Doctoral Thesis

Morphology of structures in three-dimensional diffusional growth

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Morphology of Structures in Three-dimensional Diffusional Growth

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Abstract

In our experiments, we investigate in situ three-dimensional crystals during free growth into pure supercooled liquid xenon. The undercooling, $\Delta T$, is in the range of $80 \text{ mK} \leq \Delta T \leq 118 \text{ mK}$. This corresponds to a range between $0.00135$ and $0.00199$ in dimensionless units. We report on pattern selection and morphological transitions. We enforced morphological transitions of the growing crystal from dendrite to seaweed by a cooling step. The fact that such a transition is possible indicates that a similar morphology diagram, as it is proposed by other authors for two-dimensional growth, is valid in three dimensions too. We have found doublon patterns as building blocks for seaweed patterns in three dimensions.

To describe the transition and the seaweed patterns we use the following growth parameters that have been originally introduced to describe dendritic growth: the growth velocity $v_{\text{tip}}$, the tip radius $R$ and $v_{\text{tip}} R^2$ which is proportional to the volume solidification rate of the dendrite. During the transition from dendrite to seaweed the growth velocity decreases and the tip radius increases. We observed a big excursion of $v_{\text{tip}} R^2$ away from the value of the dendrite versus time.

For a doublon it is found that the two fingers can be characterized by the tip radius of an unperturbed dendrite at the same nominal undercooling. The maximum growth velocity of a doublon is the one of an unperturbed dendrite.

We have determined the fractal dimension of the contours of seaweed patterns. The box dimension $d_f$ and the correlation dimension $\nu$ have been analyzed. For the box dimension we have implemented an optimized method, which needs less boxes to cover the fractal set than a frequently used nonoptimized method, which does not determine a minimal number of boxes. Averaged over several seaweed contours it is found $d_f = 1.48 \pm 0.07$ (optimized method) and $\nu = 1.47 \pm 0.07$. Within experimental errors no difference is found to the fractal dimension of the contours of dendrites analyzed in previous studies.

The growth of dendrites and seaweed in three dimensions is characterized by the same length scale and the same fractal dimension. Therefore we conclude that although the transition from dendritic to seaweed-like growth is initiated by a perturbation, the growth is determined by the same diffusional conditions. This means for example that both morphologies have the same typical curvature.
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Kurzfassung

In unseren Experimenten untersuchen wir in situ dreidimensionale Kristalle, während sie in eine reine Schmelze aus unterkühltem Xenon hineinwachsen. Die Unterkühlung $\Delta T$ der Schmelze liegt im Bereich von $80 \text{ mK} \leq \Delta T \leq 118 \text{ mK}$. Dies entspricht einem Bereich zwischen 0.00135 und 0.00199 in dimensionslosen Einheiten. Wir berichten über Strukturbildung und morphologische Übergänge. Mit Hilfe einer Abkühlung haben wir am wachsenden Kristall den Übergang von dendritischem zu „seaweed-artigem“ Wachstum erzwungen. Die Tatsache, dass ein solcher Übergang möglich ist, deutet darauf hin, dass in drei Dimensionen ein ähnliches Morphologiediagramm gültig ist, wie es für zwei Dimensionen von anderen Autoren vorgeschlagen wurde. Wir fanden Doublonen als Grundbausteine für Seaweed-Strukturen in drei Dimensionen.

Um den Übergang und die Seaweed-Strukturen zu beschreiben, sind folgende Wachstumsparameter benutzt worden, die ursprünglich für die Beschreibung von dendritischem Wachstum eingeführt wurden: die Wachstumsgeschwindigkeit $v_{\text{tip}}$, der Spitzenradius $R$ und $v_{\text{tip}} R^2$, welches proportional zur Volumenerstarrungsrate eines Dendriten ist. Während des Überganges vom Dendriten zur Seaweed-Struktur sinkt die Wachstumsgeschwindigkeit und der Spitzenradius nimmt zu. Wir beobachteten im zeitlichen Verlauf eine Exkursion von $v_{\text{tip}} R^2$ weg vom Wert des Dendriten.

Es wurde gefunden, dass die beiden Finger eines Doublons durch den Spitzenradius eines ungestörten Dendriten bei gleicher nominaler Unterkühlung charakterisiert werden können. Die maximale Geschwindigkeit eines Doublons ist diejenige des ungestörten Dendriten.

Wir haben die fraktale Dimension der Kontur von Seaweed-Strukturen bestimmt. Sowohl die Boxdimension $d_f$ wie auch die Korrelationsdimension $\nu$ wurden analysiert. Für die Boxdimension haben wir eine optimierte Methode implementiert, welche weniger Boxen zur Überdeckung der fraktalen Menge braucht als eine häufig verwendete Methode, welche nicht die minimale Anzahl der Boxen bestimmt. Für den Mittelwert über mehrere Seaweed-Konturen wurde $d_f = 1.48 \pm 0.07$ (optimierte Methode) beziehungsweise $\nu = 1.47 \pm 0.07$ gefunden. Innerhalb der experimentellen Unsicherheit konnte kein Unterschied zur fraktalen Dimension von dendritischen Konturen aus früheren Studien gefunden werden.

Das Wachstum von Dendriten und Seaweed-Strukturen in drei Dimensionen ist durch die gleiche Längenskala und die gleiche fraktale Dimension charakterisiert.
Wir schliessen daraus, dass, obwohl der Übergang zwischen dendritischem und seaweed-artigem Wachstum durch eine Störung ausgelöst wird, das Wachstum durch die gleichen diffusiven Bedingungen bestimmt ist. Das heisst zum Beispiel, dass beide Morphologien die gleiche typische Krümmung haben.
1. Introduction

1.1 A moving-boundary problem

Pattern formation can occur, when two phases of one compound are driven out of stationary coexistence, so that a stable phase grows at the expense of the metastable phase. The two phases are separated by an interface which moves during growth. Depending on the interfacial properties, experimental conditions and shape parameters, this interface may be unstable with respect to small positional perturbations. Such instabilities lead to the onset of pattern formation. Open questions are: Which types of spatial patterns are formed? How are these patterns influenced by the growth conditions, the properties of the two bulk phases and the properties of the interface?

We study the growth of a crystal into a supercooled melt which is the metastable phase in our experiments. Solidification is a first order phase transition, and therefore latent heat has to be removed from the solid-liquid interface. Thermal diffusion is assumed to be the only mechanism of heat transport which is growth rate limiting in the system under consideration. Kinetic effects, such as the ordering of atoms at the interface, are assumed to be fast.

For the case of a semi infinite crystal which grows into the supercooled melt, the propagation of a plane solid liquid interface is described by the classical Stefan-Problem [1]. In this problem, it is assumed that the temperature of the plane solid-liquid interface is the thermodynamic equilibrium melting temperature. The mathematical problem is the determination of the propagation respectively the position of the interface. Positional instabilities have not been discussed by Stefan. The classical Stefan-Problem can be generalized by taking into account positional instabilities and deviations of the melting temperature of the curved solid-liquid interface from the thermodynamic equilibrium melting temperature. As in the classical Stefan-Problem, the mathematical problem in the generalized case is the determination of the position of the solid-liquid interface. As the position of the interface is part of the boundary conditions of the diffusion problem we have a so-called moving-boundary problem in three dimensions.

For a quantitative discussion of the moving-boundary problem it has to be considered that the solid liquid interface is not an isothermal surface,
1. Introduction

- when the interface is not uniformly curved.
- when the interface does not proceed with the same velocity at any point.

We will now discuss the influences on the solid-liquid interface temperature. To facilitate the calculations, the following assumptions are made for the solidification process:

i) It is assumed that the melt fills an infinite space. A crystal growing into the infinite melt does not "see" any additional boundaries apart from the interface. Therefore this growth geometry is called free growth.

ii) Prior to crystal growth the whole volume of melt is homogeneously thermostated at $T_\infty < T_m$, where $T_m$ is the thermodynamic equilibrium melting temperature. The undercooling of the melt is defined by $\Delta T \equiv T_m - T_\infty$. $\Delta T$ is the only parameter to influence the system, i.e. $\Delta T$ is the only control parameter of the system.

