SOLIDIFICATION OF A LIQUID CRYSTAL:
MORPHOLOGIES AND TRANSITIONS

by

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Abstract

When a material freezes, the form it takes depends on the solidification conditions. For instance, as the undercooling is increased, one typically sees solidification into less-ordered forms. The resulting growth modes appear to be generic, with qualitative similarities between systems whose microscopic details are quite dissimilar.

I have used both optical and atomic-force microscopy to study the transitions between different growth morphologies during the solidification of a particular liquid crystal, 10 OCB. We have observed six different solidification modes, each with a distinct micro and meso structure. The front-velocity-vs.-undercooling curve has a discontinuity in its slope and, in some cases, in the curve itself at mode transitions, suggesting that these transitions are analogous to phase transitions. Such transitions have been seen in other systems, but no general rule has been found that can predict which morphology will be selected. We show that, contrary to intuition and widespread speculation, the fastest-growing mode is not always the one selected.

One of the growth modes exhibited by 10 OCB is known as banded spherulitic growth. Spherulites have been seen in a wide variety of materials including minerals, pure elements, polymers, biomolecules, and metal alloys. However, despite a century of study, there is no generally accepted theory of spherulitic growth. In particular, the cause of the concentric banding seen in many spherulites remains a mystery. Our studies of banded spherulites in 10 OCB using both optical and atomic-force microscopy show that the bands are associated with a density modulation and thus are not merely the result of a birefringent effect, as is commonly believed.

As the atomic-force microscope (AFM) is a relatively new tool, some time was spent studying its capabilities. We found that because the AFM resolution is largely determined by attractive forces between the tip of the probe and the sample, resolution can be improved
by imaging in a suitable liquid medium. We also developed a simple method for calibrating AFM cantilevers — a crucial step in using the AFM to obtain quantitative force data. This work is presented in an appendix.
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Contents

Approval ........................................... ii
Abstract ........................................... iii
Acknowledgments .................................. v
List of Tables ................................... ix
List of Figures ................................. x
1 INTRODUCTION ............................... 1
2 SOLIDIFICATION THEORY .................... 4
  2.1 Phase stability ............................. 5
      2.1.1 Phase coexistence ..................... 5
      2.1.2 Nucleation ............................. 8
  2.2 The standard model of solidification ........ 10
      2.2.1 The standard model .................... 10
      2.2.2 Other solidification models .......... 13
  2.3 The diffusion-limited regime .............. 14
      2.3.1 Planar growth fronts ................. 14
      2.3.2 The Mullins-Sekerka instability .... 16
      2.3.3 Dendrites ............................. 18
      2.3.4 Other diffusion-limited growth forms . 19
  2.4 The kinetics-limited regime .............. 20
      2.4.1 Metastable phases ..................... 20
      2.4.2 The large-undercooling regime ....... 21
      2.4.3 Defect generation ..................... 23
  2.5 Spherulitic growth ......................... 24
      2.5.1 Models of spherulitic growth .......... 24
5.2 High-resolution investigations of banded spherulites .............. 104
5.3 Spherulite stability ............................................. 110
5.4 Video microscopy of banded spherulite dynamics .................... 113
5.5 Conclusions for banded spherulitic growth in 10 OCB ............. 115
6 CONCLUSIONS ....................................................... 120

Appendices
A THE ATOMIC-FORCE MICROSCOPE .................................. 123
   A.1 Calibration of the atomic-force microscope .................. 123
      A.1.1 Scanner calibration ........................................ 123
      A.1.2 Detector calibration ........................................ 126
      A.1.3 Cantilever calibration ...................................... 127
   A.2 Lateral resolution of the atomic-force microscope ........... 129
      A.2.1 Forces involved in AFM imaging ......................... 130
      A.2.2 A model of the atomic-force microscope ................ 132
   A.3 Improving the resolution of the atomic-force microscope ... 137
   A.4 Experimental results .......................................... 138
      A.4.1 The future of AFM resolution ............................ 141
B VAN DER WAALS FORCES ............................................ 145
   B.1 The physics of dispersion forces ............................. 145
   B.2 Calculation of the Hamaker constant ......................... 147
   B.3 Calculating the van der Waals force .......................... 149

Bibliography .......................................................... 155
List of Tables

3.1 Properties of 10 OCB ........................................ 38

4.1 Lattice parameters for crystalline 10 OCB ................... 94

4.2 Major X-ray diffraction peaks for crystalline 10 OCB ........ 96

B.1 Dielectric data for typical atomic-force microscope materials .... 152
## List of Figures

2.1 Free energy for a two-phase system ........................................... 6
2.2 Phase diagram for a two-phase system ........................................ 7
2.3 Phase diagram for a dilute solution ........................................... 8
2.4 Nucleation barrier for the solid phase ....................................... 9
2.5 The diffusive instability ....................................................... 16
2.6 Dependence of growth velocity on undercooling .......................... 22
2.7 Origin of “sheaf-like” AFM nucleus ........................................ 27
2.8 Characterization of morphology transitions ............................... 32
2.9 The smectic A phase ......................................................... 35

3.1 Structure of cyanobiphenyl liquid crystals .................................. 38
3.2 Sample cell construction ...................................................... 40
3.3 The atomic-force microscope ............................................... 44
3.4 Free growth ................................................................. 46
3.5 Experimental set-up for free growth ......................................... 47
3.6 Directional solidification .................................................... 49
3.7 Sample geometry for the interface temperature estimate ............... 50

4.1 Collage of 10 OCB growth modes .......................................... 54
4.2 Growth modes of 10 OCB .................................................. 56
4.3 Measurement of the solidification front location ......................... 58
4.4 Measurement of the solidification front velocity ......................... 59
4.5 Growth front envelope ...................................................... 61
4.6 Fractal dimension of interfaces ............................................ 62
4.7 Growth velocity of 10 OCB as a function of undercooling ............ 64
5.11 Microstructure of mode E ........................................... 112
5.12 Fracture of banded spherulites ....................................... 112
5.13 “Unbanding front” during annealing .................................. 113
5.14 Change in microstructure associated with the loss of bands ....... 114
5.15 Change in X-ray diffraction peaks due to annealing .................. 115
5.16 Video sequence of banded growth ...................................... 116
5.17 Growth of successive generations of bands ............................ 117

A.1 Lateral calibration images for AFM imaging ............................... 125
A.2 Vertical calibration of AFM scanners ..................................... 126
A.3 Power spectrum of cantilever fluctuations .............................. 130
A.4 A simple model of the atomic-force microscope .......................... 133
A.5 Typical force spectrum ......................................................... 135
A.6 Force spectrum in water ......................................................... 140
A.7 Force spectra for various media ............................................. 142
A.8 Baseline interference fringes ................................................. 144

B.1 Geometry of the van der Waals interaction across a gap ............... 148
B.2 Cauchy plot for 1-bromonaphthalene ...................................... 151
B.3 Calculation of the Hamaker constant for a Si₃N₄ – air – mica system .... 152
B.4 Calculation of the Hamaker constant for a Si₃N₄ – n-propanol – mica system 153
B.5 Dependence of the Hamaker “constant” on distance ........................ 154
Chapter 1

INTRODUCTION

Everyone knows that when a molten material is cooled below its freezing point, it freezes. How it freezes, however, depends on the solidification conditions. For instance, as the undercooling — the amount of cooling below the phase-coexistence temperature — is increased, one typically sees solidification into less-ordered forms. At very small undercoolings, where the growth proceeds at near-equilibrium conditions, we may see the formation of single crystals. At these small undercoolings, diffusion of latent heat and impurities away from the front can cause a flat interface to become unstable, leading to dendritic growth. The solid is still a single crystal, but with a very complicated boundary. As we cool further, attachment kinetics at the interface become important. This may lead to non-crystallographic branching and polycrystalline solids. In some cases, such as in spherulitic growth, these microcrystals are themselves organized into a pattern. At very large undercoolings, molecular motion becomes very slow, leading to the formation of amorphous solids.

The earliest known reference to solidification patterns dates to c.135 BC China, when Han Ying observed [1]:

Flowers of plants and trees are generally five-pointed, but those of snow ... are always six-pointed.

Surprisingly, the hexagonal symmetry of snowflakes was not recorded in Europe until 1591 by Thomas Hariot [2]. The first to investigate this structure in a mathematical, rather than theological, manner was Johannes Kepler [3] in his 1611 work “The Six-Cornered Snowflake.” In this remarkable essay, Kepler speculated that the hexagonal structure may result from a microstructure of close-packed spheres, and, in doing so, began the scientific
study of pattern formation.

The past century has seen large gains in the understanding of solidification patterns. Interest has been due to both their fascinating range of shapes and to their technological importance: since the microstructure of a material determines its macroscopic properties, it is natural to seek ways to control, or at least predict, that microstructure. Stefan [4] modeled solidification as a diffusion equation with free boundaries. Ivantsov [5], in 1947, found that this model admitted a uniformly propagating solution of growing dendrites with a parabolic shape (in the absence of surface tension). Mullins and Sekerka [6] showed in 1963 that a planar front becomes unstable as the growth velocity increases, so that such a front must break up into a more complicated pattern. More recently, it has been found that surface tension and surface tension anisotropy are required for the formation of dendrites and for the selection of their size [7, 8].

In Chapter 2, I briefly review some of the models used to describe solidification. We will see that the origin of solidification patterns is the interplay between microscopic and macroscopic properties. For instance, the complex shape typical of dendrites is essentially due to the increased heat transport away from the solid surface made possible by the increased front area. The selection of the characteristic size of the dendrite on the macroscopic scale is due to the stabilizing influence of surface tension acting on the microscopic scale — arbitrarily fine dendrites would result in arbitrarily large surface energies.

The observation of growth morphologies other than dendrites, even under conditions where dendritic growth would be predicted, indicates that the problem of dendritic growth is not yet completely solved. The simplest conclusion is that the exact form of the dendrites varies with the growth conditions. However, as we shall see, the transitions between morphologies can be sharp, implying the existence of fundamentally distinct growth mechanisms.

Given a choice of possible growth mechanisms, we would like to predict which will be preferred over the others. In equilibrium thermodynamics, the phase that minimizes the free energy is "selected." Despite intensive effort, no equivalent extremum principle has been found for pattern selection in nonequilibrium systems [9]. An intuitively appealing idea is that the mode with the largest front velocity will be able to dominate the growth [10]. Ben-Jacob and co-workers have suggested that this is part of a more general selection principle: they speculate that the fastest-growing mode will dominate far from equilibrium, while (presently unknown) principles related to the microstructure may be more important.
CHAPTER 1. INTRODUCTION

closer to equilibrium.

Even with a choice of growth forms, it is not obvious a priori that a morphology diagram specifying morphology as a function of current growth conditions must exist. It is entirely possible that growth morphologies in a nonequilibrium system will depend also on the growth history. In practice, this does not seem to be the case. Computational results have shown sharp changes between growth forms for some theoretical models. Morphology diagrams have been mapped experimentally in some systems. However, the theoretical results are model dependent, while the experimental results often suffer from a lack of resolution.

The major contribution of this thesis is the measurement of a very well-defined morphology diagram for a simple solidification system (nominally pure 4-cyano-4'-decoxybiphenyl, or 10 OCB). The techniques employed in this investigation are described in Chapter 3, while the results are discussed in Chapters 4 and 5. We find that 10 OCB can solidify in a variety of growth modes, each of which is seen only in a finite range of undercooling. Sudden changes in both the growth form and the growth velocity are seen as the undercooling is varied. Some of these morphology transitions are consistent with the hypothesis that the fastest growing morphology is the one observed. However, this rule does not hold in every case, indicating that the selection principles are more complex.

We have also studied a particular growth morphology known as banded spherulitic growth. Spherulites typically form at large undercoolings from systems with a highly viscous melt [11]. This morphology has been seen in a wide variety of materials from elemental selenium to biological molecules, and is particularly important in the solidification of polymers. Despite this importance — and a century of study — there is no generally accepted theory of spherulitic growth. Even more mysterious is the origin of the concentric bands which often accompany spherulitic growth. Although the nature of these bands is known in some systems (for instance, in polymers the bands are associated with a periodic rotation of the optical axis along the spherulitic radius [12]), the mechanism responsible for their formation remains elusive. In Chapter 5, I discuss our observations of spherulitic growth in 10 OCB.

Once this tour of growth morphologies in 10 OCB is complete, the main results and conclusions are summarized in Chapter 6.
Chapter 2

SOLIDIFICATION THEORY

A comprehensive review of pattern formation during solidification is beyond the scope of this thesis. For such a review, the reader is referred to the literature (see, for example, [13, 14, 15, 16, 17]). In the following Chapter, I outline the background necessary to discuss the results of Chapters 4 and 5.

In order to understand the nonequilibrium problem of solidification, we first discuss phase equilibrium and first-order phase transitions in Section 2.1. The important points are the concept of a selection principle (minimization of the free energy), which determines which phase will be seen when more than one are possible, and the concept of a barrier to nucleation of the solid phase when a liquid is cooled below its melting point. It is this nucleation barrier which is responsible for the existence of solidification fronts. The standard thermal-diffusion model, which is often used to describe solidification fronts, is reviewed in Section 2.2. In particular, we will see that solidification patterns can arise from a diffusive instability. However, this model predicts a restabilization of the planar interface at large velocities. By contrast, a variety of solidification fronts are seen in experiments performed far from equilibrium, where diffusive instabilities are thought not to be present. This regime is discussed in Section 2.4. Here, diffusion is no longer the controlling mechanism and we must also consider growth kinetics. One solidification morphology — spherulitic growth — is singled out for additional discussion in Section 2.5. In Section 2.6, I summarize the present understanding of transitions between growth morphologies. In particular, I will discuss the possibility of a principle for nonequilibrium pattern selection analogous to the minimization of the free energy in equilibrium systems. Finally, I discuss the considerations involved in choosing a material for an experimental study of solidification morphology.
2.1 Phase stability

Before we consider the solidification process itself, it is useful to review the thermodynamics of first-order phase transitions. Consider a system at constant, uniform temperature \( T \) and pressure \( P \). The change \( dU \) in internal energy \( U \) of this system, due to an infinitesimal reversible displacement, is given by

\[
dU = T \, dS - P \, dV + \sum_{i=1}^{n} \mu_i \, dn_i,
\]

where \( dS \) is the change in entropy \( S \), \( dV \) the change in volume \( V \), \( dn_i \) the change in the quantity \( n_i \) of species \( i \), and

\[
\mu_i = (\partial U / \partial n_i)_{S,V,n_1,n_2,...,n_{i-1},n_{i+1},...}
\]

is the chemical potential of the \( i \)th component. The Gibbs free energy of the system is defined as

\[
G = U + PV - TS.
\]

From Eqs. 2.1 and 2.3, we deduce that

\[
dG = V \, dP - S \, dT + \sum_{i=1}^{n} \mu_i \, dn_i.
\]

For the system to be in equilibrium at constant pressure, temperature, and composition, the Gibbs free energy must be a minimum, so that \( dG = 0 \). From Eq. 2.4, we find that

\[
(\partial G / \partial P)_{T,n_i} = V,
\]

\[
(\partial G / \partial T)_{P,n_i} = -S,
\]

and

\[
(\partial G / \partial n_i)_{P,T} = \mu_i.
\]

Eqs. 2.5–2.7 describe the density change, latent heat production, and component segregation, respectively, when the system can exist in more than one phase.

2.1.1 Phase coexistence

If more than one phase are available, the one which minimizes the Gibbs free energy will be selected. This is shown schematically in Fig. 2.1. In the case of a pure material, \( G \) is a
function of temperature and pressure for each phase. At a fixed pressure, we can represent $G$ as a function of temperature, as in Fig. 2.1a. Here, the free energy curve for each of two phases is shown, with the solid lines indicating which phase is stable at a given temperature. The equilibrium freezing point is the temperature at which the two curves cross, allowing both phases to exist simultaneously. Note that the slope of the $G(T)$ curve is discontinuous at this point, resulting in a jump in the curve $S(T) = (\partial G/\partial T)|_P$, as shown in Fig. 2.1b. This jump, $\Delta S$, is proportional to the latent heat $L$ for the phase transition:

$$L = T \Delta S.$$  \hfill (2.8)

Figure 2.1: Free energy for a two-phase system. (a) Gibbs free energy as a function of temperature. The coexistence temperature is the point at which the two curves intersect. The stable phase (as a function of undercooling), is indicated by the solid line. (b) Entropy as a function of temperature. The jump in entropy at the phase transition is proportional to the latent heat of the transition.

The fact that the equilibrium phase of the system is fixed by the values of the parameters $P$ and $T$ (and not, for instance, by the previous history of the system), allows us to construct a phase diagram as shown in Fig. 2.2. The regions of phase stability are separated by curves where two phases coexist. At any point $(P_0, T_0)$ on these curves, the chemical potential
must be the same for either phase, so

$$\mu^I(P_0, T_0) = \mu^II(P_0, T_0),$$

(2.9)

where I and II denote the phase. Note that since this condition involves two variables, it defines a curve in the \((P, V)\) plane. Thus, three phases of a single-component system can only be in equilibrium at a single point (i.e. a triple point). In general, the number of phases that can coexist in a multicomponent system is given by Gibbs phase rule. For a two-component system, three phases can coexist over a range of pressures. The slopes of the coexistence curves are described by the Clausius-Clapeyron equations [18].

![Phase diagram for a two-phase system. Regions of stability for the two phases are separated by a coexistence curve.](image)

Figure 2.2: Phase diagram for a two-phase system. Regions of stability for the two phases are separated by a coexistence curve.

In the more general case where the system has several components, an equation similar to Eq. 2.9 holds for each component. One interesting case is the liquid-solid transition in a dilute solution. The impurity is usually less soluble in the solid phase, leading to the well-known freezing-point depression. In the small-undercooling limit, the phase diagram then resembles the one shown in Fig. 2.3. In addition to regions where the solid and liquid phases are stable, Fig. 2.3 includes an “excluded region.” If the temperature \(T\) and impurity concentration \(c\) are chosen to lie in this region, the system will phase separate into an impurity-rich liquid phase in coexistence with an impurity-poor solid phase, as indicated in Fig. 2.3. The two phases then have concentrations \(c_L\) and \(c_S\) given by the intersection of the horizontal line corresponding to the value of \(T\) with the upper and lower bounds (known as the \textit{liquidus} and \textit{solidus} lines, respectively) of the excluded region.
Figure 2.3: Phase diagram for a dilute binary solution. For finite impurity concentrations, the freezing point of the solution is usually lower than that for the pure solvent. Note that this phase diagram has an “excluded region” between the liquidus and solidus curves. For an initial condition within this region, the solution phase separates along a horizontal line into an impurity-rich liquid and impurity-poor solid.

For $c \ll 1$, the liquidus curve has the form

$$T = T_0 - \frac{k_B T_0^2}{L} (1 - k)c,$$  \hspace{1cm} (2.10)

where $k_B$ is Boltzmann’s constant, $T_0$ is the equilibrium phase coexistence point and

$$k = c_s/c_L = \exp(-\Delta F/k_B T),$$  \hspace{1cm} (2.11)

where $\Delta F$ is the free energy difference of impurity molecules in the solid phase with respect to the liquid [19], is the partition coefficient (which is usually $< 1$ for solid-liquid coexistence). The solidus curve has the same form, but with a slope that is a factor of $1/k$ larger. The freezing-point depression is typically of the order of $1^\circ \text{C/mol}\%$ impurity for the liquidus line.

### 2.1.2 Nucleation

When the parameters of a system are changed so that the initial phase is no longer stable, the system will eventually undergo a change of state to the newly stable phase. In the case of solidification, there is a barrier to nucleation of the solid phase. This can be understood by the following argument [13]: If a liquid is cooled below its freezing point, the solid phase will have a lower free energy. However, for the solid phase to form, an interface between
the growing solid and the as-yet-unsolidified melt must be formed. Thus, although there is a decrease in free energy associated with the creation of the solid, there is, at least until solidification is complete, an increase in free energy associated with the creation of the interface.

The net change in free energy for a spherical solid germ of radius $R$ can be expressed as

$$\Delta G = \frac{4}{3} \pi R^3 \Delta \mu + 4 \pi R^2 \gamma,$$  \hspace{1cm} (2.12)

where $\Delta \mu$ is the (negative) change in the chemical potential per unit volume and $\gamma$ is the surface energy per unit area. This change in free energy is plotted in Fig. 2.4, where we see that the solid droplet must be larger than some critical size, labeled $R^*$, for growth to be energetically favourable.

![Figure 2.4: Nucleation barrier for the solid phase. A sphere of solid phase in an undercooled melt will not increase in size unless it is larger than the critical radius $R^*$.
](image)

The critical radius is easily calculated by setting the derivative of Eq. 2.12 equal to zero:

$$\frac{dG}{dR} = 4\pi R^2 \Delta \mu + 8\pi R^2 \gamma = 0,$$  \hspace{1cm} (2.13)

whence

$$R^* = -\frac{2\gamma}{\Delta \mu}.$$  \hspace{1cm} (2.14)

The change in chemical potential is given by

$$\Delta \mu(T) = \mu^S(T) - \mu^L(T),$$  \hspace{1cm} (2.15)

where $\mu^S$ and $\mu^L$ are the chemical potentials in the solid and liquid phases, respectively. For small undercooling, we can expand about the coexistence temperature $T_0$, so that

$$\Delta \mu(T) = [\mu^S(T_0) - (T - T_0)s_S] - [\mu^L(T_0) - (T - T_0)s_L],$$  \hspace{1cm} (2.16)
where \( s_s \) and \( s_L \) are the entropy densities of the solid and liquid phases. From Eqs. 2.8 and 2.9, we find that for \( \Delta T / T_0 \ll 1 \),

\[
\Delta \mu(T) \approx -\frac{L \Delta T}{T_0},
\]

so that Eq. 2.14 becomes

\[
R^* = \frac{2\gamma T_0}{L \Delta T^*}.
\]

Not surprisingly, the change in chemical potential is proportional to the undercooling \( \Delta T = T_0 - T \).

Because of this nucleation barrier, it is usually necessary to undercool a liquid by some amount before solidification will take place. No minimum value is required, although the nucleation rate increases rapidly with undercooling. The nucleation barrier is also responsible for the existence of solidification fronts — solidification, rather than occurring simultaneously throughout the melt, begins at a discrete number of nuclei, which then expand at the expense of the melt. These solidification fronts determine the structure of the resulting solid.

2.2 The standard model of solidification

Several models have been developed to study solidification fronts. In the following Section, I will describe the most commonly used solidification model. This model applies to diffusion-limited growth from convection-free melts. Molecular kinetics and anisotropy are introduced as phenomenological modifications to the basic macroscopic equations. Even with these simplifications of a more complex physical system, this model shows complex behaviour.

2.2.1 The standard model

Consider a pure liquid at a some uniform temperature below the freezing point. This is an unstable system which will begin to solidify once a critical nucleus is formed. At this point, the growing solid is warmer than the surrounding liquid due to the release of latent heat at the solidification front. If the undercooling is smaller than a value of

\[
\Delta T = L / c_p,
\]

where \( c_p \) is the specific heat capacity of the solid, the heat released is sufficient to raise the temperature of the resulting solid above the melting point. Clearly, for solidification to
CHAPTER 2. SOLIDIFICATION THEORY

In the absence of convective or radiative heat transport processes, the thermal field must satisfy the diffusion equation

\[
\frac{\partial T}{\partial t} = D_h \nabla^2 T,
\]

where \(D_h\) is the thermal diffusion constant (which may have different values in the two phases).

The solution to this differential equation must satisfy two boundary conditions at the solidification front. The reason that two boundary conditions are needed is that the location of the interface is not itself specified — that is what we are trying to find. The first boundary condition is one of heat conservation: the rate of heat generation at the front must be balanced by the thermal flux away from the front. Mathematically,

\[
Lv_n = -[D_h c_p \delta \cdot \nabla T],
\]

where \(v_n\) is the component of the growth velocity along the direction \(\delta\), directed outward from the solid, and the square brackets denote the discontinuity in the heat flux across the boundary. The second boundary condition is a statement of the temperature at the interface:

\[
T_i = T_0 - \gamma \kappa T_0 / L - \tilde{\beta}(v_n).
\]

The second term on the right hand side is the modification of the equilibrium freezing point for a surface with curvature \(\kappa\), where \(\kappa\) is the reciprocal of the mean curvature. \((\kappa\) is positive if the interface bulges into the liquid phase). This is the Gibbs-Thomson effect [21]. If the liquid and solid phases are in equilibrium at the interface, the interface will remain stationary. For growth to occur, the interface must be must be out of equilibrium. This is the origin of the final term on the right-hand side. In general, \(\tilde{\beta}\) is a function of the interface speed and direction with respect to the crystal lattice. For small growth velocities \(\tilde{\beta}(v_n)\) is taken to be a linear function of velocity. We will see in Section 2.4 that this approximation is not valid far from equilibrium.

Finally, the imposed temperature \(T_\infty\) (for instance, the temperature of the walls of the sample), give us an asymptotic boundary condition at infinity:

\[
T = T_\infty
\]
far from the interface.

A convenient scaling of the temperature field is suggested by Eq. 2.19. If we choose the dimensionless thermal diffusion field to be

$$ u = \frac{T - T_0}{(L/c_p)}, $$

Eq. 2.20–2.23 become

$$ \frac{\partial u}{\partial t} = D_h \nabla^2 u, $$

$$ v_n = -[D_h \hat{n} \cdot \nabla u], $$

$$ u_i = -d_0 \kappa - \beta(v_n), $$

where $\beta(v_n) = (c/L)\tilde{\beta}(v_n)$ and $d_0$ is the capillary length given by $d_0 = \gamma c_p T_0/L^2$, and

$$ u = -\Delta, $$

far from the interface, where

$$ \Delta = \frac{T_0 - T_\infty}{(L/c_p)}, $$

is the dimensionless undercooling imposed far from the interface.

In the case of an impure material, solidification will depend on the distribution of the impurity field $c$, which must also obey a diffusion equation: $\partial c/\partial t = D_m \nabla^2 c$. Because of impurity segregation at the front, there is an impurity conservation condition analogous to Eq. 2.21. The presence of impurities at the interface also affects the interface temperature, as shown by Eq. 2.10. This provides a coupling between the temperature and impurity concentration fields. In most cases, $D_t \gg D_m$, so that heat can diffuse away from the boundary much more quickly than can impurities. The solidification process is then limited by impurity diffusion unless the impurity concentration is very small.

The similarity between the equations for thermally controlled growth and those for impurity-controlled growth suggests that both may exhibit similar behaviour. In fact, several pattern forming systems involve diffusion-controlled growth into an unstable phase. Examples include electrochemical deposition [22, 23] and amorphous annealing. Another closely related system is the displacement of a viscous fluid such as glycerine by a less viscous fluid such as air or water between two closely spaced glass plates. This system is known as a Hele-Shaw cell and has been used to mimic many of the growth patterns seen in solidification.
As we will see, the basic cause of pattern formation in diffusive systems is the enhanced diffusion of the front near points which bulge into the melt. This allows such fingers to grow faster than other points along the front, rendering a planar front unstable.

### 2.2.2 Other solidification models

Two other types of models that have proven useful in the study of solidification problems are order-parameter models and boundary-layer models [20]. The order-parameter models describe the phase of a solidifying material as a non-conserved order parameter coupled to a conserved thermal field. The advantage of this approach is that it removes computational difficulties associated with an infinitely sharp interface. The boundary-layer model replaces the physics of the infinite diffusion field with an effective temperature gradient across a narrow boundary layer at the interface. In two-dimensional computations, this allows the solidification front to be treated as a string, removing the computational difficulties of solving the full diffusion equation with a moving front. This approach has proved particularly useful in discussing aspects of dendritic growth [24].

In addition, much effort has gone into the study of the solidification process on the microscopic scale [25, 26]. This approach is necessary in order to understand solidification kinetics (described by the function \( \beta \) in the standard model) at more than a phenomenological level.

Another approach is to model the process on an intermediate level, as is done in the lattice models used to study, for instance, diffusion-limited aggregation (DLA) [27, 28]. Here, the diffusion field is represented by particles moving randomly on a lattice. These particles are taken to be larger than individual molecules, but small enough to mimic local variations in the diffusion field.

In some solidification processes, it may be necessary to consider fluid flow in the melt. There are at least three possible sources of flow: externally imposed flows, convection currents caused by the latent heat, and flow generated by the density difference between the liquid and solid phases. The first two are often important in commercially relevant solidification processes (for instance, when the melt is stirred to maintain a uniform impurity distribution). The third possibility may play an important role in solidification patterns in kinetics-limited growth, particularly in the mechanism of spherulitic growth, which will be discussed in Section 2.5.
2.3 The diffusion-limited regime

One natural division between solidification regimes occurs at a temperature where the dimensionless undercooling given by Eq. 2.29 is \( \Delta = 1 \). For an undercooling below this value, heat must be transported away from the interface for solidification to proceed. Larger undercoolings remove the requirement that heat be diffused from the interface. Then, other mechanisms must control the growth (see Section 2.4).

