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Dynamical and structural self-organization : a study of friction, liquid-crystal nucleus growth, and supramolecular polymers through simple models

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5

Phase transition by nucleus growth

5.1 Phases of liquid crystals

One of the major differences between the phases of matter such as gas, liquid or solid, is the amount of freedom the particles have. In a gas the particles can move freely within the whole system volume, and there is hardly any preferential separation between them. In liquids the particles can still move anywhere within the system, and as such, have not lost the freedom of position, however, in a liquid the particles stay closely together and hence have lost the freedom of relative position. A solid has lost almost all this freedom. Its constituents can only move inside a small cage created by the neighbors. The statistical mechanical quantity describing this type of freedom in a system is the entropy, the quantity that changes when we reversibly add heat to a system kept at a constant temperature

$$\Delta S = \frac{\Delta Q}{T} \quad (5.1)$$

where ΔS is the change in entropy, ΔQ is the heat added to the system and T the temperature at which we do this. When a first-order phase transition takes place between two phases that have different entropies at the transition temperature, the change of entropy is accompanied by what is known as the *latent heat*. For example, when sweat evaporates, it changes from a liquid to a gas, increasing its entropy. This increase in entropy must be compensated by extracting heat from the environment, thereby cooling your body down.

Besides losing spatial freedom, a particle can also lose orientational freedom. This is often the case with molecules that are far from spherically symmetric, such as rod-like or disc-like molecules. Some of these form materials that are called liquid crystals. Because of their anisotropy they have many liquid phases, that all, except one, have some sort of crystalline order, whence the name liquid crystal. If the liquid crystalline order is a function of the temperature, then the liquid crystal is called *thermotropic*. Let us look at the typical phases of a rod-like thermotropic liquid

crystal. At high temperatures the rods can move anywhere within the system and do not have any particular orientation, this purely liquid phase is called the *isotropic* phase[2]. At lower temperatures phases with several types of crystalline order exist. In the *nematic* phase the particles have lost only their orientational freedom, all rods are more or less aligned, but they can still be found anywhere within the system. The smectic phase removes one of the spatial freedoms; molecules are aligned like in the nematic phase, but they are also ordered in layers. There can be more than one smectic phase, that differ in the angle between the layers and the molecule orientation. If the angle between the long axis of the molecule and the layers is 90° the phase is called Smectic A, if the angle is different, the phase is called Smectic B, which is slightly more ordered. Higher order smectics do exist, in which there is ordering between the layers (one layer tilting in one direction, the other in the other direction). In columnar phases the liquid crystal molecules do not form layers as in the smectic phase, but they form stacks or columns of molecules that then form several types of two-dimensional lattices. Finally, in the crystalline phase, the rods are confined to a lattice position, and have lost all, or most, of their orientational freedom.

In a pure sample the transition from an isotropic liquid to a nematic liquid crystal can occur in two ways. If the isotropic phase is cooled below the so called spinodal temperature then spinodal decomposition occurs. In this temperature regime the isotropic phase is unstable, and so spontaneously, all molecules align into domains with a similar orientation. However, because there is no initial preferential orientation, these domains are not aligned amongst themselves, and the reorientation of these domains into one large nematic domain can take quite some time. If, however, the isotropic phase is cooled below the transition temperature but above the spinodal temperature, then the isotropic phase is metastable, and a change of phase can only occur through nucleation. In this case the nematic phase grows from one or several approximately spherical domains of ordered molecules surrounded by the still unaligned isotropic phase. The rate at which these spherical domains grow depends on the temperature at the edge of the domain. However, the change of phase at this edge causes latent heat that can slightly change this temperature.

In this chapter I introduce the concepts that one needs to study nucleus growth theoretically by using thermodynamic differential equations. I will apply these equations to the spherical growth of nematic order from an isotropic melt, as an introduction to Chapter 6.