At these conditions the temperature field around a crystal can be described by a solution of the diffusion equation in three dimensions [2, 3]:

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

(1.1)

with the boundary conditions given below and the thermal diffusivity $D$. Instead of the local temperature $T$, the dimensionless temperature field $u$, with

$$u \equiv \frac{T - T_\infty}{L/c_p},$$

(1.2)

is used for mathematical description. $u$ is given in units of the unit undercooling $L/c_p$. $L$ and $c_p$ are the latent heat per unit volume and the specific heat of the homogeneous melt per unit volume, respectively. In general, $u$ satisfies Eq. (1.1) separately in the liquid and in the solid with the respective values of $D$. In the symmetric model [2], where the material properties in the liquid and in the solid are assumed to be the same, only one diffusion equation has to be solved. This model greatly simplifies some of the mathematics without losing too many important features. Therefore, in the following we restrict our discussion to the symmetric model.

The condition of energy conservation at the moving interface leads to the continuity equation [2]

$$v_n = D \left( \nabla u|_{\text{solid}} - \nabla u|_{\text{liquid}} \right) \cdot \hat{n},$$

(1.3)
where \( \mathbf{n} \) is the unit vector normal to the interface, directed into the liquid, and \( v_n = \mathbf{v} \cdot \mathbf{n} \) is the component of the growth velocity normal to the interface. The subscripts indicate on which side of the interface the gradients of the temperature field are to be taken. The left-hand side of Eq. (1.3) accounts for the rate at which heat is generated at the boundary, and the right-hand side for the heat flow into the bulk phases on either side of the interface.

Finally, at the nonisothermal interface the boundary condition is [2]

\[
\begin{align*}
 u|_{\text{interface}} &= \Delta - \beta v_n - d\kappa. \quad \text{(1.4)}
\end{align*}
\]

On the right-hand side, the first term is the dimensionless measure of the undercooling,

\[
\Delta \equiv \frac{\Delta T}{L/c_p} \equiv \frac{T_m - T_\infty}{L/c_p}. \quad \text{(1.5)}
\]

The second term on the right-hand side of Eq. (1.4) is proportional to the growth rate at the interface. It relates the growth velocity to the undercooling at the interface. The third term on the right-hand side of Eq. (1.4) accounts for the deviation of the melting temperature of a curved interface from \( T_m \). It is known as Gibbs-Thomson effect [4]. The local curvature of the interface, \( \kappa \), is positive for a convex surface, i.e. if the centre of curvature is located in the solid. The proportionality \( d \) relates the curvature of a surface to the deviation of the melting temperature of the curved surface from \( T_m \). The cubic symmetry of the crystal lattice of xenon leads to a fourfold anisotropy in any plane perpendicular to a principal crystallographic axis. In the case of a fourfold anisotropic surface tension the fourfold anisotropic capillary length \( d \) is given by

\[
d = d(\Theta) = d_0(1 - \epsilon_4 \cos(4\Theta)), \quad \text{(1.6)}
\]

where \( \epsilon_4 \) is the fourfold anisotropy strength, \( \Theta \) the angle between the interface normal and a given crystallographic direction. The capillarity or averaged capillary length \( d_0 \) is defined as

\[
d_0 \equiv \frac{\gamma_{sl} T_m c_p}{L^2}, \quad \text{(1.7)}
\]

where \( \gamma_{sl} \) is the isotropic part of the interface free energy. \( d_0 \) is typically of the order of Ångströms and represents a property of the material.

Eqs. (1.1), (1.3) and (1.4) specify the symmetric model of solidification of a pure substance. One can derive the equation of motion for the surface of a crystal from these equations by eliminating the diffusion field \( u \), in favor of coordinates which describe the position of the moving boundary.
1.2 Dendritic growth

Assuming an isothermal interface at $T_m$, i.e. neglecting the Gibbs-Thomson effect and kinetic effects, Ivantsov [5] has found that an axisymmetric, parabolic needle-crystal is a solution of the moving-boundary problem given by Eqs. (1.1) and (1.3). This paraboloid of revolution can be characterized by the radius of curvature $R_{tv}$ of the tip. This radius of curvature of the tip is called tip radius and it is a typical length scale of the dendrite. The tip radius can be used for scaling the lengths. In the following dimensionless lengths are denoted with a hat, e.g. $\hat{x}, \hat{z}$, etc. The tip radius decreases with increasing undercooling. There are three main reasons, why the so called Ivantsov solution is not satisfactory:

- For a given undercooling $\Delta T$, the Ivantsov solution predicts only a value for the product $R_{tv} v_{tip}$. It is an experimental fact that for a given $\Delta T$, unique values for the tip radius and the growth velocity are selected [6, 7]. The prediction of these two parameters is the so-called selection problem.

- A rotational paraboloid is not the basic shape of experimentally observed dendrites [8].

- The Ivantsov solution is not a stable solution, i.e. it can not be observed in experiments.

Two important theories in the solution of the selection problem may be mentioned in chronological order: the marginal stability theory and the solvability theory. The marginal stability theory [9, 10, 11] formulates an additional condition which allows to select the tip radius and the growth velocity of the tip at a given undercooling. It is assumed that the selected dendrite is the one moving with the minimum speed for which the surface tension can stabilize the underlying needle-crystal. According to the solvability theory for axisymmetric dendrites [2, 12, 13] an anisotropic surface tension is necessary to stabilize the growing dendrite. The anisotropy in the surface tension acts as a singular perturbation, reducing Ivantsov’s continuous family of solutions to a discrete set of needle-crystal solutions where only the dendrite with the largest velocity is stable. The selection of the shape and the growth velocity for three-dimensional dendritic crystals of materials with cubic symmetry of the crystal lattice has been studied by Ben Amar and Brener [14].

The liquid surrounding the tip is metastable with respect to freezing. In the case of diffusion-limited growth, this may lead to a Mullins-Sekerka instability. Mullins and Sekerka [15] have shown that a planar interface, moving at a constant velocity into a metastable phase is unstable against perturbations with a spatial
wavelength longer than some characteristic stability length. The interfacial pattern formed by this instability is characterized by the wavelength corresponding to the fastest growing perturbation. Starting with an axisymmetric dendrite, in a first step such an instability can initiate the growth of fins along the dendrite [16, 17]. A second instability of the Mullins-Sekerka type destabilizes these fins and sidebranches start to grow at the ridges of these fins.

In Ref. [18], Brener has studied the contour of the dendrite in the region where four fins are observed in experiments. For materials with cubic symmetry, Brener has found an analytical solution for the contours of these fins:

$$\hat{z} \sim |\hat{x}|^{3/5}, \quad (1.8)$$

where the $z$-axis is oriented along the growth direction of the dendrite tip and the $xz$-plane contains the ridges of two of the four fins. This coordinate frame of reference can be seen in Fig. 2.2.

To avoid confusion when comparing literature we emphasis that there exist various tip radii used for scaling in different situations, e.g. the tip radius $R_{IV}$ of an Ivantsov paraboloid of revolution, the experimentally determined tip radius $R_{exp}$ and the tip radius $R_{LM-K}$ in the theory of marginal stability by Langer and Müller-Krumbhaar [9, 10, 11]. Therefore, comparing literature where a tip radius has been used for scaling, one has to find out how the tip radius has been determined. A discussion on the various tip radii can be found in [19].

Experimental studies with xenon, which crystallizes in a face-centered cubic structure (fcc), show that the shape of three-dimensional dendrites in the tip region can be described by the tip function [8]

$$\hat{z} = (0.58 \pm 0.04) |\hat{x}|^{1.67 \pm 0.05}. \quad (1.9)$$

Here, the experimental data have been scaled with the experimentally determined tip radius, $R_{exp} \neq R_{IV}$. Eq. (1.9) is in good agreement with the analytical result given in Eq. (1.8).

### 1.3 Growth morphologies

Dendritic solidification is the best known example for the formation of crystals with complex spatial patterns at conditions far from equilibrium. If the surface tension is anisotropic, a crystal nucleus finally develops into a dendritic pattern like a snowcrystal [2, 20]. The development in the case of vanishing anisotropy, however, has been studied in less details.

A theory for the fundamental two-dimensional morphologies and the most relevant parameters controlling their appearance has been developed [21, 22, 23].
Figure 1.1: Schematic morphology diagram [21, 22, 24] of undercooling $\Delta$ vs. anisotropy $\epsilon$ for the compact (C) and fractal (F), dendrite (D) and seaweed (S) growth pattern. The region surrounded by the dotted line depends on thermal noise. The growth in region K with undercooling $\Delta > 1$ is controlled by kinetics.

