boundary conditions. Images are taken 1 s apart and show a sample area of $290\ \mu\text{m} \times 220\ \mu\text{m}$.

the isotropic phase. The nucleus growth was followed in a polarizing microscope (Leitz) equipped with a Mettler FP82 hot stage and a FP80 temperature controller for an accuracy of relative temperatures within 0.1 K. The transmission image was recorded by a video camera and subsequent image analysis performed by means of standard software (Adobe Premiere, Adobe Photoshop) after inverting the images to achieve better contrast. For the determination of the growth exponents, only images during the early stages of the phase formation were used, when the germs were still well separated.

3. Experimental results and discussion

Figure 2 shows a typical sequence of (inverted) polarizing microscope images taken 1 s apart, demonstrating the nucleation and growth of TGBA* germs from the isotropic melt, as time

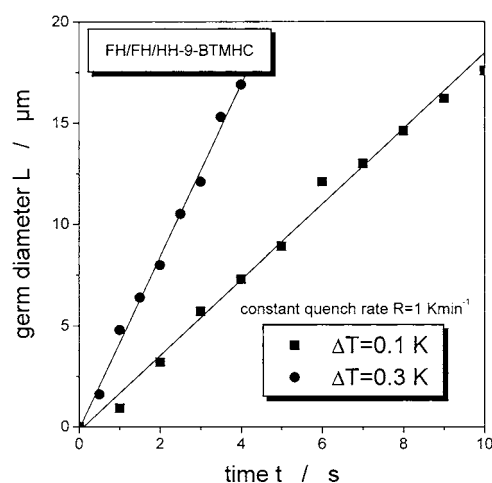


Figure 3. Experimentally determined germ diameter L as a function of time t for a variation of quench depth ΔT at constant quench rate $R = 1 \text{ K min}^{-1}$ for FH/FH/HH-9-BTMHC.

proceeds. The image size is $290 \mu\text{m} \times 220 \mu\text{m}$. From these series the germ diameter L is determined as a function of time t and a least-squares fit according to equation (1) yields the growth exponent n . Some exemplary data of the $n = 9$ homologue are shown in figure 3 for a variation of quench depth ΔT at constant quench rate $R = 1 \text{ K min}^{-1}$.

Figures 4(a)–(d) show the variation of the determined growth exponent x as a function of quench rate R , quench depth ΔT at constant and at variable quench rate, as well as cell gap d , for the two homologues under investigation. For quench rates smaller than about $R = 1 \text{ K min}^{-1}$ a growth exponent slightly larger than $n = 1$ is observed, before a basically linear growth law is obeyed in the range of $2 \text{ K min}^{-1} < R < 5 \text{ K min}^{-1}$ (figure 4(a)). For larger quench rates, the growth exponent approaches a value of $n = 1/2$, which is attributed to an insufficient regulation electronics of the temperature control. Super-cooling below the quench depth is observed, so that the sample is not at isothermal conditions after the quench at all times of the nucleus growth process. Values for quench rates of $R = 5 \text{ K min}^{-1}$ or larger should thus be interpreted with caution.

Figure 4(b) shows the growth exponent as a function of quench depth for a constant quench rate of $R = 1 \text{ K min}^{-1}$. n is found to be independent of quench depth ΔT at a value $n = 1$. For larger quench depths, $\Delta T > 0.3 \text{ K}$, the sample is clearly not at isothermal conditions before the nucleation and growth process commences. This seems to be in contrast to results reported for the growth kinetics of other liquid crystal phases [9], showing an increasing exponent from $n = 1/2$ to $n = 1$ for increasing quench depth, but can be understood, when we consider that the difference in free energy between the isotropic and the TGBA* phase should be rather large. The behaviour at variable quench rate, chosen to $R = 10 \Delta T$, is depicted in figure 4(c). Here, a decrease of the growth exponent from $n = 1$ to $n = 1/2$ is observed for increasing quench depth. Again, we have to keep in mind that values obtained for larger quench rates should be taken with caution.

Generally, the phase occurrence, transition temperatures and material properties of TGB phases are highly sensitive to preparation conditions, especially the cell gap of the used sandwich cells (at least for planar boundary conditions). For the here used cells with homeotropic boundary conditions, a constant, cell gap independent transition temperature was observed for the Iso.–TGBA* phase transition, as the gap was varied between $d = 2 \mu\text{m}$