5.2 Order parameters

Entropy is often not the most suitable parameter to describe a phase, especially when studying a very specific transition between two phases. In a transition between phases one can often identify one specific property, that one can describe by means of what is called an *order parameter* (here denoted by m), that is not present in one of the phases, and that is present in the other. The order parameter is then zero in the

first phase, which will be called the disordered phase, and nonzero in the other, the ordered phase. For instance, in the transition from the isotropic phase to the nematic phase of a rod-like liquid crystal the orientation changes from completely random, to more or less aligned. The order parameter that is usually taken to describe the order in the nematic phase, is a tensor^[1]

$$Q_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^N \frac{3}{2} \hat{u}_{i\alpha} \hat{u}_{i\beta} - \frac{1}{2} \delta_{\alpha\beta} \quad (5.2)$$

where \hat{u}_i is the unit direction vector of molecule i , and N is the number of molecules. In the next chapter we will not take the direction of ordering into account, and we will use the simpler, scalar version of the nematic order parameter

$$m = \left\langle \frac{3 \cos^2(\theta) - 1}{2} \right\rangle, \quad (5.3)$$

where $\langle \cdot \rangle$ denotes an average over the particles in the system, and θ is the angle of a particle with respect to the average orientation of the particles in the system. $\theta = 0$ therefore means that the particle is exactly aligned with the average orientation, and if all particles are perfectly aligned, then $m = 1$. If the particles are randomly oriented, then

$$m = \left\langle \frac{3 \cos^2(\theta) - 1}{2} \right\rangle = \int_0^\pi \frac{3 \cos^2(\theta) - 1}{2} \sin(\theta) d\theta = 0 \quad (5.4)$$

So $m = 0$ in the isotropic phase, and $0 < m \leq 1$ in the nematic phase, with $m = 1$ describing a perfectly aligned, nematic phase¹.

If the transition from the isotropic phase to the nematic phase occurs via nucleus growth, then the nematic order parameter is a *nonconserved* order parameter. The total order, defined by the integral of the order parameter over the system volume V , steadily changes from zero in the isotropic phase, to V in a perfectly aligned, nematic phase. In other phase transitions instead, the order parameter is conserved, namely locally the order changes, but the total order is conserved. For example, at high temperatures some oils completely mix in water, while at lower temperatures they demix into two layers. A good order parameter to describe this transition is the oil density ρ_{oil} minus some scaled version of the water density $a\rho_{\text{water}}$, i.e. $m = \rho_{\text{oil}} - a\rho_{\text{water}}$. If we choose a correctly, then in a totally mixed system $m = 0$, while in a demixed system $m < 0$ in the water phase and $m > 0$ in the oil phase. The total order parameter, chosen this way, is conserved.

5.3 The Landau expansion of the free energy

To describe a transition that is driven by a difference in the free energies of the system, it is most convenient to have an accurate description of the free energy in terms of the

¹ In Chapter 6 we use a scaled version of m .

order parameter. However, for all but the simplest of systems this is far too complex. We can however use an approximate description, based on the way we expect the free energy to change if we change the order. In a second order phase transition we know that the order parameter is zero above the transition temperature T_c , i.e. $m = 0$ at $T \geq T_c$ and continuously changes to nonzero values at $T = T_c$. In other words, close to T_c the order parameter is very small. This inspired Landau to write the free energy as a series expansion in the order parameters, expanded around the disordered phase, i.e. $m = 0$, at the phase transition temperature T_c [4]

$$F(m, T) = F_0 + \alpha(T)m + A(T)m^2 + B(T)m^3 + C(T)m^4 + D(T)m^5 + \dots \quad (5.5)$$