Analytically a kinetic phase diagram, morphology diagram or morphologic diagram in the plane ($\Delta$, $\epsilon$) has been developed (see Fig. 1.1). It represents regions of different morphologies and the lines of transitions between them [21, 23, 24]. Compact structures (C) are distinguished from fractal structures (F). Compact structures or compact growth means growth at a constant average density, irrespective of the value of this density, while in a fractal pattern the density varies with length scale. A complementary classification uses orientational order in the structure for characterization. A structure with pronounced orientational order is called dendritic (D), and without apparent orientational order it is called seaweed (S). A necessary condition for dendritic growth is that the anisotropy in the solid-liquid surface tension is sufficiently large to stabilize the shape of the dendrite. Seaweed patterns are predicted to occur for small or vanishing anisotropy and high undercooling. The basic building blocks for seaweed patterns in two dimensions are the so-called doublons. A doublon consists of two fingers with a narrow groove of liquid along the axis of the symmetry between them. This groove with a width of $h$ will be called inner groove thereafter (see Fig. 1.2). It has a parabolic envelope [23]. For higher undercooling seaweed patterns are predicted.

Although substantial progress has been made in describing growth phenomena
in two-dimensional geometry, much less is known on the development in three dimensions, where the interface between the growing solid and the nourishing fluid is a two-dimensional object. Using a phase-field model Abel, Brener and Müller-Krumbhaar [26] have found that for \( \Delta \approx 1 \) dynamically stable objects in three dimensions, analogous to doublons in two dimensions, are formed. It consist of three cooperating fingers which form a triplet pattern.

According to Fig. 1.1 it should be possible in experiments to enforce a transition from dendrites to seaweed by increasing undercooling for a given material. We show in Sec. 3.1 that for three-dimensional growth, the morphology can be changed from dendrite to seaweed by an approximation of a cooling step. The procedure to approximate a cooling step is described in Sec. 2.2. The perturbations caused by the cooling step will be classified as very weak, weak and strong. In Sec. 3.3 we present experimentally found patterns in three dimensions which have a doublon-like structure. These patterns are the building blocks of the growth pattern when the morphology of our system has changed from dendritic to seaweed-like due to the cooling step. In Sec. 3.3 we also show single, isolated doublon patterns without additional occurrence of seaweed morphology.
They are formed after the perturbation, when tip-splitting of the front tip of the crystal occurs and the perturbation is too weak to enforce a complete transition to seaweed. The fractal dimension of seaweed patterns will be analyzed in Sec. 3.2.

In the following the term "crystal" stands for any crystal with dendritic, seaweed or doublon structure. If it is not denoted explicitly as fcc- or crystallographic structure, the word "structure" is used as synonym for pattern.
2. Experimental setup and methods

2.1 Experimental setup

In our experiments, we observe in situ the growth of three-dimensional crystals into pure supercooled liquid xenon. We use xenon in our studies of pattern formation as a transparent model substance for metals. Xenon crystallizes in a fcc structure. In Appendix A, selected properties of xenon are given (Tab. A.1).

The cryostat used in this work is converted from the one utilized in Ref. [27]. The experimental setup, depicted in Fig. 2.1, is designed similarly to the one used in previous experiments [28, 29]. Modifications and improvements are done on the optical system, the image capturing, the camera and the positioning system of the camera.

To improve the spatial resolution of our raw data we have developed a new optical imaging system and a new illumination system. For imaging we have designed a symmetrical periscope with three optical stages adjusted in unit conjugation ratio, i.e. each stage images in the scale one to one. The optical resolution of the system is about 1 μm, i.e. two parallel lines 1 μm apart can be resolved. In order to make use of this resolution we magnify the picture to such an extent that the pixel size is not relevant. For wide view images we use a smaller magnification (zoom lens). To facilitate contour extraction the periscope has been designed to provide contours of high contrast. The illumination tube is designed to focus the image of the homogeneous light source into the plane of the crystal. Infrared wavelengths, which might heat the growth vessel, are filtered out carefully. No influence of illumination on temperature of the melt can be detected with an uncertainty of ±10⁻⁵ K. For image capturing we use a digital CCD-camera mounted on a high precision linear positioning system.

The growth vessel is immersed completely in a heat bath of isopentane. Its volume is large enough (≈ 100 cm³) to ensure “free growth” of the crystal. Before each experiment we purify the xenon to 99.9999 % (specification of the manufacturers). The pure melt is supercooled in the range of 80 mK ≤ ΔT ≤ 118 mK.
Figure 2.1: Experimental setup. 1, growth vessel with the capillary; 2, periscope; 3, illumination system; 4, heat bath (isopentane); 5, tube to provide a laminar flow in the heat bath; 6, stirrer; 7, big mass of stainless steel to reduce the vibrations of the stirrer; 8, liquid nitrogen; 9, adjustable helium gas atmosphere to control the cooling power; 10, heater; 11, temperature sensor; 12, combined rotary and linear motion drive to lift and to rotate the capillary; 13, zoom lens (1x-7x); 14, digital CCD-camera; 15, power supply for the camera and output to the computer interface; 16, high precision linear positioning system; 17, field lens.
This corresponds to a range between 0.00135 and 0.00199 in dimensionless units. During the experiment, the temperature of the liquid xenon, measured far away from the crystal, is stabilized to better than $\pm 10^{-4}$ K.

The growth of the crystal is initiated by means of the capillary injection technique [28, 30]. Free growth starts after the crystal has left the capillary. Because of the cubic symmetry of the crystal lattice of xenon, six dendrites develop. In the following, the direction approximately along the direction of gravity is denoted as [100]-direction. The crystal growing in [100]-direction is the one we usually take our pictures from. Four dendrites develop in horizontal directions. The one in [100]-direction is not found because it would direct along the capillary. Considering the [100]-dendrite, four fins in the [010]-, [010]-, [001]- and [001]-directions are formed. We orient the dendrite by rotating the capillary such as to turn two of the four fins in the plane perpendicular to the object plane of the periscope. In addition the dendrite can be moved up and down by means of a vertical feed-through manipulator for the capillary.

The growing crystal is illuminated homogeneously by a cold light source in the visible spectrum and imaged by means of a periscope to the chip of a digital camera (1280 pixel \(\times\) 1024 pixel) outside the cryostat. The camera writes directly into the memory of the computer so that no digitizing of video pictures is necessary. Because of limited memory capacity pictures are not taken continuously but in discrete time steps. We denote the pictures with image #1, image #2, image #3 and the crystals with crystal one, crystal two and so on. The undercoolings $\Delta T$ of the melt where a crystal has been grown, are shown in Tab. 2.1.

In our experiments the growth directions of the observed dendrites are tilted from the direction of the gravitational field by an angle $\phi$ between 0° and 29°. After rotating two fins into the plane perpendicular to the object plane of the periscope the growth direction is generally not parallel to the object plane. There is a non-vanishing angle between the growth direction and the object plane. To determine the orientation of the growth direction we take an additional picture at the beginning of the experiment which shows the crystal rotated by 90°.

An example of a stored digital picture is shown in Fig. 2.2 a). Because of the high contrast of these pictures the contours of the crystals can be extracted automatically, i.e. without any influence of the operator. We bring the contour into a coordinate frame of reference, where the dendrite tip stays in the origin and the growth axis is oriented along the $z$-axis as shown in Fig. 2.2 b). Finally, we scale the contour according to the fact that the growth direction was not in the object plane of the periscope. The scaling factor can be calculated by means of geometrical considerations.

Contours prepared in that way are the raw data for most of our investigations.
Experimental setup and methods

Figure 2.2: Image processing [29]. a) Digital picture of a dendrite. The extracted contour of the dendrite is shown as a white line. b) The same contour brought into a coordinate frame of reference, where the tip of the dendrite lies in the origin and its growth direction is parallel to the $z$-axis. The $xz$-plane contains the ridges of two of the four fins of the dendrite. Lengths are given in $\mu$m.

Table 2.1: Experimental values of the undercooling of the melt, $\Delta T$, which is the only control parameter of our system.