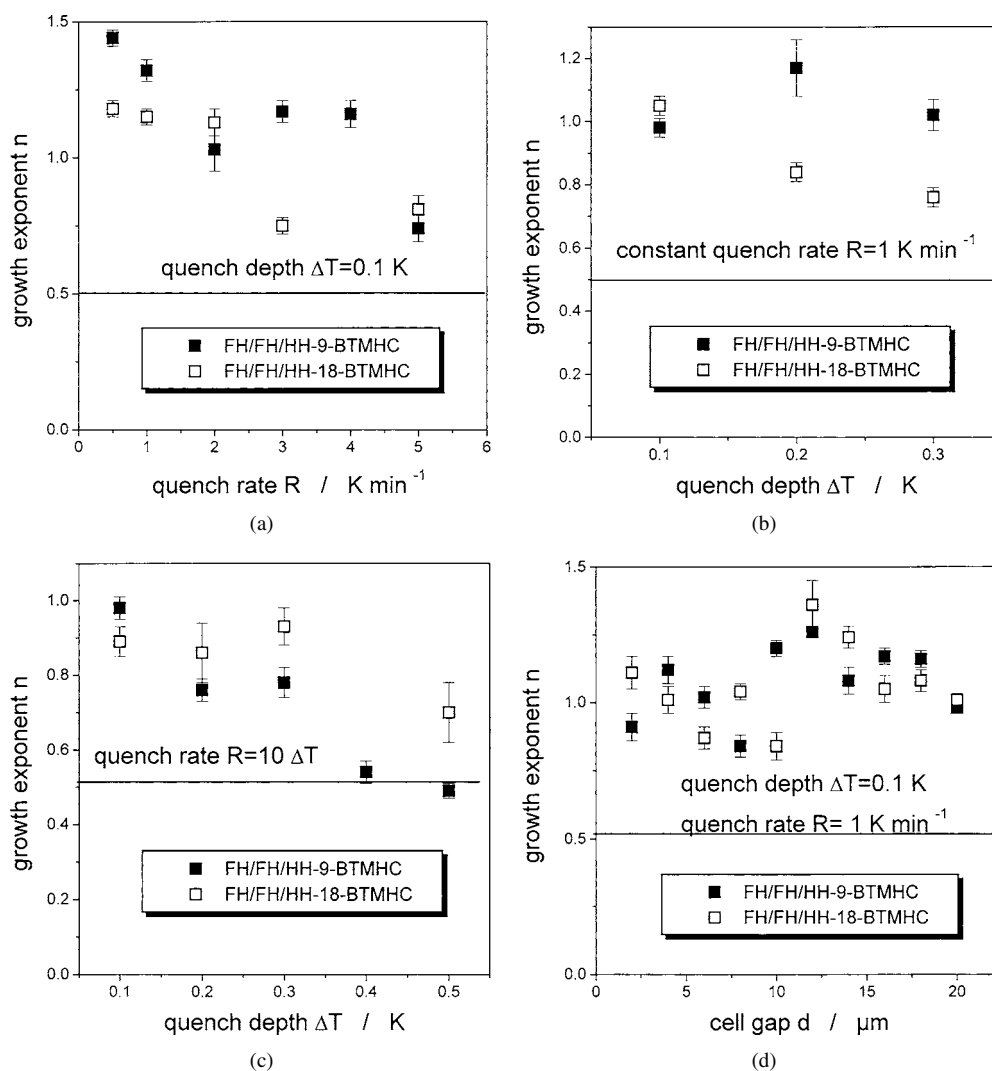


Figure 4. Experimentally determined growth exponent n as a function of (a) quench rate R , (b) quench depth ΔT at constant quench rate $R = 1$ K min^{-1} , (c) quench depth ΔT at variable quench rate $R = 10 \Delta T$ and (d) cell gap d , for compounds FH/FH/HH-9-BTMHC (closed symbols) and FH/FH/HH-18-BTMHC (open symbols).

and $d = 20$ μm . Transition temperatures were constant within an accuracy of 0.1 K. Also for the growth exponent no peculiarities were observed as the cell gap was varied. Although values do scatter quite a bit, one can observe a growth exponent basically being equal to $n \approx 1$, independent of sample geometry (figure 4(d)). There seems to be no observable crossover from a two-dimensional to three-dimensional growth process as observed for the late time coarsening process of a BPII phase [11].

4. Conclusions

The nucleus growth of spherical germs of an ordered liquid crystalline TGBA* phase from the disordered isotropic melt was investigated with respect to quench rate, quench depth and

sample geometry. For isothermal conditions after the quench, the growth of a characteristic length L (in this case the germ diameter) with time t is described by a universal growth law of the form $L(t) \sim t^n$, with a growth exponent of $n \approx 1$. The observation of growth exponents being of the order of $n \approx 1$ is in good qualitative agreement with investigations for other liquid crystalline phases [9]. It confirms that in the present system with an isotropic to TGBA* transition, the volume driving term plays the dominant role in the phase ordering process.

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References

- [1] Mazenko G F and Zannetti M 1985 *Phys. Rev. B* **32** 4565
- [2] Allen S M and Cahn J W 1979 *Acta Metall.* **27** 1085
- [3] Hashimoto T, Nishimura K and Takeuchi Y 1978 *Phys. Lett. A* **65** 250
- [4] Wang G-C and Lu T-M 1983 *Phys. Rev. Lett.* **50** 2014
- [5] Chuang I, Turok N and Yurke B 1991 *Phys. Rev. Lett.* **66** 2472
- [6] Lifshitz I M and Slozov V V 1961 *J. Phys. Chem. Solids* **19** 35
- [7] Coniglio A and Zannetti M 1989 *Europhys. Lett.* **10** 575
- [8] Demikhov E, Stegemeyer H and Blümel T H 1994 *Phys. Rev. E* **49** R4787
- [9] Diekmann K, Schumacher M and Stegemeyer H 1998 *Liq. Cryst.* **25** 349
- [10] Li M-H, Laux V, Nguyen H-T, Sigaud G, Barois P and Isaert N 1997 *Liq. Cryst.* **23** 389
- [11] Schumacher M and Stegemeyer H unpublished results
Schumacher M 1996 *Thesis* Paderborn