Kinetics of Phase Transitions in Liquid Crystals

Stephen A. Barr

December 14, 2006

Abstract

When a liquid crystal system is quenched across a phase boundary, it is observed that nuclei of the ordered phase form and then grow. This growth can be described by a universal growth law. There are many other systems which are also described by a universal growth law and much work has been done in understanding those systems. Only recently, however, has this been investigated in systems that form liquid crystals. In this paper I will discuss the experiments performed to determine the growth laws and the size distribution of the nuclei in liquid crystal systems and how the results compare with the general theoretical predictions for these quantities.

1 Introduction

Liquid crystals are partially ordered systems with long-ranged order that is between a completely isotropic phase, or a liquid, and a completely ordered phase, or a crystal. The molecules that form liquid crystals are anisotropically shaped, usually rod-like, and it is this anisotropy that leads to many of the different liquid crystal phases which have varying degrees of long-ranged order, both in the center of mass positions of the molecules as well as their orientations. In the isotropic phase, there is not long-ranged order in either the centers of mass or in the orientations of the molecules. In the nematic phase, the molecules do have long-ranged orientational order, that is they are all pointing in the same direction, however the centers of mass of the molecules do not have long-ranged order. The cholesteric phase is the chiral version of the nematic phase, in which there are nematic layers which are continuously rotated with respect to each other. In the smectic A and smectic C phases, in addition to orientational order, there is also positional order in one direction. Other combination of long-ranged order are also possible leading to a large number of liquid crystal phases [1]. In order to determine what phase the system, or a particular part of the system, is in, an order parameter is used. For liquid crystals, the order parameter is a tensor, however using a scalar order parameter S, give by

$$S = \frac{1}{2} < 3\cos^2\theta - 1 > \ , \tag{1}$$

is sufficient to describe the orientational order in nematic liquid crystals. Here, θ is the angle between the long axis of a single molecule and the director, or the average direction of the long axis of all the molecules, and the brackets denote a temporal and spatial average. The order parameter is zero in the isotropic phase and non-zero in the nematic phase [1].

If a liquid crystal system is originally in the isotropic phase and the temperature is decreased quickly across a phase transition, it is found that nuclei of the low temperature state, the nematic phase for example, appear spontaneously and grow [2]. The process of nucleation and growth has been studied extensively for many years. It is not only interesting from a fundamental perspective, but is also important in industrial applications, since many material properties depend on the thermal history of the material [3]. While much work has been done in understanding this process in other systems, like crystallization and the phase separation of binary alloys, only recently has the phase ordering process been studied in systems that form liquid crystals [3]. Systems that form liquid crystal are a good candidate for studying phase ordering kinetics since it can be directly observed by conventional polarizing microscopy. Other methods for studying phase transitions include differential scanning calorimetry, which only provides information about the temperature of a phase transition, and X-ray investigations, which can only determine structural information. Polarizing microscopy, however, can be used to determine both the temperature of the phase transition and structural information. In addition, the structural information obtained with polarizing microscopy allows for better characterization of structural features than X-ray investigations [1].

Nucleation growth in liquid crystal systems, as well as in many other systems, can be described by a universal growth law. This means that the domain structure is independent of time if scaled by the appropriate function, $L(t) \sim t^n$, where t is the time after a temperature quench and n is the growth exponent [4]. This function can be determined experimentally by measuring nuclei growth as a function of time where L would represent the size of a nucleus [5]. For liquid crystal system, and other systems which are described by a non-conserved order parameter, the growth exponent n is expected to depend on the quench depth, and vary from 0.5 at small quench depths to 1 at large quench depths [5]. In addition to a variation with quench depth, there are two distinct growth regimes at different times, nucleus growth at short-times and coarsening at long-times. These are each described by separate growth exponents [6].