In the diffusive limit, the standard model is a natural tool for the study of growth processes. In this section, we will examine typical features of growth in the diffusive limit in terms of the standard model of solidification.

2.3.1 Planar growth fronts

The simplest interface shape is that of a planar front. However, it is easy to show that a planar front propagating at a constant speed cannot exist for \( \Delta < 1 \) [16, 29].

We begin by assuming a planar front moving with a constant velocity \( v \) along the \( \tilde{z} \)-axis. If we transfer to the frame of reference moving with the front, by using the transformation

\[
\tilde{z} \rightarrow z - v_0 t,
\]

the diffusion equation becomes

\[
\frac{\partial u}{\partial t} - v \frac{\partial u}{\partial z} = \nabla^2 u. \tag{2.31}
\]

For a shape preserving front, this becomes,

\[
\nabla^2 u + \frac{2}{\ell} \frac{\partial u}{\partial z} = 0, \tag{2.32}
\]

where \( \ell = 2D_h/v \) is the diffusion length.

The solution of Eq. 2.32 with the boundary conditions given by Eqs. 2.26 and 2.27 for an interface at \( z = 0 \) is, neglecting kinetics:

\[
u(z) = \begin{cases} 
\exp\left(-\frac{2z}{\ell}\right) - 1 & \text{for } z \geq 0 \text{ (liquid)} \\
0 & \text{for } z < 0 \text{ (solid)}
\end{cases}. \tag{2.33}
\]

Note that the velocity is not specified by this solution, but the undercooling at infinity is: \( u \rightarrow -1 \) as \( z \rightarrow +\infty \). Thus, this analysis predicts a steady-state planar solution for unit undercooling.
A planar interface at a smaller undercooling will accumulate excess latent heat at the interface, causing the solidification to slow. This can be shown by constructing a “similarity solution” for Eq. 2.25. We assume that the solution \( u(z,t) \) has the form

\[
  u(z,t) = U(w),
\]

where \( w = z/\z(t) \) and \( \z(t) \) is the interface position. With this solution, Eq. 2.31 becomes

\[
  \frac{d^2U}{dw^2} + \frac{\z(t)\dot{\z}(t)}{D_h} \frac{dU}{dw} = 0,
\]

where \( \dot{\z}(t) \) is the front velocity. Since \( \z(t) \) and \( \dot{\z}(t) \) are time dependent, the product \( \z\dot{\z} \) must be equal to a constant for the similarity solution to exist. We can then write

\[
  \z\dot{\z} = 2D_h P,
\]

where \( P \) is a constant. This can be written as

\[
  \frac{1}{2} \frac{d}{dt} \z^2 = 2D_h P.
\]

Integration of Eq. 2.37 results in

\[
  \z^2 = 4D_h Pt + C,
\]

from which we determine that the motion of the front relaxes to

\[
  \z(t) = \sqrt{4D_h Pt},
\]

where we can neglect the integration constant \( C \) for large times. Thus, the front velocity decreases as \( 1/\sqrt{t} \).

If we solve Eq. 2.35, we find that the constant \( P \) and the undercooling \( \Delta \) are related by

\[
  \Delta = \sqrt{\pi} P e^P \text{erfc}(\sqrt{P}),
\]

where

\[
  \text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-y^2} dy
\]

is the complementary error function.

Undercoolings for which \( \Delta > 1 \) eliminate the need for latent heat to be diffused away from the front. A steady-state front is then possible. The temperature rise due to the latent
heat will result in a front temperature of $1 - \Delta$. The front velocity can then be determined from Eq. 2.27:

$$v = \beta^{-1}(\Delta - 1),$$

(2.42)

where $\beta^{-1}(u)$ is the inverse of the kinetic undercooling function. For small growth velocities, $\beta(v)$ is approximately a linear function of velocity: $\beta(v) \approx \beta_0 v$. Then the velocity for $\Delta > 1$ becomes

$$v \approx \frac{\Delta - 1}{\beta_0}.$$ 

(2.43)

### 2.3.2 The Mullins-Sekerka instability

In the previous section, we saw that for any undercooling $\Delta < 1$, a planar front must slow as latent heat builds up in front of the interface. In fact, Mullins and Sekerka showed that such a front is unstable and will break up into a nonplanar shape [6, 30]. The basic mechanism is that if part of an otherwise planar front manages to grow ahead of the front, it will protrude into a region of greater undercooling (remember that the front is heated by the release of latent heat). This will result in a larger temperature gradient near that finger, leading to a greater heat flux, which allows the finger to grow faster than the surrounding front, as described by Fig. 2.5.

![Figure 2.5: The diffusive instability. A protrusion ahead of a planar solidification front compresses the isotherms near the finger, resulting in faster growth. Note that, due the the Gibbs-Thomson effect, the finger is also at a lower temperature than the planar parts of the front.](image)
The instability of the planar front can be shown by means of a linear stability analysis. In this approach, we represent deviations from a planar front by sinusoidal perturbations in the front position. Since we are considering a linear system, an arbitrary small perturbation can be represented as a Fourier series of such terms. This can be done for a general planar solution at $\Delta < 1$, but the basic result can be seen in the simpler case of unit undercooling with a constant front velocity.

Consider a perturbation to a planar interface at $z = 0$ (in the reference frame moving with the front), of the form

$$\zeta(x, t) = A \exp(ikx + \omega_k t) + \text{c.c.}$$  \hspace{1cm} (2.44)

where $\omega_k$ is the growth-rate, to be determined, of a perturbation with wavenumber $k$. This perturbation in the front position will modify the diffusion field given by Eq. 2.33. We expect this effect to decay with distance from the origin, so we write

$$u(z) = \begin{cases} 
\exp(-\frac{2z}{\ell}) - 1 + B \exp(ikz - qz + \omega_k t) + \text{c.c.} & \text{for } z \geq 0 \\
B \exp(ikz - \bar{q}z + \omega_k t) + \text{c.c.} & \text{for } z < 0 
\end{cases}$$  \hspace{1cm} (2.45)

The perturbation described by Eq. 2.44 will grow for $\omega_k > 0$ and decay for $\omega_k < 0$. Since we are only interested in checking the stability of the perturbed solution, not its long-term behaviour, we solve for $\omega_k$ in the limit of a small perturbation, where we can use linearized equations. By substitution into Eq. 2.31, we can show that $q$ and $\bar{q}$ are the positive solutions of

$$q^2 - (2/\ell)q - k^2 = \omega_k/D$$
$$\bar{q}^2 + (2/\ell)\bar{q} - k^2 = \omega_k/D,$$  \hspace{1cm} (2.46)

where we are assuming that the thermal diffusivity is the same in both phases.

After evaluation of Eqs. 2.27 and 2.26 at the interface, we find that

$$\omega_k = v \left[q - \frac{2}{\ell} \right] - D(q + \bar{q})d_0 k^2.$$  \hspace{1cm} (2.47)

For $k\ell \gg 1$, $q \approx \bar{q} \approx k$, so Eq. 2.47 becomes

$$\omega_k \approx kv[1 - d_0 \ell k^2].$$  \hspace{1cm} (2.48)

Here we have taken $\omega/D \ll k^2$, since we are looking for the points where $\omega = 0$. We see that perturbations grow for all wavenumbers $k$ such that

$$k < (d_0 \ell)^{-1/2}.$$  \hspace{1cm} (2.49)
Larger wavenumbers, corresponding to shorter wavelengths, are stabilized by surface tension. Note that the characteristic size of a growing perturbation is of the order of

$$\lambda \sim 2\pi \sqrt{d_0 \ell}.$$  \hspace{1cm} (2.50)

This emphasizes the fact that the resulting pattern arises from a competition between a microscopic property — the capillary length $d_0$ — and a macroscopic property — the diffusion length $\ell$. The capillary length is typically of the order of Ångstoms and is roughly equal to the thickness of the interface. The diffusion length, which depends on the velocity, is of the order of millimeters for the typical velocities measured in this thesis. The result is a structure with characteristic length scales of the order of micrometers.

A full analysis of Eq. 2.47 reveals that the planar front will be stable to perturbations of all wavelengths above a critical velocity $v_s$ given by

$$v_s = \frac{D_h}{d_0}.$$  \hspace{1cm} (2.51)

Physically, this is because the diffusion length $\ell$ (which characterizes the destabilizing mechanism) decreases with increasing velocity. When $\ell$ falls below the the capillary length (which describes the stabilizing effect of surface tension), the planar front becomes stable. Thus, the Mullins-Sekerka analysis predicts featureless solidification fronts at large enough velocities. This restabilization has been observed in directional solidification experiments performed at high velocity [31]. We will see in Section 2.4 that in many cases, diffusion is not the mechanism controlling growth at large velocities and undercoolings. In those cases, complicated patterns, rather than featureless fronts, are seen.

It is important to note that a linear stability analysis can only determine the stability of a solution — it tells us little about the structure seen in the long term. The linear equations describe exponentially growing perturbations. For any steady-state structure, this growth must be limited by nonlinear terms.

### 2.3.3 Dendrites

We have seen that a planar solidification front cannot move at a constant speed, except at unit undercooling. However, this is not the case for all interface shapes.

One familiar steady-state solidification morphology is that of dendritic growth. In dendritic growth, needles, which may be sidebranched, grow at constant velocity into the melt. The tips of these needles are nearly parabolic in shape.
CHAPTER 2. SOLIDIFICATION THEORY

It has long been known [5] that in the limit of vanishing surface energy, the standard solidification model allows a steady-state solution in which the interface has a parabolic shape. This can be seen by transforming Eqs. 2.25–2.28 to parabolic coordinates moving with the front. We then arrive at the famous Ivantsov solution, which states that

$$\Delta T = \begin{cases} \frac{Pe^P E_1(P)}{\sqrt{\pi Pe^P} \text{erfc}(\sqrt{P})} & \text{3-dim} \\ \frac{Pe^P E_1(P)}{\sqrt{\pi Pe^P} \text{erfc}(\sqrt{P})} & \text{2-dim} \end{cases}$$

(2.52)

where the Peclet number $P$ is defined in terms of the growth velocity $v$ and tip radius $\rho$ by

$$P = \frac{\rho v}{2D} = \rho/\ell.$$  

(2.53)

Here, $E_1$ is the integral

$$E_1(P) = \int_{\rho}^{\infty} \frac{e^{-t}}{t} dt$$

(2.54)

and erfc(x) is the complementary error function.

The Ivantsov solution relates the tip radius and growth velocity to the undercooling, but does not select a specific velocity or dendrite size. Experimentally, however, it is known that a unique dendrite is selected for given growth conditions [32]. It was not until recently that this problem was solved by the *microscopic solvability condition* [7, 8]. The essential ingredient for this condition was the realization that the surface tension and its anisotropy act as singular perturbations to the needle crystal solution, so that even small surface tension has a large influence on the solution.

2.3.4 Other diffusion-limited growth forms

Although many of the features of dendritic growth are now understood, dendrites are not the only growth form seen in the diffusion-limited regime. One that has received a great deal of attention recently is known as the dense-branched (or “seaweed”) morphology (DBM) [33, 34, 35, 36]. The DBM is characterized by fingers with a fairly uniform width oriented radially within a roughly circular envelope. The DBM fingers undergo repeated tip-splitting allowing them to spread throughout the sample. This mode is distinguished from dendritic growth, which it superficially resembles, by tip splitting and from diffusion-limited aggregation (DLA) by the fact that it is not a fractal structure. This morphology has been studied experimentally in Hele-Shaw cells [24, 37] and electrodeposition [35, 36], and discussed theoretically in terms of solidification models, particularly the boundary-layer model. It is typically seen in systems with zero or small surface tension anisotropy.
In addition to the faceted, dendritic, and DBM solidification modes seen in diffusion-limited growth are the patterns seen at larger undercoolings when kinetics become important.

### 2.4 The kinetics-limited regime

The crossover to the kinetics-limited regime occurs when the dimensionless undercooling $\Delta > 1$. When the undercooling is increased above this level, we expect a change in growth morphology as kinetic effects begin to dominate the solidification process. The restabilization of the planar front at large enough velocities (roughly those seen at the crossover to the kinetic regime) suggests that kinetics-limited growth may be characterized by smooth fronts. In fact, experimental studies in that regime reveal a variety of phenomena, including defect generation, metastable phases, and, at the highest undercoolings, glass formation.

Here, I will briefly discuss the morphologies appearing in the kinetic limit.

#### 2.4.1 Metastable phases

Many materials have more than one solid phase available for solidification from the melt. Well-known examples of elements with multiple solid phases are carbon and tin. Although only one of the solid phases can be favoured thermodynamically, solidification into a metastable phase can occur.

The most obvious way to obtain a metastable phase is to first solidify a material at a temperature where the desired phase is stable, and then change the temperature to a value where the resulting solid is metastable. If the barrier to nucleation of the stable phase is high, the metastable phase can persist for a long time. For instance, the diamond form of carbon is the stable phase when grown at high pressures, but it is metastable with respect to graphite at room temperature and atmospheric pressure.

Metastable phases can be formed directly if the nucleation barrier for the metastable phase is lower than that for the stable phase. In such a case, it is possible for growth of the metastable phase to dominate the system. One way to lower a nucleation barrier is to introduce impurities at which heterogeneous nucleation can occur. Preferential nucleation of the metastable phase can occur if the lattice of the impurity is more similar to the lattice of the metastable phase than it is to that of the stable solid. Nucleation of the metastable
phase then occurs by epitaxy [38]. Similarly, a metastable phase may nucleate along with the stable phase, but have a higher growth velocity.

Another mechanism for the formation of a metastable phase can occur when it is possible for a system to pass through, or near (in order-parameter space), a metastable phase en route to the stable solid [39, 40]. A finite quantity of the metastable phase can be formed dynamically if the interface between the melt and metastable phase moves faster than the interface between the metastable and stable phases, allowing the solidification front to split.

Experimentally, metastable phases are often produced by quenching liquids at very high cooling rates (cooling rates of up to $10^8 \, ^\circ C/s$ have been attained experimentally [41]). The emphasis on cooling rate, though often seen in the literature, is, I believe, very misleading. It is the undercooling, not the cooling rate, which controls growth phenomena. The utility of large cooling rates is that they make it possible to cool a material to a large undercooling before nucleation begins. In some systems, more modest cooling rates are sufficient. For example, multiple solid phases in liquid crystalline materials are common [42, 43, 44, 45, 46, 47]. When nucleation occurs before the melt has stabilized at the desired undercooling, the relative amounts of the solid phases formed will depend on the rate of cooling.

2.4.2 The large-undercooling regime

As the undercooling increases, the change in free energy, which drives the solidification process, becomes larger. As a result, the solidification velocity usually increases with undercooling, for small undercoolings. The functional form of this increase depends on the specific growth mechanism. The growth velocity has been modeled as [48]

$$v = \frac{g_0 D_s}{d} [1 - \exp(-\Delta G/k_BT)],$$

(2.55)

where $\Delta G$ is the decrease in free energy due to solidification. In this model, solidification is described as a process in which molecules in the melt arrive at the interface and stick with some probability $g_0$ of order unity. Since the melt is disordered, each molecule must diffuse a distance of the order of the molecular size, $d$, before it becomes incorporated in the ordered lattice. Thus, the growth velocity depends on the self-diffusion constant $D_s$.

For small undercoolings, the growth velocity described by Eq. 2.55 is proportional to $\Delta G$ and, therefore, to the undercooling (recall Eq. 2.17). This dependence is relevant for the growth of a rough interface. Burton, Cabrera, and Frank [49] have shown that when the
growth of faceted solids is dominated by steps spiraling around screw dislocations (Frank-Read sources), the growth velocity depends on undercooling as \( v \propto \Delta T^2 \).

In either case, the growth velocity depends on the self-diffusion constant, which is related to the fluid viscosity. As the undercooling increases, the viscosity increases and diffusion decreases in accordance with the Stokes-Einstein relation \( D = k_B T / 6 \pi a \eta \), where \( a \) is the hydrodynamic radius of the molecule and \( \eta \) is the fluid viscosity. This can be described by an activation energy \( F \) and associated Arrhenius factor so that \( D_s \propto \exp(-F/k_B T) \). In some cases, it is also useful to consider a nucleation barrier \( U \) for material to be incorporated into the solid (i.e., a "surface nucleation" barrier). Including the temperature dependence of the diffusion constant and the dependence of the growth rate on surface nucleation, Eq. 2.55 becomes [50]

\[
v = \exp\left(-\frac{U}{k_B T}\right) \exp\left(-\frac{F}{k_B T}\right) [1 - \exp(-\Delta G/k_B T)].
\]

(2.56)

At low enough temperatures, the kinetics of diffusion and surface nucleation dominate and the solidification velocity slows. Schematically, the solidification velocity has a dependence on undercooling similar to the one shown in Fig. 2.6.

![Figure 2.6: Dependence of growth velocity on undercooling. For small undercoolings, the growth rate increases linearly with the undercooling, and hence the change in free energy. At large undercoolings (low temperatures), the velocity curve turns over as the kinetics become slow.](image)

One result of this slowing of kinetics and the associated increase in the viscosity of the melt is that some materials, if cooled quickly enough, form amorphous solids. This is known
as the “glass transition” [51].

Another consequence of the growth law indicated in Fig. 2.6 is that for large enough undercooling (i.e. past the maximum in the growth rate), the warming of the sample due to the release of latent heat leads to an increase in the growth velocity. This results in a positive feedback: the increase in velocity causes an increase in the rate of heating, increasing the velocity further. This is known as “explosive crystallization.” Generically, positive feedback can result in saturation at a steady state, or in feedback oscillations. This thermal instability has been observed in the crystallization of amorphous materials, where it can lead to surface undulations [52].

Our discussion of solidification processes has, so far, been mostly concerned with pure materials. As we noted in Section 2.2.1, similar behaviour can be expected of solidification controlled by impurity diffusion. As an example, mineral crystallization is often modeled as solidification limited by impurity diffusion. Since this crystallization typically occurs at large undercoolings and growth velocities, the boundary conditions at the interface must reflect the departure from equilibrium. Oscillatory banding in minerals, for instance, has been modeled using a velocity-dependent expression for the partition coefficient $k$ at the front [53].

2.4.3 Defect generation

Solidification models in the diffusive limit usually tacitly assume that the growing solid phase is comprised of a small number of perfectly ordered domains. This is not always the case in the diffusive limit; in the kinetics limit, it is rare. Driving the growth process far from equilibrium (for example, by increasing the undercooling or the growth velocity) causes a stress in the growing solid, which results in the introduction of defects.

Several types of dislocation mechanisms have been studied [54]. For instance, thermal stresses due to temperature gradients within the solid during growth can result in a mechanical stress due to the dependence of density on temperature. Other mechanical stresses can arise from viscous flow of the melt due to the density change upon freezing. Impurity particles can also generate defects by the epitaxial force due to alignment of the local crystal lattice with the lattice at the surface of the impurity particle.

These dislocations can result in a variety of patterns in the regime between perfect crystalline solids and amorphous solids. As an extreme example, a grain boundary is a chain of dislocations. Many of the morphologies seen in the kinetics regime consist of aggregates
of individual crystals. One such example, in which the aggregate may itself become ordered on a larger scale, is known as spherulitic growth.

2.5 Spherulitic growth

Spherulitic growth typically occurs in materials solidified at a large undercooling from a highly viscous melt. Spherulites consist of radially oriented microcrystals arranged at non-crystallographic angles within a spherical envelope. During spherulitic growth, the front velocity remains constant with radius. The front velocity is usually small: in polymeric systems, where most of the detailed studies have been performed, typical growth rates are 1–10 μm/min. This morphology has, however, been seen in a wide variety of materials including elemental selenium [55, 56, 57], polymers [11, 12, 58, 59, 60, 61], low molecular-weight systems with polymeric impurities [62], organic materials [63, 64] biological molecules [61], mineral aggregates [65, 66, 67], and liquid crystals [46, 68]. Many spherulites show bands concentric about the domain nucleus. Despite a century of study in these materials, there is no generally accepted theory that can make quantitative predictions about the growth properties.

Spherulites are the typical crystallization mode for polymers (although not all polymer solids are crystalline) and therefore are important in the determination of the mechanical properties of the resulting solid. Similarly, the carbon in cast iron often forms spherulites [69], resulting in a metal which is much less brittle than cast iron in which the carbon forms graphite sheets. Here, the formation of spherulites is desirable. In biological sciences, where large single-crystals are required for X-ray structural determinations, spherulites are a common "failure-mode" [61, 70]. Clearly, an understanding of how and why spherulites form would benefit many areas of science and technology.

2.5.1 Models of spherulitic growth

The similarities between spherulites in diverse systems suggest a common underlying physical mechanism. Identifying spherulites in a wide range of materials is, therefore, important in sorting out which properties are fundamental to spherulitic growth.

Early models of spherulitic growth suggested that spherulites were formed by the regular branching of microcrystals at a few crystallographic angles [71]. This mechanism was used to explain observations that spherulite envelopes are occasionally faceted, particularly at
small radii. Further microscopic studies revealed, however, that the individual crystallites do not appear to be crystallographically related [74]. Nevertheless this model has been invoked more recently to describe the shape of selenium spherulites [56].

In 1963, Keith and Padden [11, 72] proposed that the size of the crystallites is set by the diffusion length, $\ell_m = D_m/v$ (where $D_m$ is the diffusivity of impurities), which characterizes the width of the impurity-rich layer which builds up at the interface during crystallization at a velocity $v$ from an impure melt. They argued that noncrystallographic branching can result from misaligned structures with sizes of $\ell_m$ because these will be large enough that they can grow without being incorporated by the surrounding solid, but not so large as to themselves be subject to the same instability. This paper is noteworthy in that it predates the Mullins and Sekerka paper on the diffusional instability of planar solidification fronts. However, improved optical and electron microscopy, the latter aided by the discovery of improved techniques, particularly permanganic etching of polymer spherulites [59, 73], determined that the typical crystal sizes did not scale with $\ell_m$ [74, 75].

A more recent idea is that spherulites are the result of the dense-branched morphology described in Section 2.3.4 [76, 77]. The characteristic finger width in this model is predicted to scale as $\sqrt{d_0 \ell_m}$, in accordance with the Mullins-Sekerka instability. However, the DBM consists of fingers branching from single crystalline domain. It is not clear that this diffusion-limited growth form is relevant to spherulitic growth, which forms multicrystalline aggregates under conditions far from equilibrium.

At the most basic level, the elements required for spherulitic growth are crystallization into needles and a mechanism to align the needles into a radial direction. Whatever the mechanism for the formation of needle-crystals, the radial orientation of these crystals needs to be explained. In polymers, SEM studies have shown the crystals to be ribbon-like, or lamellar. These lamellae are made up of folded polymer chains aligned roughly perpendicular to the lamellae. Polymer crystals are rarely perfect, so many dangling chains extend from the lamellar surfaces. Bassett, Keller, and Mitsuhashi have proposed that the entropic pressure of these “cilia” between the lamellae can account for the radial splay in polymers [59, 78, 79].

In other materials, Tiller [80] has proposed that the splay is due to viscous flow of the melt caused by the density change on solidification. This density difference forces fluid to flow through the narrow channels between needle crystals (into the spherulite if the solid
is more dense than the liquid). This generates a pressure $\Delta P$, according to the Hagen-Poiseuille equation, given by

$$\Delta P = 8\rho_L \nu vt f / \lambda^2,$$

(2.57)

where $\rho_L$ is the fluid density, $\nu$ its viscosity, $t$ is the channel length, $v_f$ is the fluid velocity, and $\lambda$ is the channel width. As the needles grow, they thicken. Since solidification is, in general, accompanied by a density change, this growth will result in fluid flow. In the case of a cubic array of cells of volume $\lambda^3$ bordered along the edges by twelve filaments (each of which is shared by four other cells), fluid conservation demands that the change in fluid velocity across a single cell cell satisfies

$$6\pi R \left( dR / dt \right) \lambda \Delta \rho = \Delta v_f \rho_L \lambda^2,$$

(2.58)

where $R$ is the radius of the needles and $\Delta \rho$ is the density change. From this, Tiller predicts that the pressure differential required for flow through the channels must have the form

$$\Delta P = Cv \Delta \rho vt / \lambda^4,$$

(2.59)

where $v$ is the growth velocity, $r$ the tip radius of the needles, and $L = vt$ is the spherulite radius. The constant $C$ is treated as an undetermined parameter which accounts for the fact that the tube walls are not solid.

This pressure increases with viscosity (and, hence, with undercooling), as well as with the spherulite radius. Tiller predicts that a transition from an initially crystallographic array of needles to a spherulite with radially oriented needles will occur at a critical spherulite radius $L^*$, which scales as

$$L^* \propto \nu^{-1/2} \lambda^2 \nu^{-1/2} v^{-2}.$$

(2.60)

The bend in individual needles is then made permanent by induced dislocations in the crystals.

Experiments on the solidification of water/glycerol solutions show stages of this evolution from a crystallographic, polyhedral shape to a shape with radial symmetry [81]. Moreover, the transition radius $L^*$ was shown to scale in the manner predicted by Eq. 2.60. This model explains naturally the observation that spherulites form from high-viscosity fluids.

Another feature of spherulitic growth in need of an explanation is the overall spherical shape. Caroli, et al. [82] have suggested that fluid flow generated by the density change $\Delta \rho$ plays an important role in stabilizing the spherical morphology.
2.5.2 Spherulite nucleation

The idea that the spherulite morphology is the result of a bending of microcrystals into the radial direction is strengthened by observations of spherulite nuclei which are decidedly asymmetric. Typical spherulite nuclei have a form which is known in the spherulite literature as "sheaf-like," due to their resemblance to a tied sheaf of wheat. The standard explanation [66, 71] is that the spherulite initially nucleates as a single needle, from which new needles branch out, eventually resulting in radial growth. If there is a maximum branching angle, the result is an asymmetric nucleus with two cavities which are inaccessible to crystals branching from the original nucleus, and a defect line where needles from opposite ends of the nucleus meet. This process is shown schematically in Fig. 2.7.

![Figure 2.7: Origin of "sheaf-like" AFM nucleus. The sheaf structure is thought to be due to branching from an initial needle crystal, eventually resulting in a nearly circular envelope. If there is a maximum branching angle, two cavities remain near the nucleus.](image)

Alternatively, Tiller's model would predict that the holes left near the nucleus are due to an initial radius of curvature of the bending fibers. In either case, the sheaf structure stems from the evolution of a nearly radially symmetric structure from an initially anisotropic nucleus.

2.5.3 Banded spherulites

Although there is some agreement about the overall structure of spherulites, the mechanism responsible for the large-scale structure remains unknown. Even less is understood about
the origin, or even the nature, of banding in spherulites.

Some of the early investigators of spherulites concluded that the bands represent concentric shells of crystallites separated by less-ordered material [83]. In this picture, the bands are the result of a rhythmic growth process. The density modulation due to the structural variation would then act as an optical diffraction grating. The belief was that the contrast mechanism in optical microscopy of bands with spacings on the order of microns was the result of diffraction of light outside of the accepting cone of the microscope objective.

Careful studies of bands in polymer spherulites using the polarizing microscope, primarily by Keller [12, 83, 84], have indicated that banding in spherulites is due to a birefringent effect. These observations suggest that the optical axis of the crystals follows a helical path about the spherulite radius. When viewed through crossed-polarizers, a dark band will be seen at radii where the optical axis lies along the line of site. This hypothesis is supported by observations of an apparent shift in the bands when the sample is tilted, thus rotating the optic axis about the tilt axis.

The observation of bands with unpolarized light can also be readily explained by this model. The rotation of the index ellipsoid results in a variation in the index of refraction along the spherulite radius, causing the bands to act as a diffraction grating, as in the rhythmic growth model described above. If the optical axis lies perpendicular to the radial direction, there will be no variation in the refractive index for light polarized along the spherulite radius, so that the bands are not visible when illuminated by light linearly polarized in this direction. This dependence on polarization direction has been seen experimentally [83, 84].

Less easily explained by this picture are the ridges that have been observed on the surfaces of spherulites prepared in thin layers. It has been suggested [84] that branching of the spherulite fibers is inhibited by the sample walls, resulting in periodic gaps as the crystal axes rotate. Alternatively, these apparent ridges may be an artifact resulting from the difference in contrast between edge-on and face-on polymer lamellae [84].

Twist in the unit cell orientation has been confirmed in some systems by electron microscopy [59, 60, 61, 74, 85], microbeam X-ray analysis [86], and micro-Raman spectroscopy [87]. The existence of this twist can be due to either a continuous twist about the radial direction in individual lamellae or a dependence on radius of the average orientation of untwisted crystals. The second possibility is generally believed to be more likely [61, 85]. However, some electron micrographs indicate that the lamellae are flat throughout most of
a band and twist rapidly in a short distance \cite{59, 61, 85}. Apparent screw dislocations have been observed at the boundaries of the bands \cite{60}, though it is unknown whether these are the cause, or the effect, of the bands — if two initially parallel ribbons twist, their edges may interact, causing the ribbons to lock together. Topographically, this contact point resembles a screw dislocation and may initiate spiral growth \cite{88}.