The terms of the expansion also depend on the pressure, but in this and the following chapter I will assume that the transition occurs at a constant pressure. If the expansion is possible around $m = 0$ then one can truncate this series at a certain point. The values of the higher order terms should then be less important than those of the lower order terms and so around T_c we can assume (as an approximation) that only $\alpha(T)$ and $A(T)$ are temperature dependent, and fill in the values at T_c for the other terms

$$F(m, T) = F_0 + \alpha(T)m + A(T)m^2 + B(T_c)m^3 + C(T_c)m^4 \quad (5.6)$$

This is the Landau expansion in its most general form. Its global minimum at a certain temperature T is the thermodynamically most stable phase, local minima are metastable phases. Note that only the order parameters at these minima, that I will denote by \bar{m} , are real thermodynamic variables, m is only a mathematical construct (for example, in some cases it is not physically possible for m to be less than zero, while mathematically it is). By eliminating terms and choosing the right form of the remaining terms, one can tailor the expansion to describe very specific phase transitions. As an example I will approximately follow Landau's original application, that of a second order phase transition from $\bar{m} = 0$ to $|\bar{m}| \neq 0$ at $T = T_c$. If we assume $F(m) = F(-m)$ then we can immediately eliminate all odd terms, i.e. $\alpha \equiv 0$, $B(T_c) \equiv 0$ and $D(T_c) \equiv 0$, leaving us only to deal with A and C . The free energy must have a global minimum, and so the fourth order term must be positive, namely $C(T_c) = c$, with $c > 0$ a positive constant. If the disordered phase, i.e. $\bar{m} = 0$, must be most stable at high temperatures, and must change continuously from $\bar{m} = 0$ to $\bar{m} \neq 0$ at $T = T_c$, then A must be zero at $T = T_c$, larger than zero at higher temperatures, and smaller than zero at lower temperatures. To first order in temperature therefore, $A(T) = a(T - T_c)$, where $a > 0$ is again a positive constant. If we truncate the series at the fourth order, we get

$$F(m, T) \approx F_0 + a(T - T_c)m^2 + cm^4 \quad (5.7)$$

with

$$\bar{m} = \begin{cases} 0 & \text{for } T \geq T_c \\ \pm \sqrt{\frac{-a(T - T_c)}{2c}} & \text{for } T < T_c \end{cases} \quad (5.8)$$