2 Small Quench Depth

In order to understand why the the growth exponent should have a particular value, it is important to understand what causes domains to grow. One factor is the difference in bulk free energy between the nematic state and the isotropic state. If the system is quenched to just below the critical temperature, this difference in free energy is small and does not contribute to domain growth. In this case the main driving force which causes a nucleus to grow is the movement of antiphase boundaries, which separate two domains with different order parameters. The velocity of the antiphase boundary is equivalent to the change in the radius R of a domain and is proportional to the curvature K of the interface [7]. If the domains are spherical, then $K = 1/R$. This leads to an equation for the domain radius given by

$$\frac{dR}{dt} = \frac{M}{R} , \tag{2}$$

where M is a constant. Solving for $R(t)$ yields

$$R(t) \sim t^{1/2} , \tag{3}$$

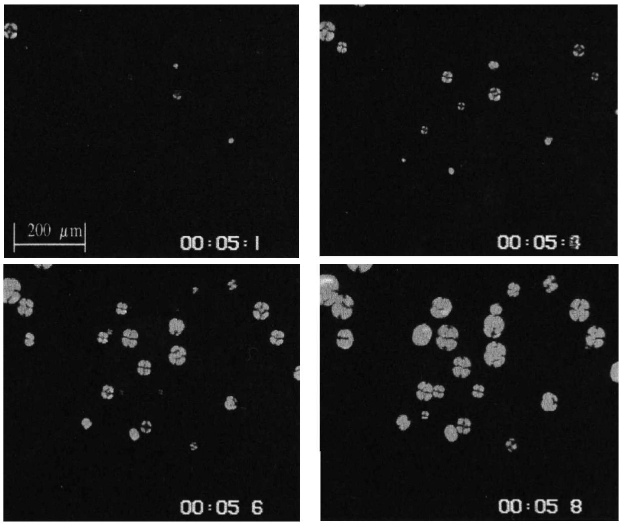

Figure 1: Snapshots of nematic nuclei growing out of the isotropic phase. In the lower right corner the time after the temperature quench is given. The nematic domains are roughly spherical and grow in time. Taken from [5].

which is the universal growth law for a liquid crystal system that has been quenched just below the isotropic to nematic phase transition temperature. This result can also be derived starting from the time-dependant Ginzberg-Landau equation [4], and the generalization to arbitrarily curved surfaces was done by Allen and Cahn [7].

Experiments carried out by Diekmann *et al.* confirm this growth exponent for small quench depths [5]. The molecule studied is PCH5, which undergoes an isotropic to nematic phase transition at 54.5 °C. Polarizing microscopy was used to observe the growth of nuclei and the process was captured using a CCD camera. The nuclei diameters were determined using either digital image processing or direct on-screen measurement and the liquid crystals were confined between glass plates with a cell thickness of 12 μm. As shown in Fig 1, the nuclei are roughly spherical and grow in time. For a quench depth of 0.05 °C, the growth exponent is found to be 0.50, in excellent agreement with the theoretical prediction.

3 Large Quench Depth

As the quench depth is increased in experiments, the observed growth exponent varies from 0.5 at small quench depths to 1 at large quench depths. Figure 2 shows

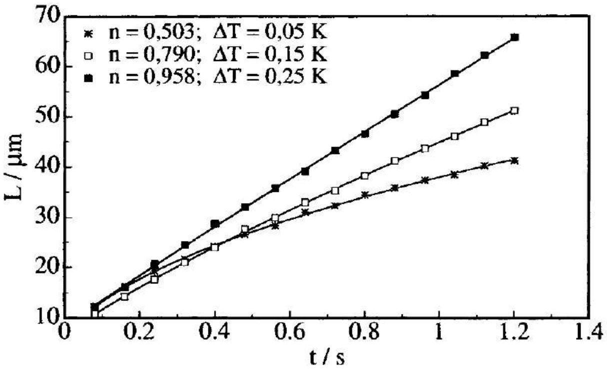

Figure 2: Diameter of nematic domains as a function of time for various quench depths, ΔT. As the quench depth is increased, the nematic domains grow faster and the growth exponent goes from 0.5 to nearly 1. Taken from [5].

how the growth exponent increases, again using PCH5. Increasing the quench depth to 0.15 °C from 0.05 °C increases the growth exponent from 0.50 to 0.79. At an even larger quench depth of 0.25 °C, the growth exponent reaches a value of 0.96 [5].