There is no theory that explains why the optical axis should have such a twist, or why such a twist would be in phase over large enough domains to create visible bands. Moreover, this picture raises problems of a geometric nature: it is difficult to imagine the structure of a dense arrangement of twisted ribbons \cite{60, 71, 88}.

Suggestions for the cause of the twist in spherulite microcrystals have included buckling due to surface energy — small crystals may twist due to a difference between the lattice constants at the surface and in the bulk \cite{71} — and strain induced by screw dislocations \cite{89}. A more elaborate explanation for the twist, as well as for the S-shaped cross-section of lamellae often observed in electron micrograph studies \cite{59, 85}, relies on an energy difference between the sides of the lamellae \cite{88}. This model suffers the disadvantage that it is only valid for polymer spherulites. Moreover, it has been recently observed that an arbitrary cross-section of a twisted ribbon will be S-shaped, even if the cross-section in a direction perpendicular to the twist axis is flat \cite{90}.

### 2.5.4 Overview of spherulitic growth models

While high-resolution studies have allowed a detailed characterization of the spherulitic structure, there is little agreement on the origin of this structure. It is accepted that the radial alignment of individual fibers originates from a pressure between the fibers, though the origin of that pressure may differ from system to system.

Similarly, banding in spherulites is accepted to be a birefringent effect resulting from the rotation of the optic axis about the spherulite radius. However, there is no accepted theory that explains the cause of this rotation or the reason why neighbouring fibers would twist in concert. Indeed, such a twist in closely packed lamellar crystals in polymer spherulites requires a periodic intersection of these crystals.

Most of the recent quantitative studies of banded spherulites have been performed in polymeric systems. In order to determine the important features of spherulitic growth, it is desirable to perform equivalent high-resolution studies in other systems. One such study will be described in Chapter 5.
2.6 Morphology transitions

We have seen that solidification can take several forms. These can be divided into the broad categories of diffusion-limited growth, where heat or impurities need to be transported away from the growth front, and kinetics-limited growth, where such transport is not required and the growth is limited by microscopic details of the solidification process. Within these categories, several different growth morphologies have been studied. Given that several solidification morphologies are available to take the place of the unstable planar front, we would like to be able to determine which is seen.

The simplest possibility is that the growth form can change continuously as the growth conditions are altered. In this case, the different growth modes would be limiting cases in regimes where different mechanisms dominate (i.e. diffusion-limited growth at small \( \Delta T \) and kinetics-limited growth at large \( \Delta T \)). Then, given an accurate model of the solidification process, the growth morphology could be predicted for any set of growth parameters. We would expect to see smooth transitions between the various regimes while quantities such as the undercooling are varied. In particular, quantities such as the growth velocity would be analytic functions of the undercooling.

This approach has been successfully applied to problems in polymer crystallization ("regime theory" [91, 60]) and metallurgy (the "LKT" theory [92, 93, 94]). For instance, the "regime theory" of polymer crystallization considers the growth process to be a combination of surface nucleation and lateral growth. Three regimes are defined: (I) lateral growth dominated crystallization, (II) nucleation and lateral growth approximately equal, and (III) growth limited by the rate of surface nucleation. Although each regime has a somewhat distinct dependence on undercooling, the boundaries between these regimes are not sharp [60].

Continuous transitions between morphologies are not, however, the only possibility. For instance, the dense-branched morphology is observed in experimental and numerical models under conditions where a dendritic solution is known to exist [10, 95, 96, 97], suggesting that a selection rule between distinct morphologies (each of which has its own dependence on growth conditions) is at work. These models, as well as theoretical discussions [98, 99], show that transitions between morphologies with variations of the growth parameters can be sharp. The question then becomes: can one determine which of the available growth morphologies is seen?
CHAPTER 2. SOLIDIFICATION THEORY

A long-time goal of a number of researchers in nonequilibrium physics has been to formulate the problem of pattern selection in terms of an extremum principle analogous to the minimization of free energy discussed in Section 2.1.1. No general kinetic potential for nonequilibrium systems has been found, though several approaches have proved useful [9]. Since nonequilibrium processes are, by definition, time dependent, it is possible that such a potential cannot by found — the growth form may depend on the growth history, as well as on the current growth conditions. The only theoretical recourse is then to examine the stability of each possible pattern on an individual basis.

If, however, a steady-state morphology determined by the growth conditions alone does exist for any given growth conditions, and if there are sharp changes between morphologies as the growth conditions are varied, it must be possible to divide the space of the growth parameters into a phase diagram. The existence of a phase diagram is equivalent to the existence of selection principles which determine which morphology is seen. Experimentally, such phase diagrams have been mapped in various systems.

Ben-Jacob, et al. [10, 24, 95, 100], have discussed morphology transitions and selection principles in terms of the average growth velocity, which can be thought of as a response function to the driving force in the system (e.g. the undercooling, supersaturation, etc.). The average velocity is a measure of the rate of approach towards equilibrium. Since the rate of change in free energy at the interface is given by the integral of velocity along the interface, the appropriate average velocity must take the shape of the interface into account. They go on to propose two types of morphology transitions. In the first kind (which they call a first-order morphology transition), the velocity is discontinuous at the transition point. A second-order morphology transition is characterized by a continuous velocity, but has a discontinuous derivative. These two types of morphology transitions are illustrated in Fig. 2.8.

In the nomenclature of dynamical systems, a transition involving a jump, as in Fig. 2.8b, is called a “subcritical bifurcation” (Fig. 2.8a shows a “transcritical” bifurcation [9]). The two modes can coexist in some range of undercooling, though one mode will be metastable with respect to the other. In practice, fluctuations usually prevent the spinodal points (the point where a solution becomes absolutely unstable) from being seen.

Ben-Jacob, et al., have proposed that the fastest growing morphology is the one dynamically selected [10, 95, 97]. This selection principle is intuitively appealing because a faster mode would be able to grow ahead of any competing growth mode, eventually surrounding it.
Figure 2.8: Characterization of morphology transitions in terms of the growth velocity-vs.-undercooling plot. The competing morphologies have velocity curves that overlap for a range of undercooling. In both cases, the selected morphology is indicated by a solid line, while the curve for the competing morphology is shown by a dashed line. (a) Second-order morphology transition. In a second-order morphology transition, the derivative of the growth velocity with respect to growth conditions (here, the undercooling) is discontinuous. The transition occurs at the undercooling where the velocity curves of the two competing morphologies cross. In this case, the fastest-growing morphology, indicated by the solid curve, is assumed to be the one selected. (b) First-order morphology transition. In a first-order morphology transition, the velocity itself is discontinuous at the transition point. In the example given, mode 2 is selected throughout its range of existence, though mode 1 is, in general, metastable for undercoolings as large as the crossing point of the dashed lines shown.

and preventing further growth. The velocity-vs.-undercooling curve expected in this case is indicated in Fig. 2.8a. This is not claimed to be a complete selection rule, but part of a more general scheme. In analogy to the entropy term dominating the equilibrium free energy at high temperature, the growth velocity, representing the rate of entropy production, may be the most important term far from equilibrium. A more general selection principle may also include variables associated with the microscopic equilibrium properties of the interface.

It should be noted that the fastest-growing mode hypothesis cannot describe a first-order morphology transition. In Fig. 2.8b, the morphology transition and velocity jump occur because mode 2 does not exist below some critical value of the undercooling.

One caution in this discussion of mode transitions is that the term mode has remained undefined. Part of the difficulty is that the very existence of these modes is determined by the time- and length-scales of the observations. Clearly, the complicated microstructure
of the growth morphologies is not an equilibrium structure. In principle, the morphology is defined by the kinetic structure of the interface during growth; in practice, the resulting structures persist for times ranging from minutes to years. Another difficulty is that the growth process is subject to fluctuations so that, near a transition point, a large enough front will always show coexistence of more than one mode. This will result in some smearing of the transitions.

In our discussion, growth morphology will refer to the shape of the growth front and resulting structure of the solidified material. The morphology may vary smoothly with growth parameters. Our operational definition of a growth mode will be a morphology whose growth is easily distinguished from other morphologies. In order for this distinction to be made, the modes must be separated by relatively rapid changes in growth morphology with growth conditions. The case where the change is associated with discontinuous changes in measurable properties (such as growth velocity, derivative in growth velocity, and interface roughness) on a local scale will be of most interest to us.

Morphology transitions have been observed in both experimental and computational work. In many cases, particularly patterns observed in the Hele-Shaw cell and in simulations of diffusion-limited growth, the fastest growing mode hypothesis holds. Other clear examples have been seen in the measurement of growth velocities in metal alloys [101]. On the other hand, we are aware of one counterexample in the literature [102]: measurements of growth velocity in pure nickel and copper-nickel alloys show an apparent morphology transition associated with a decrease in the slope of the velocity curve — i.e., to a slower mode. In this case, the relevance to morphology transition schemes was not discussed.

There is a clear need for additional experimental studies of morphology transitions. There are few examples in the literature in which the variation in growth morphology (let alone the velocity, which is often not measured at all) has been characterized well enough to distinguish between continuous and sharp transitions. One of the goals of this thesis is to help to remedy this situation. In particular, I perform accurate measurements of the growth velocity along with visualization of the growth morphology. This will allow us to discuss the mechanisms of the different growth modes and how they are selected.
2.7 The choice of an experimental system

As we have seen, similar solidification morphologies can be seen in a wide range of materials. Thus, studies of solidification in one material may have applications to others.

In the experiments presented in this thesis, we chose to study solidification of a liquid crystal. We will see that these materials allow one to perform experiments that would be difficult or impossible with other materials. In fact, many of the growth characteristics seen are common to other systems as well, suggesting that the results of our studies can yield insights applicable to solidification in other materials.

Before we continue, we shall recall some basic facts about liquid crystals. If we examine a material in the solid phase on the microscopic scale, we find that its atoms are arranged, at least locally, on a lattice. This implies a translational symmetry, where we find no change in the local atomic arrangement as seen from locations separated by integral numbers of lattice vectors. Such an arrangement is called a crystal. In a liquid, on the other hand, no such lattice exists. While we can still predict the average distance between nearest-neighbour atoms in a liquid, the direction is random and constantly changing. The liquid phase is invariant under any translation, not just a lattice of translations.

For some materials, other phases between the solid and liquid exist. These are called liquid crystals. In a liquid crystal, some, but not all, of the translational symmetry of the liquid is lost. By way of example, consider the structure of the smectic A phase, as illustrated schematically in Fig. 2.9. The smectic A phase consists of molecules arranged in layers with a well-defined average thickness. The translational symmetry represented by the layers can be thought of as a one-dimensional crystal. The smectic A phase is invariant under any two-dimensional translation in the smectic plane. Within this layer, there is no lattice and the molecules behave somewhat as a two-dimensional liquid. It is worth noting that the liquid crystal phases are true thermodynamic phases and the transition of a liquid crystal phase is usually first order (and is accompanied by the release of latent heat).

Liquid crystals have long been used for the study of phase transitions. In the past, a great deal of attention has been focussed on the variety of phase transitions that can occur in liquid crystalline materials. However, another feature of these materials is that the dynamics of growth are typically on a convenient time scale: slow enough to be conveniently observed by microscopy at modest frame rates, but not so slow as to preclude detailed studies. The reason for this can be understood by the following simple argument [103]:
CHAPTER 2. SOLIDIFICATION THEORY

Figure 2.9: The smectic A phase. In this state of matter, molecules form layers with a well-defined layer spacing, yet remain fluid within the layers. This can be thought of as a state intermediate to the liquid and solid state. Note that this diagram is schematic only: fluctuations usually result in a far greater spread in average positions for individual molecules.

Solidification from a melt can be thought of as the ordering of molecules, initially in the liquid phase, into a regular lattice. A natural velocity scale can be formed by considering the ratio of the effective thickness of the front \( \ell_{\text{eff}} \) divided by the time scale for diffusion across the front, \( t_0 \sim \ell_{\text{eff}}^2 / D \). Thus, the natural velocity scale for solidification is \( v_0 \sim D / \ell_{\text{eff}} \). This is not meant to be an estimate of the solidification velocity — that will depend on the growth conditions. Rather, \( v_0 \) is an estimate of velocities at which the microscopic kinetic processes can occur. As solidification velocities approach this value, we expect the resulting solid to become increasingly disordered.

Consider first the solidification of a pure low-molecular-weight material. In this case, the solidification time is set by diffusion of latent heat generated by solidification away from the interface. Thermal diffusion constants for simple materials are usually of the order of \( D_k \sim 10^{-3} \) cm\(^2\)/s. If we take for the thickness scale the atomic size of the material, \( \ell_{\text{eff}} \sim 10^{-8} \) cm, the velocity scale becomes \( v_0 \sim 10^5 \) cm/s.

Next, consider the case of a binary alloy. In this case, we need to consider both heat diffusion away from the interface and mass diffusion of the solidifying materials to appropriate sites on the lattice. Since mass diffusion is typically one hundred times slower than heat diffusion, this becomes the rate-determining step. Then \( v_0 \sim 10^{-5} / 10^{-8} \sim 10^3 \) cm/s. Such velocities are typical in “rapid solidification” of metal alloys [104].

Next, we consider the solidification of a liquid crystal. The molecules of these materials are larger than those considered above — on the order of \( \ell_{\text{eff}} \sim 2 \times 10^{-7} \) cm. The diffusion
time will again be set by mass diffusion of impurities [106]. Taking $10^{-7}$ cm$^2$/s as a typical diffusion constant for these materials, we find $v_0 \sim 0.5$ cm/s.

Finally, we consider the solidification of a polymer. Polymeric fluids usually have very long diffusion times due to the tangled arrangement of the long polymer molecules. Time scales now depend on the length of the molecules. For high-weight polymers, we can estimate $v_0 \sim 10^{-11}/10^{-5} \sim 10^{-6}$ cm/s using the arguments of Ref. [103] for a polymer length of $10^4$. In fact, spherulite growth velocities in polymers are usually of the order of microns per minute [105].

These values of $v_0$ give some idea of the relative velocities at which similar effects might be expected in different materials. Of course, some effects might be material-specific while others may depend on factors not considered here (such as viscous flow due to the density change on freezing). Nevertheless, this does serve to explain why we might choose to study solidification in a liquid crystal, despite the added complexity of freezing from an anisotropic phase. The solidification is much slower than is seen in metals, so the front motion may be followed, but not so slow as in a polymer where the low front velocities result in very long experiments.
Chapter 3

EXPERIMENTAL METHODS

Unlike a technical journal, where the limited space and terse style precludes a detailed discussion of the methods used, a thesis allows the freedom of a complete description of the experimental methods. This information is likely to be more useful to a reader planning similar experiments than any other part of this work, most of which will be published elsewhere.

This chapter is divided into three sections. In the first, I will discuss the materials used and the samples made. The second section describes the various imaging techniques used to make the many pictures appearing in this work. In the third section, I discuss the types of solidification experiments that have been done and describe the the apparatus I used. The description of the actual use of this equipment will be left to Chapters 4 and 5.

3.1 Sample preparation

It is no secret to workers in the experimental sciences that the key to obtaining unambiguous results is in the sample preparation. Despite its importance, this subject is often neglected in favor of discussions of the results obtained and conclusions drawn. In this section, I discuss the materials studied and the steps necessary to prepare useful samples.

3.1.1 Materials

As discussed in Section 2.7, the properties of liquid crystals make them a convenient choice for the study of solidification. Given that liquid crystals, as a class of materials, are likely to
CHAPTER 3. EXPERIMENTAL METHODS

have desirable time and velocity scales, we need only decide which of the many liquid crystals to use. We would prefer one that is chemically very stable and available in highly-pure form. Two such families of liquid crystals are the cyanobiphenyls and oxycyanobiphenyls [107], which have the generic structures diagrammed in Fig. 3.1. A particularly good choice is 4-cyano-4'-decyloxybiphenyl (10 OCB) because its transition to the true solid state occurs at 59.5°C and it will readily undercool to room temperature. This means that all of our solidification experiments can be performed near room temperature. Some of the physical and chemical parameters for 10 OCB are listed in Table 3.1.

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_n \begin{array}{c} \text{O} \\ \text{C} \equiv \text{N} \end{array} \\
\text{n CB}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_n \begin{array}{c} \text{O} \\ \text{C} \equiv \text{N} \end{array} \\
\text{n OCB}
\end{align*}
\]

\[
\begin{align*}
\text{O}-\begin{array}{c} \text{C} \equiv \text{N} \\
\end{array} \\
\text{10 OCB}
\end{align*}
\]

Figure 3.1: The cyanobiphenyl family of liquid crystals. The cyanobiphenyls (nCB’s) and oxycyanobipheyls (nOCB’s) have the structures indicated. One example is 10 OCB.

<table>
<thead>
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<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical name</td>
<td>—</td>
<td>4-cyano-4'-decyloxybiphenyl</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Formula</td>
<td>—</td>
<td>C(<em>{23})H(</em>{29})ON</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>(M_{100\text{CB}})</td>
<td>335.49</td>
<td>g/mol</td>
<td>—</td>
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<td>—</td>
<td>70247-25-5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Density (solid)</td>
<td>(\rho)</td>
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<td>g/cm(^3)</td>
<td>[146]</td>
</tr>
<tr>
<td>Thermal diffusivity (SmA)</td>
<td>(D_h)</td>
<td>(\sim 10^{-3})</td>
<td>cm(^2)/s</td>
<td>[108]</td>
</tr>
<tr>
<td>Specific heat (SmA)</td>
<td>(c_p)</td>
<td>(\sim 2)</td>
<td>J/g°C</td>
<td>thesis</td>
</tr>
<tr>
<td>Latent heat of solidification</td>
<td>(L)</td>
<td>115</td>
<td>J/g</td>
<td>thesis</td>
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<td>°C</td>
<td>[107]</td>
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<tr>
<td>Smectic A-isotropic transition</td>
<td>(T_{\text{SmA-I}})</td>
<td>84</td>
<td>°C</td>
<td>[107]</td>
</tr>
</tbody>
</table>

Table 3.1: Properties of 10 OCB.

In most of the experiments to be discussed here, the 10 OCB was used as purchased
with no additional purification. The major impurity is expected to be water which has a 0.15% solubility limit in 10 OCB. Studies with purified 10 OCB as well as samples in which impurities were deliberately added showed the same behaviour.

Of course, one complication in using a liquid crystal is that solidification occurs from the supercooled liquid crystal phase instead of from a supercooled, isotropic melt. As we will see, the anisotropy of this "melt" seems to have no qualitative effect on solidification.

3.1.2 Sample cells

The samples used in this study usually consisted of a thin layer of 10 OCB sandwiched between two glass plates, as indicated in Fig. 3.2. In many cases, no spacer was used, resulting in a sample thickness between 8 and 10 μm. The wire spacers, when used, ranged in thickness between 12.5 and 120 μm. Sample cells with spacers were glued together [109] while applying even pressure to ensure parallel glass surfaces. As shown, the bottom plate was chosen to be slightly larger than the top one, allowing the cell to be glued without any glue spreading to the underside of the cell, which would affect the thermal contact with the oven. The size of the bottom plate was usually chosen to be 25 mm to allow it to fit into the temperature control stage.

In most cases, we used thin glass plates (cover slips ~170 μm thick) to allow thermal diffusion times to be as short as possible. This is important both to allow the system to reach equilibrium quickly when it is first undercooled to the desired temperature as well as to allow fast response to changes in the undercooling. Studies with glass plates 1 mm thick gave similar results; differences could be attributed to longer time constants of the glass.

Glass cleaning

When preparing samples for liquid crystalline materials, it is essential to use extremely clean surfaces. This makes chemical treatment for the desired anchoring (see below) characteristics far more reliable. Good results were obtained with the following procedure:

I first rinsed the plates for about one minute to remove large dust particles. The first washing stage consisted of rubbing in soapy water. After this, plates were placed in beakers small enough (10 and 20 mL) to force the plates to stand vertically and only make contact with the beaker at a few points on the bottom and sides of the beaker. To avoid contamination, the plates remain in the beakers for the remainder of the cleaning procedure.
CHAPTER 3. EXPERIMENTAL METHODS

The plates and beakers are rinsed by filling with distilled water 20–30 times. Next, the beakers are filled with acetone and placed in an ultrasonic cleaner at 60°C for 20 minutes. This is followed by another cycle of 20 rinses.

For the final washing stage, the beakers are filled with a soap solution [110] and ultrasonicated at 60°C for a full hour. The soap solution is removed by a cycle of 50–100 rinses in distilled water followed by 10–20 rinses in distilled, de-ionized water.

Most of the water is removed from the slides by blowing dry nitrogen across the surface. The plate is then returned to the beaker and placed in an oven at 120°C for one hour.

**Anchoring**

Since liquid crystal phases are anisotropic, it is necessary to induce an alignment direction to achieve a homogeneous sample. The induced alignment is referred to as the anchoring and is usually accomplished by treating the walls of the sample container. The interaction of liquid crystal molecules at the surface is usually sufficient to cause a stable orientation (which may, in general, be position-dependent) through the bulk of the material.
10 OCB has only one liquid crystal phase: the smectic A phase described in Section 2.7. In most cases, we wanted the layers of the smectic to be parallel to the glass plates — a situation known as homeotropic anchoring. In homeotropic anchoring, all directions within the smectic plane are equivalent, so we expect no favored directions within the plane of the sample cell during subsequent solidification experiments. Another possibility would be to anchor the material so that the molecular axes lie in the plane of the sample, resulting in smectic planes perpendicular to the cell. This form of anchoring is called planar anchoring.

To achieve homeotropic anchoring, we treated the plates with an organosilane [111]. Organosilanes have the generic structure $R_nSiX_{4-n}$, for $n = 1-4$. Here, $X_i$ denotes a group such as Cl, or a methoxy or ethoxy group, which can hydrolyze in the presence of water, while the $R_n$s are non-hydrolyzable groups. Typical organosilanes for liquid crystal anchoring have the structure $RSiH_2OCH_3$. In the presence of water, the methoxy group dissociates according to

$$RSiH_2OCH_3 + H_2O \rightleftharpoons RSiH_2OH + CH_3OH.$$ 

The resulting silanol molecule can then bond to SiOH groups on a glass surface by the condensation reaction

$$RSiH_2OH + SiOH \xrightarrow{\text{condensation}} RSiH_2 - O - Si + H_2O.$$

The properties of the modified surface are determined by the choice of the $R$ group. For anchoring liquid crystals, one of the organic groups will often be an organic chain which sticks out of the surface, promoting a similar orientation in liquid crystal molecules at the surface.

In order to achieve this anchoring, we used a 1% solution of the organosilane ZLI 2510 [112] in a 50/50 solution of toluene and dichloroethane. The beakers containing the glass plates were filled with this solution and left standing for about 1 minute. The silane solution was then returned to the bottle for re-use and the plates allowed to stand in a humid environment for another minute to promote hydrolysis of the silanes. The solvent was removed by transferring the beakers to an oven at $\sim 70^\circ C$ for 20 min. Note that care must be taken to limit the exposure of the silane solution to water to prevent the silane molecules from bonding with each other to form dimers. In practice, a fresh solution needed to be made every six months from organosilane stored in an argon atmosphere.

A peculiarity in this surface treatment is that anchoring was usually improved if the silanated plates were rubbed firmly with a paper cloth [113] before use. This presumably
CHAPTER 3. EXPERIMENTAL METHODS

removed any organosilane which precipitated from the evaporated solution without chemically bonding to the glass. Plates with a good silane coating felt noticeably more slippery than plates with an uneven coating.

For a few experiments, we wanted planar anchoring. This was achieved by slowly drawing (~1 mm/min) the plates from a beaker containing a polyimide solution [114]. This forms a thin layer with polymer molecules aligned roughly in the drawing direction. Baking in an oven at 150°C removed the solvent and promoted polymerization and chemical bonding with the glass. The interaction between this layer and the 10 OCB causes the liquid crystal molecules to align parallel to the surface. The surface is gently rubbed with a fine cloth (controlled mechanically for consistency [115]) in the drawing direction to select the anchoring direction.

Filling

Once the glass plates have been cleaned and treated, and sample cell built, the final step is to fill the cell with the liquid crystal. For cells with a spacer, this was done by heating the cell to ~90°C and placing a small amount of solid 10 OCB at an open edge. The 10 OCB would melt into the isotropic phase and flow into the cell by capillary action.

For cells without a spacer, the bottom plate was heated and a small amount of 10 OCB added to the center. Once the 10 OCB was melted, the second plate was placed on top, momentarily cooling the sample into the smectic phase. When the system again reached the isotropic phase, the 10 OCB would spread evenly below the top plate.

3.2 Instrumentation and apparatus

Several techniques were employed to study the growth morphologies seen during solidification. Most of these were standard techniques, which need not be described in detail. For instance, much of the imaging was done by optical microscopy. The electron microscope was also used for imaging solidified surfaces. Non-imaging techniques included grazing-incidence X-ray diffraction and differential scanning calorimetry (DSC). Details of the operation of these instruments will be given in Chapters 4 and 5.

One instrument that deserves more discussion is the atomic-force microscope.
3.2.1 Atomic-force microscopy

Since its invention in 1986, the atomic-force microscope [116] (AFM) has become an increasingly important tool for studying surfaces at the atomic level. A diagram of the AFM is shown in Fig. 3.3. Surfaces are imaged by means of a sharp tip attached to a weak cantilever spring. The deflection of the cantilever is measured, in our case, by the optical lever technique [117]. In this method, cantilever deflection is measured by sensing the motion of a laser beam reflected from the cantilever using a position-sensitive dual-photodiode detector. This device measures the position of the laser beam as the difference between intensity measured by two diodes separated by \( \sim 10 \ \mu \text{m} \). A feedback loop is used to maintain a constant deflection as the sample is raster scanned below the tip by a piezoelectric actuator. The vertical motion necessary to achieve this constant deflection as the sample moves under the tip provides a measure of the surface topology.

The key to the success of the AFM lies in the construction of the cantilever and tip. These are usually fabricated as an integral device from silicon or \( \text{Si}_3\text{N}_4 \) using lithographic techniques. This makes it possible to produce tips which terminate in points with radii of curvature \( <100 \ \text{Å} \) [118]. The cantilevers themselves are typically 50–100 \( \mu \text{m} \) long, 2 \( \mu \text{m} \) or less thick, and have spring constants as small as 0.02 N/m. These small tips and delicate springs allow surfaces to be imaged at near-atomic resolution. Unlike its close cousin, the scanning tunneling microscope (STM), the AFM is able to image non-conducting samples. An advantage over techniques such as electron microscopy is that little or no sample preparation beyond mounting is required.

Despite this ease of use, there are obstacles to obtaining quantitative information from the atomic-force microscope. Most notable is the fact that despite its apparent similarities with the STM, atomic resolution is rarely achieved. This is essentially due to long-ranged forces such as the van der Waals force which act between the tip and sample. These forces, which are usually attractive, cause the tip to contact the sample in a finite area (typically \( >30 \ \text{Å} \) across), thus limiting the resolution [119].

In order to estimate the resolution or to make quantitative measurements of these long-ranged forces, we need to characterize accurately the properties of the cantilevers. Variability in spring constants and tip radii from cantilever to cantilever make it necessary to measure these parameters on an individual basis whenever quantitative work is performed.

Another difficulty with the AFM is that of calibration of the scanner. In order to
CHAPTER 3. EXPERIMENTAL METHODS

Figure 3.3: The atomic force microscope.
precisely move the sample by the small amounts required for sub-nanometer imaging, we used piezoelectric scanners. However, this results in motion that is not linear in the applied voltages and which depends on the previous scan history.

A fair amount of effort was placed into understanding and dealing with these limitations before the AFM was used for the experiments that are the main subject of this thesis [119, 120, 121]. As these details are not germane to the story of solidification morphologies, they are included as appendices.

3.3 Solidification experiments

There are two standard types of solidification experiments: free growth and directional solidification. In free growth, a sample in the liquid phase is cooled to a temperature below its equilibrium freezing point, causing it to freeze. In directional solidification, the sample is moved through a temperature gradient so that the liquid begins at a temperature above its freezing point and travels into a region below its freezing point.

These two techniques give complementary information: in free growth, we set the undercooling and allow the sample to choose a front velocity; in directional solidification, we choose the average front velocity and allow the front to stabilize at an undercooling appropriate for that velocity. In either case, the growth morphology is selected by the growth conditions.

3.3.1 Free growth

The standard arrangement for free growth is shown schematically in Fig. 3.4. A liquid is undercooled to a temperature set by a heat bath in contact with the sample walls. Although the undercooled liquid phase is metastable, the nucleation barrier ensures that solidification does not begin immediately. Once a critical nucleus is formed, the solid phase begins to grow, as in Fig. 3.4.

At this point, one could make several objections about the experiment. Most notably, one might be concerned that the generation of latent heat at the interface will raise the local temperature at the interface, resulting in growth at an unknown undercooling which is smaller than the one set by the heat bath. We will see in Section 3.3.3 that this problem can be partially avoided by using samples thin enough that most of the latent heat is conducted
Figure 3.4: Experimental arrangement for free growth. Solidification occurs in a liquid held at a temperature below the freezing point by the sample walls which are in contact with a heat bath.

away by the cell walls rather than by the sample. We will also see that when the glass plates of the sample are thick and the undercooling large, we cannot neglect the latent heat.