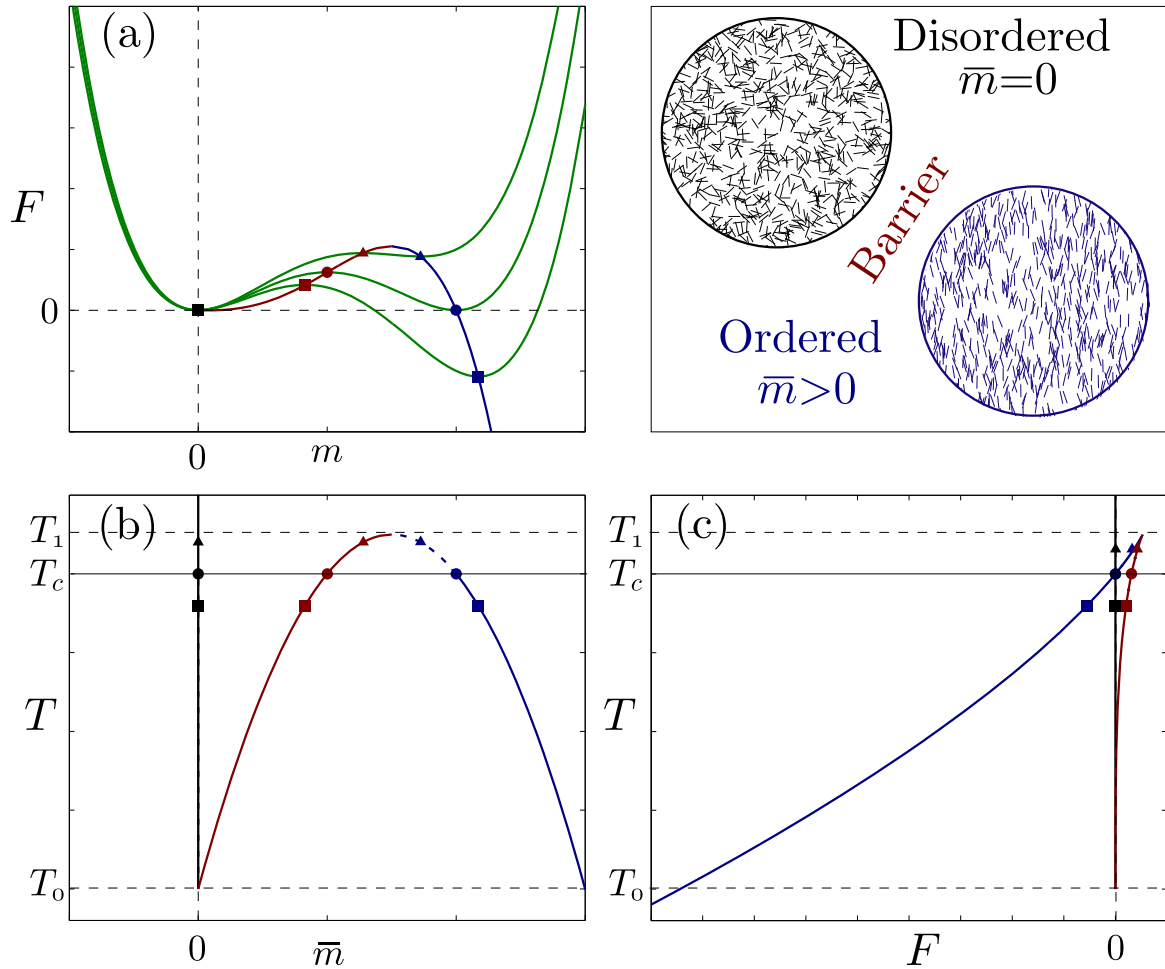


Figure 5.1: Illustration of the Landau expansion for a first-order phase transition with an asymmetric order parameter (Eq. 5.12). In all panels blue lines and symbols depict the order parameter \bar{m}_o in the ordered phase, red lines and symbols the order parameter \bar{m}_b on top of the barrier, and black lines and symbols the order parameter of the disordered phase $\bar{m}_d = 0$. A square symbol depicts a temperature below the coexistence temperature T_c , where the ordered phase is most stable. A circle depicts a system at the coexistence temperature, where both phases are equally stable, and a triangle depicts the system at a temperature above T_c . (a) Free energy F as a function of the order parameter m . The green lines depict the free energy at three different temperatures within the binodal regime, the shape of the symbols placed at the extrema of the curves denote the temperature, as explained before. At $m = 0$ and $F = 0$ the square symbol, the triangle and the circle fall on top of each other. (b) Position of the extrema \bar{m} as a function of temperature. (c) Free energy as a function of temperature of the ordered phase (blue) the disordered phase (black) and the barrier (red).

The series expansion is allowed for second order phase transitions, because close to T_c the order parameter describing both phases and the free energy in both phases are almost equal. Although a series expansion of the free energy around a first-order phase transition seems less obvious, since the order parameter changes discontinuously, it is still possible[3]. In a first-order phase transition there is a range of temperatures, called the binodal regime, where both phases are either stable or meta stable (e.g. for $T_0 < T < T_1$ in Fig. 5.1). The application of Eq. 5.6 must have the same properties, i.e. in a small temperature regime it must have a minimum both at $\bar{m} = 0$, and, separated by a maximum, a minimum at $\bar{m} \neq 0$. Above the binodal temperature regime only $\bar{m} = 0$ may be stable, below the binodal $\bar{m} = 0$ must be unstable. The regime where only one of the phases is stable is called the spinodal regime. There are two ways to achieve this behavior. For the studies of the next Chapter 6 I will choose the second description.