The dependence of the growth exponent on quench depth is not predicted by Allen-Cahn theory because it assumes that the free energy of the two states are equal [5]. This assumption is true at small quench depths when T is just below the critical temperature, however this fails at large quench depths where the free energy difference between the isotropic state and the ordered state is large. In order to account for this, Bray suggested adding a term to Eq. 2 which represents the free energy difference between the two phases. The new equation is given by

$$\frac{dR}{dt} = \frac{M}{R} + \beta \, , \tag{4}$$

where β is proportional to the free energy difference ΔF. ΔF itself is a function of quench depth, ΔT, where a deeper temperature quench results in a larger difference in free energy. The resulting formula for β can be written as

$$\beta = A \Delta F(\Delta T) \, , \tag{5}$$

where A is a constant [4].

The growth exponent cannot be obtained from Eq. 4 analytically. However, it is possible to numerically determine the growth exponent given specific values

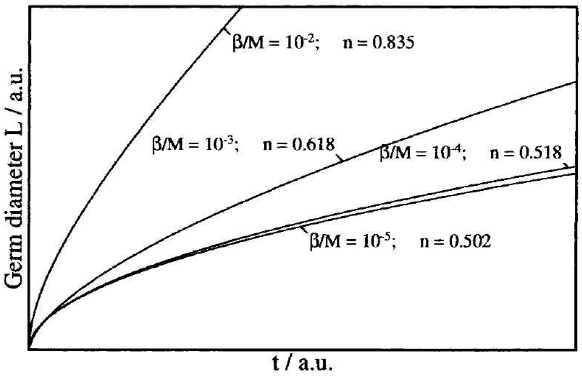

Figure 3: Numerical data for the domain diameter as a function of time in reduced units. As β, which represents the quench depth, becomes larger, the growth exponent increases from 0.5 to 1. This agree with experimental results. Taken from [5].

of β and M. This is shown in Fig. 3 for different values of the ratio between these two quantities, β/M. When $M \gg \beta$, the growth exponent is 0.5, which is expected since this case represents the situation where ΔF is small and the growth is curvature driven. As β is increased, the free energy difference becomes more important and adds to the driving force. When this happens, the growth exponent increases, reaching a value of 1 if $\beta \gg M$. This is in good qualitative agreement with the experimental results where the same behavior is observed, as shown in Fig 2 [5].

This quench depth dependant growth exponent only describes nucleus growth at short times, usually under a minute. After this time, experiments observe a different growth exponent [6]. This suggests that there is a different process which becomes dominant at long times. This behavior can be seen in Fig. 4, which shows the average nucleus diameter as a function of time for a deep temperature quench. At short times, the growth exponent is about 1, however at longer times, the growth exponent changes, and a value of about 0.5 is observed. These two different behaviors are referred to as nucleus growth and nucleus coarsening respectively. The time at which the onset of nucleus coarsening occurs depends on many factors. A larger cooling rate, for example, leads to a quicker onset of coarsening. The growth exponent itself, though, is independent of the cooling rate, the cell gap, and the quench depth in this long time regime. This suggests that the long-time process is controlled by diffusion [6].

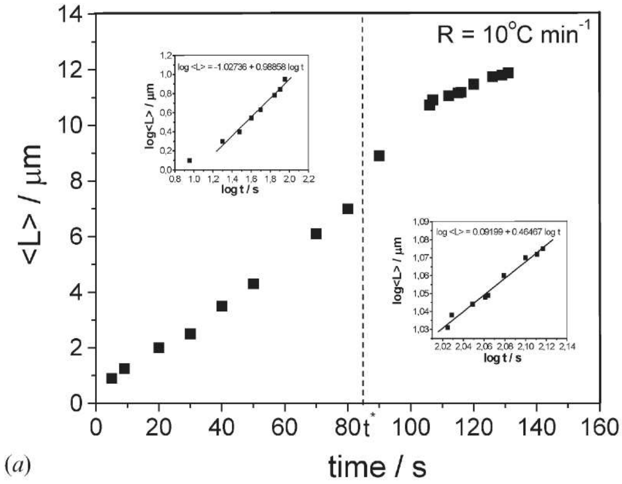

Figure 4: Average nucleus diameter as a function of time after a temperature quench. The short-time nucleus growth and the long-time coarsening processes are separated at a time $t*$. The insets show each process in a log-log plot in order to determining the growth exponents. A growth exponent of about 1 is found at short times and a growth exponent of about 0.5 is found for long times. Taken from [6].