<table>
<thead>
<tr>
<th></th>
<th>undercooling $\Delta T$ [mK]</th>
<th>undercooling $\Delta T$ [dimensionless]</th>
</tr>
</thead>
<tbody>
<tr>
<td>crystal one</td>
<td>95</td>
<td>0.00160</td>
</tr>
<tr>
<td>crystal two</td>
<td>91</td>
<td>0.00154</td>
</tr>
<tr>
<td>crystal three</td>
<td>118</td>
<td>0.00199</td>
</tr>
<tr>
<td>crystal four</td>
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<td>0.00176</td>
</tr>
<tr>
<td>crystal five</td>
<td>80</td>
<td>0.00135</td>
</tr>
</tbody>
</table>
2.2 Selection of growth morphology

After a crystal has left the capillary and entered the homogeneously supercooled melt, there is a transient state at the end of which the crystal grows with a stationary velocity \( v_{\text{tip}} \). The growth direction of the stationary growing crystal is oriented along the principal crystallographic axis. Thus the stationary growing crystals at our standard conditions are dendrites, corresponding to the region D in the morphology diagram Fig. 1.1. The question, whether our dendrites are fractal (region F) or compact (region C), is discussed in Sec. 4.3. The morphology diagram Fig. 1.1 has been developed [22, 24] for two-dimensional systems. If it is assumed that a three-dimensional system with low anisotropy behaves similarly, then one may expect that an enhancement of undercooling leads to a transition from dendritic to seaweed-like morphology. It is experimentally not possible to enhance the undercooling in the liquid homogeneously by a cooling step. But in order to initiate a morphological transition it is possible to change the temperature of the melt in the environment of the growing dendrite: Latent heat is set free at the crystal surface during free growth. Therefore the melt close to a crystal has a temperature close to \( T_m \). The melt far away from the dendrite has the temperature \( T_{\infty} < T_m \). Shifting the crystal downwards to the colder region in the growth vessel provides a cooling step for the crystal.

In the experiment we observe that the morphology of the crystal can be changed by shifting the crystal from the center of the growth vessel to the bottom of the vessel. Such a temperature step corresponds to a crossing of the phase boundary in the morphology diagram Fig 1.1 from region D to region S. Thus, it is possible to decide whether a dendrite or a seaweed will be grown. It is necessary to pull up the crystal back to the original position because the shifted crystal leaves the field of view of the camera. Because of pulling up, the crystal leaves the region S again. One might expect that its morphology changes back to dendritic after a transient time.

Dendrites and seaweed can be distinguished by means of the shape and of the growth parameters. In the following sections we will show how to characterize growing crystals.
2.3 Growth parameters

2.3.1 Growth velocity

The growth velocity is a good parameter to describe the system. In our images the growth velocity is determined from the times when two pictures are taken and the positions of the crystal at these two pictures. The growth velocity is always measured in the direction of the maximum growth velocity even if it does not coincide with a principal crystallographic axis.

In previous studies with xenon it has been found that the growth velocity of an isolated dendrite $v_{\text{tip}}$ is constant in time [28] for a given $\Delta T$. It increases with increasing undercooling $\Delta T$ [7]:

$$v_{\text{tip}} = (188.8 \pm 8.6) \Delta T^{(1.745 \pm 0.017)}$$

where $v_{\text{tip}}$ is given in $\mu m/s$ and $\Delta T$ in K.

2.3.2 Tip radius

In this work there are three different types of crystals where the tip radius has to be measured: dendrite, seaweed without a doublon at the front tip and seaweed with a doublon at the front tip. The following paragraphs discuss how to determine these different radii.

The notion $R_{\text{exp}}$ stands for a tip radius experimentally determined by means of the mathematical methods developed for the dendrite, independent of the type of the crystal.

Tip radius of a dendrite

It has been mentioned in a previous section that there exist several definitions of tip radii of dendrites, e.g. $R_{\text{iv}}$, $R_{\text{exp}}$ and $R_{\text{LM-K}}$. In the following we use the experimentally determined tip radius, $R_{\text{exp}}$. In general, the radius of curvature $R$ of a function $f(x)$ in two dimensions is given by

$$R = \frac{(1 + f'(x)^2)^{3/2}}{f''(x)}.$$

We used two ways to measure $R_{\text{exp}}$. Both have some disadvantages:

- *Parabola fit*: A parabola cannot be fitted in a unique way to a contour. Fitting a parabola to a contour leads to a tip radius decreasing with decreasing fitting height $H$. $R_{\text{exp}}$ is obtained by extrapolating the fitted tip radius to $H \rightarrow 0$ [7, 31].
2.3. Growth parameters

- **Power law fit**: The tip function given in Eq. (1.9) does not define a smooth function at \( \hat{z} = 0 \). Therefore no tip radius can be found (see Eq. (2.2)). However by fitting the power law \( z = a|x|^{1.67} \) and comparing the resulting value for the fitting parameter \( a \) with the dimensionless tip function Eq. (1.9) \( R_{\text{exp}} \) can be determined.

For dendritic growth, both methods lead, within the error of measurement and fit procedure, to the same result. According to Ref. [7], \( R_{\text{exp}} \) decreases with increasing undercooling \( \Delta T \) as

\[
R_{\text{exp}} = (5.2 \pm 0.4) \Delta T^{-0.83\pm0.03},
\]

where \( R_{\text{exp}} \) is given in \( \mu m \) and \( \Delta T \) in K. For a dendrite, both the tip radius \( R_{\text{exp}} \) and the growth velocity \( v_{\text{tip}} \) are constant in time. The parameters in Eqs. (2.3) and (2.1) are independent of undercooling.

**Tip radius of a seaweed pattern without a doublon at the front tip**

The tip radius for such a pattern is measured with the methods developed for the dendrite. The tip radius of a seaweed without a doublon at the front tip is denoted as \( R_{\text{exp}} \).

**Tip radius of a seaweed pattern with a doublon at the front tip**

It is not obvious which definition of a radius of curvature makes sense in a discussion of doublon patterns. There are two concepts: firstly, the radius \( R_{\text{env}} \) of the envelope and secondly, the tip radius of one of the fingers. As consequence of the results in Sec. 3.3 the tip radius of a doublon is determined as tip radius of the so-called prime finger (see Sec. 3.1.3) of the doublon. As it is measured with the mathematical methods developed for the dendrite, the tip radius of the prime finger is denoted as \( R_{\text{exp}} \) too.

2.3.3 Stability constant

The stability of parabolic dendrites has been analyzed by Langer and Müller-Krumbhaar [9, 10, 11], treating surface tension as a linearized perturbation. They found that the continuum of Ivantsov's solutions is divided into a stable and an unstable region. It is assumed that the dynamical operating state selected by the physical system corresponds to the point of marginal stability dividing the stable and unstable region. This marginal-stability hypothesis led to an additional relation between \( v_{\text{tip}} \) and the tip radius \( R \):

\[
\sigma^* = \frac{2Dd_0}{v_{\text{tip}}R^2},
\]
where $\sigma^*$ is usually referred to as the *stability constant*. It is assumed to be independent of undercooling, but as $\nu_{\text{tip}}R^2$ is proportional to the volume solidification rate, which should vanish for $\Delta \to 0$, $\sigma^*$ should show a dependence on undercooling at least in the limit $\Delta \to 0$. Experimentally, it is found that the value of $\sigma^*$ varies from substance to substance and seems to depend on undercooling for some substances [6, 32, 33].

In our experiments $D$ and $d_0$ are assumed to be independent of temperature in the considered range of undercooling. Therefore it is sufficient to measure $\nu_{\text{tip}}R^2$. For $R$ we use the experimentally determined tip radius $R_{\text{exp}}$. 
2.4 Fractal dimension

Far away from the crystal tip nonlinear interactions between neighboring side-branches are significant. No reproducible parameters have been found to characterize individual sidebranches far away from the tip [7]. This behavior is typical for chaotic dynamical systems. “Integral” parameters, which describe properties of the whole crystal, are suitable to characterize crystals as these parameters account for the nonlinear interactions between the different sidebranches. One of these integral parameters is the fractal dimension of the crystal. For a review of fractals and fractal dimensions see Ref. [34, 35, 36]. There are two well known methods to determine the fractal dimension of an experimental data set, the box counting method and the correlation dimension method.

Numerical calculations of fractal dimensions are often difficult and sometimes may lead to inconclusive results, e.g. if too few data points are available [37]. To obtain a physically meaningful and reproducible fractal dimension the scaling range should exceed one order of magnitude.

2.4.1 Box dimension

In the approach of the box counting method, the fractal set embedded in a D-dimensional space is covered by a D-dimensional grid with volume elements of box size \( \varepsilon \). \( \varepsilon \) is also denoted as length scale. The minimum number of “boxes” needed to cover the entire fractal set, \( N(\varepsilon) \), is given by

\[
N(\varepsilon) = L^{d_f} \left( \frac{1}{\varepsilon} \right)^{d_f},
\]

where \( L \) is the volume of the fractal set in the D-dimensional space and \( d_f \) the box counting dimension. Applying the logarithm on both sides of Eq. (2.5) leads to

\[
\log N(\varepsilon) = d_f \log L + d_f \log \left( \frac{1}{\varepsilon} \right).
\]

In the limit of small \( \varepsilon \) where \( d_f \log L \ll d_f \log (1/\varepsilon) \) the following linear relationship

\[
\log N(\varepsilon) \sim -d_f \log \varepsilon
\]

is valid and can be used to determine the fractal dimension \( d_f \). In practice, Eq. (2.7) holds only over a limited range of \( \varepsilon \). The concept breaks down for values of \( \varepsilon \) smaller than the typical minimal distances of the system, such as the pixel
size or the length scale of the structure, and for values of $\varepsilon$ larger than the size of
the entire system. An example for a length scale is the tip radius.