- If $F(m) = F(-m)$ then the odd terms vanish again, and one needs a sixth order term to ensure a global minimum

$$F(m, T) \approx F_0 + a(T - T_0)m^2 - cm^4 + em^6 \quad (5.9)$$

with

$$\bar{m} = \begin{cases} 0 & \text{for } T \geq T_c \\ \pm \sqrt{\frac{c + \sqrt{c^2 - 3ea(T - T_0)}}{3e}} & \text{for } T < T_c \end{cases} \quad (5.10)$$

where $T_c = T_0 + \frac{c^2}{4ea}$, and where all coefficients are positive. Note that T_0 now refers to the lowest temperature where the disordered phase is (meta) stable, and T_c is the temperature at which the disordered and the ordered phase have the same free energy and are therefore equally stable. $T_1 = T_c + \frac{c^2}{3ea}$ is the temperature above which the ordered phase becomes unstable. The binodal regime therefore is given by $T = [T_0, T_1]$.

- If $F(m) \neq F(-m)$, with a single ordered phase at $\bar{m} > 0$, then still $\alpha \equiv 0$, because otherwise the disordered phase will not be at $\bar{m} = 0$. The third order term then causes the asymmetry that we need to have only one ordered phase and the fourth order term is enough to have a global minimum.

$$F(m, T) \approx F_0 + a(T - T_0)m^2 - bm^3 + cm^4 \quad (5.11)$$

$$= F_0 + a(T - T_c)m^2 + \frac{1}{c}m^2 \left(\frac{b}{2c} - m \right)^2 \quad (5.12)$$

with

$$\bar{m} = \begin{cases} 0 & \text{for } T \geq T_c \\ \frac{3b + \sqrt{9b^2 - 32ac(T - T_0)}}{8c} = \frac{3b + \sqrt{b^2 - 32ac(T - T_c)}}{8c} & \text{for } T < T_c \end{cases} \quad (5.13)$$

where $T_c = T_0 + \frac{b^2}{4ac}$, $T_1 = T_0 + \frac{9b^2}{32ca}$, and again all coefficients are positive. Equation 5.12 is more insightful than Eq. 5.11; at $T = T_c$ the free energy is clearly a double well potential with minima at $\bar{m} = 0$ and $\bar{m} = \frac{b}{2c}$, while the temperature dependent term shifts the position and value of the second minima. In Figure 5.1 I illustrate the properties of this realization of the Landau expansion.

5.4 Spatially inhomogeneous systems

The order parameter is a coarse grained description of the order in a system. It is often calculated by taking some spatial average over for instance the particle positions. In simple models, such as Ising models or lattice models of atom positions in a crystal, the order parameter can be calculated directly from the model, and the Landau expansion can be a very useful tool to study their phase transitions. By taking thermodynamic derivatives one can calculate the entropy change during the transition, or the heat capacity of a system. And if the order parameter is influenced by an external field, then the effect of this field on the transition can be studied by adding the appropriate term to the free energy expansion.

Until now I have assumed that the order parameter is the same throughout the system, but that need not be the case. The order parameter can fluctuate, and thus becomes spatially dependent, $m = m(\vec{r})$. The Landau expansion of the free energy will now be valid only locally, and we must add an expansion in terms of the fluctuations ∇m , $(\nabla m)^2$, ... to model the effect of spatial inhomogeneity on the free energy. As the free energy must increase for all fluctuations, the lowest order term must be $(\nabla m)^2$. If we call $f[m(\vec{r})]$ the free energy density at \vec{r} , then the total free energy is given by an integral over all space of the free energy density plus the terms that take the fluctuations into account

$$F = \int_V \{f[m(\vec{r})] + s\xi (\nabla m(\vec{r}))^2\} d\vec{r} \quad (5.14)$$

where s is proportional to the surface tension and ξ is a measure for the width of the interface.