4 Size Distribution

In addition to describing the growth behavior of the nematic domains, it is also possible to describe the size distribution of the nematic domains using the model of reversible aggregation [8]. This model not only describes the size distribution, but also allows for a better understanding of the difference between the short-time and long-time growth behaviors. In the model, non-equilibrium structures are formed by linking individual dynamical units into aggregates, which are metastable. These aggregates have a definite lifetime and are continually formed and reformed, which means this process is reversible. The number n of aggregates of size y is given by

$$n(y) = a y^p \exp\left(-\frac{yu}{kT}\right) , \tag{6}$$

where a is a constant, k is the Boltzmann constant, T is the absolute temperature, u is the aggregation energy per unit, and p is related to the dimension of space, D, through the relation $p = D - 1$. Multiplying $n(y)$ by y yields the statistical size distribution of the aggregates $h(y)$, given by

$$h(y) = a y^{p+1} \exp\left(-\frac{yu}{kT}\right) , \tag{7}$$

In general, a non-zero minimum aggregate size, y_0, has to be taken into account. Also, there may be multiple statistical ensembles as a result of the different components in a multi-component system. Taking these generalizations into account results in a distribution function given by

$$h(y) = \sum_{i=1}^{N} a_i (s_i - s_{0i})^{p+1} \exp\left(-\frac{y_i u_i}{kT}\right) , \tag{8}$$

where N is the number of statistical ensembles. Here the aggregate size, y, is replaced by the aggregate area, s, which is easy to determine experimentally from the aggregate diameter, L [2].

Studying a multi-component mixture has the advantage that there is a two phase region. The presence of this region makes it easier to study both the short-time and the long-time growth processes. Bronnikov *et al.* investigated a particular multi-component liquid crystal system, ZLI-5014-100, which exhibits a two phase region at the isotropic to cholesteric transition over a temperature range of about 1 K [2]. This size distribution was measured experimentally in a sandwich cell with a thickness of 4 μm using polarizing microscopy. The distribution was