Another concern is that the initial growth form may not resemble the morphology observed at asymptotically long times. The initial morphology may differ because of the relatively high curvature at the nucleus, as well as transients in impurity concentration and flow fields before a steady state is established. In most cases, we will be considering growth at distances far enough from the nucleus that we need not worry about initial transients, though there will be exceptions.

The actual free growth experiments were performed with the experimental set-up sketched in Fig. 3.5. Solidification occurs at the temperature maintained by a computer-controlled hot stage [122] with a heater plate holding the temperature above a point set by a water bath [123]. The purpose of the water bath is to allow rapid cooling when fluctuations increase the temperature above the set-point. The sample is placed in a copper cell with a \(\sim 2\) mm hole to allow observation, which is placed inside the oven. Once the cell is inserted and the oven lid closed, an insulated teflon box with a glass window (not shown in Fig. 3.5) is placed over top. With this arrangement, temperature stability of 10 mK and temperature gradients of the order of 10 mK/mm (inferred from interface shapes [124]) were typical.

In a typical experiment, the sample is heated into the isotropic phase for \(\sim 30\) s to remove
Figure 3.5: Exploded cross-section of the experimental set-up for a free growth experiment. A sample in the isotropic phase is transferred to a sample holder in a temperature controlled oven. Visualization of the resulting growth is by means of an optical microscope.
all traces of structure from previous experiments. At this point the insulation, oven lid, and sample holder lid are removed from the temperature stage. The sample is then quickly transferred to the sample holder and the oven reassembled. The solid phase nucleates at random points and is observed by optical microscopy [125].

As most of the experiments were performed in a temperature range between 20 and 50°C, the perturbation to the oven temperature was usually small enough that the oven relaxed to its initial state before solidification started.

In some cases, the field of view allowed by the microscope was too small to adequately estimate the direction and magnitude of the solidification velocity. This typically occurred at small undercoolings, where the growth front becomes very rough. For experiments at these high temperatures, the microscope was replaced with a camera lens [126]. In this case, the cover of the sample holder had to be omitted to allow a larger region of the sample to be imaged.

A final modification was made in order to investigate the dynamics of the front morphology. In this arrangement, the sample holder was replaced by a movable “tongue” attached to an (x, y) translation stage. This allowed the sample to be moved in order to keep the front in view for a long period, allowing observations while the oven temperature was changed. Of course, in this arrangement the sample is in poorer contact with the heat bath, resulting in large temperature gradients and long time constants before changes in temperature manifested themselves by changes in the growth morphology.

3.3.2 Directional solidification

Another class of solidification experiments is that of directional solidification. The essential idea of this type of experiment is illustrated by Fig. 3.6. A sample initially at a temperature above the freezing point (usually well above, in our case), is driven at constant velocity through a temperature gradient and ends up at a temperature below its freezing point.

In practice, part of the sample usually begins in the solid phase at the cold side of the gradient. This eliminates the need to wait for nucleation to occur before solidification can be observed. After the motion starts and initial transients die away, a steady-state growth front is seen. In a steady state, the front establishes itself at a constant position and temperature within the gradient, which conveniently results in a front that is stationary in the laboratory frame.
CHAPTER 3. EXPERIMENTAL METHODS

Figure 3.6: Directional solidification apparatus. In directional solidification, the sample is pushed through a temperature gradient at a constant velocity. Here, the undercooling is unspecified, allowing the growth front to adopt one appropriate to the velocity.

The main weakness of the directional solidification method is that it is difficult to determine the undercooling at the interface. The position and magnitude of the temperature gradient is affected by the heat conductivity and velocity of the sample, as well as by the control temperatures. The magnitude of the gradient in our apparatus under typical conditions has been measured [127]. In this work, I made no attempt to measure interface undercoolings in directional solidification experiments.

3.3.3 Temperature rise at the interface

One of the goals of this work is an accurate measurement of solidification velocities in free-growth experiments as a function of undercooling. Thus, accurate measurements of the local interface temperature are needed. The thin-sample geometry allows the latent heat released by the growing solid to be removed through the glass walls of the sample cell, rather than through the sample itself. This allows a constant growth velocity, rather than one that slows with time, as discussed in Section 2.3.1. However, the latent heat will result in a constant interface temperature which is higher than the heat bath temperature. I will estimate this temperature rise in a manner previously described in the literature [128].

We begin with the assumption of a planar interface of thickness $d$ in the $y$-direction propagating at a constant velocity $v$ in the $x$-direction, as shown in Fig. 3.7a. We take the
length of the front in the \( z \)-direction as infinite. By transforming to the frame moving with the front, as discussed in Section 2.3.1, we find that the temperature field must satisfy the diffusion equation

\[
D \nabla^2 T + v \frac{\partial T}{\partial x} = 0. \tag{3.1}
\]

We will take the diffusion constant as equal for both glass and sample. At large distances, the temperature must be equal to \( T_\infty \), the bath temperature.

![Sample geometry for the interface temperature estimate. (a) Side view of a planar front of thickness \( d \) (and infinite length along the \( z \)-axis) moving along the \( x \)-axis with velocity \( v \). (b) Approximation treating the interface as an infinite cylinder with circumference \( d \) stationary in a conductive medium, which is moving to the left with velocity \( v \).](image)

If we assume a solution to Eq. 3.1 of the form

\[
T = T_\infty + u(x, y) e^{-x/\ell}, \tag{3.2}
\]

where \( \ell = 2D/v \), we find that \( u \) must satisfy the equation

\[
\nabla^2 u - \frac{1}{\ell^2} u = 0. \tag{3.3}
\]

If we approximate the front as a cylinder of circumference \( d \), as shown in Fig. 3.7b, it is convenient to work in cylindrical coordinates. If we further assume that the temperature is
constant on the cylinder, \( u \) must be a function of the radial coordinate only. In cylindrical coordinates, the equation for \( u(r) \) is then

\[
r^2 \frac{d^2}{dr^2} u + r \frac{d}{dr} u - a^2 r^2 u = 0, \tag{3.4}
\]

where \( a = 1/\ell \). This is a modified Bessel equation of order zero, which has the general solution

\[
u(r) = A I_0(ar) + B K_0(ar), \tag{3.5}
\]

where \( I_0(x) \) and \( K_0(x) \) are the modified zeroth-order Bessel functions of the first and second kind \([129]\).

The function \( I_0(x) \) diverges for large \( x \), so \( A = 0 \). The constant \( B \) is determined by a boundary condition at the interface. Solidification generates latent heat at the interface at a rate of \( Lvd \) per unit length (here, \( L \) is the latent heat per unit volume). For a steady state, this heat must be transported away from the interface. The temperature gradient at the interface causes a heat flux of \( J = \kappa T \vec{v} T \), where \( \kappa_T \) is the thermal conductivity. Note that \( \kappa_T = D \rho C_p \), where \( \rho \) is the material density and \( C_p \) is the heat capacity at constant temperature per unit mass. Thus, the condition of heat conservation at the interface is

\[
Lvd = -2\pi r_0 \kappa_T \frac{\partial T}{\partial r} \bigg|_{r=r_0}, \tag{3.6}
\]

where \( r_0 = d/2\pi \) is the radius of the cylinder.

If \( ar \ll 1 \), we can use the approximation \( K_0(x) \approx -\ln x \) \([129]\) to determine \( B \). We then find that \( B = Lvr_0/\kappa_T \) so that

\[
T = T_\infty + \frac{Lvr_0}{\kappa} e^{-ax} K_0(ar) \tag{3.7}
\]

throughout the system. The temperature rise at the interface is then

\[
\Delta T = \frac{Lvd}{2\pi D \rho c} \ln \frac{vd}{4\pi D}, \tag{3.8}
\]

again assuming \( ar \ll 1 \).

Note that a more accurate estimate could be made by integrating the Green's function for this problem (which is simply the modified Bessel function \( K_0 \)) over the interface in Fig. 3.7a. This would also provide the temperature distribution across the solidification front. For the purposes of our discussion, the estimate provided by Eq. 3.8 will be sufficient.
For a sample thickness of 10 μm Eq. 3.8 predicts a temperature rise of ~0.08°C at 
v = 10 μm/s and ~0.6°C at v = 100 μm/s, using the values listed in Table 3.1. The 
temperature rise at 10 μm/s is not much larger than the fluctuations in the temperature 
control. Even the rise of 0.6°C is not large compared to the 20°C undercooling required 
to achieve growth velocities of 100 μm in our samples. For a cell of thickness 100 μm and 
a solidification velocity of 100 μm/s, the temperature rise will be ~4°C, which may be of 
more concern.
Chapter 4

SOLIDIFICATION MODES AND MODE TRANSITIONS

As we have seen in Chapter 2, the form that a material takes on freezing depends on the solidification conditions. I chose to study the solidification behaviour of 10 OCB because of the rich variety of solidification morphologies exhibited by this material.

In this Chapter, I present our studies on the solidification modes and mode transitions of 10 OCB. In the first section, I describe the various growth modes observed when 10 OCB is solidified at different undercoolings. The second section examines the transitions between modes. Next, I discuss the effect of control parameters other than the undercooling. This is followed by a brief discussion of X-ray diffraction results. Finally, the results are summarized in Section 4.5.

4.1 Growth modes

Aside from the material properties, there are many parameters that can be important in the solidification of a material. For instance, we might be concerned with undercooling, impurity concentration, stirring of the melt, pressure, and thermal conductivity of sample walls. In this study, the main control parameter will be the undercooling, although I will briefly discuss the effect of impurities and thermal conductivities. The sample size will also turn out to be important because it controls the rate at which heat can be conducted out of the sample.
The first hint of the variety of modes available for solidification in 10 OCB can be gleaned from the following very simple experiment: when a sample being solidified at high speed in a directional solidification apparatus is suddenly stopped, the solidification front, which is initially at a finite undercooling, continues to move until it reaches a point in the temperature gradient where the interface temperature equals the equilibrium melting point. It can then freeze no further, so the front velocity must relax to zero. In the case of 10 OCB, the texture of the solidified material changes several times as the velocity decreases from \(\sim 150 \mu m/s\) to zero. This is shown in Fig. 4.1.

![Figure 4.1: Growth morphologies exhibited by 10 OCB when the solidification velocity is decreased to zero from \(\sim 150 \mu m/s\). This is collage of several optical micrographs spanning the region of decreasing front velocity. The growth direction was to the right. Note that the change in texture as the velocity changed required the light level to be adjusted twice during this sequence.](image)

Although directional solidification is useful for rapidly scanning the various solidification modes and for growing oriented samples, it is difficult (though not impossible [131]) to determine the undercooling corresponding to a non-zero front velocity. Thus, we mostly studied solidification by free growth, where an undercooling is imposed and the sample chooses its front velocity and growth morphology.

We photographed the solidification fronts for undercoolings up to \(40^\circ C\) (corresponding to a dimensionless undercooling of \(\Delta \sim 0.7\)). The procedure, as discussed in Section 3.3.1, was
to transfer a sample, initially in its isotropic liquid phase (at ~90°C), into a temperature-controlled oven set at the desired undercooling. It is difficult to extend the measurements below room temperature (40°C undercooling) as this generally causes the solid phase to nucleate before the sample has cooled to the oven temperature, resulting in growth at an unknown undercooling. Measurements at low undercooling (< 5°C) were limited by the decreased rate of nucleation and slow rate of growth near the freezing point of the material (59.5°C). In any case, no evidence of new growth modes at higher or lower temperatures was ever seen.

A collection of micrographs of 10 OCB solidification fronts is shown in Fig. 4.2. In order to maintain consistency with our first publication on this solidification system [130], these pictures are labeled modes A through F.

Several of these growth modes are similar to morphologies seen in other materials. Faceted needle crystals (mode B) have been seen in many materials. Similarly, dendrites with sidebranching (mode C) are a common growth mode and are characteristic of diffusion-limited growth seen in materials including inorganic salts, organic solids, and metals. Spherulitic growth (modes E and F) is important in the solidification of many materials and will be the subject of Chapter 5.

4.2 Mode transitions

In this section, we take a closer look at the mode transitions with the dual aim of verifying that discontinuous changes in the growth morphology do occur and attempting to understand the rules governing such changes. First we will discuss the optical measurement of the interface velocity and structure. These measurements will then be used to study apparent morphology transitions. Finally, I summarize the results.

4.2.1 Velocity and roughness measurements

One of the most important parts of the optical analysis was the accurate measurement of front velocities. The front velocities were obtained by measuring the change in front position over several frames of digitized movies recorded by computer using a CCD video camera [132] and frame grabber [133].

Once the images were stored, we measured the location of the fronts by digital image processing techniques. The procedure is illustrated in Fig. 4.3. First, the pixel values of
Figure 4.2: Collection of micrographs of 10 OCB solidification fronts. Each micrograph is the result of a separate experiment performed at the indicated undercooling. (A) Mode A. At small undercooling, the growth is in the form of tangled fibres. (B') Mode B'. In this mode, long straight needle crystals travel ahead of a front that otherwise resembles mode A. (B) Mode B. In this undercooling range, the front consists of large needle crystals. (C) Mode C. At larger undercooling, growth is in the form of dendrites with sidebranching. (D) Mode D. The crystals of mode D are of a size comparable to those of mode C, but are often seen to bend. Branching occurs at non-crystallographic angles, unlike the sidebranching seen in mode C. (E) Mode E. The crystals seen in mode E are too small to see optically, resulting in a front that appears smooth. (F) Mode F. At still larger undercooling, the crystals, which are still too small to see optically, are arranged in a banded pattern. This growth mode is known as banded spherulitic growth. Note that the scale of image (F) differs from that of (A)-(E).
each frame are divided by the corresponding pixels of a background image which was taken before the solidification front reached the field of view of the camera. This removes spatial variations in intensity across the image, whether they be due to uneven illumination or scratches and dust on the sample surfaces. Next, the image is thresholded at an intensity level between those of the solid and smectic A phases [134]. This level was chosen by hand, but usually the intensities are different enough that the exact choice of level in a fairly large range has negligible effect on the measured position of the front. Scattering from the inhomogeneous solid phase generally causes it to appear darker than the well aligned smectic. At this point, all regions completely surrounded by solid regions are filled in. This prevents intensity variations within the solid from appearing as false interfaces, but has the drawback of ignoring pockets of unsolidified material enclosed by the advancing front. The resulting binary image is "eroded," removing all pixels which border at least one white pixel of the smectic phase. The front is then taken to be the set of eroded points.

Once the set of pixels comprising the front has been determined, its change in position over time needs to be measured to determine the velocity. This was done by fitting a circular arc to each set of interface points. This is possible because the sample cell is small enough that any domain must nucleate close enough to the field of view of the microscope that its overall envelope shows a noticeable curvature about the (offscreen) nucleation point. This could be reliably done for the relatively smooth interfaces seen in modes E and F. In other cases, with rougher growth fronts, the center of the best fit circular arc was dependent on the range of points used by the fit and was quite different for different frames of the video sequence. In order to deal with this problem, the center of the fit was forced to lie at the average of a first set of fits, after which only the radius of the arc was allowed to vary. A plot of this radius for each frame against time then yields the average front velocity. An example of this analysis is shown in Fig. 4.4.

There are a few subtleties in this procedure that are worth mentioning. First, the chi-squared value, \( \chi^2 \), which is minimized by standard curve fitting algorithms is calculated by summing the squares of the vertical distances between the data points and the model curve. In other words, for data points of the form \((x_i, y_i)\), and a model curve of the form \( y = f(x) \), the \( \chi^2 \) is defined as

\[
\chi^2 = \sum_i \frac{(y_i - f(x_i))^2}{\sigma_i^2},
\]

where \( \sigma_i \) is the uncertainty in the value of \( y_i \). This measurement of \( \chi^2 \) can give very poor
Figure 4.3: Measurement of the solidification front location. (a) Digitized image of the solidification front. The growth direction is indicated by the arrow. (b) Background image. (c) Normalized image of solidification front obtained by dividing (a) by (b). (d) Thresholded image differentiating between the solidified material (black) and the smectic A phase (white). (e) Image (d) with all points enclosed by the front set to black to remove noise. (f) Pixels at the boundary between the phases (obtained from an exclusive OR between image (e) and the erosion of image (e)). (g) Boundary superimposed on the original image (a).
Figure 4.4: Measurement of the solidification front velocity. (a) Set of pixels on the solidification front for several frames spaced at 2 second intervals (intervening fronts spaced at 0.5 s are omitted for clarity). A rotation to a horizontal orientation has been performed. (b) Circular arc fit to the top interface of (a). (c) Plot of radius vs. time to determine the average growth velocity.

\[ v = 57.7 \, \mu m/s \]
results for sections of circular arcs, essentially because it neglects uncertainties in the values of \( x_i \) — if the derivative \( \frac{dy}{dx} \) is large, a small change in \( x_i \) results in a large change in the \( \chi^2 \). The obvious answer is to measure \( \chi^2 \) in terms of the radial distance of data points from the fit arc. However, we found that we could obtain good results simply by ensuring that the data points were aligned as close as possible to a horizontal direction. This was accomplished by a rigid rotation of all of the data points, as in Fig. 4.4.

Another problem is that, due to thermal gradients in the solidification stage, the growth velocity was not exactly uniform across the cell. As a result, the growth fronts were not quite circular. This effect was not noticeable for the 1 mm field of view of the microscope at low power, but can be seen in images captured with the camera lens (cf. the discussion of the mode B' transitions, below).

Finally, for very rough interfaces, as are seen in modes A, B', and B, as well as at the small undercooling ends of the mode C and mode D regions, it was difficult to fit the interface reliably.

Both the problem of thermal gradients and the problem of rough interfaces presented little difficulty to the measurement of the front velocity. As long as the data points were roughly along the \( x \)-axis, so that the center of the arc was near the \( y \) axis, the precise location of this center had little effect on the estimated front velocity. Therefore, even poor fits were useful. The main difficulty is in obtaining a consistent estimate of the interface roughness.

It is clear from Fig. 4.2 that the interface roughness changes with undercooling and with the growth mode. We measured the roughness of the growth fronts in three ways. The first method was to simply measure the root-mean-square values of the deviations of the data points from a fit to the interface. Though the location of the center of the circular arcs fit to the front had little effect on the velocity estimate, it did have a large effect on the roughness measurement. For this reason, we chose to measure the RMS deviations from a quadratic fit to the data. As individual parabolas were fit to each front in a growth sequence, without regard to trends in the growth direction, this has the effect of neglecting contributions to the true interface roughness on length scales comparable to the image size.

One complication of this roughness measurement is that for very rough fronts, the interface cannot be represented as a function, due to the overhang of individual tips. Usual methods of roughness analysis can therefore not be employed. One remedy is to convert the points into a single-valued function by representing the interface by its envelope. This
was done by selecting the points at the largest radius from the average fit center discussed above, to obtain a function in polar coordinates: \( r(\theta) \). An example is shown in Fig. 4.5. The RMS values of these functions can be used to characterize the roughness.

The RMS values of these functions can be used to characterize the roughness.

![Figure 4.5: Growth front envelope. (a) Growth front shown in Fig. 4.3. (b) Envelope of growth front. Note that the envelope tends to broaden non-vertical features.](image)

The final measure of the roughness was to estimate the fractal dimension of the interface. The fractal dimension of a one-dimensional curve in a two-dimensional image is a measure of how the length of the curve scales with the scale on which it is measured. More precisely, the fractal dimension \( D \) of such a curve can be defined as [135]

\[
D = -\lim_{\epsilon \to 0} \frac{N(\epsilon)}{\epsilon},
\]

where \( N(\epsilon) \) is the number of squares of edge \( \epsilon \) on a fixed grid required to cover the curve (i.e. the number of squares on such a grid which contain at least part of the curve). (Of course, this definition can be extended to higher-dimensional objects simply by using a grid with an appropriate dimension.) With this definition, the fractal dimension of a straight line or a circle will be 1, whereas the fractal dimension of a disk will be 2. For most real objects, the length or surface area depends on the resolution used in the measurement. For fractal objects, the value of \( D \) given by Eq. 4.2 is constant over almost two orders of magnitude for \( \epsilon \). Clearly, this value cannot be constant to atomic dimensions for real objects; however, we
found that our interfaces were approximately fractal over the length scales we are concerned with, as shown in Fig. 4.6.

Figure 4.6: Fractal dimension of interfaces. A log-log plot of the number of boxes required to cover the interface vs. the box size can be used to estimate the fractal dimension of the interface. The interface used in this example is shown in Fig. 4.3. The slope of the straight line indicates that the growth front has a fractal dimension of approximately 1.4, at the scale of the image.

One might argue that none of these schemes provides a complete description of the growth front. However, we will see that each of these provides a very clear signal of sudden changes in the growth morphology.

As mentioned earlier, one of the reasons for using 10 OCB for these solidification experiments is that its natural solidification time-scale allows many experiments to be performed, leading to a high degree of accuracy. The danger in acquiring large amounts of data, is that one is then obliged to analyze it. The velocity and roughness analysis was largely automated [136, 137, 138].

4.2.2 The growth velocity curve

It is not obvious from the pictures in Fig. 4.2 alone whether there are fundamental differences between the growth modes or whether the morphology changes smoothly with undercooling, making the boundaries between these modes subjective. In order to resolve this issue, we can measure interface quantities as a function of undercooling. For example, Fig. 4.7 shows the growth velocity as a function of undercooling. This curve can be divided into sections
corresponding to the different modes illustrated in Fig. 4.2. Note that the boundaries
between modes are the points where the curve or its derivative are discontinuous. This
claim will be further justified in Section 4.2.

4.2.3 The C–D and D–E transitions

Let us start in the middle, in the regions labeled modes C–E in Fig. 4.7. An expanded
view of this region, as shown in Fig. 4.8a, suggests that the slope of the velocity curve
is discontinuous near $\Delta T = 15^\circ C$ and $\Delta T = 18.5^\circ C$. These apparent discontinuities are
accompanied by an obvious change in the growth morphology, as illustrated by the sequence
of micrographs shown in Fig. 4.9. The data point symbols in Fig. 4.8 indicate the growth
mode corresponding to each point, based on the apparent morphology. The pictures in
Fig. 4.9 suggest that the change in growth morphology is accompanied by a change in the
interface roughness. This is illustrated by Fig. 4.8b and c. The estimated fractal dimension,
shown in Fig. 4.8d, also indicates sharp changes in the front morphology.

Additional evidence that the growth modes C–E are, indeed, distinct can be found by
observing a stable growing front when the undercooling is suddenly changed to a value
favoring a different mode. For example, Fig. 4.10 shows a typical sequence during the
transition from mode C to mode D. When the undercooling is increased, needles of mode D
appear and grow ahead of the smooth mode C front. When these grow far enough ahead of
the front, they branch, allowing the new mode to spread laterally and eventually take over
the growth.

Similarly, when the undercooling of a mode D front is decreased to a value where mode
C would normally be observed, the transition to mode C takes place by nucleation and
lateral spreading, as illustrated by the sequence of images in Fig. 4.11. The sudden change
in growth morphology and the necessity of the new mode to nucleate and grow laterally
clearly indicate that modes C and D are distinct growth modes and not merely different
expressions of the same mode. The increase in $dv/d(\Delta T)$ at the transition indicates that the
selection between modes C and D always favors the fastest growing mode, as hypothesized
in Section 2.6.

Transitions between modes D and E also support the “fastest mode wins” hypothesis.
However, the nature of the transitions is not as clear. In Fig. 4.9e–g, we see that as the
undercooling is increased, less and less of the front is made up of mode D needles, while
more and more is composed of the very smooth mode E. Apparently, modes D and E coexist
Figure 4.7: Growth velocity of 10 OCB as a function of undercooling. Note that separate branches of this curve are marked by discontinuities in slope and, in some cases, in the curve itself. The labels indicate the modes illustrated in Fig. 4.2. The data points at small undercoolings were measured using a camera lens in place of the microscope to provide a larger field of view.
Figure 4.8: Velocity and roughness data for modes C–E. The symbols for the data points indicate the growth morphology, as determined from images such as those shown in Fig. 4.9. (a) Velocity as a function of undercooling. Note the apparent discontinuities near $\Delta T = 15^\circ C$ and $\Delta T = 18.5^\circ C$. (b) RMS roughness of the growth front as a function of undercooling. Note the sudden changes in roughness at the discontinuities in the velocity curve. Sudden changes also occur in measures of (c) the RMS roughness of the radial envelope of the front and (d) estimates of the fractal dimension of the front.
Figure 4.9: Sequence of front morphologies for modes C–E. Each of the frames (a)–(g) shows the front morphology at the undercoolings indicated. Beginning with mode C in frame (a), we see that the growth front gets smoother with increasing undercooling until frame (d), where the interface has become very rough and has a morphology clearly distinct from that of (a)–(c). This is mode D. As the undercooling increases still further, the front again becomes smoother until very few needles extend ahead of a macroscopically smooth front as in (f) (note the domain of smooth mode E in the upper right-hand corner). In frame (g), the front is composed entirely of mode E. The scale bar, corresponding to 200 μm, is the same for each image.
CHAPTER 4. SOLIDIFICATION MODES AND MODE TRANSITIONS

Figure 4.10: Transition from mode C to mode D. When the undercooling of a growing mode C front is suddenly increased to a value favoring growth of mode D (from $\sim 12^\circ C$ to $\sim 16^\circ C$), needles of mode D grow ahead of the mode C front and branch out to take over the front. The time interval between frames is 1s. (Scale bar is 200 $\mu m$.)

over a finite temperature range. The sharpness of the transition indicated by the velocity and roughness data is then somewhat surprising. The roughness data for mode D varies linearly until they reach the nearly constant value for mode E. The fractal dimension data in Fig. 4.8, at least, suggests a transition between two values over a 1$^\circ C$ range centered at an undercooling of 18$^\circ C$.

While the transition from mode E to mode D when the undercooling is decreased proceeds by a nucleation and lateral growth process, as illustrated in Fig. 4.12, the transition from mode D to E shows a different behaviour. Mode E forms regions throughout the sample long before mode D disappears. The needles of mode D become buried by the mode E front when they curve away from the direction normal to the mode E front. It appears that the tip velocity of the mode D needles remains at least as fast as the average velocity of the mode E front during this process. However, the average front velocity for mode D is less than that of mode E since the direction of this growth is not always the same as the
Figure 4.11: Transition from mode D to mode C. Mode C nucleates from mode D when the undercooling is decreased from $\sim 16^\circ$C to $\sim 12^\circ$C. The temperature was changed $\sim 1$ min before frame 1. The mode C region nucleates within mode D and pushes ahead of the mode D front. It is then able to branch laterally until it covers all of mode D. The interval between frames is 4s. The sample was moved every two frames to keep the front in view. The scale bar is again 200 $\mu$m.
average direction of the growth. This is shown in Fig. 4.13.

Figure 4.12: Nucleation of mode D from mode E. This frame shows two domains of mode D nucleating from the smooth front of mode E after the undercooling was changed across the transition point. The needles of mode D have grown ahead of the mode E front and have begun to branch.

One final note on the transitions between modes C, D, and E is that, near the transition points, the velocity curve in Fig. 4.8 appears to be double-valued with branches corresponding to the two modes involved in the transition. This is easily explained if we realize that even if only one mode is stable at a given undercooling, it will not necessarily be the mode that nucleates when solidification begins. This could be due, for instance, to differing nucleation barriers for the different modes or to changes in the temperature after growth has begun. The finite sample size then dictates that the expected mode may not nucleate before the growth front passes the field of view of the microscope. With a larger sample size, we would expect this to occur less frequently.

If the fastest-growing mode is always the one selected, we would expect an increase in the slope $dv/d(\Delta T)$ at each mode transition. However, it is not clear that this is always the case in the complicated velocity curve shown in Fig. 4.7. Therefore, we will need to examine each of the other transitions before forming any conclusions about the selection principles.
CHAPTER 4. SOLIDIFICATION MODES AND MODE TRANSITIONS

Figure 4.13: Transition from mode D to mode E. Mode E takes over the front as the mode D needles curve away from the growth direction and are buried by the advancing mode E front. The dark fibres in the solid region behind the front are mode D fibres that have already been buried.

4.2.4 The B–C transition

One region of Fig. 4.7 with an apparent decrease in slope is at the transition between modes B and C. From Fig. 4.2c and d, these two modes seem to be quite different. However, these two pictures were taken at well-separated undercoolings. An examination of the morphologies at intermediate temperatures, as well as the evolution when the growth temperature is changed does not show a sharp transition. Moreover, during a mode transition, no obvious nucleation point is seen: either nucleation occurs everywhere, or the transition is continuous.

What then is the difference between modes B and C? What I have labeled mode B generally consists of wide, faceted, crystals without side branches. These decrease in width with increasing undercooling. Mode C is characterized by crystals of nearly constant width throughout its region of stability. The crystals of mode C exhibit clear crystallographic sidebranching.

As with the analysis of transitions between modes C–E, we turn to a measurements of the growth properties. The velocity is plotted as a function of undercooling in Fig. 4.14a. We see that the front velocity increases with undercooling in the mode B limit, but remains essentially constant once we are well into mode C. However, this velocity curve is not particularly clean at the mode B end. This is because mode B growth is very rough, making it difficult to determine the average front position. The data shown in Fig. 4.14a.
were obtained using a camera lens, as described in Section 3.3.1, which provided a large enough field of view (~1 cm) to define the front at the expense of increased sensitivity to temperature gradients within the sample.