If the overall free energy of the system can be lowered by changing the order of the system, then the order parameter may also become time dependent, $m = m(\vec{r}, t)$. In the case of a nonconserved order parameter, we expect the order parameter profile $m(\vec{r})$ to change in the direction of lowest free energy, which can be expressed by the time dependent Landau-Ginzburg equation

$$\frac{\partial m}{\partial t} = -\frac{1}{\tau} \frac{\delta F[m(\vec{r})]}{\delta m(\vec{r})} \quad (5.15)$$

where δ denotes a functional derivative, and τ sets the time scale of the transition. In the case of a conserved order parameter, the order parameter moves in the direction

of lowest free energy fluctuations, as the total free energy density f (i.e. the free energy without the spatially varying terms, in a homogeneous phase of volume V : $f = F/V$) is conserved. In this case Eq. 5.15 is not valid, and equations such as the Cahn-Hilliard equation, of the form[5]

$$\frac{\partial m}{\partial t} = \Gamma \nabla^2 \frac{\delta F[m(\vec{r})]}{\delta m(\vec{r})}, \quad (5.16)$$

should be solved.

After choosing the correct terms of the Landau expansion of the free energy density, performing the functional derivation of the right hand sides of 5.15 and 5.16, and starting from a suitable initial order parameter profile, both the Landau-Ginzburg equation, and equations such as the Cahn-Hilliard equation, result in a partial differential equation. In special circumstances, and often by using some approximations, these partial differential equations can be solved analytically. Luckily, they can always be integrated numerically, either on a simple grid using finite difference integration schemes, or on more involved geometries using for instance finite element methods.

5.5 Temperature and latent heat

The change of entropy between different phases can be measured by the heat $L = \Delta Q$ that is added to convert from one phase to the other at a constant phase transition temperature T_c

$$L = \Delta Q = T_c \Delta S \quad (5.17)$$

where ΔS is the change of entropy. Heat injected into a system at a certain point does not only increase the temperature at that point, the heat also diffuses away and heats up the surrounding material². The thermal diffusion equation describes how the change of heat is related to a change in temperature.

$$\frac{\partial T}{\partial t} = D_T \nabla^2 T + \frac{1}{c_p} \frac{\partial Q}{\partial t} \quad (5.18)$$

where c_p is the specific heat and D_T is the thermal diffusivity. To keep the energy of the closed system constant during the transition to a more ordered phase ($\Delta S < 0$), the entropy change must be balanced by the latent heat

$$\frac{\partial Q}{\partial t} = -T_c \frac{\partial S}{\partial t} = T_c \frac{\partial^2 F}{\partial t \partial T}, \quad (5.19)$$

² The diffusion of heat in the isotropic phase is different from that in the nematic phase. In anisotropic liquids like a nematic liquid crystal, the diffusion of heat in the direction of the average molecule orientation is different from that perpendicular to this direction. In this thesis we use the scalar heat diffusion equation as an approximation.

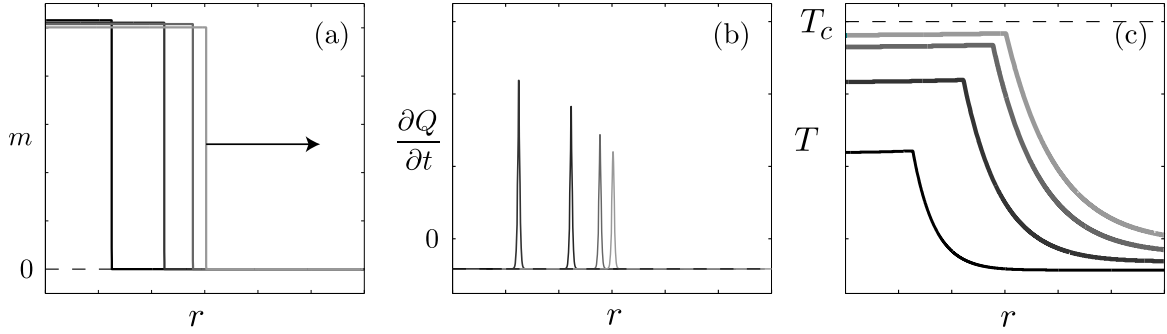


Figure 5.2: Illustration of a one dimensional system with a changing order parameter profile. Later times are denoted by lighter gray lines. (a) The order parameter as a function of position r , for four different times. The order increases, and so the order parameter profile moves to the right. (b) A change of the order parameter profile results in latent heat. (c) Due to the latent heat of panel (b) the temperature increases. At the same time the heat diffuses away, and heats up the surroundings. As the velocity of the order parameter interface in panel (a) depends on the temperature at the interface (panel c), the velocity of the interface decreases.