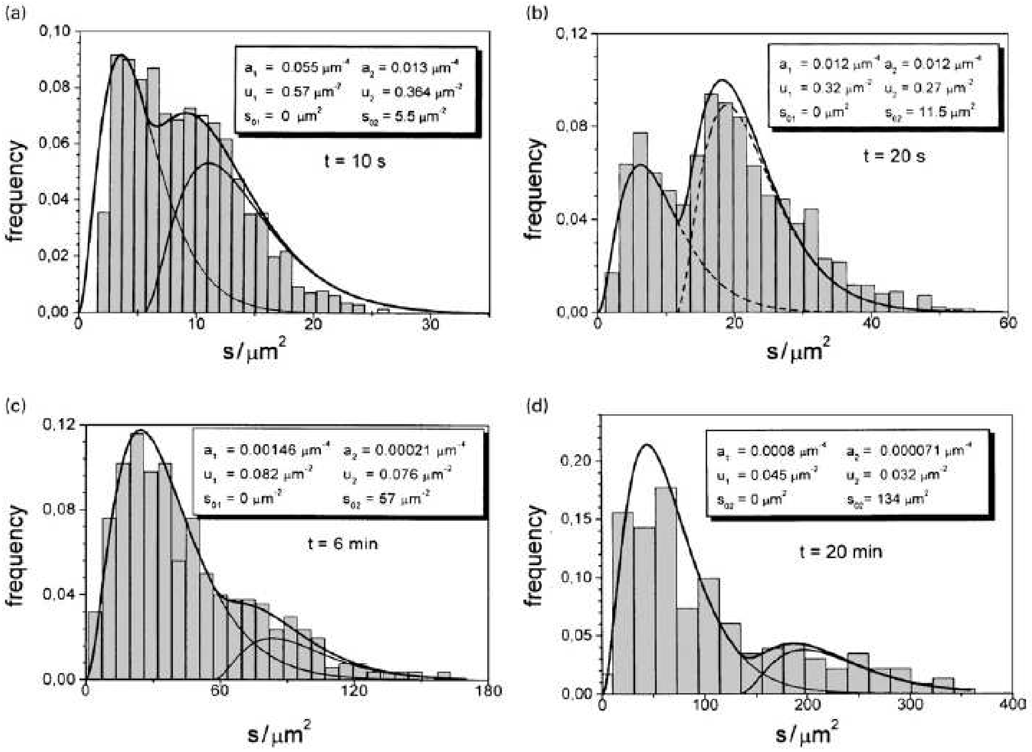

Figure 5: Statistical distribution of nuclei area. This data is fit to Eq. 8 with the fitting parameters a_i, u_i, and s_i given in the inset. There is good agreement between Eq. 8 and the experimental results. Taken from [2].

then fit to Eq. 8 with $p = 1$, since the samples were restricted in one dimension, and $N = 2$ from inspection of the distribution. As shown in Fig 5, the theory accurately describes the observations. The fact that there are two distinct distributions suggests that there are likely two dominant components in the mixture. In addition to the size distribution, the average nucleus size L, was also determined. A log-log plot of L as a function of time, shown in Fig. 6, clearly shows two growth regimes which are separated by a plateau at about 100 s, when nucleus growth ceases for a short time. In this case, both the short-time and the long-time regimes have the same growth exponent of about 0.5 [2].

By fitting the experimental distributions to Eq. 8 at different times, it is possible to obtain the fitting parameter u_i for each distribution as a function of time. The results of this are shown in Fig. 7, and from this plot it is clear that there is an abrupt change in behavior at about 100 s, which corresponds to the time

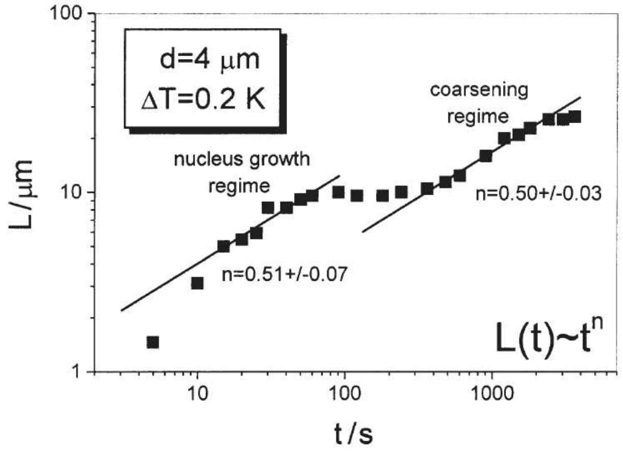

Figure 6: Average nucleus diameter as a function of time. In this log-log plot it is clear that there are two regimes separated by a plateau. In this example, both the long-time and the short-time growth exponents are approximately the same with a value of 0.5. Taken from [2].

separating the short-time and the long-time growth processes. This demonstrates that there are indeed two distinct growth regimes which are controlled by different mechanisms. At short times, u for both ensembles decreases rapidly. The sharp decrease in aggregation energy causes a significant increase in the average nucleus size. This provides evidence that the short-time process is related to nucleus growth, which includes the coalescence of nuclei. The long-time growth process is not controlled by the aggregation energy, but instead is believed to be related to domain coarsening. This is a diffusion controlled process in which material from smaller domains diffuses to the larger domains, similar to Ostwald-ripening [2].