The front roughness, as measured from camera lens images, is plotted in Fig. 4.14b. The roughness curve seems to be continuous throughout modes B and C, but, like the velocity curve, the scatter makes it difficult to determine the precise behaviour.

The speeds of individual needles are shown in Fig. 4.14c. These were measured from the change in position of individual tips with time in movies imaged with the microscope at low power. As the individual needles, particularly in mode C, do not always grow in the direction of the average front growth, this measurement is not equivalent to the front velocity measurement in Fig. 4.14a (clearly, the front velocity must be less than or equal to the tip velocity). This measurement shows a kink between mode B and the constant velocity mode C. However, the associated change in slope in the front velocity curve seems to take place over a broader range.

The needle width, plotted in Fig. 4.14d, appears to be a continuous function of undercooling in this region, but may show a change in slope at the transition. Again, there is a fair bit of scatter in these data points. Observations of mode B needle growth show that these needles thicken as they grow and branch by a mechanism in which the tip splits into several smaller tips. This makes the determination of the maximum tip width difficult.

The crystallographic sidebranching mechanism for mode C is quite different from the branching shown by mode B. Another difference between the modes is the orientation. The needles of mode B are generally pointed along the growth direction. During the transition to mode C, the average tip-growth direction rotates until the tips align at an approximate 45° angle to the front. Fig. 4.15 shows this evolution between modes after the growth temperature was suddenly changed. Note, though, that some needles deep into the mode B regime do show some sidebranching, while not all mode C microcrystals exhibit sidebranches or an alignment away from the growth direction.

Despite the differences in the mode B and mode C morphologies, we measure a continuous evolution between modes. Thus, we are forced to conclude that modes B and C are not fundamentally different growth modes. Instead, they seem to represent different limits of a single growth mode. In mode B, wide needles form and branch by tip-splitting. In mode C, the individual crystals are much thinner and branch by dendritic sidebranching. The apparent transition between the two modes corresponds to the onset of sidebranching.
Figure 4.14: Front measurements for modes B and C. Note that (a) and (b) include data measured using both the microscope and a camera lens. The overlap of these two data sets shows that the two measuring procedures are consistent with each other. (a) Front velocity as a function of undercooling measured using low magnification images of the font obtained with a camera lens. The scatter in the data is primarily due to the roughness of mode B and temperature gradients in the sample cell, which are not as evident at higher magnifications. (b) Front roughness. The roughness was also measured from low-magnification camera images. (c) Tip velocity. The average speeds of individual tips along their growth directions is plotted as a function of undercooling. These were measured from series of frames imaged through the microscope. (d) Needle width. The maximum crystal width was estimated from series of microscope images at several undercoolings.
Figure 4.15: Tip rotation in the B-to-C transition. During this transition, the needles of mode B gradually bend. In this micrograph, this process has resulted in needles aligned away from the normal to the growth front. By the time the front is well into mode C, the needles are at an angle of approximately 45° to the front. The scale bar represents 200 μm.

Plausibly, the change in orientation of the individual crystals seen in mode B is due to the onset of sidebranching: growth will always be favoured in an average direction normal to the front because of temperature and impurity gradients generated by the solidification process. When crystallographic branching occurs at the nearly 90° angles, a rotation by 45° allows both the tips and sidebranches to grow at equal rates.

4.2.5 The E–F transition

Another region where the velocity curve shown in Fig. 4.7 exhibits non-trivial behaviour is near an undercooling of 23°C. We identify this region as the transition between mode E, for which the front velocity increases rapidly with undercooling for ΔT<21°C, and mode F, for with the front velocity increases less rapidly with undercooling. Again we ask: is the transition between these modes sharp? If so, what are the selection rules governing the transition?

As seen in Fig. 4.2, the microcrystals making up the solid are too small to resolve optically in modes E and F. Little structure can be seen in mode E. However, in mode F, we see a pattern of bands with a spacing of approximately 2 μm parallel to the front direction. This solidification mode is known as “banded spherulitic growth” and will be the subject of Chapter 5.
Although the velocity data in this region reveal a complicated function of undercooling, with a local minimum and maximum, they do not suggest a discontinuous transition. However, this observation does not rule out the possibility of a coexistence of modes E and F, resulting in a continuous evolution of properties between dissimilar modes. As the front is quite smooth for these modes, we cannot use the front roughness as an indicator for the mode transition, as we did for modes C–E. Instead, I have measured the wavelength and correlation length (in the growth direction) of the bands.

These quantities can conveniently be estimated from the autocorrelation of the optical data. For our purposes, we can define the two-dimensional autocorrelation function (ACF) as

\[ C(r) = \langle (I(r_0 + r) - \bar{I})(I(r_0) - \bar{I}) \rangle, \tag{4.3} \]

where \( I(r) \) is the image intensity at position \( r \), \( \bar{I} \) is the average intensity, and the average is over all positions \( r_0 \) of the image. The autocorrelation function measures the average structure in a two-dimensional function, here the intensity of an image. The ACF will be maximum at values of \( r \) for which points in the original image that are separated by the vector \( r \) tend to have similar values. Thus, the ACF is able to reveal periodic structures, as well as the characteristic length over which a 2D image is correlated. The definition for the ACF given in Eq. 4.3 is essentially a convolution integral of the intensity function. If we recall that the Fourier transform of the convolution of two functions, \( f \) and \( g \), is equal to the product of their Fourier transforms, \( F \) and \( G \), respectively, i.e.

\[ \mathcal{F}\left\{ \int_{-\infty}^{\infty} dr \, f(r-r_0)g(r) \right\} = FG, \tag{4.4} \]

we see that the ACF of the intensity function, \( I(r) \), is simply the inverse Fourier transform of the magnitude squared of the the Fourier transform of \( I \). Since the magnitude squared of the Fourier transform of a function is simply its power spectral density (PSD), we can conveniently calculate the ACF as the inverse Fourier transform of the PSD. This is the Wiener-Kinchin Theorem [136].

The procedure for measuring the wavelength and correlation lengths of the mode F bands is illustrated in Fig. 4.16. Once the ACF (Fig. 4.16c) has been calculated, we extract a cross-section perpendicular to the bands, as in Fig. 4.16d. The parameters are extracted by fitting this data to a function of the form

\[ f(x) = ae^{-x/\xi}\cos(2\pi x/\lambda) + b + cx + dx^2, \tag{4.5} \]
where $\xi$ is the correlation length of the bands (in the direction perpendicular to the bands), $\lambda$ is the wavelength, $a$ is a scaling factor, and $b$, $c$, and $d$ are constants to allow for a quadratic fit to the baseline. In practice, the baseline is reasonably flat, so the fit parameters $c$ and $d$ are small ($5 \times 10^{-5} a/\mu m$ for $c$ and $1 \times 10^{-6} a/\mu m^2$, measuring relative to the amplitude $a$). We can see from Eq. 4.5 that $\xi$ gives an idea of the distance over which the bands remain well-ordered.

Of course, the PSD contains exactly the same information as the ACF, so we could extract the desired information without performing the autocorrelation. The wavelength could be calculated from the positions of the peaks in the PSD, while the correlation length could be related to the width of these peaks. However, in the absence of a functional form for the bands and, hence, for their Fourier transform, it is simpler to fit an exponential decay to the envelope of the ACF bands: even if a sinusoidal function is a poor representation of the bands, this fit will give a good estimate of the decay length.

The wavelength and correlation length are plotted along with the velocity data in Fig. 4.17. We find that the decrease in wavelength with undercooling can be fit well to a power-law (better than to, for instance, an exponential) diverging from an undercooling of $\sim 22^\circ C$, in the middle of the negative-slope region of the velocity curve. The correlation length of the bands increases sharply at an undercooling of $\sim 24^\circ C$, near the local minimum in the velocity curve. As shown in Fig. 4.18, the bands first become well-defined in this region: below this undercooling, a characteristic spacing can be measured from the autocorrelation function, but the coherence length is not much larger than a single wavelength.

Note that in Fig. 4.17c, the autocorrelation begins to decrease slightly with undercooling at large undercooling. This is an artifact of the measurement technique. The measurement works well when the bands are nearly straight lines — i.e. far from the nucleus. However, the domains are never infinite in extent, so there is always some curvature. The result is that the measured correlation length is shorter than it would be if we did a more difficult measurement of radial correlation. In order to minimize curvature effects, the autocorrelation was performed on images of bands as far as possible from the domain nuclei. At small undercoolings, we usually grow a few large spherulitic domains, so we can image bands at distances of up to a centimeter from the nuclei. However, large undercoolings result in many spherulitic domains whose diameters may be less than 1 mm. In these cases, curvature effects are unavoidable and the correlation is artificially attenuated. Despite this, the correlation length still provides a good indication of the onset of banding.
Figure 4.16: Measurement of the band wavelength and correlation length. (a) Original image of a banded spherulite (grown at an undercooling of 25°C). The scale bar measures 50 μm. (b) Power spectral density. Zero spatial frequency is at the center of the image. The dominant features are the peaks (dark regions) corresponding to the band frequency and its harmonics. (c) Autocorrelation function. The image intensity represents correlation with respect to zero distance (located at the center of the image). The autocorrelation function reveals the average band structure. Note that the bands in the correlation function have a limited length because of a loss of lateral correlation due to random drift in band position and sudden jumps in the band phase. The autocorrelation also decays in the direction normal to the bands, showing a gradual loss of coherence. It is this correlation length that we will use to characterize the band ordering. The line indicates the growth direction. (d) Cross-section of the autocorrelation image along the line shown in (c). The fit is to the decaying sinusoidal function of Eq. 4.5.
Figure 4.17: Wavelength and correlation length for modes E and F. (a) Velocity-vs.-undercooling curve. (b) Wavelength of bands. A power-law fit suggests a divergence from a transition temperature of 22.3°C in the negative-slope region of the velocity curve. (c) Correlation length of the bands in a direction perpendicular to the bands. The correlation length has been normalized to the band spacing, although this has little effect on the shape of the curve. Note that the degree of order in the bands increases suddenly at an undercooling near the local minimum in the velocity curve.
Figure 4.18: Development of band ordering at the E-to-F transition. (a) Typical images of the banded morphology at various undercoolings. The scale bar spans 50 μm. (b) Autocorrelation images corresponding to (a). (c) Cross-sections along the growth direction (normal to the bands) of the autocorrelation function of the images shown in (a). Each is fit to Eq. 4.5.
The apparent divergence in the wavelength of the bands and the sharp change in their coherence when the undercooling is varied suggests a sharply defined transition between the banded and non-banded growth modes. We can then ask, "is the fastest-growing mode selected?" We are faced with two scenarios: If we consider the negative-slope region of the velocity curve to be a transition region, then the transition takes us from mode E, where the growth velocity increases rapidly with undercooling, to mode F, whose velocity is a less-strongly increasing function of undercooling — i.e., to a slower mode. On the other hand, the velocity curves need not be linear. It may be that mode E reaches a maximum velocity near an undercooling of 22°C, after which its velocity decreases with undercooling. The transition is then to a faster mode at the point where the velocity curves for modes E and F cross.

The nature of the bands is discussed in more detail in Chapter 5.

4.2.6 Mode B'

So far, we have considered mode transitions at which the growth velocity is a continuous function of undercooling. Recall, however, that Fig. 4.7 shows the velocity curve to be discontinuous near an undercooling of 10°C. The morphology corresponding to this velocity "spike" shown in Fig. 4.2B' is one of thin needles growing well ahead of the remainder of the front, which otherwise resembles the hair-like mode A. Numerous attempts have failed to produce growth velocities between that of modes B and B', suggesting that there is a true discontinuity.

The velocity evidence alone provides good evidence that mode B' is distinct from either modes A or B. We have also measured the front roughness, as shown in Fig. 4.19b. The overall roughness of mode B' is similar to that of mode A, and larger than that of mode B. The roughness curve does not seem to be discontinuous, but does show a large degree of scatter. This is a result of the large roughness, which required measurements using the larger field of view of a camera lens, rather than a microscope. In fact, I believe that the roughness is on too large a scale even for the camera lens, resulting in inconsistent data.

A clearer signal of the phase transition is given by the maximum thickness of the needle crystals, as shown in Fig. 4.19c. Although this plot also shows scatter, it does indicate a clear discontinuity between the thicknesses in modes B' and mode B, where the crystals are much larger. The characteristic thickness was not measured for mode A, since it is smaller than the resolution of the optical microscope (i.e., \( \lesssim 1 \mu m \)). It is clear that the
Figure 4.19: The mode B’ transitions. (a) Velocity data for modes A, B’, and B, and D (see below). Note that the transition to mode B’ is discontinuous. The points indicated by squares mark a distinct morphology only occasionally seen (see Section 4.2.7). (b) Roughness data for mode A, B’, and B. (c) Typical maximum thickness for crystals of modes B’ and B. The transition between these modes is clearly discontinuous. The thickness of mode A crystals are too small to estimate optically.
mode B' crystals are larger than the mode A crystals.

The large increase in velocity exhibited by B' is surprising. One possibility is that this mode is a result of the sample geometry; since both modes B' and B have crystal thicknesses as large or larger than the sample thickness, we would expect them to modified from the form they would take for truly three dimensional growth. This has no bearing on any conclusions about the mode transitions. Our focus has been on the mode transitions with no reference to the modes themselves. However, this idea can be investigated by considering sample cells of different thicknesses.

Fig. 4.20 is a plot of growth velocities for mode B' in cells of different thicknesses. We find that for thicker cells, mode B' exists over a wider temperature range and grows at even higher velocities than for thinner cells. Surprisingly, the growth velocities in the 50 μm cell were larger than those in either the 10 or 120 μm cells, so that the maximum velocity at any given undercooling must reach a maximum at some intermediate thickness. However, the latent heat released by solidification will cause a larger temperature rise at the interface for thicker cells, so the actual undercoolings for the velocities plotted for the 120 μm cell are expected to be smaller than the values inferred from the oven temperature (cf. Section 3.3.3). This will be explored further in Section 4.3.1.

A further complication is that the morphologies observed for mode B' in the thicker cells are quite different from those seen in the thin cells. A comparison of the morphologies at similar undercoolings in different cell thicknesses is shown in Fig. 4.21. For the thicker cells, mode B' consists of large crystals with sidebranching and does not appear to be very different morphologically from mode B. However, both modes are seen in the thicker cells and grow at quite different velocities. In fact, Fig. 4.22 shows the nucleation of mode B' from mode B in a thick cell.

Another observation is that a low-velocity mode is occasionally seen in the undercooling range where mode B' would be expected (see Fig. 4.19). This is taken as further evidence that B' is a separate mode: more than one mode can exist, but B' is the one selected in a particular undercooling range. The appearance of other modes is evidence for a relatively large nucleation barrier for mode B'. It is interesting to note that the morphology of the modes corresponding to these points (cf. Fig. 4.23, below) does not resemble any of the modes A, B', or B very closely. The long, curved needles without sidebranching are reminiscent of mode D, but lie well outside the previously studied undercooling range for mode D. This observation will be discussed further in the next section.
CHAPTER 4. SOLIDIFICATION MODES AND MODE TRANSITIONS

Figure 4.20: Effect of sample thickness on mode B' velocities. For thicknesses of 50 and 120 μm, mode B' grows at a larger velocity and is observed over a wider range of undercooling than for samples of 10 μm thickness.

Figure 4.21: The dependence of mode B' on sample thickness. As the sample thickness increases, the microcrystals of mode B' become wider and begin to resemble mode B. The scale bar spans 200 μm.
CHAPTER 4. SOLIDIFICATION MODES AND MODE TRANSITIONS

Figure 4.22: Nucleation of mode B' from mode B in a 120 μm thick cell. These two images (separated by 5s) show the growth of a domain of mode B' (with approximate boundaries indicated by white lines) which has nucleated from a mode B front. The scale bar denotes 1 mm. The poor contrast was typical of images obtained with a camera lens rather than a microscope — nevertheless, the front is well-defined. Note that the needles of mode B' have a preferred growth direction with little side branching, leading to a slow rate of lateral spreading relative to the growth velocity of the needles. The concave growth front is due to the meeting of two domains, as well as to thermal gradients over the (large) field of view.

Since mode B' is distinct from both modes A and B, the transition from this mode, by either increasing or decreasing the undercooling, is to a mode with a smaller growth velocity. Indeed, as discussed in Section 2.6, no transition involving a discontinuous change in growth velocity can be explained by a scheme involving the intersection of two response functions. If the transition does not involve a selection between two response functions, both of which coexist over a finite range, then the transition may occur because one or another of the modes ceases to be an allowed choice at some critical undercooling. For this to be the case, one would expect some of the measured quantities to exhibit a singularity at the boundaries of the allowed undercooling range. However, no sign of the impending change is seen in either the velocity or the roughness curves.

We are then left with the possibility that there is a selection rule other than the “fastest-growing mode” hypothesis at play. Ben-Jacob, et al., have suggested that although the fastest mode is likely to be favoured far from equilibrium, the general selection rule may involve an additional contribution related to the structure of the modes. Our observations suggest that mode B' lacks an effective mechanism for lateral spreading. For example, the
structure of this mode in thin cells shows very little sidebranching (see Fig. 4.21). Even in thick cells, where the mode B' needles are larger and do sidebranch, lateral growth seems to be slow. Fig. 4.22 shows a mode B' front in a thick cell growing rapidly ahead of a mode B front, but making much slower progress along the mode B front.

Although these observations do not explain how a slower mode can overtake a faster one, it is likely that the difference in the lateral growth-rate plays a role. The precise mechanism may involve a time-dependent competition between the individual needles at the boundaries of the growth fronts, rather than the overall motion of the average fronts.

4.2.7 Mode D at small undercooling

As discussed earlier, a low-velocity mode is occasionally seen at undercoolings where mode B' is usually observed. Two examples of this growth front are shown in Fig. 4.23. Of the growth modes discussed so far, these fronts resemble mode D the most strongly. They have the same structure of tufts of needles consisting of curved fibers with no sidebranching. Moreover, the front velocities fall close to the velocity curve extrapolated from mode D.

Figure 4.23: Mode D at low undercooling. (a) Picture of this morphology, which does not resemble any of the modes more commonly seen in this undercooling range. The overall shape is reminiscent of mode D (cf. Fig. 4.2D), but with a coarser structure. (b) This picture shows several examples of needles which have broken during growth. The scale bar measures 200 μm.
The growth fronts pictured in Fig. 4.23 are much rougher than the mode D growth fronts measured earlier. This is consistent with the hypothesis that this small-undercooling mode is an example of mode D — the roughness of mode D increased with decreasing undercooling in Fig. 4.8 — but makes a quantitative comparison difficult.

Another difference between this mode and the original mode D is that the tips of the fibers are often curled through $>180^\circ$ (note the top region of Fig. 4.23b). These curls maintain a nearly constant shape as the front grows. Although this makes the tips look like they are static so that growth occurs by increasing the fiber length elsewhere than at the tip, a more likely explanation is that the fibers are uncurling as they grow. This may be due to the fact that the fibers also thicken as they grow in length: a point on the fiber that is initially part of a curl will require an increasingly greater force (presumably supplied by viscous flow in the smectic A phase due to the density change resulting from solidification) to maintain the curved shape as the fiber gets increasingly wider. The result is that only a short length near the tip is thin enough to remain bent at any time.

One of the consequences of the mechanical motion of material in these fibers is that they frequently break when they grow against neighbouring fibers. Fig. 4.23b shows a few examples of this, one of which is near the center of the image. It is clear that, although this growth mode is appearing at an undercooling well inside the diffusive limit, non-diffusive mechanisms, in particular, viscous flow, do play a role in its structure. In fact, motion caused by fluid flow in the melt is also seen in the entangled fibers of mode A, where the front velocity is even smaller.

Further measurements of this growth front would help to determine if it is, in fact, a small-undercooling example of mode D. If we accept this to be the case, then this front offers strong support for the "fastest mode wins" rule: mode D then has a small range of stability (or at least metastability) with respect to mode B'. It is not seen at slightly larger undercoolings — there, mode B, which has a larger front velocity, is selected. At still larger undercoolings, mode B turns into mode C, which has a velocity that increases much more slowly with undercooling. At some point, the mode-D velocity becomes larger than that of mode C, and a second domain of mode D appears. Both transitions favour the fastest mode.
4.2.8 Directional solidification results

Some of the solidification experiments discussed above can be examined in more detail by direction solidification. Recall that directional solidification is, in some sense, a complementary technique to that of free growth. In directional solidification, we fix the growth velocity rather than growth undercooling. If the mode transitions discussed above are, in fact, discontinuous, we would expect to observe this in directional solidification with, perhaps, some differences due to the imposed temperature gradient.

Using directional solidification, we have been able to observe morphologies similar to all those found in free growth, with the exception of mode B' (Fig. 4.24). This exception is not surprising if we consider that for the velocity range corresponding to mode B', more than one morphology at more than one undercooling can be observed. At the large velocities required for modes B', E, and F, the entire sample cell passes through the directional solidification apparatus in less than two minutes. This may not allow enough time for the most stable mode to be established, particularly if the nucleation barrier is large compared with that of the other possibilities. In fact, the velocities recorded in Fig. 4.24 do not agree well with the velocity ranges for the corresponding modes in free growth. This may be the result of transient morphologies — the apparatus had to be started from rest so that growth begins as a low-velocity mode — or it may be that the selection rules need to be modified for directional solidification.

Even in the absence of nucleation barriers, directional solidification can be an inconvenient choice of techniques for the study of mode transitions. For instance, if the growth velocity goes through a maximum and minimum, as is the case for the mode E to F transition, we might expect a hysteretic effect: when the motion of the sample is begun, any morphology up until the one at the local maximum can be attained, but still larger velocities will cause a “jump” to a morphology existing at an undercooling past the local minimum. Similarly, when the velocity is decreased from a value well beyond the local maximum, the morphology can change continuously until the local minimum of the velocity curve is reached. After this, the morphology must change discontinuously to one well into mode E.

Nonetheless, directional solidification provides an alternative view of our mode transitions. In the case of the second-order mode transitions, C–D and D–E, the sharp transition is recovered. The selection rule, which has been seen by other authors [139], becomes the
CHAPTER 4. SOLIDIFICATION MODES AND MODE TRANSITIONS

Figure 4.24: Examples of growth morphologies in directional solidification. Modes analogous to all of those seen in the free growth experiments have been seen. The scale bar indicates 200 μm. These experiments were performed with an imposed temperature gradient of 60°C.

selection of the mode stable at the smallest undercooling. Due to the imposed gradient, this mode will then lie at a point ahead of any front at a larger undercooling, effectively choking it off.

In addition, directional solidification allows an easy measurement of the lateral growth velocity of the mode selected when the imposed velocity is made to cross a transition point (see Fig. 4.25). This may prove to be a useful technique in future studies of morphology transitions.
4.3 Control parameters other than undercooling

So far, we have looked at the effect on growth morphology of varying the control parameter $\Delta T$. There are several other parameters under our control. The amount of data necessary to define our morphology diagram increases drastically if we increase the dimensionality of our phase space by including these other parameters, so a full study is not feasible. Here, I present preliminary studies of the effects of sample thickness and impurity concentration.

4.3.1 Thickness effects

A full investigation of thickness effects is beyond the scope of this investigation. We have made a preliminary study by observing growth at a few different thickness. Because the B and B' crystals are very thick (up to 30 $\mu$m), the $B'$--$B$ transition was the one that varied most with sample thickness, over the range explored (10 $\mu$m to 120 $\mu$m).

Fig. 4.26a is shows the velocity-*vs.-*undercooling curve for three sample thicknesses. As we saw earlier, the most striking change when sample thickness is increased is the increased existence range for mode B'. It is also evident that the slope of the velocity curve is smaller for larger undercoolings. This is consistent with the hypothesis that reheating due to the release of latent heat raises the interface temperature above that set by the sample stage, thus shifting the true value of the undercooling to lower values. The change in interface
temperature is given by Eq. 3.8. Fig. 4.26b shows the velocity curve with the undercooling scale corrected by Eq. 3.8 using the values for the physical constants of 10 OCB listed in Table 3.1 (except for the value of $D_h$). For $D_h$ — the least accurately known of these constants — I used a value of $1.25 \times 10^{-3}$ cm$^2$/s, as this provided an overlap between the curves for undercoolings between 18 and 23°C that was noticeably better than the agreement found using the tabulated value. Either value led to a markedly improved agreement between the curves in that undercooling range, however.

Eq. 3.8 does not improve the overlap of the velocity curves for the large velocities found in mode B' and in mode F above 25°C undercooling. In the case of mode B', an improvement is not expected — the growth front is far from planar, so the assumptions involved in Eq. 3.8 do not apply. It is clear from Fig. 4.26 that the actual temperature rise is less than that given by Eq. 3.8. The roughnesses of the fronts encountered in mode F, however, are much less than the sample thickness. We believe that the poor results for the undercooling correction in this case are due to an overestimate of the undercooling during solidification: at large undercoolings, solidification began before the sample had cooled to the temperature set by the sample stage.

Most of the morphologies observed for thin cells are preserved when the thickness is increased. Modes A, B, E, and F seem to be unchanged in the thick cells. Mode B' has a slightly different appearance and extended range but is seen in thick cells. The morphology of modes C and D is, however, altered in a thick cell. Throughout this range, the observed morphology seems to be a coexistence of these two modes. The front consists of long needles resembling those of mode D, with collections of smaller needles like those of mode C, which nucleate just behind the front. This process is shown in Fig. 4.27. As the undercooling is varied, the relative amount of the two coexisting morphologies changes.

In summary, sample thickness has little effect on the solidification velocity of 10 OCB, aside from well-understood results due the increased interface temperature. Most of the growth morphologies are also unchanged, aside from those for which the characteristic width of the microcrystals is comparable to the sample thickness. However, modes B', C, and D are noticeably different, with corresponding differences in the velocity curve. A study of the evolution of morphology with sample thickness at a fixed undercooling would, no doubt, be interesting, but will not be undertaken in this study.
Figure 4.26: Effect of thickness on the velocity curve. (a) Velocity data for three sample thicknesses. (b) Data from (a) corrected to account for reheating due to the generation of latent heat.
Figure 4.27: Sequence of micrographs illustrating the front morphology at an undercooling of 16.4°C in a sample of thickness 50 μm. The frames were taken 1s apart. Note that the front appears to be a coexistence of two modes with different sizes of crystals. The scale bar represents 200 μm.

4.3.2 Impurity effects

We have been considering the growth mode transitions of 10 OCB with little attempt to understand the details of the mode themselves. One of the most basic questions we can ask is whether or not the morphologies are impurity driven. For instance, in mode A, very thin fibers (~1 μm) can be grown at low velocity in very thin sample cells (<10 μm). Presumably, the latent heat generated by the solidification can be easily pumped away by the sample walls. The lack of a smooth front is then somewhat puzzling unless it is due to the diffusion of impurities (which are trapped by the sample walls). We attempted to estimate the impurity concentration by calorimetry.

A common technique for estimating the purity of a material is differential scanning calorimetry (DSC). A DSC apparatus measures the difference in heat required to maintain an equal temperature between a sample enclosed in a metal sample container and a reference blank while the temperature is raised. Thus, when the sample undergoes a phase transition, additional heat must be supplied to the sample to provide the latent heat of transition. If the sample holder and blank are identical, the difference in heat required for the temperature rise allows one to calculate the specific heat of the sample, while the total heat energy supplied during the transition gives a measure of the latent heat. In practice, the sample holder and blank are not identical and the instrument is not perfect, so various corrections need to be made. For our purposes, a discussion of these techniques is not necessary (see, for example, [140, 141]).

The data for a DSC run [142] using as-purchased 10 OCB as a sample are shown in Fig. 4.28. This sample goes through two phase transitions: solid to smectic A at ~60°C, and
smectic A to isotropic liquid at $\sim 84^\circ$C. The absorption of latent heat at these transitions manifests as a spike in the supplied energy. For a pure sample and a very slow rate of heating, these spikes would be delta functions — all of the material would change state before any further temperature rise was possible. In reality, impurities in the sample, as well as the instrumental response time due to finite thermal conductivities, result in an observed melting range. The impurity level can be estimated from the width and shape of the latent heat spikes. As a rule of thumb, the width of the peaks are of the order of one degree per mole percent of impurity. This would imply an unrealistically large impurity for our sample, if the solid to smectic A transition is considered. However, this width depends on the partition coefficient $k$, which we have not measured. Note that $k$ is usually close to unity for a smectic-isotropic transition since impurities are easily incorporated into the smectic phase [143]. This results in a much narrower peak for that transition.

![Differential scanning calorimetry data for 10 OCB.](image)

Figure 4.28: Differential scanning calorimetry data for 10 OCB. The solid-to-smectic A and smectic A-to-isotropic transitions are indicated by the two peaks at $\sim 60^\circ$C and $\sim 84^\circ$C, respectively. Values for the heats of transition are calculated from the integrated power in each peak, while the specific heat capacity is estimated by the height of the curve away from the transitions, where it is a measure of the power required to heat the sample. The sample had a mass was 2.4 mg, and was heated at a rate of 1°C/min.