When computing the box dimension, it is not always easy to find a minimal
covering of the fractal set. There is a commonly used method to compute the box
dimension that takes no notice of this problem. Instead of looking for a minimal
covering of the set with boxes of size $\varepsilon$, the fractal set is covered with a square
mesh of size $\varepsilon$, i.e. regularly placed, non-overlapping boxes of size $\varepsilon$. The number
$N(\varepsilon)$ of these non-overlapping boxes needed to cover the entire set is determined.
The fractal dimension $d_f$ is computed using Eq. (2.7). We call this method the
nonoptimized method. In an optimized method we try to find a minimal covering,
i.e. a minimal number of boxes. For each box size $\varepsilon$ we compute the number
of boxes for each three $x$-, $y$- and angular positions of the square mesh. The smallest
of these numbers of boxes is set as $N(\varepsilon)$.

In Sec. 3.2.2 the optimized method is compared with the nonoptimized method.

2.4.2 Correlation dimension

The correlation dimension method has been developed by Grassberger and Pro-
caccia [38]. The approach relies on correlation functions and is more efficient than
box counting. The correlation function $C(r)$ is defined as

$$C(r) = \lim_{m \to \infty} \left( \frac{1}{m^2} \sum_{i,j=1}^{m} H(r - |\vec{x}_i - \vec{x}_j|) \right), \quad (2.8)$$

where $r$ is the variable radius of a hypersphere in the $D$-dimensional embedding
space, $m$ is the number of points in the fractal set and $\vec{x}_i$ and $\vec{x}_j$ are the coordinates
of points in the set. $H$ is the Heaviside function defined by $H(x) = 1$ for positive
$x$ and 0 otherwise. Roughly speaking, $C(r)$ measures the density of points within
a “circle” with radius $r$ around a point in the fractal set. This density is averaged
over all points in the fractal set. Grassberger and Procaccia showed that

$$C(r) \sim r^{\nu}, \quad (2.9)$$

or taking the logarithm on both sides

$$\log C(r) \sim \nu \log r, \quad (2.10)$$

where $\nu$ is defined as correlation dimension. This linear relationship can be used
to determine the fractal dimension $\nu$. It is found in theoretical considerations
that in general one expects $d_f > \nu$, although usually $d_f \approx \nu$ is measured [38]. As
in the case of box counting, the linear relationship, Eq. (2.10), holds only over a
range of $r$ limited by a typical length and the overall dimensions of the set.
3. Experimental results

3.1 Morphological transitions

In our discussion of the morphology diagram Fig. 1.1 in Sec. 1.3 we have suggested that it might be possible to change the growth morphology by changing the temperature of the environment of the crystal. To verify this conjecture we have pushed a dendrite into the colder region of the growth vessel, i.e. we push the crystal downwards out of the centre of the growth vessel. It is possible to control the influence of the cold environment by shifting the crystal into the cold region for a limited time \( \tau \). After the duration \( \tau \) we pull the crystal back to the field of view of the camera for further observation of the growth. In the following we denote this procedure as a perturbation of crystal growth. Depending on \( \tau \) we call the perturbation very weak (when \( \tau \) is very short), weak (\( \tau \) being short) or strong (\( \tau \) being long). For a quantitative characterization of the response of the crystal to the perturbation we determine the following growth parameters:

1. the growth velocity \( v_{\text{tip}} \)
2. the tip radius \( R_{\text{exp}} \)
3. \( v_{\text{tip}} R^2 \), which is proportional to the inverse of the stability constant \( 1/\sigma^* \).
   For \( R \) we use the experimentally determined tip radius \( R_{\text{exp}} \).

In addition the following properties are used to describe the crystal:

4. the shape of the contour of the crystal close to its tip
5. the growth of sidebranches.

The following discussion of the development of crystals includes selected examples taken out of a great number of data.
3.1.1 Very weak perturbation ($\tau < 60s$)

The dendrite continues to grow as before, no change in growth parameters can be observed. The perturbation is too weak to cause any changes.

3.1.2 Weak perturbation ($60s < \tau < 150s$)

Fig. 3.1 a) shows a dendritic crystal in a stationary state before pushing it into the cold region. Fig. 3.1 b) shows the same crystal immediately after a perturbation of $\tau \approx 120s$. We compare the growth parameters of the stationary growing dendrite with the ones of the perturbed crystal:

i) The growth velocity has decreased from 2.3 $\mu$m/s for the dendrite to 1.9 $\mu$m/s for the perturbed crystal.

ii) The tip radius has increased from 25.7 $\pm 0.15$ to 27.4 $\pm 0.5$ $\mu$m.

In Fig. 3.1 c) the contours of both crystals a) and b) are superposed. The contours are extracted and brought into a coordinate frame of reference as described in Sec. 2.1 The thick line in Fig. 3.1 c) represents the perturbed crystal and the thin line the dendritic one. The contour of the dendrite can be fitted by the power law $z \sim |x|^{1.67 \pm 0.05}$ (dashed line) up to a fitting height of 250 $\mu$m, where sidebranches start to develop. Sidebranching of the perturbed crystal starts already in a distance of about 135 $\mu$m from the tip, and the sidebranches of the perturbed crystal have a much coarser appearance than those of the dendrite.

The environment of the perturbed crystal is at a lower temperature than the one of the stationary growing dendrite. From Eq. (2.1) and Eq. (2.3) one would expect for a dendrite that the growth velocity increases and the tip radius decreases with increasing undercooling. This is in contradiction to our observations. Therefore we conclude that crystals undergo a morphological transition during a perturbation. Between 3 and 4 minutes after a perturbation, the morphology of the crystal changes back to a dendrite. A morphological transition can be studied in more detail after a strong perturbation.

3.1.3 Strong perturbation ($\tau > 150s$, or stirring the melt)

Fig. 3.2 shows a crystal after a strong perturbation. The preferential growth along the principal crystallographic axes, which is typical for dendritic growth, is lost. According to the morphology diagram Fig. 1.1 we call the resulting morphology seaweed. If the perturbation is performed by pushing the crystal out of the centre of the growth vessel, then it is impossible with our present setup to observe
3.1. Morphological transitions

Figure 3.1: Weak perturbation [crystal five]:

a) A dendritic crystal before pushing it downwards
b) The same crystal some seconds after pulling it up again
c) Comparison of the contours of the dendrite a) and the perturbed crystal b) and the fitted tip function of the dendrite a)
3. Experimental results

Figure 3.2: Seaweed pattern with doublons as typical substructures. Although one can see in this picture only the projection of the crystal in the two-dimensional image plane, the crystal grows in three dimensions and it has a three-dimensional shape. The seaweed pattern shown in this figure is grown after a strong perturbation. The horizontal size of the whole image is about 1650 μm. [crystal one, image #19]

a morphological transition as it takes place. It is also possible to change the temperature distribution around a growing dendrite by stirring the melt. This can be done by rotating the crystal vigorously, i.e. by adding turbulence and extra convection. This kind of perturbation allows the continuous observation of a transition from a dendrite to seaweed. To demonstrate such a transition we have selected a crystal growing at a nominal undercooling of ΔT ≈ 95 mK. Sequences of contours extracted from images of this crystal are superposed in Fig. 3.3 (images #6 to #20) and Fig. 3.5 (images #22 to #26). The images are not taken in equidistant time steps. Image #6 is the first image after the perturbation and it is taken some seconds after the perturbation. Image #20 is taken 623 s after the image #6. Some seconds before taking image #22, which is shown in Fig. 3.4, the crystal was rotated about the vertical axis by 90° to change the field of view. The sequence of superposed contours starting with image #22 is shown in Fig. 3.5.