The difference between the two regimes can also be seen by counting the number of nuclei observed as function of time. As shown in Fig 8, this is rapidly decreasing in time. Even though the number of nuclei decreases in both regimes, albeit at dramatically different rates, it is directly observed that two different mechanisms cause this decrease. In the nucleus growth regime, it is observed that coalescence is the main cause for the decrease in the number of nuclei. There are many nuclei during this phase and they are all close together. When two nuclei meet, they merge into a single, larger nucleus. At later times, during the coarsening process, there are fewer domains and this decreases the chances for coalescence. This suggests that a diffusion controlled mechanism must be dominant. It is also directly observed that the smaller domains vanish without coalescing with the larger

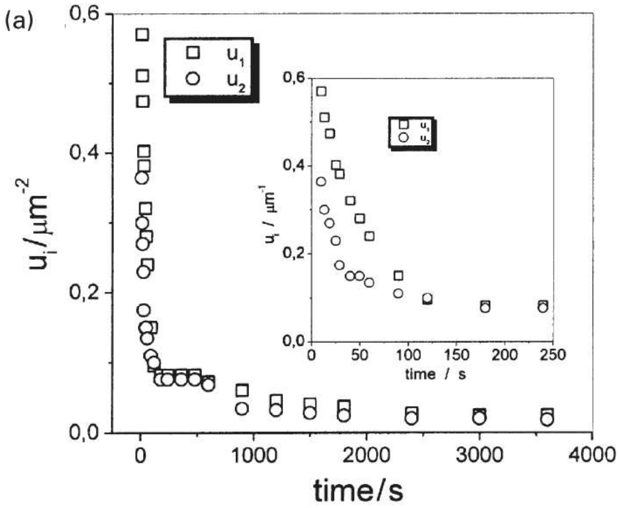

Figure 7: Aggregation energy for both ensembles as a function of time. This was obtained by fitting Eq. 8 to the experimental distributions. The abrupt change in behavior at $t = 100$ s corresponds to the change from the short-time regime to the long-time regime. Taken from [2].

domains. At the same time the larger domains do indeed grow with time. These finding provide even stronger evidence that the long-time process is controlled by diffusion [2].

5 Conclusion

Liquid crystal systems that undergo a temperature quench across a phase boundary exhibit nucleation growth and coarsening and follow a universal growth law. The mathematical descriptions of these processes are generic to many systems undergoing a phase transition and have indeed been able to describe many other systems. Only recently, however, have these phenomenon been investigated in liquid crystal systems. By using polarizing microscopy it is possible to directly observe these processes in liquid crystals, and therefore, they provide a good example system and can further the understanding of systems in which direct observation is not possible.

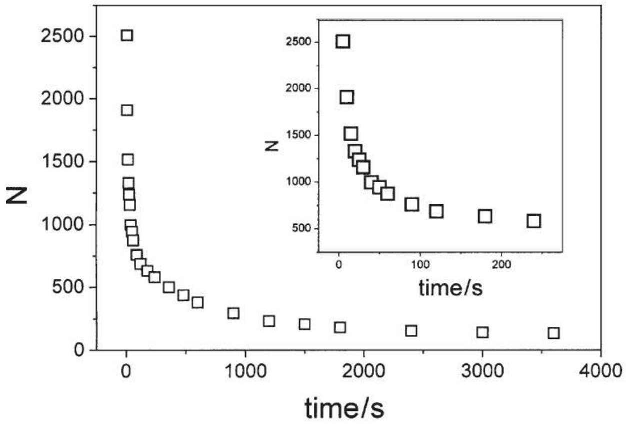

Figure 8: Number of nuclei observed in the microscope as a function of time. The initial decrease is attributed to coalescence during the the nucleus growth regime. Taken from [2].

References

[1] I. Dierking. *Textures of Liquid Crystals*. Wiley-VCH, Weinheim, 2003.

[2] S. Bronnikov and I. Dierking. *Phys. Chem. Chem. Phys*, 6:1745, 2004.

[3] S. Bronnikov and I. Dierking. *Physica B*, 358:339, 2005.

[4] A. J. Bray. *Adv. Phys.*, 43:357, 1994.

[5] K. Diekmann, M. Schumacher, and H. Stegmeyer. *Liq. Cryst.*, 25:349, 1998.

[6] S. Bronnikov, C. Racles, A. Nasonov, and M. Cazacu. *Liq. Cryst.*, 9:1015, 2006.

[7] S. M. Allen and J. W. Cahn. *Acta Met.*, 27:1085, 1979.

[8] H. G. Kilian and B. Zink. *J. Chem. Phys*, 107:8697, 1997.