It is likely that the sample, as purchased, consists of several solid morphologies, which
may have slightly different melting points. Similar conclusions have been made for other solidified liquid crystals that have been studied in this way [42, 43, 44, 45, 46, 47].

The DSC data, then, is not useful for the estimation of the impurity concentration. It has been used to estimate the values for the latent heat, specific heat capacity, and transition temperatures tabulated in Table 3.1.

A more direct way of evaluating the effect of impurities is to explicitly set the impurities in the sample. 10 OCB is available in nominally pure form, but generally contains \(~0.15\%\) water at the saturation limit. A “pure” sample was prepared by heating a small quantity of 10 OCB above 100°C in an open beaker under vacuum. Bubbles formed for about an hour before no further change in the material was obvious. After another hour of pumping, the purified 10 OCB was used to make a thin sample. DSC was not applied to this sample, but optical microscopy during very slow heating revealed a melting range of \(<0.1°C\). The solidification morphologies, velocities, and transition temperatures were, to within experimental resolution, completely unaltered.

A second sample was made by dissolving \(~2.7\%\) by mole of \(\text{C}_2\text{Cl}_6\) in unpurified 10 OCB. This impurity level is well above the total amount of impurity expected in 10 OCB and, thus, should be the dominant impurity contribution in the doped sample. Hexachloroethane was chosen because it is expected to be rejected from the 10 OCB solid phase (i.e. the partition coefficient is much less than one) and has been successfully used in other solidification experiments involving cyanobiphenyl liquid crystals [144].

The solidification morphologies were unaltered, even at this high impurity level. This contrasts with solidification systems such as succinonitrile, where impurities can be very important. This implies that the solidification of 10 OCB is limited by thermal diffusion. Additional studies with different impurities may prove useful.

4.4 X-ray diffraction results

We have established that 10 OCB can solidify into a variety of growth morphologies. One may wonder if the different morphologies have different crystal structures. In order to answer this question, we performed X-ray analyses of several different growth modes.

Because of the thin samples under investigation, we used grazing-incidence X-ray diffraction [145] to maximize the reflection from the sample while minimizing the contribution from the glass substrate. Samples of thickness \(~100 \mu\text{m}\) were chosen to maximize the amount of
solid and, hence, the intensity of the diffracted beam. This large thickness is, in light of the discussion of the effect of sample thickness, a poor choice — most of the morphology data were measured in thinner samples. Even with the thick samples, runs of up to several hours duration were required, raising the possibility of radiation damage.

Another concern is that the thin sample geometry constrains crystals to grow in the plane of the sample. This will be particularly true for growth modes B', B, C, and D. In such cases, the sample does not form a true three dimensional powder and thus will not exhibit all Bragg planes in the diffraction data. Despite these concerns, the X-ray data provide some interesting information.

Solid 10 OCB has been previously determined to have a monoclinic crystal structure [146] with the lattice parameters in Table 4.1. This study did not consider the possibility of different crystal structures which may result from growth under different conditions. In other studies of liquid crystal solid phases, multiple solid crystal structures have often been observed [43, 147, 148]. In fact, it has been suggested that the existence of more than one solid structure is a generic feature of liquid crystals — the very molecular properties that allow various liquid crystal phases are conducive to more than one solid phase [46, 150]. For example, the hydrocarbon chain present in many liquid crystal molecules is able to take on several configurations with minimal change in the free energy of the resulting crystal. In fact, even in a single solid phase, disorder in these hydrocarbon chains is often present [149].

<table>
<thead>
<tr>
<th>Lattice constant</th>
<th>Value</th>
</tr>
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<tr>
<td>a (Å)</td>
<td>9.041 ± 0.020</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.220 ± 0.016</td>
</tr>
<tr>
<td>c (Å)</td>
<td>31.099 ± 0.067</td>
</tr>
<tr>
<td>β (deg.)</td>
<td>92.336 ± 0.160</td>
</tr>
</tbody>
</table>

Table 4.1: Lattice parameters for crystalline 10 OCB available in the literature [146].

Our X-ray diffraction data for several of the growth modes are shown in Fig. 4.29, with major peaks tabulated in Table 4.2. All of the diffraction patterns have several peaks in common. This indicates that unit cells for all modes are approximately the same size, ~31 Å, which is approximately the length of the 10 OCB molecule. However, there are several differences, the most obvious ones at angles of ~5°, ~13°, and the range from 18–22°. Whether these differences are due to actual structural differences, different unit cell orientations (recall that not all Bragg reflections will be observed if the orientation
of the microcrystals is constrained), or radiation damage (note that the difference is most pronounced at large angles, measured late in the run), is unknown.

Figure 4.29: Grazing incidence X-ray diffraction data for five 10 OCB growth modes. Each mode was grown at the indicated temperature in a 120 μm thick sample. All data are normalized to the first peak and offset on the intensity axis. Copper K-α radiation was used.

Regardless of the cause of these differences, we can comment on the similarities. The data indicate that modes A and B have the same structure and orientation. Similarly, there is no apparent structural difference between modes E and F at the molecular level, despite the morphological differences on the microscopic scale. Other than differences at large angles, corresponding to small Bragg spacings, all four of these modes may have the same crystal structure. The differences could be attributed to radiation damage, or to the poorer resolution of the mode E and F diffraction curves. This loss of resolution is most likely due to the much smaller size of the microcrystals of modes E and F (as will be discussed in Section 5, the microcrystals for mode F have thicknesses as small as 600 Å — a mere twenty spacings of the long dimension of the unit cell). Mode D, on the other hand clearly differs from the other modes measured.
CHAPTER 4. SOLIDIFICATION MODES AND MODE TRANSITIONS

20

spacing Nearest plane $d_{hkl}$ (Å)

<table>
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<tr>
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<th>Nearest plane</th>
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<tr>
<td>(°)</td>
<td>$(hkl)$</td>
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<tr>
<td>20.25</td>
<td>1.84</td>
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</table>

Table 4.2: Major X-ray diffraction peaks for crystalline 10 OCB.

Some of the peaks tabulated in Table 4.2 are tentatively assigned Miller indices and compared with peaks expected from the unit cell of Table 4.1. Although these X-ray data do not contradict the results expected for the proposed unit cell, several expected peaks (notably $hkl = [100]$) are clearly missing, while no strong candidates were found for others.

4.5 Summary of mode transitions in 10 OCB

We have studied the solidification of a liquid crystal, 10 OCB. We found that this material can solidify into several morphologies, depending on undercooling, some of which have been seen in other systems. The major contribution of this study is a careful measurement of the growth velocity and other quantities as a function of undercooling, which allowed us to show conclusively that sharp transitions between growth morphologies occur. Thus, we conclude that the different morphologies in question correspond to distinct growth modes, each with its own micro- and macro-structure and velocity curve.

In every case involving a sharp mode transition and continuous velocity curve, the change in velocity is consistent with the intuitively reasonable "fastest mode wins" rule. In these cases, the transition favors the faster-growing mode, which goes on to take over the front. A particularly striking example is given by mode D. This mode is seen in two undercooling ranges separated by a region in which modes B and C are selected. The small-undercooling region ends when the velocity of mode B becomes larger than that of mode D. However, as the undercooling increases, mode B changes smoothly into mode C. Mode D reappears when its velocity curve overtakes that of mode C, which has levelled off.
There are transitions, however, for which the velocity curve is not continuous. Such a situation cannot be explained by such a simple selection rule. In this case, there is either an unknown general rule at work or the general explanation lies in a specific stability analysis of each possible stationary state. This is the situation that many people believe holds in nonequilibrium systems [9].

If, as Ben-Jacob, et al., have suggested, there is a general rule, the mechanism by which mode B' is able to lose to the slower mode B may give an important insight into the nature of this rule. Our observations suggest that the lack of an effective branching mechanism for lateral spreading is responsible. Thus, it is a property related to the structure, rather than the velocity, of this mode which allows a mode with a slower growth velocity, but more rapid lateral growth, to overtake it.

Although our findings for the selection rules at work in second-order morphology transitions agree with those proposed by Ben-Jacob, et al., some of our observations are difficult to reconcile with the phase diagram analogy. In particular, a bifurcation of the type shown in Fig. 2.8a generally involves an exchange of stabilities at the critical value of the control parameter. If this point is crossed, the mode that was stable is expected to become absolutely unstable. Instead, we find that it is relatively unchanged, and continues to grow, stopping only when the faster mode nucleates and spreads to take over the front. It may be that the kinetics of changing an existing front are much slower than the rate of nucleation of a new phase.

Coexistence of modes is more easily explained in the case of a first-order morphology transition, as we found for mode B'. A subcritical bifurcation, as indicated in Fig. 2.8b allows two phases to coexist over some range of parameters. Outside of this range, the selection principle is trivial: only one of the two modes exists. Within this range, there may be a selection rule determining which mode will be expressed. Alternatively, the selection may be governed by initial conditions. Experimentally, however, we find no evidence of singular behaviour at either end of the existence range for mode B'.

In summary, we have mapped a morphology phase diagram for the solidification of 10 OCB. We find both first and second order transitions. The second order transitions support a proposed selection principle. However, there are questions that need to be addressed if morphology selection is to be treated analogously to equilibrium phase transitions.
Chapter 5

BANDED SPHERULITES

So far, we have been studying growth modes and mode transitions without much reference to the nature of the modes involved. In this Chapter, we will examine one of the modes, mode F, in more detail. We have identified this growth mode as banded spherulitic growth, based on its similarities with spherulites in other systems (see Section 2.5). Individual mode F domains grow at a constant velocity with a circular envelope (until they impinge on other domains). Further, this mode grows at larger undercoolings than do other modes such as the dendritic morphology. Unlike spherulites of most other materials, however, these grow at high enough velocities to make feasible a detailed study of their properties as a function of undercooling. Moreover, we are able to grow 10 OCB spherulites to sizes on the order of 1 cm, resulting in domains 10,000 band spacings in diameter.

5.1 Optical observations

Optically, these spherulites show a banded structure with occasional radial lines perpendicular to the bands, as shown in Fig. 5.1. In fact, these lines are the most obvious feature at lower magnifications and have, in the past, occasionally been mistaken for radial fibers. In Fig. 5.1, these lines can be seen to be nothing more than phase shifts between adjacent banded domains. High-resolution studies (Fig. 5.7) show that there is no continuity of microcrystals along these lines.

Although spherulitic growth is usually from an isotropic fluid, the anisotropy of the smectic A phase does not seem to affect the spherulitic growth mode. For example, spherulites grown from samples with planar anchoring, rather than the usual homeotropic anchoring,
Figure 5.1: Optical micrograph of a domain of banded spherulitic growth. Note that the spherulite consists of banded domains separated by shifts in the phase of the bands. This sample was solidified at an undercooling of about 40°C, resulting in a band spacing of 1.7 μm. The scale bar measures 50 μm.
differ only in a growth velocity anisotropy: the growth was slowest in the anchoring direction. The result is oval "spherulites" with an aspect ratio of ~0.9, as shown in Fig. 5.2. This velocity difference may be due to the anisotropy in the molecular alignment. The molecules are aligned parallel to the growth front in the direction of fastest growth. If this is the alignment of the molecules when they are incorporated into the microcrystals, this would result in faster growth than when the molecules must rotate from a perpendicular direction.

On the other hand, the growth anisotropy may stem from an isotropy on a larger scale. During the anchoring procedure described in Section 3.1.2, ridges formed in the polyimide layer parallel to the surface of the polyimide solution as the glass plates were drawn from the beaker. This allowed faster fluid flow along the ridges, which may have allowed faster growth in these directions. Fluid flow certainly takes place during spherulitic growth. We have measured dust particles in the smectic A phase moving at speeds well in excess of 100 μm/s when the front is still several hundred micrometers away. Presumably, this flow is due to the change in density during solidification.

We estimated the change in density by measuring the change in size of small droplets (200–800 μm in diameter) sandwiched between glass plates held 25 μm apart as they are solidified. Since the solid phase is denser than the smectic A, the drops shrink during solidification, as shown in Fig. 5.3. Note that the solid drop is not perfectly circular because the solid phase does not usually nucleate at the center. This results in increased flow from the regions further from the nucleus. We found that the density change is approximately 10% for spherulitic growth, although the thin film of material left on the plates as the droplet shrinks makes a precise estimate difficult. We were unable to establish a trend in the density change with undercooling, although increased nucleation times made it difficult to extend the measurements beyond the temperature range for mode F. We will see that the spherulitic morphology is not compact on the microscopic scale. Thus, this density change must be regarded as an average value over the spherulite domain.

These spherulites can also be grown by directional solidification. With this technique, it is possible to grow very large spherulites so that the entire sample consists of essentially one domain. Of course, the growth is constrained to the direction of motion, resulting in bands with negligible curvature. Surprisingly, even though directional solidification imposes a temperature gradient, as well as a growth velocity on the sample, the spherulitic structure seems to be unmodified from that in free growth. In fact, even the relation between band spacing and growth velocity is preserved. In Fig. 5.4, the band spacing for both free growth
Figure 5.2: Oval spherulites in a planar anchored sample. The top image shows a growing spherulite in a sample with planar anchoring (in the horizontal direction). The bottom image is a close-up of the center of this spherulite. Both show an elliptical shape, indicating that growth was faster in the anchoring direction. The scale bar represents 100 μm in the top image and 25 μm in the bottom.
CHAPTER 5. BANDED SPHERULITES

Figure 5.3: Density change during solidification of a small droplet of 10 OCB at an undercooling of 30°C between glass plates 25 μm apart. The density change causes the droplet to shrink. The original shape is still visible because of a thin (estimated from the depth of field to be ~1 μm) film of material which freezes to the glass plates.

and direction solidification is plotted as a function of growth velocity. Both sets of data fall on a single curve, indicating that the growth is not sensitive to the details of the temperature gradient at the interface.

In addition to existing in samples with a wide range of thicknesses, it is possible to grow spherulites in very small and irregularly shaped droplets. Fig. 5.5 shows banded growth in droplets as small as 10 μm in diameter and in irregular droplets with necks on the order of a single band in width. These drops are also quite thin (<5 μm, as measured by the change in focus between the edges and center). The observation that the behaviour is unchanged as the sample size is made small argues that the structure of the flow and impurity fields at distances of more than several micrometers from the front cannot be important to the formation and ordering of the bands. The important length scales are then expected to be of the order of the band spacing.

In addition to the characterization of the band spacing, we can use optical microscopy to measure the domain structure. For instance, we measured the coherence of the bands in Section 4.2.5. We also attempted to measure the characteristic lateral size of the banded domains (i.e. along the band direction). This is a rather difficult measurement to make:
measurements of the lateral correlation length are very sensitive to curvature and sharpness of focus in the original image, while direct counting of the number of domains involves a subjective choice of what constitutes a domain boundary. We were unable to produce consistent enough results to determine if the lateral size depends on wavelength. It is clear however, that since the domains have the same average width at both large and small distances from the spherulite nucleus, new domains must be formed as the radius (and, hence, the circumference) increases.

Although banding is usually explained as a birefringent effect, the bands in our spherulites are visible in unpolarized light. This is not surprising — any nonuniformity in optical properties can be expected to have visible effects — and has been seen in other spherulites. When the spherulites are viewed through crossed polaroids, a dark “Maltese cross” is seen in addition to the bands. This is expected from the radial structure. Fig 5.6 shows a comparison of the band visibility in unpolarized vs. polarized light.

If we view spherulites illuminated by unpolarized light through a single polarizer, we find that the band contrast is greatest when the polarizer is aligned parallel to the bands.
Figure 5.5: Spherulitic growth in irregular droplets. The bands are able to propagate through features of the order of the band spacing. In addition, banding is seen in droplets only two bands across.

When the polarizer passes light polarized perpendicular to the bands, the contrast is so weak that the bands cannot be distinguished. This indicates that the contrast is due to an attenuation of the component of light polarized along the bands. As the samples are too thin for there to be much absorption, the loss must be due to scattering. Higher-resolution studies are necessary to determine whether the variations in the refractive index that cause this scattering are due to a rotation of the unit cell along the radius, as discussed in Section 2.5, or to variations in the density.

Since the band spacing is on the order of optical wavelengths, these spherulites form circular diffraction gratings. Several orders of diffraction spectra can be seen. This is consistent with the belief that the visibility of the bands in unpolarized light can be attributed to diffraction of light outside of the acceptance cone of the microscope [83].

5.2 High-resolution investigations of banded spherulites

In order to learn more about the structure of these spherulites, higher resolution studies are needed. We have examined the structure using atomic-force microscopy. Previous AFM
Figure 5.6: Spherulite bands viewed in (a) unpolarized light and (b) between crossed polarizers. In both cases, the bands are easily visible, though in (b) they are obscured by the extinction along the polarizer directions. This sample was solidified by dropping it into liquid nitrogen, resulting in the rapid nucleation of many domains.
CHAPTER 5. BANDED SPHERULITES

studies of spherulites have been performed [151, 152, 153, 154], but, as far as we are aware, this is the first such study in a non-polymeric system.

Fig. 5.7 shows AFM micrographs of banded regions. The imaging was performed with a commercial AFM [155] using Si$_3$N$_4$ tips (with nominal radii of curvature of 400 Å and spring constants of the order of 0.1 N/m). Scan rates ranged from 1–4 Hz.

These samples were prepared by prying sample cells apart, causing them to cleave at the sample-glass interface. We see that the bands are made up of needles aligned perpendicularly to the bands. The needles in Fig. 5.7b have widths of approximately 600 Å and lengths that do not often extend beyond a single band spacing. This image also shows a phase discontinuity. Note that the jump in phase is very sharp — adjacent microcrystals can clearly be identified as belonging to separate domains.

The fact that the bands are visible in Fig. 5.7 implies that they are associated with a height modulation on the surface. However, it is important to recall that the AFM really measures the sample height required to maintain a constant force on the cantilever. This results in the measurement of both topographical information (for example, scanning over valleys forces the sample holder to rise to maintain a constant cantilever deflection) and mechanical properties (a softer sample will deform more, again forcing the sample holder to rise to maintain cantilever deflection [156]). Thus, the contrast seen in atomic-force microscopy is, in general, a mixture of topology and mechanical properties.

In Fig. 5.7b, the region between bands does not seem to contain well-formed crystals. However, this is most likely due to the decreased resolution in the softer regions of the sample. The X-ray diffraction data in Fig. 4.29 show no evidence of a decrease in crystallinity between modes E and F and, more importantly, some images, such as Fig. 5.7a, show clearer definition of the region between bands. Spherulites grown at larger undercoolings tended to have larger gaps, spanned by fewer microcrystals, between the bands. However, for reasons discussed below, the difficulties in imaging 10 OCB using the AFM did not permit us to quantify this statement.

Our interpretation is that the contrast mechanism of the spherulitic bands in our AFM images stems mainly from mechanical effects: a reduced density of microcrystals between bands results in smaller elastic constants. The amplitude of the modulation in the average density increases with undercooling.

Note that these images show no evidence of any twist in the microcrystals, although such a twist is not ruled out. The resolution in these images is ~100 Å. This poor (by AFM
Figure 5.7: Atomic-force micrographs of spherulitic bands. The samples were grown between glass plates, which were subsequently pried apart to allow AFM imaging. The bands are composed of needles with lengths on the order of the band spacing. (a) Spherulite grown at $\Delta T=25^\circ C$. At small undercoolings many of the crystals span several bands, resulting in little contrast between the bands. (b) Spherulite grown at $\Delta T=32^\circ C$. Here, there is a large contrast between bands. Note, as well, the sharp jump between different domains of banding.
resolution is apparently due to large adhesion between the 10 OCB and the AFM tips. Permanent sample modification is typically seen after only a few scans and streaks due to material picked up by the tip during a scan are often present. Fig. 5.8 shows a scan of a region of sample after several minutes of imaging at a smaller scale. The permanent sample modification due to imaging is clearly visible. In fact, the individual crystals which make up the bands are more visible in this region. This may indicate that a thin (<100 nm) layer at the surface (which is grown in contact with glass plates) has a different form than the bulk. Chemical treatments of the AFM tip to reduce adhesion to the sample may result in better images in future studies.

Figure 5.8: Sample damage of 10 OCB by AFM imaging. This scan was performed after several minutes of AFM imaging at a smaller scale. The earlier scan area is clearly visible as a permanently modified region of the surface. The scan direction was horizontal. Note the streak (~1/5 of the way from the top) which indicates material being picked up by the tip.

One of the drawbacks of the AFM is that it is only able to examine surfaces. Thus, the AFM alone is not able to determine whether the bands extend through the bulk of the sample or whether they are a surface effect. We have performed scanning electron microscopy studies which reveal that the bands do extend through the thickness of the sample (Fig. 5.9).
Like the AFM, the scanning electron microscope (SEM) is sensitive to sample surfaces. The SEM measures the intensity of secondary electrons emitted when a focused electron beam is incident on the sample. This allows it to image topology (the secondary electrons can escape from peaks and ridges more easily than from pits and valleys), as well as sample density (a denser region has a larger interaction with the incident beam). One advantage of the SEM over the AFM is that it is able to scan the sides of samples. Fig. 5.9 shows the edges of fractured spherulites with bands clearly extending through the width of the sample.

![Figure 5.9: Scanning electron microscope image of a 10 OCB banded spherulite. The sample was prepared between highly-doped silicon (to provide a conducting substrate) and a glass plate, both of which were treated for homeotropic anchoring. The image shows a fractured spherulite showing bands in both the surface and bulk of the sample. The growth direction was to the lower left.](image)

Note that this micrograph also shows a collection of needle crystals that have detached from the spherulite. As expected from the AFM pictures, these have lengths on the order of a single band spacing.

A disadvantage of the SEM is that the electron beam charges the sample and deposits heat. The 10 OCB is nonconducting, so it charges quickly, distorting subsequent imaging.
Moreover, heating the spherulites to within 5°C of their melting point (59.5°C) causes an irreversible change in structure (cf. Section 5.3). As a result, it was difficult to form good images — the sample was damaged in less than one second. Often, samples are coated with a conducting layer prior to imaging to remove these problems. In this case, we were able to obtain useful images without resorting to such techniques. This success requires careful adjustment of the electron beam current so that the incident flux is balanced by the electrons emitted from the sample [157].

A close examination of Fig. 5.6 shows that the innermost concentric bands are not perfectly circular. Atomic-force microscope images (Figs. 5.10a and b) show that the nuclei have the classic sheaf form discussed in Section 2.5, but with the additional complication of banding. Unlike Figs. 5.10a and b, Fig. 5.10c does not show a sheaf, but, rather, a two-armed spiral. This may be due to heterogeneous nucleation at a dust particle.

We can also use the AFM to study the microstructure of mode E, which, like mode F, has microcrystals too small to be seen optically. In Fig. 5.11, we see that the microcrystals in mode E seem to have a ribbon-like shape with clear branching.

### 5.3 Spherulite stability

Although the spherulites are stable enough that it is possible to study their structure, it is important to understand that they are not the stable phase for solidified 10 OCB. This is not surprising since they are grown far from equilibrium. In fact, it has been observed that spherulites of some materials can break up with explosive force [11]. We have seen evidence of a built-in stress in our spherulites, as well.

Our spherulites often fracture concentrically along the bands, as in Fig. 5.12, within a period of hours, especially when grown at large undercooling. Over a period of several days, the bands disappear completely. This process can be accelerated when the spherulites are heated above room temperature. If the spherulites are annealed at a few degrees below the solid-to-smectic A transition temperature, the bands disappear in a matter of minutes. There seems to be a well-defined front associated with this change, as shown in Fig. 5.13. The velocity of this front depends on the growth temperature of the original spherulite, as well as on the temperature to which the spherulite is heated. The front in this figure has a velocity of \( \sim 10 \ \mu \text{m/s} \).

When we examine the microstructure of the "unbanding transition," we find that a clear
Figure 5.10: AFM images of spherulite nuclei. (a) and (b) "Sheaf-like" nuclei (to be compared with Fig. 2.7). (c) Two-armed spiral.
CHAPTER 5. BANDED SPHERULITES

Figure 5.11: Microstructure of mode E imaged by atomic-force microscopy. The microcrystals are ribbon-like and highly branched.

Figure 5.12: Fracture of banded spherulites. Within a period of hours, 10 OCB spherulites solidified below room temperature (to an undercooling of ~40°C, in this case) often fracture in concentric cracks along the bands, indicating a built-in stress. There are also radial cracks emanating from the origin.
change in the morphology has occurred. Fig. 5.14 shows an initially banded region after the bands have disappeared. The microcrystals are now much larger and all remnants of the band ordering have vanished. The difference is also apparent in the change in the X-ray diffraction pattern, as shown in Fig. 5.15.

5.4 Video microscopy of banded spherulite dynamics

Thus far, we have been considering the microstructure of banded spherulites grown under a variety of conditions. If we are to learn more about how this mode grows, it is useful to study the dynamics of spherulitic growth. We did this by video microscopy using a camera with a 30 Hz frame rate. Each frame consists of two interleaved frames, allowing us to use digital image processing to extract two frames separated by 1/60th of a second from each frame.

Fig. 5.16 shows a two-frame sequence of the growth with differences between frames highlighted in black. The major difference between the frames is that the band that has nucleated in the first frame has spread laterally without much growth in the direction normal to the bands. The longer video sequence of Fig. 5.17 shows this lateral growth repeated
Figure 5.14: AFM micrograph of a banded region after annealing at a temperature 5°C below the melting point. Note that the bands have vanished.

Our observations suggest that the nucleation of lateral growth generally occurs at points that lag neighboring portions of the front. These bands then grow tangentially along the front until they end at a step at the end of a domain or meet another growing band. Large domains of in-phase spherulites are then the result of a local effect: each band in a given domain grows from a single nucleation point, over top of the previous band, resulting in a periodic band structure.

There are some difficulties with this model, however. It is not obvious why growth would occur laterally along the front or, if this does happen, why this growth, which would be the fastest growth direction, does not become the radial velocity of the growth front. The radial growth of the bands would need to be limited by some effect which stops the growth before the next band covers it.

In any case, the information we are interested is at the limit of optical resolution of our
Figure 5.15: Change in X-ray diffraction peaks due to annealing. The samples were solidified by free growth, resulting in growth in all directions within the sample plane.

5.5 Conclusions for banded spherulitic growth in 10 OCB

In summary, we have studied the growth of spherulites in 10 OCB. The characteristics of the microcrystalline arrangement into bands and the sheaf morphology at the nucleus indicate that these spherulites are very similar to those seen in other materials.

We saw no evidence of either twist in individual microcrystals or a rotation in the orientation of successive crystals. It may be that our images lack the resolution to show this twist, but the arrangement of the microcrystals themselves indirectly suggests that this twist cannot exist in 10 OCB. Since the microcrystals are, at some undercoolings at least, only a single band spacing in length, they are too short to carry a continuous twist from band to band. On the other hand, the microcrystals are too long for the bands to result from a succession of untwisted microcrystals whose orientation depends on radial position.
Figure 5.16: Video sequence of banded growth. The top and bottom images are separated by 1/60th of a second, with differences between frames highlighted in black. This sequence suggests nucleation and lateral growth of a band over top of a relatively static growth front.
Figure 5.17: Longer video sequence. The images are again separated by \(1/60\)th of a second.
CHAPTER 5. BANDED SPHERULITES

— each crystal extends an entire band spacing, regardless of its starting point.

Moreover, in the birefringence models, it is generally assumed that the phase coherence of the bands within a single domain is inherited: each microcrystal in a single domain can be traced to a common ancestor. In that case, we would expect to see new domains nucleate and grow from an initially small region of the front. Each new domain would have to be associated with two boundaries in the form of phase discontinuities. Instead, we find that new domains often arise as the result of a single new phase discontinuity forming within an existing domain. Such an observation favors our lateral growth model. Such domains could form if bands nucleated at two points within a single domain, creating a new phase jump due to mismatch when they meet.

On the other hand, we have provided clear evidence that the banding is associated with a modulation in the density of microcrystals. This suggests that even though twist is present in other spherulites, it may not be the fundamental feature of banding.

Given that we now have some understanding of what the bands are, we would like to address the question of how they are formed. Again, we have not arrived at a definitive answer. However, we do have hints as to which quantities may be important and which are certainly not.

Spherulitic growth in irregular droplets and through narrow necks allows us to eliminate temperature, impurity, and flow fields at distances of more than a few band spacing from the front as important quantities. Directional solidification, with a large imposed temperature gradient, resulted in an unchanged morphology. The overall structure and coherence of bands is thus the result of very local properties.

If we discard the idea that the bands arise from a twist in microcrystals with a phase inherited from parent crystals, the most obvious possibility remaining is that they form spontaneously at the front. Our attempts to model this growth focused on front instabilities.