From the Landau expansion we get the free energy as a function of the order parameter m , and so we have to rewrite the change of heat in terms of the order parameter

$$\frac{\partial Q}{\partial t} = T_c \frac{\partial}{\partial t} \frac{\partial F}{\partial m} \frac{\partial m}{\partial T} = T_c \frac{\partial^2 F}{\partial m \partial T} \frac{\partial m}{\partial t} \quad (5.20)$$

and so the temperature changes as

$$\frac{\partial T}{\partial t} = D_T \nabla^2 T + \frac{1}{c_p} T_c \frac{\partial^2 F}{\partial m \partial T} \frac{\partial m}{\partial t}. \quad (5.21)$$

This partial differential equation governs the way latent heat, that is generated by the change of the order parameter, changes the temperature of the material. The change of the order parameter is described either by the Landau-Ginzburg equation (Eq. 5.15) for a nonconserved, or by the Cahn-Hilliard equation (Eq. 5.16) for a conserved order parameter[5]. And together the heat diffusion equation (Eq. 5.21) and the order parameter evolution (5.15 or 5.16) form a coupled set of partial differential equations that must be solved simultaneously to study the growth of order in a first-order phase transition, if the diffusion of latent heat is important[6]. In Figure 5.2 I illustrate the way the change of a nonconserved order parameter profile $m(r)$ changes the temperature $T(r)$, via the release of latent heat. In general the rate of change of the order parameter profile depends on the temperature, and so the increase of temperature due to the latent heat slows down the growth of the nematic nucleus.

In Chapter 6 I will study the growth of nematic nuclei, growing from an undercooled isotropic melt in more detail. Experimentally, these ordered liquid crystal

nuclei have been found to grow roughly as a power-law of the time, with a growth exponent that describes an S-shaped curve as a function of the quench depth, i.e. the amount of undercooling of the isotropic liquid. We suspected that the diffusion of the latent heat might explain this S-shaped curve, and set out to solve the time-dependent Landau-Ginzburg equation, coupled to a thermal diffusion equation, for this case. We cannot, however, numerically solve the coupled equations directly, because the thermal diffusivity of liquid crystals near the isotropic to nematic transition is very high, and because the difference in entropy between the nematic and isotropic phase is very small. The time and length scales of the heat diffusion equation and the order parameter evolution equation are very different and solving both at the same time is intractable. I circumvent this problem by solving the order parameter equation analytically for a spherically symmetric nucleus, calculating the latent heat analytically as well, and only treating the temperature diffusion numerically. By employing a multiscale method in which I increase the grid spacing and the time step as the temperature field widens, I am able to simulate the growth of these nuclei exponentially faster than by conventional, direct integration.

In Appendix 6.A I derive the shape and the velocity of the order parameter profile, and the latent heat resulting from this changing order parameter profile. Then, in Appendix 6.B I calculate the surface tension, and show that it is equal to what the classical nucleation theory predicts. In Appendix 6.C I derive the coupled equations in more detail, and show how to calculate the parameters of the model from experimentally measurable quantities. Then, in appendix 6.D I show how to solve the coupled equations numerically, and how to do the same semi-analytically. Finally, in Appendix 6.E, I compare my calculations to experimental measurements on octylcyanobiphenyl (8CB). I show that nematic nuclei grow diffusively, but that latent heat diffusion is too fast to account for their slow growth.

5.6 References

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