The growth parameters change upon perturbation:

i) The growth velocity $v_{tip}$ has been determined for the time intervals between two images as shown in Fig. 3.6a) and in Fig. 3.7a). Images #3 to #5 have been taken during stationary dendritic growth. Then the transition
3.1. Morphological transitions

Figure 3.3: Contours of a growing crystal during a morphological transition from dendrite to seaweed. The figure describes the development of the crystal during 623 seconds. The individual time steps are not identical. Image #6 is taken some seconds after the perturbation, so the shape of the crystal is still very close to the shape of a dendrite. The short, thick arrows indicate the occurrence of tip-splitting. [crystal one]
3. Experimental results

Figure 3.4: Image #22, which is taken 780 s after image #6. The crystal is now rotated by 90° compared with the images up to #20. The front tip has split and a doublon pattern has developed. Additional tip-splitting of the sidebranches is marked with arrows. The crystal looks a little bit squeezed together because it is tilted by 29° backwards. [crystal one]

Figure 3.5: Contours of the images #22 to #26 [crystal one]. The prime finger develops towards to a dendrite again. The original image #22 is shown in Fig. 3.4.
3.1. Morphological transitions

has been initiated by stirring the melt by rotating the crystal. We observe a reduction of the growth rate by 30% to 50%.

ii) The tip radius increases after the initiation of the transition almost up to a factor 3 (Fig. 3.6b) and Fig. 3.7b).

iii) At the beginning of the experiment the shape of the crystal is that of a dendrite. This shape is preserved in image #6, the first image taken after the perturbation. Then the tip region widens and in image #17, the tip splitting starts and a doublon pattern is formed. In Fig. 3.5 it is shown how this fingered system continues to grow. The right finger grows slower than the left one (image #26). The faster growing, surviving finger is denoted as prime finger. The other, slower finger is called secondary finger.

iv) In Fig. 3.8 and Fig. 3.9 the development of \( v_{\text{tip}}R^2 \) is shown. We observe a big excursion away from the value of the dendrite.

v) Fig. 3.3 shows that the side branches also undergo tip splitting. The growth is quite isotropic as expected for seaweed.

Looking at the shapes of the contours in Fig. 3.5 one might assume that the prime finger develops to a dendrite again. This idea is supported by the following observations:

- Fig. 3.6a) shows the values of \( v_{\text{tip}} \) for the prime and the secondary finger denoted as full black and grey symbols, respectively. Starting with image #22 the tip velocity of the prime finger approximates the velocity of the dendrite while the velocity of the secondary finger decreases.

- In Fig. 3.6b) starting with #17, where tip splitting of the front tip occurs, the tip radius of the doublon pattern is very close to the radius of the unperturbed dendrite. This is found both for the original angle of view and for in the view rotated by 90°.

In Sec. 3.3 it will be discussed in detail how to measure the tip radius of a doublon pattern.

- In Fig. 3.8, similar to the growth velocity and the tip radius, \( v_{\text{tip}}R^2 \) shows changes due the morphological transitions. It relaxes back to the values of the stationary dendrite after a transition time.

Tip radius, growth velocity, stability constant and shape indicate that the system relaxes slowly and returns back to dendritic growth.
Figure 3.6: a) Growth velocity and b) tip radius of the crystal vs. the image number. The horizontal dashed lines mark the values of the velocity and the radius measured at the unperturbed dendrite (images #3 to #5). The transition starts with image #6. Starting with image #22 the images are taken from a view rotated about the vertical axis by 90°. The grey triangles denote the velocity of the secondary finger. [crystal one]
3.1. Morphological transitions

Figure 3.7: a) Growth velocity and b) tip radius of the crystal vs. time. Apart of the horizontal axis, everything is similar to Fig. 3.6.
Figure 3.8: $v_{tip}R^2$ vs. the image number. The horizontal dashed line indicates the values of $v_{tip}R^2$ obtained from the unperturbed dendrite (images #3 to #5). The transition starts with image #6. Note that the values for a doublon pattern (images #22 to #26) are on the level of the original dendrite. [crystal one]

Figure 3.9: $v_{tip}R^2$ vs. time. Apart of the horizontal axis, everything is similar to Fig. 3.8.
3.2 Fractal dimension

3.2.1 Reliability of data

For the determination of a fractal dimension it is necessary to use enough data points otherwise wrong results may be obtained [37]. Therefore we use for the determination of the fractal dimension of seaweed images with large imaging areas and long contours (images #15, #20 of crystal one and image #7 of crystal two). We have tested by two methods whether or not the amount of data is sufficient for a determination of a fractal dimension.

First we have produced data sets with various amounts of data by using a fraction of the available contour length. Starting from the tip in z-direction the contours are cut off at a distance corresponding to a certain fraction of the size of the original contour. The fraction is measured in percent. Then the correlation dimension $\nu$ of these contours is calculated according to Sec. 2.4.2 and plotted in Fig. 3.10 versus the fraction in percent. Starting with a short piece of a line the correlation dimension is $\nu = 1$. With increasing complexity of the contour used for the analysis, the correlation dimension increases and reaches finally a saturation value of $\nu = 1.464$.

A second independent test has been performed which shows that the set of data points, provided by the whole contour, is a sound basis for the determination of the correlation dimension. According to [37] the following relationship has to be satisfied:

$$\nu \leq \frac{2 \log N_{\text{data}}}{\log f}.$$  \hspace{1cm} (3.1)

In our case, the number of data points $N_{\text{data}}$ is larger than 5000. And $f = r_{\text{max}}/r_{\text{min}}$ is about 300, where $r_{\text{max}}$ and $r_{\text{min}}$ are the upper and the lower limit of the correlation radii used to determine the correlation dimension. So we obtain

$$\nu < 2 \log (5000)/ \log (300) \approx 3,$$  \hspace{1cm} (3.2)

meaning that the condition Eq. (3.1) is satisfied.
3. Experimental results

3.2.2 Box dimension

We compare the non-optimized and the optimized box counting dimension of a seaweed pattern. For both methods the number of boxes $N(\varepsilon)$ to cover the contour versus the box size $\varepsilon$ is plotted in Fig. 3.11. The number of boxes $N(\varepsilon)$ for the non-optimized method are shown as thin line, the ones for the optimized method as thick line. To cover the contour, for every box size the optimized box counting method needs an equal or smaller number of boxes than the nonoptimized box counting method. Although the two graphs look similar there are differences in the slopes and hence in the box dimension $d_f$. The optimized method leads to a larger box dimension than the nonoptimized method for all seaweed contours that we have analyzed. In all studies dealing with the box dimension, the data points form curved lines. Therefore, a determination of a fractal dimension according to Eq. (2.7) does not lead to a unique result. In order to find out the range of $\varepsilon$, where the scaling relation Eq. (2.7) holds, the local slope is determined [36], i.e. we take a subset of the data points of the log-log-plot, which includes the box sizes $\varepsilon_{\text{sub}}$ with

![Figure 3.10: Correlation dimension $\nu$ vs. the fraction of the contour used to calculate the correlation dimension. Starting from the tip in z-direction the contours are cut off in a distance corresponding to a fraction of the size of the original contour [image #20, crystal one]. The fraction is given in percent. With increasing percent the values of $\nu$ saturate at $\nu = 1.464$, denoted with the full thin line. The dashed line at $\nu = 1.51$ indicates the averaged correlation dimension of dendrites [28].](image)
3.2. Fractal dimension

Figure 3.11: Number of boxes $N(\varepsilon)$ vs. box size $\varepsilon$ in a log-log-plot for the nonoptimized method (thin line) and the optimized method (thick line). The analyzed contour is one of a seaweed pattern [image #20, crystal one]. The box size is measured in $\mu$m. The box size is increased in steps of one $\mu$m. As expected the number of boxes to cover the contour is smaller for the optimized method. The two lines meet in the limit of very small boxes (not shown). Linear regression leads to different box dimensions $d_f$, e.g. for the range 60 ... 600 $\mu$m one gets $d_f = 1.453 \pm 0.004$ for the optimized method and $d_f = 1.368 \pm 0.005$ for the nonoptimized method. For both methods the data point are not on a straight line.
3. Experimental results

\[ a -1.25 \]

\[ \log [\text{Box Size } \varepsilon [\mu m]] \]

Figure 3.12: Local slope of the curves in Fig. 3.11 vs. \( \log \varepsilon \).

\( \varepsilon_{\text{low}} \leq \varepsilon_{\text{sub}} \leq \varepsilon_{\text{high}} \) and \( \varepsilon_{\text{high}} = 2 \varepsilon_{\text{low}} \). In this subset the local slope was calculated by means of linear regression and plotted at \( \varepsilon = \varepsilon_{\text{low}} \sqrt{2} \). In Fig. 3.12 the local slopes of Fig. 3.11 are plotted versus \( \varepsilon \) for the optimized and the nonoptimized method of boxcounting. Fig. 3.12 shows graphically two problematic properties of the boxcounting method:

- The slope and hence the box dimension \( d_f \) depends on the method to arrange the boxes. For \( \log \varepsilon > 2 \), respectively for \( \varepsilon > 100 \mu m \), the frequently used nonoptimized method leads to a lower fractal dimension than the optimized method.