One possibility that we considered is the “explosive crystallization,” mechanism discussed in Section 2.4. In our case, this mechanism does not seem relevant. Although there is a region near the onset of the banding where the velocity does decrease with increasing undercooling (and any successful model will need to explain this), the average growth velocities for the banded spherulites extends to much higher velocities than the local maximum. Also, since this mechanism is highly dependent on the details of the temperature rise at the interface, the temperature for the onset of banding and the resulting wavelength would be expected to depend on sample thickness. This has not been seen experimentally.
Another possibility is that the bands are somehow produced by stress induced by viscous flow in the melt. We have seen that there is a large amount of stress built into the spherulites. We have also observed rapid fluid flow, caused by the density change during solidification, far from the spherulites during solidification. Although we have already shown that the far field is unimportant, this flow must also exist near the interface, where the relevant length scale will be the size of the channels between microcrystals. As discussed in Section 2.5, this flow will induce a stress in the growing needles [80], causing them to bend or perhaps even break. The stress will also change the free energy and, hence, the growth velocities of the crystals. Thus far, we have not been able to demonstrate an instability in simple models of this process.

Both of these models treat spherulitic growth by a “coarse graining” over the separate microcrystalline domains which form the spherulite. It may be that the essential physics lies in the nucleation of these needles, rather than in their growth [11]. The formation of the bands would then be due to a collective phenomenon in which the nucleation of one domain influences that of others near by. This might be expected, for instance, when the individual crystals are comparable in size to the critical nucleus. Such a process is consistent with our observation of lateral growth of the spherulite bands.

As discussed in Section 2.4, growth can be regarded as a process of nucleation and lateral growth of new domains. The size of domains formed in this manner must scale as $\xi=(v_g/I_d)^{1/(d+1)}$, were $v_g$ is the growth velocity, $I_d$ is the nucleation rate per unit volume, and $d$ is the dimension of the model [158] (in this case $d=2$ since we are considering secondary nucleation at the surface of the spherulitic domain). Both $v_g$ and $I$ decrease with increasing supercooling. The characteristic domain size will become small if $v_g$ is the more rapidly decreasing function. Measurements of crystal size in most materials, including 10 OCB, show that crystal size usually becomes small at large undercoolings. Of course, neither $v_g$ nor $I_d$ are expected to remain constant, as assumed by this simple discussion, when the domain sizes become small enough to interact.
Chapter 6

CONCLUSIONS

We have, in the space of a few pages, considered a very complicated solidification system. The freezing of 10 OCB results in a large variety of complex and, in some cases, surprising and previously unknown growth modes. Even in restricting our attention to the transitions between these growth modes and ignoring the details of the growth mechanisms themselves, we were left with a great many observations. In one case, we departed from this strategy and delved into the mysteries of the banded spherulite. (In addition, our studies with the atomic-force microscope required an understanding of its inner workings and fundamental limitations. The details of this I leave to Appendix A.) Ultimately, we can hope for an understanding of solidification phenomena that is complete enough to explain all of these observations. For now, we will have to be satisfied to separate out those observations that allow us to make immediate conclusions and which suggest future experiments.

First of all, we have found a material that exhibits a wealth of solidification morphologies. Several morphologies — such as faceted dendrites, sidebranched dendrites, tip-splitting, non-crystallographic branching, and spherulitic growth — are known from other systems. Our observations are all in a regime where diffusion is expected to be important (the dimensionless undercooling was less than 0.7 for mode F), but some of the morphologies, particularly spherulitic growth, are far from pure diffusion-limited growth: there, kinetics are also important (the fronts are space-filling, characteristic of kinetics-limited growth). Although such behaviour is not unknown in other systems, 10 OCB has the advantage of convenient time and temperature scales. This convenience makes a detailed study of the morphology diagram possible.

Our studies of spherulitic growth reveal a morphology that is strikingly similar to the
spherulites seen in other systems. However, we find no evidence that the explanation of banding for these other systems is relevant to spherulites in 10 OCB: atomic-force microscope studies have not revealed a periodic rotation in the orientation of the microcrystals which make up the spherulites. These AFM studies do, however, show that the bands are associated with a modulation in the density of these microcrystals. Experimental goals for future studies of 10 OCB spherulites are to verify the nature of the bands and to study their growth with greater spatial and temporal resolution. On the theoretical side, we suggest that the search for a general mechanism for the growth of banded spherulites should focus on a search for a front instability or cooperative nucleation effect that can lead to a periodic density modulation.

We have presented clear evidence that sharp transitions between growth morphologies do occur in solidification, even beyond the diffusion-limited regime. These transitions are signaled by pre-transitional effects and are accompanied by sudden changes in the microstructure and in the behaviour of the growth velocity. Moreover, when the undercooling is changed during growth, we see nucleation and front propagation, rather than a smooth cross-over to the new morphology. Clearly, then, the different growth modes represent fundamentally distinct processes, only one of which is selected for any particular undercooling. The “exception that proves the rule” is that for undercoolings near a morphology transition, successive experiments will sometimes result in different morphologies. This indicates that, though two morphologies can exist, some selection principle determines which is more stable, and is hence ultimately observed. We attribute the fact that it is, in fact, the less stable mode that is occasionally observed to transient effects: both modes have similar stability near the transition, but we are confident that with a big enough sample, the most stable mode will win.

No universal set of morphology selection rules has been provided from theoretical considerations, though it has been proposed that the mode with the fastest growth rate will eventually take over the growth front. We find that this rule is consistent with our observations in cases where the growth velocity, but not its slope, is continuous across the transition (i.e. for second-order transitions). This is made particularly clear by the selection of mode D, which occurs in two separate undercooling ranges. Between these ranges, the growth velocity of mode B increases with undercooling more rapidly than that of mode D, so that mode B becomes the faster-growing mode. Mode D reappears at a larger undercooling when the velocity curve of mode C levels off and drops below the velocity curve for mode D (which
continues to increase with undercooling).

However, the transition to one of the growth modes (mode $B'$) is accompanied by a jump in the velocity (and so is termed a first-order morphology transition). A different selection rule is clearly needed in this case. Although the selection principles at work here — if any — remain unknown, it is likely that mechanism allowing the slower of two modes to be selected involves the structure of the modes (specifically, the lateral branching mechanism and the detailed dynamics of individual tip growth).

In studying primarily the transitions between growth morphologies, we have left several questions about the modes themselves unanswered. Some of these modes are deserving of individual study. In particular, it would be interesting to understand the growth mechanism responsible for the entangled “spaghetti” of mode A which occurs even at the smallest undercoolings, as well as the reason for the sudden appearance, and equally sudden disappearance, of the rapidly-growing mode $B'$. Nor have we exhausted the possibilities for studying morphology transitions: in measuring the morphology as a function of undercooling for a single sample, we have traced but a single path through morphology space. Other parameters may reveal new behaviour. For example, we have studied the effect of thickness enough to know that it is important for certain modes.
Appendix A

THE ATOMIC-FORCE MICROSCOPE

As discussed in Section 3.2.1, the atomic-force microscope (AFM) is a device for imaging surfaces at the near-atomic level. Here, I will discuss a few technical details necessary for the quantitative interpretation of AFM data. The scope of this discussion exceeds that which is necessary for the study of spherulites in a liquid crystal; however, it is also a record of the early part of my thesis work [119, 120, 121].

A.1 Calibration of the atomic-force microscope

Before the AFM can be used to obtain accurate quantitative data, several calibrations must be performed. In the remainder of this section, I will discuss the calibration of the sample translation stage, the cantilever deflection detector, and the cantilever spring constant.

A.1.1 Scanner calibration

One of the difficulties of scanning probe instruments is that they use piezoelectric actuators to control the sample position as it is scanned beneath the probe. Although piezoelectrics, with their ability to generate controlled motion at the sub-angstrom level, have made scanning probe instruments possible, their linearity characteristics still leave something to be desired. Hysteresis during a motion cycle and creep in the piezo extension when the applied voltage remains constant create problems when the goal is to obtain quantitative results.
In practical terms, the response of a piezo to changes in applied voltages involves a set of relaxation time constants whose values range from microseconds to tens of seconds. Thus, results often depend on previous scan history.

In the latest generation of instruments, the solution has often been to measure the piezo extension independently, for instance, by optical interferometry. In older instruments, the only solution is to perform calibrations under a variety of conditions (i.e., scan speed and size) and to perform all quantitative measurements under these conditions.

We performed lateral calibrations with two standards: one for large area scans, and one for scans at the atomic scale. For large area scans (1–100 μm), a set of calibration images of a two-dimensional 1 μm diffraction grating was used. For smaller scans, calibrations were usually based on scanning tunnelling microscope (STM) images of a freshly cleaved graphite surface. Two such calibration images are shown in Fig. A.1. It is worth emphasizing that calibration is as much a function of scan speed as it is of scan size. However, the dependence is not so dramatic as to require calibrations for every possible scan condition for qualitative work.

It is clear from Fig. A.1a that the calibration is not constant over the image. This leads to a nonlinear distortion. Provision has been made to correct this in the imaging software, but this correction is a simple stretching correction \((X, Y) \rightarrow (X', Y')\) of the form

\[
X' = f(X), \quad Y' = g(Y)
\]

and neglects cross-terms. Furthermore, these nonlinear corrections will also depend on scan conditions so a single pair of functions is not appropriate. Another approach is to use a calibration image such as Fig. A.1a as a map to correct the image. We had no need of this procedure for the imaging included in this report.

In addition to calibrating the piezoelectric scanner in the \(x\) and \(y\) directions, it is necessary to perform a calibration in the \(z\) direction. Several methods for this calibration have been discussed in the literature. Most rely on imaging samples with known changes in height, such as atomic steps on flat surfaces [160, 161], viruses [162], and polystyrene spheres [163]. For our work, we required an accurate \(z\) calibration for force spectra (see Appendix A.4). Since these are measured at relatively low speed, we found that it was sufficient to measure piezo displacement using a linear variable differential transformer (LVDT) displacement transducer [164]. The vertical range of the piezo was approximately one micrometer in our case, which is a small displacement, even for relatively sensitive LVDTs.
Figure A.1: Calibration images for two scan sizes. (a) AFM image of a two-dimensional diffraction grating. (b) STM image of a graphite surface. Note that this is a honeycomb lattice with atom positions at the vertices. A bias voltage of 0.02 V and set-point current of 0.53 nA were used.
(ours had a full range of ~1 cm). The sensitivity of an LVDT depends on the transformer driving frequency. By using the highest available frequency, a high gain, and averaging over several sets of data, we found that we could perform adequate calibrations [120].

A sample piezo calibration is shown in Fig. A.2a, where several individual runs have been averaged. The $y$ axis of this plot was calibrated using the LVDT, which was itself calibrated with a micrometer. The $x$ axis is recorded in units corresponding to the digitized voltage output from the AFM control module. The curve is accurately modeled as a quadratic, as evidenced by the fit residuals shown in Fig. A.2b.

![Piezo calibration graph](image)

Figure A.2: Measurement of vertical piezo displacement as a function of applied voltage in terms of the binary channel set by the AFM control unit. (a) Displacement of the piezo measured by an LVDT. (Average of 32 runs.) (b) Residuals of a quadratic fit to the data

A.1.2 Detector calibration

Several methods of detecting cantilever deflection are in use. In our case, cantilever deflection is measured using the optical-lever technique [117]. In this detection system, a laser beam
is reflected from the back of the cantilever onto a position-sensitive photodetector (PSPD). The cantilever deflection is then measured as a difference signal between the two halves of the PSPD. This signal is not likely to be linear with the deflection; rather, it depends on the cross-sectional intensity distribution of the reflected laser beam, which will be different each time the laser is adjusted for a new microlever [165].

Once the vertical response of the piezo scanner has been calibrated, we can calibrate the detector by measuring its signal as a function of piezo extension. The measurement of cantilever deflection as a function of piezo extension is termed a "force spectrum." If we assume that the compliance of the weak cantilever is smaller than that of either the tip or the sample [166], then the deflection of the tip and the displacement of the sample must be equal once the two are in contact. This allows us to use the regions of force spectra where the tip and sample are in contact as calibration curves for the detector. As we only need to calibrate the detector for deflections smaller than a few nanometers, we can use a linear fit to a small portion of the force spectrum.

A.1.3 Cantilever calibration

The atomic-force microscope is increasingly being utilized to probe surface forces at very small scales. The accuracy of such measurements depends upon a knowledge of the physical properties of the spring and tip that probe these forces. In particular, one needs to estimate the force constant of the cantilever spring to which the tip is attached.

Despite this need for calibration of individual cantilevers, the force constants of cantilevers are rarely measured; rather, they are inferred from theoretical estimates based on the geometry and elastic properties of the cantilevers [167]. Often, the calculations themselves are suspect, since they are generally based on a simple, rectangular-beam geometry while the actual springs are "V"-shaped [168].

The spring constant of a cantilever spring of length $\ell$, width $w$, and thickness $t$ is given by the formula [169]

$$k = \frac{Ewt^3}{4\ell^3},$$

(A.1)

where $E$ is the Young's modulus for the cantilever material. The spring constant for a V-shaped lever is then estimated by doubling the value calculated for a single arm, assuming a rectangular geometry. Recently, more refined calculations have been performed [168, 170], but these still suffer from the problems discussed below.
The cantilevers are often made of multiple materials (e.g., gold on silicon nitride), making a proper estimate of their elastic properties difficult. More important, this approach neglects the possibility of variation in the force constants of individual springs due to structural defects and variations in the lever geometry and composition. For example, since the spring constant depends on the lever thickness $t$ as $t^3$, even small variations in the thickness will result in large variations among the force constants of nominally identical springs.

A more direct way to measure the force constant of a spring is to measure the response to weights attached to the tip. This procedure has been carried out by Hansma, et al. [171]. The drawback of this procedure is that it is not easy to place objects at the end of a cantilever that may be less than 50 μm long, and it is difficult to reliably estimate the mass of weights of the appropriate small sizes. Moreover, once this is done, the tip is unusable for subsequent measurements, owing to the difficulty in removing the weights without damaging the tips.

We have developed a direct method for estimating the spring constant that does not damage the tip or cantilever [120]. The basic approach involves the measurement of thermal fluctuations in the cantilever.

A harmonic oscillator in equilibrium with its surroundings will fluctuate in response to thermal noise. The Hamiltonian of such a system is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2$$

where $q$ is the displacement of the oscillator, $p$ is its momentum, $m$ is the oscillating mass, and $\omega_0$ is the resonant angular frequency of the system. By the equipartition theorem, the average value of each quadratic term in the Hamiltonian is given by $k_BT/2$, where $k_B$ is Boltzmann’s constant and $T$ is the temperature. In particular,

$$\langle \frac{1}{2}m\omega_0^2 q^2 \rangle = \frac{1}{2}k_BT.$$  

As $\omega_0^2 = k/m$, the force constant may be obtained from a measurement of the mean-square spring displacement as

$$k = \frac{k_BT}{\langle q^2 \rangle}.$$  

For a spring constant of 0.05 N/m, typical of relatively weak AFM cantilevers, thermal fluctuations will be of the order of 3 Å at room temperature. For such small deflections, we can approximate an AFM cantilever as a simple harmonic oscillator with one degree of
freedom. (Other elastic modes of the cantilever have a much higher force constant and thus do not contribute much to the value of \( \langle q^2 \rangle \).) This implies that if we measure the RMS fluctuations of a freely moving cantilever with a sampling frequency much higher than its resonant frequency (to avoid averaging out the fluctuations), we can estimate the spring constant. However, other noise sources are present.

In order to isolate the contribution due to thermal oscillations, we examine the data in the frequency domain. In the absence of additional noise sources and in the limit of small damping, the power spectral density of the fluctuations in the spring displacement has a Lorentzian line-shape [172]. Other noise sources add a background to this thermal response. As none of the other noise sources is likely to have a resonance at the resonant frequency of the cantilever, it is a simple matter to subtract this background. The area below the remaining peak is then a measure of the power of the cantilever fluctuations. Since the integral of the power spectrum equals the mean-square of the fluctuations in the time-series data [136], the estimate of the spring constant becomes

\[
k = \frac{k_B T}{P}, \tag{A.5}
\]

where \( P \) is the area of the power spectrum of the thermal fluctuations alone. An example of the power spectrum of cantilever fluctuations is shown in Fig. A.3.

This method has recently been adopted as part of the standard software package used by the Topometrix corporation in their commercial AFMs [173].

A.2 Lateral resolution of the atomic-force microscope

Imaging with atomic resolution requires a probe of atomic dimensions. In the scanning tunneling microscope, this requirement is fulfilled by the exponential decay of the electron tunneling current with the tip-sample separation. The decay length of this current is approximately 1 Å, so the total current is dominated by electrons flowing through the single tip atom that is closest to the sample surface. Thus, even though STM tips have a macroscopic radius of curvature that is rarely smaller than 100 Å, the effective tip size is a single atom, allowing it to produce images that have atomic resolution.

The AFM obtains its topographical information from the short-ranged repulsion resulting from the overlap of electronic shells between tip and sample. If this short-ranged force were the only one present, the AFM would operate in the same manner as the STM —
APPENDIX A. THE ATOMIC-FORCE MICROSCOPE

Figure A.3: Power spectral density of cantilever fluctuations. The data are fit to a Lorentzian curve in order to estimate the spring constant $k$. The disagreement of the calculated value with the value of $k = 0.064 \text{ N/m}$ claimed by the manufacturer underscores the importance of cantilever calibrations.

through a single atom — and one would be able to again produce images of atomic resolution. However, the presence of long-ranged interactions cause a deformation of the tip which results in a degradation of the image resolution.

The purpose of this section is to explore the undesired effects of these long-ranged forces and to suggest a way to control them. In order to do this, we will first need to discuss the various forces that may act. I single out one of the forces — the van der Waals interaction — for detailed study. In the second part of this section, we study the effect of these forces with a simple model of the AFM. The third section examines possible ways to improve this resolution. Finally, I will show some experimental results that illustrate the conclusions of the first two sections.

A.2.1 Forces involved in AFM imaging

The operation of an atomic-force microscope is based on the interaction between the tip and the sample. There are many forces that can be important. I will discuss several of these in turn.

The most important force in AFM imaging is the short-ranged repulsion. It is this force
that we rely on to provide information on the topography of a surface. It is usually modeled by one of the following three potentials [174]: a hard-sphere potential,

\[ w(r) = \begin{cases} 
0 & \text{for } r \geq r_0 \\
\infty & \text{for } r < r_0 
\end{cases}, \quad (A.6) \]

where \( r_0 \) is the hard-sphere diameter, a power-law potential,

\[ w(r) = (c/r)^n, \quad (A.7) \]

where \( n \) is often chosen to be 12, or an exponential potential,

\[ w(r) = ce^{-r/r_0}, \quad (A.8) \]

with a value of about 0.2 Å assigned to the parameter \( r_0 \). In fact, the exact form of this potential matters little, save that it be short-ranged.

Another force which is always present is the spring force of the cantilever to which the tip is attached. For the small displacements involved in typical imaging, this deflection of the cantilever is small, so the force can be modeled as a Hooke’s-law force.

The third ubiquitous force is the the van der Waals attraction. The van der Waals (vdW) potential between two molecules, being the result of induced dipole–induced dipole interactions, has the familiar \(-C/r^6\) form. If we take a continuum approach and integrate this interaction over the volumes of the tip and surface, we find that, for small distances the potential has the approximate form [175]

\[ W(D) = -\frac{AR}{6D}, \quad \text{for } D \ll R, \quad (A.9) \]

where \( D \) is the separation between the sphere and surface, and \( A \equiv \pi^2 C \rho_1 \rho_2 \) is the so-called Hamaker constant, where \( \rho_1 \) and \( \rho_2 \) are the densities of the two solids. Although this simple pair-wise addition neglects many-body effects, the result of these is to change the value of the Hamaker constant, but not to change the form of the potential. Retardation effects, which limit the interaction for large distances, have also been neglected, but these are unimportant for a tip in hard-sphere contact with the surface.

In general, the electrodynamic van der Waals interaction will be swamped by any electrostatic forces that are present. For instance, large forces will be experienced if the tip or sample become electrically charged. This can be a problem for imaging in vacuum. Imaging in an ionic fluid will usually allow the tip and sample to discharge, but leads to electric
double-layer forces [176] due to concentration of ions at the surfaces. Imaging in humid air will also allow the surfaces to discharge, but will often lead to the formation of a thin film of water on the surface. The resulting meniscus forces can lead to a very large attraction between the tip and sample when in contact.

In the following model, I will assume that the vdw force is the only long-ranged interaction acting, because, in contrast with the various electrostatic forces, this force will always be present.

A.2.2 A model of the atomic-force microscope

We will model the AFM as a spherical tip of radius \( R \) supported by a spring of force constant \( k \), as shown in Fig. A.4. The actual tip geometry is more complicated (our measurements were performed using tips that are nominally four-sided pyramids ending in a rounded tip with a radius of about 400 Å), but we can safely ignore the details of the tip geometry because the vdw forces are dominated by the tip atoms that are closest to the sample. Moreover, retardation effects limit the effective range of the van der Waals force to several hundred Ångstroms, allowing us to ignore the contributions to the vdw forces for atoms outside the ball at the end of the tip. In Fig. 3.3a, \( Z \) is the height of the bottom of the tip above the surface in the absence of external forces — i.e. for an undeflected cantilever. Short- and long-ranged forces act on the tip to cause a deflection \( \delta \) from this height \( Z \), so that the actual tip-sample separation is \( D = Z + \delta \).

In the absence of the short-ranged repulsion, the equilibrium tip position will be one where the vdw and spring forces balance. This point may be determined by finding the energy minimum for the system. The potential energy may be written as

\[
E(\delta, Z) = \frac{AR}{6(Z + \delta)} + \frac{1}{2}k\delta^2,
\]

(A.10)

where \( Z \) is determined by the piezo extension and acts as a control parameter. This energy function has a singularity at \( \delta = -Z \), when the tip-sample distance is zero. Of course, contact forces will always limit the approach distance to a few Ångstroms. Local minima of the energy function may be found by setting its derivative equal to zero:

\[
\frac{dE(\delta, Z)}{d\delta} = \frac{AR}{6(Z + \delta)^2} + k\delta = 0.
\]

(A.11)

Thus, the critical values of \( E \) are the solutions of a cubic equation and so can be calculated analytically. Note that Eqs. A.10 and A.11 may be scaled so that they depend on only
Figure A.4: Simple model for the tip-surface interaction. (a) A tip of radius $R$ is suspended a distance $D$ above a surface. The tip is acted on by vdw forces, causing the spring to stretch and the tip to move by an amount $\delta$ from the spring equilibrium height $Z$ above the sample. Note that in the case of an attractive vdw interaction, shown here, $\delta$ is negative. (b) The snapping instability causes the tip to hit the sample. Finite elastic moduli cause the tip and sample to deform. As suggested here, the sample is usually softer than the tip and deforms more.
one parameter, $\ell \equiv \sqrt{AR/k}$, which is the length scale at which the vdW forces are able to deflect the spring significantly.

Solving Eq. A.11 for $\delta(Z)$, we find

$$
\delta(r) = \left\{ \begin{array}{ll}
\frac{2}{3} \left| Z \cos\left(\frac{1}{3}\arctan\sqrt{\frac{a}{b}}\right) - Z \right| & \text{for } A < 0 \\
(a + \sqrt{b})^{1/3} + (a - \sqrt{b})^{1/3} - \frac{2Z}{3} & \text{for } A > 0, b > 0 , \\
\frac{2}{3} \left| Z \cos\left(\frac{1}{3}\arctan\sqrt{\frac{a}{b}}\right) - Z \right| & \text{for } A > 0, b < 0
\end{array}\right.
$$

(A.12)

where

$$a = \frac{Z^3}{27} - \frac{\ell^3}{12}$$

and

$$b = \frac{\ell^3}{18} \left( \frac{\ell^3}{8} - \frac{Z^3}{9} \right).$$

Not surprisingly, $\delta = 0$ for large tip-sample distances. As $Z$ is decreased, moving the tip and sample together, an attractive vdW interaction ($A > 0$) will cause the tip to be deflected toward the sample. When $Z$ is decreased to $3^{2/3}\ell/2$, the solution given by Eq. A.12a becomes unstable — the magnitude of the gradient in the vdW force has become larger than that in the spring force. This occurs at a tip-sample distance of $D = Z + \delta = 2Z/3 = \ell^{\sqrt{3}}$ from the sample. At this point the tip will “snap” into contact with the surface [177]. For typical values of the Hamaker constant, tip radius, and spring constant ($10^{-19}$ J, 500 Å, and 0.1 N/m, respectively), the tip will jump into contact with the surface when it is about 26 Å away. At this point the separation is large enough that atomic scale roughness will have little effect on determining the snapping point, but small enough that the assumption in Eq. A.9 that $D \ll R$ is justified.

Once in contact, the vdW force and any applied spring force is balanced by the repulsion of the relatively few tip atoms in contact with the sample. It is in this mode that most AFM imaging is performed.

The tip-sample interaction can be measured as a “force spectrum,” where the cantilever deflection is measured as a function of sample extension,$Z$. Figure A.5 sketches the general shape of a force spectrum. The approach curve shows the snap to contact discussed above. On retraction, the tip remains in contact with the sample, even a finite negative applied force. This is due to the adhesive forces and has important consequences to the image resolution of the AFM.

If both sphere and surface were infinitely rigid, they would touch at just one point. However, as both have a finite elastic modulus, they each deform and make contact over a
APPENDIX A. THE ATOMIC-FORCE MICROSCOPE

Figure A.5: Typical force spectrum showing the cantilever deflection as a function of piezo position. The solid line is the approach curve and the dashed line shows the deflection as the piezo is retracted. Note the snap to contact after which the tip remains in contact even with a negative applied force.

small circle of radius $a_0$, as illustrated in Fig. 3.3b. Long ago, Hertz found that the size $a_{H}$ of this circle for an external loading $F$ of a sphere of radius $R$ is given by

$$a_{H}^3 = \frac{RF}{K}, \quad (A.13)$$

where $1/K$ is given by

$$\frac{1}{K} = \frac{3}{4} \left( \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right), \quad (A.14)$$

where $\nu$ is Poisson’s ratio and $E$ is Young’s modulus for materials 1 and 2 (tip and sample) [178, 179].

We can use this to estimate the maximum loading force permitted for atomic resolution. For typical values of the Young’s modulus ($1.5 \times 10^{11}$ N/m$^2$ for Si$_3$N$_4$), Hertz theory predicts that in order to have a contact radius of atomic dimensions, say 3 Å, between a sample and a tip with a 400 Å radius of curvature, the loading force may not exceed 90 pN. This force is considerably smaller than the vdW force between the tip and sample in cases relevant to AFM operation in air. If we continue to approximate our deformed tip as a sphere, the force between it and the sample may be calculated by differentiating Eq. A.9 with respect
APPENDIX A. THE ATOMIC-FORCE MICROSCOPE

where $D_0$ is the minimum distance between sphere and surface allowed by the repulsive contact forces. Eq. A.15 gives a value of 37 nN for the system discussed above, assuming values of $10^{-19}$ J for $A$ and 1.5 Å for $D_0$.

While the Hertz theory may provide a sufficiently accurate model for the case of repulsive vdW forces, it neglects the effect of surface forces. In our model, the vdW interaction, in addition to providing the loading force, acts as a surface force between the tip and sample. This causes deformation of the surfaces, increasing the contact area (cf. Fig A.4b). A calculation that includes the effect of adhesive forces, due to Johnson, Kendall, and Roberts [180], yields the formula

$$a^3 = \frac{R}{K} \left[ F + 3\pi R W_{12} + \sqrt{6\pi R W_{12} F + (3\pi R W_{12})^2} \right]$$

for the radius $a$ of the contact region between a sphere of radius $R$ and a plane. In Eq. A.16, $F$ is the external loading force and $W_{12}$ is the adhesion energy, which here is due to the van der Waals interaction. In the absence of an external load, the contact radius remains finite and is given by

$$a_0 = (6\pi R^2 W_{12} / K)^{1/3}.$$  \hspace{1cm} (A.17)

Adhesion causes the surfaces to remain in contact, even with small negative loads, until a critical value, given by

$$F = 3\pi R W_{12}/2,$$  \hspace{1cm} (A.18)

when the value of $a$ given by Eq. A.16 becomes complex. At this point, the contact area abruptly goes to zero as the surfaces detach. The minimum radius that can be reached by applying a negative load before separation occurs is given by

$$a_{min} = (3\pi R^2 W_{12} / 2K)^{1/3} = a_0/4^{1/3}.$$  \hspace{1cm} (A.19)

As an estimate the adhesion energy, assume that the tip and sample surfaces are flat over the region of interest. Then the energy per unit area required to separate the surfaces is [181]

$$W_{12} = A/12\pi D_0^2.$$  \hspace{1cm} (A.20)
Combining Eqs. A.19 and A.20, we see that the minimum radius $R$ of the contact area of a sphere and surface is given by

$$R = \left( \frac{R^2 A}{8K_D^2} \right)^{1/3}.$$  \hspace{1cm} (A.21)

For the values of the parameters considered above, we find a minimum contact radius $R \approx 19 \, \text{Å}$.

As the AFM exploits the short-ranged repulsion of the sample to map out a surface, it is clear that the resolution of the AFM is determined by this contact area. A contact area with the radius $a_0$ given by Eq. A.17 is established as soon as the tip snaps into contact and can only be decreased slightly to $R$ by pulling with a negative force without losing contact with the surface. Clearly, these contact radii are too large to allow atomic resolution. It is still possible to image the surface of an ordered material, but the image will be a moiré pattern resulting from an interaction between the lattices of both tip and sample. It is possible to measure lattice constants in this fashion, but local features will not be resolved. Such "moiré" images are characterized by perfect lattices with no local defects. When the AFM is used to image non-periodic structures, such as DNA, the resolution does not exceed 30–50 Å.

Clearly this discussion of the resolution in terms of continuum mechanics must break down as $R$ approaches atomic scales. However, to attain such a small $R$, the vdW forces must be smaller than 1 nN. Atomic-level simulations of AFM operation generally predict that atomic resolution is possible if the contact force can be kept small enough (< 5 nN) [182]. Thus, this discussion should be adequate at resolution down to atomic scales.

### A.3 Improving the resolution of the atomic-force microscope

The discussion above showed that under typical conditions, the resolution $R$ is no better than 20 Å and in practice is often larger. This conclusion is well-known and suggests two strategies for improving AFM resolution. The most obvious one is to decrease the effective tip radius. To date, the limit in this approach has been the development of tips with nominal radii as low as 100 Å [118]. A second strategy, which we discuss below, is to modify the Hamaker constant itself.

As is shown in Appendix B, this may be done by immersing tip and sample in a liquid medium. If a medium with dielectric properties intermediate to tip and sample is used, this
will cause the van der Waals forces to be repulsive. This can be understood intuitively by realizing that if the sample is more attracted to the liquid medium than it is to the tip, the tip is effectively repelled by the sample. This is the same principle that causes a block of wood to rise under the influence of a gravitational field when it is immersed in a body of water: one can say that in the presence of water, the gravitational interaction between the Earth and the wooden body is repulsive.

Eq. B.13 of Appendix B is a good starting point in selecting a suitable medium. Although approximate, it is simple enough to quickly check candidate fluids.

By choosing a liquid medium for which the vdW interactions are repulsive, we avoid the snapping instability, and any sample damage which is associated with the snap to contact. If the fluid is tailored to make the vdW interaction as small as possible, the loading force, rather than being set by the long-ranged interactions, is chosen by the operator. The resolution will then no longer be given by Eq. A.21, but will depend instead on the area of the tip brought into contact with the sample by the applied spring force. The first priority, then, is to have a purely repulsive interaction. Given a repulsive interaction, the weaker it is the better, so as to minimize deformation of the surface when the tip is moved closer to the sample.

A.4 Experimental results

Our goal, then, was to find a liquid medium for which vdW interactions between tip and sample were repulsive and weak. To proceed, we measured deflection-vs.-piezo extension curves for a collection of Si$_3$N$_4$ tips and muscovite mica samples immersed in various media. To prevent contamination, a new mica sample was used for each different medium. This sample was fixed in a liquid cell, which allows operation of an AFM with both tip and sample immersed, and cleaved after immersion in the medium to be studied. (Mica cleaved in air is rapidly coated by a thin film of water.) Tips were rinsed in the immersion medium for an hour before use. In addition, at least one new tip was used for each medium.

We used a modified version of the force-spectrum routine in our AFM driver software to acquire individual spectra of 4096 points each. Ordinarily, such routines average the force spectra over several cycles. We found, however, that small thermal drifts, which can be caused by evaporation of the medium as well as by overall temperature fluctuations in the experimental apparatus, cause an offset of the curves in successive cycles, smearing out
the information contained in the narrow range where vdW forces can be seen to act. For this reason, single-cycle force spectra were recorded and values of the force parameters were averaged after extraction. The approach speed was set to 1400 Å/s, which is slow enough that viscosity effects are unimportant, except for very viscous fluids, yet fast enough that drift in the electronics and temperature is not a problem. Up to thirty spectra were recorded for each tip-medium combination.

We used cantilevers with low spring constants to increase the deflection caused by the forces. Since these cantilevers are longer than those with higher spring constants (200 µm as opposed to 100 µm), they are also better able to endure being repeatedly pressed through several thousand angstroms in contact with the surface. The cantilevers used had nominal spring constants of 0.032 and 0.064 N/m [118].

One possibility for an imaging medium would be water. Although this might be a useful fluid for biological applications, it yields little improvement in the long-ranged forces. The very high static dielectric constant and low (relative to Si₃N₄ and mica) refractive index guarantee that the vdW interaction will remain attractive in the presence of water for most samples. An example of a force spectrum measured in water is shown if Fig. A.6. This curve is presented in raw form, with x- and y-axes uncalibrated. The large hysteresis in the deflection signal shows the importance of a calibration scheme. This force spectrum shows that water can introduce an additional complication — since it is generally a good solvent for ionic compounds, a long-ranged repulsive force resulting from the electric bilayer forces can be seen. This repulsive force is not helpful in improving the imaging resolution because the vdW attraction still causes a snap to contact and a large imaging force when the tip gets close to the sample.

Eq. B.12 suggests that in order to minimize the vdW interaction, we should choose a medium with a dielectric constant and a refractive index close to those of either the tip or the sample. Since both mica and Si₃N₄ have rather high refractive indices (1.574 and 1.986, respectively [183, 184]), very few liquids meet these criteria. The dielectric constants of mica and Si₃N₄ are 5.4 and 6.34, respectively [184, 185]. For this study, three liquids were chosen: ethanol (which has a refractive index of nₑ = 1.3594 and a dielectric constant of εₒ = 24.55), 1-bromonaphthalene (nₑ = 1.6582, εₒ = 5.12), and 1-methylnaphthalene (nₑ = 1.6170, εₒ ~ 5) [186, 187]. Eq. B.12 suggests that the vdW interaction should be attractive, repulsive, and small, respectively.

We can use the force spectra to estimate the strength of the vdW interaction. The most
Figure A.6: Unprocessed force spectrum measured in water. There is a large difference between the approach (solid line) and withdrawal (dashed line) curve due to hysteresis in the piezoelectric scanner. The approach curve near contact is expanded in the inset. In water, an overall long-ranged repulsion due to electric bilayer forces is seen in addition to the attractive van der Waals interaction that occurs at shorter distances.

A convenient method for attractive interactions is to simply measure the size of the jump to contact. In order to do this, one needs to be able to calibrate the vertical axis of the force spectrum. This is easily done by assuming that when the tip and sample are in contact, changes in the piezo height must result in equal changes in the tip deflection. (We assume that the compliance of the cantilever is smaller than those of the tip and sample. This has been tested in other studies where cantilevers with much larger force constants were used [166].) Solving Eq. A.11 for \( \delta(Z) \), reveals that the Hamaker constant can be calculated as

\[
A = \frac{3k\Delta^2_+}{R},
\]  

(A.22)

where \( \Delta_+ \) is the snapping distance. For repulsive interactions, we can simply measure the tip deflection at \( Z = 0 \). The \( Z = 0 \) position may be located by finding the intersection between the baseline for the undeflected tip and the line asymptotic to the force spectrum when the tip and sample are in contact. We then find

\[
A = \frac{6k\Delta^2_-}{R},
\]  

(A.23)

where \( \Delta_- \) is the measured deflection. A better procedure, which we have implemented as well, is to fit the full force spectrum curve using predictions based on Eq. A.10. The full fit was used to calculate the solid lines shown in Fig. A.7.
Fig. A.7 shows representative experimental curves for the three media. These curves indicate the tip deflection as the tip approaches the sample. We did not use the curves for tip withdrawal since adhesion forces can depend on the contact area history, which varies from run to run.

We note that the vdW interaction is strongly attractive in the case of ethanol, as one would expect. Both other liquids give a repulsive interaction. The interaction for 1-bromonaphthalene is smaller than that for 1-methylnaphthalene. The reverse ordering for the naphthalene derivatives is not very worrisome: these liquids have dielectric properties similar to that of mica, so that small errors in the dielectric data can change the sign of the predicted Hamaker constant. In fact, more accurate and much longer calculations that I did (see Appendix B) based on the Lifshitz theory predict that the interactions will be attractive in all three cases. Even these predictions must be treated with care, for they are only as precise as the dielectric data used as input. In particular, good data for mica is difficult to obtain as the physical properties vary from sample to sample. The overall difference between the results for ethanol and those for the naphthalenes is nonetheless in agreement with expectations based on Eq. B.12.

Although, images of mica suggest that the image contrast does improve when a repulsive medium is used, images of a perfect mica surface are a poor standard to use to judge image quality. A better demonstration of an improvement in image resolution would be to compare images of a step, defect, or adsorbed molecule produced with different media. A clear improvement in resolution of DNA strands was observed by Hansma et. al. upon imaging in 1-propanol compared with images taken in ethanol [188, 189]. Here, the experimental force curve is weakly repulsive; thus, the improvement in image resolution is consistent with the ideas developed above. Both Eq. B.12 and the more exact Lifshitz theory predict an attractive vdW interaction in this case. Other long-range forces (e.g., electrostatic) are presumably responsible for the discrepancy.

A.4.1 The future of AFM resolution

In order to improve AFM resolution when attractive vdW forces operate, there are two strategies: decrease the tip radius \( R \) (make the tip sharper) or decrease the Hamaker constant \( A \) (reduce the long-ranged forces). In this study, we have pursued the latter strategy. A further step clearly would be to combine the strategies. We note that the relatively high value of the index of refraction for silicon nitride will lead to a large van der Waals
Figure A.7: Representative deflection vs. piezo extension curves for a Si$_3$N$_4$ tip interacting with a mica sample across various media. The data have been scaled so that the $x$-axis gives $Z$, the distance between the sample and the undeflected tip position. Solid curves are fits of a van der Waals interaction to the data. In each case, the value of the Hamaker constant, $A$, has been calculated from the fitting parameter $\ell \equiv \sqrt{AR/k}$ for the plot, assuming the nominal values for $R$ and $k$ (400 Å and 0.064 N/m, respectively). (a) Attractive interaction in ethanol ($\ell = 44.9$ Å). (b) Small repulsive interaction in 1-bromonaphthalene ($\ell = -22.2$ Å). (c) Repulsive interaction in 1-methylnaphthalene ($\ell = -56.9$ Å).
force whatever the choice of liquid medium. Thus, a related strategy is to try to find a tip material that will minimize the tip’s contributions to $A$ and yield a sample-independent improvement. It is clear that such a tip material will have to be an insulator rather than a metal or semiconductor.

We have shown experimentally that both attractive and repulsive vdW interactions can be measured using the AFM. This has important implications for image resolution and raises the possibility of using the AFM to map out local variations of the Hamaker constant [190]. And most importantly, we have shown that by careful choice of an immersion medium, long-ranged forces may be eliminated, allowing the AFM to operate using the short-ranged repulsion between the sample and a single-atom tip.

Such studies were not pursued by us for the simple reason that the cantilever detection system of our AFM did not appear to be up to the task without time-consuming modification. One of the major problems is that the design of the cantilever deflection sensor allowed much of the light from the laser to miss the sample. Some of this light is able to scatter into the detector diode and interfere with the light reflected by the cantilever. The result is that a periodic oscillation in the deflection signal is superimposed on the desired signal, as in Fig. A.8. In this case, we were using a scanner with a small range for maximum resolution, so little more than one period can be seen. The magnitude, phase, and exact form of these fringes depends on the details of the reflections from both cantilever and sample, and, therefore, changes every time the tip or sample is changed. This made it impossible to model the baseline well enough to enable accurate force spectra to be made. This problem could be eliminated by designing a different cantilever deflection system, something that is often done in custom-designed instruments [191]. Amusingly, this “problem” has recently been exploited to calibrate the vertical motion of AFM scanners [192].
Figure A.8: Baseline interference fringes. Interference between light reflected from the cantilever and light scattered from the sample results in a set of interference fringes superimposed onto the cantilever deflection signal.
Appendix B

VAN DER WAALS FORCES

The model of atomic-force microscope (AFM) operation presented in Appendix 3.2.1 assumes that the van der Waals (vdW) interaction is the only long-ranged interaction acting. Though this is unlikely to be the case in a typical experiment, the vdW force is the only long-ranged force that must be considered in all situations. The discussion of AFM resolution in terms of the vdW force then gives the best resolution we can hope to achieve. Thus, it is important to understand the origin of this interaction and to be able to estimate its strength.

The purpose of this Appendix is to present the reader with the minimum background necessary to understand and compute van der Waals forces. For rigorous treatments, the reader is referred to the literature [193, 194, 195, 196]. In the first section, I provide an intuitive discussion of the origin of this interaction. The second section expands on this with a quantitative estimate of these forces. Finally, a procedure for accurately calculating these forces is given in Section B.3.

B.1 The physics of dispersion forces

The van der Waals (vdW) force is often first encountered in the study of non-ideal gases. It is introduced as an attraction between molecules which causes departures from the ideal-gas law. An intuitive picture is usually given which describes the interaction as arising from the interaction between fluctuation-induced dipole moments in otherwise non-polar molecules. This interaction was extended to solid bodies by integrating the interaction between molecules over the volumes of the bodies. This approach is somewhat unsatisfactory.
as it ignores many-body effects: interactions between particles in a solid do not allow us to treat each pair-wise interaction as a separate contribution.

A more modern approach is to study the interaction between extended bodies. The familiar form for the vdW interaction can then be recovered as the limiting case as the bodies are reduced to small spheres.

Consider two half-spaces containing some medium separated by a constant gap of thickness $d$. Fluctuations in the charge distributions of the two materials will produce transient electric fields. These fluctuations exist even at absolute zero because of "zero-point" motion. For non-zero temperatures, the fluctuations are increased by thermal effects. Because the two spaces are not isolated from each other, the fluctuations are not independent. A correlation between fluctuations in the two bodies leads to a lowering of the total electromagnetic energy of the system.

The fields existing in the gap must satisfy the boundary conditions at the interface. These boundary conditions are set by the dielectric properties in the three regions. This is where the materials properties enter into the problem. Naturally, these boundary conditions lead to a quantization of the allowed fields in the gap. The average energy of these quantized "surface modes" can be calculated as a function of temperature.

Now, if we take the derivative of this energy with respect to the temperature of the system, we find the specific heat of the system. This calculation was done by Planck, when he considered black-body radiation. The energy also depends on the size of the gap. Thus, if we differentiate the energy with respect to $d$, we find the force acting between media 1 and 3. This is the van der Waals (or dispersion) interaction and exists between any two bodies. It happens that calculations based on pair-wise addition of the usual dipole potential integrated over both bodies give a force-law with the same form as one calculated using the scheme outlined above.

Note that the frequencies at which charges in a body fluctuate are those at which the material is able to absorb electric fields. Thus, a full knowledge of the absorption spectra will allow us to calculate the vdW interaction (this has led to the use of the term dispersion forces to describe the electrodynamic vdW interaction). It is this fact that leads to the specificity of the vdW interaction. Like bodies will always attract, across any medium, more than dissimilar bodies because of the "resonance" of the electromagnetic fields in the two bodies.
B.2 Calculation of the Hamaker constant

The interaction free energy per unit area between two half-spaces, 1 and 2 separated by a material 3 of thickness $d$, as shown in Fig. B.1, has the form

$$E_{123}(d) = -\frac{A_{123}}{12\pi d^2},$$  \hspace{1cm} \text{(B.1)}$$

where $A_{123}$ is known as the Hamaker constant. This was first calculated by Hamaker [175] by integrating an assumed $-C/r^6$ vdW potential over the volumes of the two half-spaces. The more rigorous derivation by Lifshitz [194] predicts this same form and gives us an equation for the Hamaker constant which takes into account the many-body nature of the interaction. According to this theory,

$$A_{123} = -\frac{3k_B T}{2} \sum_{n=0}^{\infty} \left. \int_0^\infty dx \ln(1 - \Delta_{12;n} \Delta_{32;n} e^{-x}) \right|,$$

where

$$x = 2k_B d,$$

$$\Delta_{jk;n} = \frac{\epsilon_j(i\xi_n) - \epsilon_k(i\xi_n)}{\epsilon_j(i\xi_n) + \epsilon_k(i\xi_n)},$$

and

$$\xi_n = n \left( \frac{2\pi k_B T}{\hbar} \right),$$

and where the prime on the first summation indicates that the $n = 0$ term is given half weight. At room temperature, the $\xi_n$ have a spacing of about $2.5 \times 10^{14}$ s$^{-1}$. Note that $-1 < \Delta_{jk;n} < 1$. Since $x > 0$, it must be true that $\Delta_{12;n} \Delta_{32;n} e^{-x} < 1$. This allows us to expand the log term as a power series. Integrating term by term, we finally find that

$$A_{123} = \frac{3k_B T}{2} \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \frac{(\Delta_{12;n} \Delta_{32;n})^s}{s^3}. \hspace{1cm} \text{(B.3)}$$

Thus, the interaction energy depends on the differences between the dielectric properties of the materials given by the functions $\epsilon(i\xi)$. Evaluating the dielectric response at the imaginary frequency $i\xi$, is a bit worrisome at first, but we can directly relate it to physically well-understood quantities through the Kramers-Kronig relation [197]

$$\epsilon'(\omega) = 1 + \frac{2}{\pi} \text{P} \int_0^\infty \frac{x \epsilon''(x)}{x^2 - \omega^2} \, dx, \hspace{1cm} \text{(B.4)}$$
where $\varepsilon''(\omega)$ is the imaginary part of the dielectric response

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega),$$

and is proportional to the absorption at frequency $\omega$. Note that this is a principal value integral since the integrand diverges when $x = \omega$. We can now calculate the function $\varepsilon(i\xi)$ by taking $\omega = i\xi$ in Eq. B.4 to get

$$\varepsilon(i\xi) = \varepsilon'(i\xi) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \varepsilon''(\omega)}{\omega^2 + \xi^2} d\omega.$$  \hfill (B.5)

As can be seen, the $\varepsilon(i\xi)$ function is real and decreases monotonically in $\xi$ (from $\epsilon_0$ at $\xi = 0$ to 1 as $\xi \to \infty$). Furthermore, it is constant in frequency ranges where the absorption $\varepsilon''$ is zero. These constraints allow us to use approximate forms for $\varepsilon(i\xi)$ without significant loss of accuracy (see Section B.3 below). Armed with a knowledge of the absorption spectra of the media, we can calculate the vdW interactions between the tip and the sample.

Note that since $\varepsilon(i\xi) \geq 1$, the Hamaker constant will be positive if the gap is empty (so that $\varepsilon_2(i\xi) = 1$). This means that the vdW interaction is always attractive across vacuum. However, if the gap is composed of a material with dielectric properties intermediate to the two interacting bodies, the $\Delta_{12}$ and $\Delta_{32}$ terms will have opposite signs, resulting in a negative Hamaker constant and a repulsive interaction. This simply reflects that fact that one surface may attract the opposite surface less strongly than it does the intervening medium, resulting in a net repulsion between the bodies. A similar effect occurs when a
One further complication is that of retardation effects at long distances. Because of the finite speed of light, a fluctuation in one body cannot affect the other for a time \( t_c = \frac{d}{c_3} \), where \( c_3 = c/\sqrt{\varepsilon_3} \) is the (frequency dependent) speed of light in the intervening medium. This means that the effect of the field induced in body 2 by a fluctuation in body 1 is not felt for a time \( t_c \), by which time it will be out of phase with the fluctuating fields in body 1, decreasing the interaction energy. If we assume that the speed of light is the same in all three media, this can be dealt with by multiplying the right-hand side of Eq. B.3 by the factor

\[(1 + r_n)e^{-r_n},\]

where \( r_n = 2d\varepsilon_3^{1/2}/c \) [195]. Note that \( r_n \) is simply the ratio of the travel time of an electric field of frequency \( \xi \) across the gap and back, to the period of the signal \( (1/\xi) \).

We can see that the attenuation due to this “retardation term” increases with gap size \( d \) and with frequency \( \xi \). Thus, the contributions of high-frequency fluctuations are always the most attenuated. For very large separations, it is only the zero-frequency term representing the static dielectric constant that contributes.

### B.3 Calculating the van der Waals force

To calculate Hamaker constants, we need an explicit representation of the functions \( \varepsilon(i\xi) \) for each of the materials involved. In principle, this would require measuring the absorption spectrum for all frequencies, which is impractical. However, Ninham and Parsegian [198] have shown that \( \varepsilon(i\xi) \) for insulators can be adequately approximated by functions of the form

\[
\varepsilon(i\xi) = 1 + \sum_{j=1}^{N} \frac{C_j}{1 + (\xi/\omega_j)^2}.
\]

They assume that there are \( N \) absorptions with strengths \( C_j \) in narrow frequency bands located at frequencies \( \omega_j \). If we set \( \xi = 0 \), we see that the \( C_j \) must obey the relationship

\[
\varepsilon_0 = 1 + \sum_{j=1}^{n} C_j.
\]

The absorption spectra for most materials is due to vibrational and rotational modes, which lie in the infrared, and electronic absorptions, which lie in the ultraviolet. As relatively
few infrared terms contribute to the sum in Eq. B.3, we ignore details of the infrared spectrum and approximate this region by a single term in Eq. B.6. For many materials, the absorption spectrum in the ultraviolet region is simple enough that it, too, can be approximated by a single term. Then

\[ \epsilon(i\xi) \approx 1 + \frac{C_{\text{IR}}}{1 + (\xi/\omega_{\text{IR}})^2} + \frac{C_{\text{UV}}}{1 + (\xi/\omega_{\text{UV}})^2}. \]  

The IR and UV absorptions can be inferred from the static dielectric constant, \( \epsilon_0 \), and refractive index, \( n(\omega) \), data for each medium [196].

For instance, in the visible region, \( \xi \gg \omega_{\text{IR}} \) and Eq. B.8 becomes

\[ \epsilon(i\xi) \approx 1 + \frac{C_{\text{UV}}}{1 + (\xi/\omega_{\text{UV}})^2}. \]  

Taking \( \xi = -i\omega \), and recalling that \( \epsilon(\omega) = n^2(\omega) \), we find that

\[ \epsilon'(\omega) = \epsilon(\omega) = n^2(\omega) = 1 + \frac{C_{\text{UV}}}{1 - (\omega/\omega_{\text{UV}})^2}. \]  

Rearranging, we find that

\[ n^2(\omega) - 1 = \left[ n^2(\omega) - 1 \right] \frac{\omega^2}{\omega_{\text{UV}}^2} + C_{\text{UV}}. \]  

Thus, \( 1/\omega_{\text{UV}}^2 \) and \( C_{\text{UV}} \) are the slope and intercept of a linear fit to the plot of \( n^2(\omega) - 1 \) against \( [n^2(\omega) - 1]\omega^2 \). An example of this method of analysis, which is known as the “Cauchy plot,” is shown in Fig. B.2.

We can estimate \( C_{\text{IR}} \) and \( C_{\text{UV}} \) without detailed knowledge of \( n(\omega) \) by noting that if \( \omega_{\text{IR}} \ll \omega \ll \omega_{\text{UV}} \), Eq. B.10 yields

\[ n^2 = 1 + C_{\text{UV}} \]

so that

\[ C_{\text{UV}} = n^2 - 1. \]

Then, from Eq. B.7, we have

\[ C_{\text{IR}} = \epsilon_0 - n^2. \]

Of course, this approach makes no prediction about the effective absorption frequencies \( \omega_{\text{IR}} \) and \( \omega_{\text{UV}} \).
APPENDIX B. VAN DER WAALS FORCES

Figure B.2: Cauchy plot for 1-bromonaphthalene. Note that very little data for the index of refraction, n, is required to estimate the effective UV absorption frequency and strength.

Israelachvili has taken the approximation one step further and assumed the absorption frequencies to be the same for all three media. Then, by replacing the infinite sum by an integral, he found

\[ A_{132} = \frac{3}{4} k_B T \left( \frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left( \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) \]

\[ + \frac{3h\nu_e}{8\sqrt{2} (n_1^2 + n_3^2)^{1/2} (n_2^2 + n_3^2)^{1/2} ((n_1^2 + n_2^2)^{1/2} + (n_2^2 + n_3^2)^{1/2})} \]

where \( \nu_e \) is the effective UV absorption frequency. Given that the calculation shown in Eq. B.3 is not difficult to perform, the usefulness of Eq. B.12 for calculating Hamaker constants is questionable. However, Eq. B.12 is useful as an order-of-magnitude estimate and to predict the sign of the interaction.

As an example of this method, consider the calculation of the Hamaker constant for a Si\textsubscript{3}N\textsubscript{4} – air – mica system. This is often the system of interest in atomic-force microscopy, where many tips are fabricated from silicon nitride, and many samples are placed on a flat mica surface. The \( \epsilon(i\xi) \) data were calculated using the data in Table B.1 and are shown in Fig. B.3a. The terms in the sum in Eq. B.3 (for \( n \leq 2000 \) and \( s \leq 20 \)) are shown in Fig. B.3b. Note that the largest terms occur in the infrared region, but that the overall interaction is dominated by the larger number of terms in the ultraviolet.

Fig. B.4a and b show a similar calculation for a Si\textsubscript{3}N\textsubscript{4} – 1-bromonaphthalene – mica
Figure B.3: Calculation of the Hamaker constant for a Si$_3$N$_4$ – air – mica system. (a) Dielectric data. For any material, $\varepsilon(\omega)$ decreases monotonically from $\varepsilon_0$ to one (for air, $\varepsilon(\omega) = 1$ at all frequencies, to good accuracy). (b) Terms of the Hamaker constant in the non-retarded limit. Since the frequencies $\xi_n$ are evenly spaced (the frequency is plotted on a logarithmic scale, here), the contributions in the ultraviolet range dominate. Note that the zero-frequency term has been shifted to $1.1 \times 10^{13}$ rad/s for plotting convenience.

<table>
<thead>
<tr>
<th>Medium</th>
<th>$C_{IR}$</th>
<th>$\omega_{IR}$ ((\times 10^{14}) s$^{-1}$)</th>
<th>$C_{UV}$</th>
<th>$\omega_{UV}$ ((\times 10^{16}) s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$_3$N$_4$</td>
<td>2.558</td>
<td>4.008</td>
<td>2.782</td>
<td>1.303</td>
</tr>
<tr>
<td>mica</td>
<td>3.917</td>
<td>1.884</td>
<td>1.483</td>
<td>1.57</td>
</tr>
<tr>
<td>ethanol</td>
<td>22.702</td>
<td>6.31</td>
<td>0.848</td>
<td>1.96</td>
</tr>
<tr>
<td>n-propanol</td>
<td>18.41</td>
<td>6.31</td>
<td>0.915</td>
<td>1.936</td>
</tr>
<tr>
<td>1-bromonaphthalene</td>
<td>2.370</td>
<td>5.76</td>
<td>1.750</td>
<td>1.069</td>
</tr>
</tbody>
</table>

Table B.1: Dielectric data for typical atomic-force microscope materials
system. In this case, the contributions in the infrared region are actually repulsive, but are overwhelmed (in the non-retarded limit) by the more numerous terms at higher frequencies.

![Graph](image)

Figure B.4: Calculation of the Hamaker constant for a Si$_3$N$_4$-1-bromonaphthalene-mica system. (a) Dielectric data. (b) Terms of the Hamaker constant in the non-retarded limit. Note that the repulsive terms in the IR are overwhelmed by the attractive terms in the UV.

As shown by Eq. B.1, the vdW interaction between two planar materials depends on distance as $d^{-2}$. Retardation effects result in an additional distance dependence. If we express the retarded interaction as

$$E_{123}(d) = -\frac{A_{123}}{12\pi d^a}, \quad \text{(B.13)}$$

where $A_{123}$ is the non-retarded Hamaker constant, the value of $a = a(d)$ gives an indication
of the distance-dependence of the vdW interaction. I have plotted the Hamaker “constant” and the effective exponent \( a(d) \) as a function of distance in Fig. B.5. Note that the interaction becomes repulsive when \( d \) is large enough that the high-frequency components are attenuated by the factor \( r_n \). For still larger distances, the low-frequency repulsive terms are also attenuated, and we are left with the attractive static contribution which again varies as \( d^{-2} \). When the Hamaker constant changes sign, \( a \) diverges, as shown in Fig. B.5b. Of course, this is not a concern, as the Hamaker constant itself is zero at these points.

![Graph](image)

Figure B.5: Dependence of the Hamaker constant on distance for a \( \text{Si}_3\text{N}_4 - 1\)-bromonaphthalene – mica system. (a) Due to the finite speed of light, the contributions to the Hamaker constant from Fig. B.4b are attenuated with distance. This effect is greatest at higher frequencies, so the force becomes repulsive when the contribution of the attractive terms in the UV is attenuated below that of the IR range. The inset shows that at large distances the interaction is again attractive due to the zero-frequency term. (b) Effective power-law exponent for the vdW interaction. Note that in a restricted range of distances, the interaction becomes repulsive, leading to a diverging exponent at the ends of this region.

Retardation effects have been measured experimentally using the “surface-forces apparatus” [199]. We have also attempted to measure this effect with the AFM [121], although the magnitude of the vdW force is at the limit of sensitivity for our AFM at distances where retardation effects are expected to be important.
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