- For both techniques the local slope depends on \( \varepsilon \). We will see in Sec. 3.2.3 that data points from the correlation dimension fit much better to a straight line than in the case of a box dimension. This difference has been observed for dendrites [28] too. We do not know the reason for this behavior.

In the following we use the optimized method, which is closer to the definition of the box dimension given in Sec. 2.4.1. The box sizes \( \varepsilon \) have been taken to be equidistant on a logarithmic scale \( \varepsilon = (\sqrt{2})^n \times \mu m \), where the range is
2 \leq \varepsilon \leq 2048 \times \mu m. Fig. 3.13 shows the number of boxes necessary to cover the seaweed pattern versus \varepsilon. The local slope of this dependence versus \varepsilon is given in Fig. 3.14. Despite the dependence of the local slope on \varepsilon, we select the range of the box size between 100 \mu m and 1000 \mu m. Within the uncertainties, this diagram indicates a more or less constant slope in this \varepsilon-range. Furthermore these limits are far away from the limits of the scaling range given by the tip radius of the dendrite (R_{\text{tip}} \approx 20 \mu m) and the overall size of the seaweed patterns (\approx 1300 \mu m). The fractal dimension obtained by linear fitting for 100 \mu m \leq \varepsilon \leq 1000 \mu m in Fig. 3.13 is \overline{d}_f = 1.451 \pm 0.019. Averaging over three crystals leads to a fractal dimension for seaweed patterns of \overline{d}_f = 1.48 \pm 0.07. The error has been determined by comparison with other ranges of \varepsilon. This averaged value of the fractal dimension is not different from the box dimension \overline{d}_f = 1.42 \pm 0.05 found in [28] for contours of dendrites, within the limits of experimental uncertainties. This box dimension is different from the dimension of the topological contour, therefore the contours of the seaweed pattern are fractal in the sense of the definition given in Ref. [35].
Figure 3.13: Calculating the box dimension of a seaweed pattern [image #20, crystal one]. The box size $\varepsilon$ was chosen to be $\varepsilon = (\sqrt{2})^n \times \mu m$ with $2 \leq \varepsilon \leq 2048 \times \mu m$. The data points in the plot are not on a straight line so the box dimension $d_f$ depends on the selected range. Compare with Fig. 3.14 where the local box dimensions are calculated. The range 100...1000 $\mu m$, corresponding to the range 2...3 in logarithmic units, is used for linear fitting and calculating the box dimension of the contour. This range is denoted as thick black line. It was selected on the basis of the discussion in Fig. 3.14. The fitted straight line is shown as thin line. The magnitude of its slope corresponding to the fractal dimension is $d_f = 1.451 \pm 0.019$. 
3.2. Fractal dimension

Figure 3.14: Local slope according the data set of Fig. 3.13. According to this plot, we select the range of the box size to calculate the box dimension $d_f$ of the considered data set as follows: box sizes smaller than 100 $\mu$m are ignored, because in that range the local slope is not constant. Points with box sizes larger than 1000 $\mu$m are cut off because of their large error. The resulting scaling range is one order of magnitude and shown as thick line. The local slope in this range can be taken as constant within the uncertainties. The fractal dimension $d_f = 1.451 \pm 0.019$ gained by linear regression in the selected range is denoted as a thin line.
3.2.3 Correlation dimension

Fig. 3.15 shows a plot of $\log C(r)$ versus $\log r$, where $C(r)$ is the correlation function and $r$ the correlation radius. $C(r)$ has been calculated for the contour of a seaweed pattern. The slope corresponds to the correlation dimension $\nu$ according to Sec. 2.4.2. Saturation occurs at the upper end of the scaling range where $r$ is of the order of the overall size of the crystal which is about 1300 $\mu$m. As the data points are not exactly on a straight line we use the local correlation dimension in Fig. 3.16 to choose the range for calculating the slope:

- For small correlation radii the local dimension increases with increasing radius. The lower limit is selected where this behaviour breaks down for the first time. This limit is reached at a correlation radius of about 30 $\mu$m which is larger than the tip radius $R_{\text{exp}}$ of the unperturbed crystal.

- The upper cut-off point is chosen as the point where the local slope decays rapidly. This point is near 600 $\mu$m, far away from the overall size of the crystal.

The correlation dimension of the same three seaweed contours as for the box dimension (Sec. 3.2.2) is calculated in the selected range. Averaging over the three dimensions leads to $\bar{\nu} = 1.47 \pm 0.07$. The error estimate is determined by comparison with the correlation dimension of other selected ranges. Within the precision of our measurements, $\bar{\nu}$ has the same value as the correlation dimension of dendrites which was found to be $1.51 \pm 0.07$ [28].

It is interesting to note that the error according to linear regression is much smaller for the correlation dimension than for the box dimension. The data points of the correlation dimension fit better to a straight line as in the case of the box dimensions. This is reflected in the statistical error (corresponding diagrams Fig. 3.16 $\leftrightarrow$ Fig. 3.14) of the local slope and in the uncertainties of the linear regression (Fig. 3.15 $\leftrightarrow$ Fig. 3.13) in the selected ranges.
Figure 3.15: Calculating the correlation dimension of a seaweed pattern [image #20, crystal one]. The logarithm of the correlation function $C(r)$ vs. the logarithm of the length scale $r$ is plotted. The slope of the linear fit (thin line) is $\nu = 1.464 \pm 0.006$. The thick line indicates the range of the linear regression. The range of the linear regression is chosen by means of the local slope shown in Fig. 3.16.
Figure 3.16: Local slope according to the data set of Fig. 3.15. Error bars determined from statistical error of the linear regression are of the size of the data points and therefore not visible. According to this diagram the range selected to calculate the correlation dimension \( \nu \) is chosen between 30 \( \mu \text{m} \) and 600 \( \mu \text{m} \), corresponding to 1.47 and 2.78 in logarithmic units. The scaling range is about one order of magnitude and the ranges where the scaling breaks down are ignored. The selected scaling range is indicated by the thick line. Linear regression in this range leads to a correlation dimension \( \nu = 1.464 \pm 0.006 \) shown as thin line.
3.3 Doublons in three dimensions

We found that doublon patterns can be formed after a perturbation, especially as consequence of tip-splitting of the front tip (see Fig. 3.26 for tip-splitting of the front tip). These patterns can be observed either isolated, meaning that no additional changes to seaweed morphology can be found, or to be part of a seaweed pattern as it has been described in Sec. 3.1.3. In Fig. 3.17 an isolated doublon pattern without additional seaweed morphology can be seen. The contours extracted from this crystal are shown in Fig. 3.18. In both cases the doublon patterns behave similar:

- The doublon fingers in three dimensions are dynamically stable up to several minutes after tip-splitting. Both grow with the same, constant velocity (time range $A$ in Fig. 3.19 and Fig. 3.20). The growth velocity of the doublon pattern is lower than the one of the unperturbed dendrite (see also images #18 to #20 in Fig. 3.6). This is at variance with the model of two-dimensional growth [39, 40] where doublons are predicted to grow faster than dendrites.

- Some minutes later in the experiment the secondary finger slows down (time range $B$ in Fig. 3.19 and Fig. 3.20), whereas the faster growing prime finger slowly changes its morphology back to the one of a dendrite.

All doublon patterns actually observed have a fully three-dimensional shape, i.e. they do not simply correspond to a two-dimensional shaped doublon with a certain, constant thickness or extension in the third dimension: In the plane perpendicular to the one defined by the growth directions of the doublon fingers, two fins develop at each finger as shown in Fig. 3.21 and in Fig. 3.22. In Sec. 3.1.3 we observed also that the shape of the pattern in the plane mentioned before behaves like a dendrite.

It is not obvious which definition of a radius of curvature makes sense in a discussion of three-dimensional doublon patterns. Two concepts may be compared: In a first one the radius $R_{\text{env}}$ of the envelope over the doublon’s double finger has been proposed in Ref. [40] for two-dimensional doublons. As a second one we propose to use the tip radius $R_{\text{exp}}$ of one of the fingers. We tried to analyze both cases. We fitted the data to a parabola, as it is well known from the Ivantsov solution, as well as to a power law (Eq. (1.9)) as its experimentally and theoretically found for three dimensional dendrites.
Figure 3.17: Isolated doublon pattern observed after perturbation. Apart from the doublon on the tip, no changes to seaweed morphology are found. The horizontal size of the image is about 1650 \( \mu \text{m} \). The contour of this doublon is shown as the last contour in Fig. 3.18. [Crystal three, image #12]
3.3. Doublons in three dimensions

Figure 3.18: Doublon pattern [crystal three]. The original dendrite was perturbed by shifting it for 75 seconds down to the cold temperature field. The first picture shows the crystal immediately after pulling it up again. This means that tip splitting, leading to a doublon pattern, has taken place in the colder region of the melt, invisible to the camera. The time difference between the first and the last image is 166 seconds. The original image #12 is shown in Fig. 3.17.
Figure 3.19: Growth velocity of the two fingers of a doublon pattern vs. the image number. The growth velocity of the stationary growing dendrite at the same nominal undercooling ($\Delta T = 118$ mK) is displayed as dashed line. The black triangles indicate the velocity of the surviving prime finger of the doublon. The individual time steps between the images are not identical. In time range $A$ where the two fingers are dynamically stable they grow with the same velocity. Fig 3.17 shows that the two fingers are equal up in to growth direction. Some minutes later, in time range $B$ the secondary finger, marked with open triangles, become slower. The prime finger now will change its morphology and relax slowly back to a dendrite. [crystal three]

Figure 3.20: Growth velocity of the two fingers of a doublon pattern vs. time. Apart of the horizontal axis, everything is similar to Fig. 3.19.
3.3. Doublons in three dimensions

Figure 3.21: The doublon pattern has a fully three-dimensional shape, i.e. it does not simply correspond to a two-dimensional shaped doublon with a certain, constant thickness or extension in the third dimension: In the plane perpendicular to the one defined by the growth directions of the doublon fingers, i.e. in the plane perpendicular to the object plane, two fins develop at each finger (see Fig. 3.22 too). The arrows in the figure point to two of these fins. [image #10, crystal three]

Figure 3.22: Schematic contour of a doublon in a plane perpendicular to the growth direction. The thick arrows point to the fins which correspond to the marked fins in Fig. 3.21. Each of the two fingers looks like a dendrite with an inner groove instead of the fourth fin.
3. Experimental results

Figure 3.23: The data set to fit the radius of the envelope is plotted as two thick black lines. The borders of the data set are given by \(P1\) and \(P2\). At \(P2\) the envelope separates from the crystal. \(P1\) indicates the start of sidebranching, where a small kink is seen. The image is the same as in Fig. 3.21. [image #10, crystal three]

3.3.1 Radius of the envelope

First we discuss the doublon envelope as concept to determine the curvature of doublon patterns. This concept has been proposed in Ref. [40] for two-dimensional doublons. The radius of the envelope is denoted as \(R_{\text{env}}\).

Compared with a contour of a dendrite the range of the contour of a doublon which can be used for fitting is much more restricted (see Fig. 3.23). There are two limits for the fitting procedure:

- Far from the tip, the evaluation of the data set for fitting is similar to the evaluation for the contour of a dendrite. The range of fitting is limited by the point where sidebranching occurs, denoted as point \(P1\).

- In the region close to the tip the fitting range is limited by the point where the finger’s contour separates from the contour of the envelope. We call this point \(P2\).

We do not have a good criterion for the exact determination of \(P2\) as \(P2\) determines the gradual approach of two curves which have approximately the same slope (Fig 3.23). However, a large area near the tip has to be ignored for fitting. Thus, the number of data points for fitting is quite low. Despite the low precision of the data one can conclude:
3.3. Doublons in three dimensions

- \( R_{\text{av}} \geq 2R_{\exp} \) where \( R_{\exp} \) is the tip radius of the unperturbed dendrite. Up to now \( R_{\exp} \) has been used as a typical length scale for the whole dendrite. There is no evidence found in the experiments that the length scale of the crystal is changed by more than a factor 2 because of the formation of doublon patterns.

- All growth theories rely on quantities like \( \sigma \) or \( \sigma^* \) which are both inversely proportional to \( v_{\text{tip}}R^2 \). \( v_{\text{tip}}R^2 \) is a measure for the solidification rate and a rough characterization of the heat flow around the growing dendrite. In our experiments \( v_{\text{tip}}R^2 \) increases by factor between 4 and 10 during developing a doublon pattern. But only little influence of the formation of doublon patterns on the heat flow and hence to \( v_{\text{tip}}R^2 \) has to be expected.

Based on these results we conclude that the radius of the doublon envelope is not appropriate to describe doublon patterns in three dimensions.

3.3.2 Tip radius of the prime finger

The second concept uses the tip radius of one of the fingers. In this work we focus on the prime finger of doublon. The growth directions of the two fingers are not exactly parallel as well as the boundaries of the liquid inner groove are not exactly parallel. One can split the contour of one of the fingers by the \( z \)-axis which goes through the tip and which is parallel to the growth direction of the finger under consideration, see Fig 3.24. The shape of the fingers are not symmetric. We are interested in the tip radius \( R_{\exp} \) of the outer side far away from the groove. In order to improve the stability of the tip fitting algorithm we mirror the outer contour of the tip at the \( z \)-axis. There are two methods to measure \( R_{\exp} \) from a given contour shown in Sec. 2.3.2. Results of both methods are shown in Fig 3.25:

- The full circles denote the radius gained by fitting the power law \( z = a|x|^{1.67} \) to the contour up to various fitting heights \( H \). For a dendrite the tip radius \( R_{\exp} \) determined by this method is independent of the fitting height. For the finger of the doublon pattern analyzed in Fig 3.25 the same behavior is found. For this comparison we use the dimensionless data of \( R_{\exp} \) found in earlier studies [28] about dendrites.

- Fitting a parabola to the contour leads to a tip radius which decreases with decreasing fitting height \( H \) depicted as triangles. The tip radius \( R_{\exp} \) of the contour is calculated by linearly extrapolating to \( H \to 0 \) the radii. For the tip radius of doublon patterns we found that this method leads to the same \( R_{\exp} \) as fitting the power law within the precision of measurement, as it has been found for a dendrite.
Figure 3.24: Contour of the prime finger of a doublon pattern (thin full line) brought into a coordinate frame of reference. The secondary finger and the liquid inner groove are not shown at the left side. The thick dashed line indicates the data set for calculating the tip radius obtained by mirroring and cutting off. [image #39, crystal one]
3.3. *Doublons in three dimensions*

Figure 3.25: Tip radius of the prime finger of a doublon pattern [image #39, crystal one]. The tip radius gained by fitting a power law is independent of the fitting height $H$ (full circles for data points, thick line for averaging). Fitting parabolas to the contour and extrapolating the tip radii to the fitting height $H \to 0$ (triangles for data points, thick line for extrapolating by linear regression) leads to a tip radius which is within the precision of our measurements the same as the tip radius deduced from the power law fit, i.e. the tip radius is within 21 and 22 μm. Dashed lines are denoting the estimated errors.

For this reasons, we suggest that the significant tip radius of a doublon pattern is the tip radius of the prime finger. The shape of a finger on the side turned away from the inner groove is dendrite-like. These conclusions are supported by the investigations in Sec. 3.1.3. For the images #22 to #26 where tip-splitting has taken place and where the tip forms a two-fingered system, the tip radius is determined as described above, i.e. mirroring the outer side of the prime finger and fitting by the power law. Analyzing the images with the radius obtained in this way the doublon pattern behaves like a dendrite at the same undercooling. This is shown in Fig. 3.6 and Fig. 3.8. There, the radius of curvature determining the behavior of the doublon has been determined by measuring the tip radius of the prime finger tip. The growth parameters of the doublon pattern have the same values as the ones of the unperturbed dendrite.
Figure 3.26: Tip-splitting after a perturbation leading to a doublon pattern. The time difference between the first and the last picture is 482 seconds. In contrast to most of the other pictures the crystal has not been rotated to bring the fins into the object plane of the camera. The horizontal size of each of the images is about 820 μm. [crystal four]
4. Discussion and conclusions

4.1 Seaweed patterns and morphological transitions

The solvability theory predicts a stable growth of dendrites for materials with sufficient anisotropic surface tension $\gamma_{sl}$. It does not predict the morphology, which can be observed in the case of low or vanishing anisotropy of $\gamma_{sl}$. For two-dimensional systems a phase-diagram of morphologies has been developed [21, 22, 23]. In agreement with these theoretical predictions, seaweed and doublons are observed in thin-film directional solidification experiments of dilute alloys when the anisotropy of the surface tension is low [41, 42, 43, 44]. In thin-film directional solidification experiments the anisotropy and the surface tension $\gamma_{sl}$ can be varied by changing the crystallographic orientation. The growth velocity is the control parameter and thus plays the role of the undercooling in free growth. Depending on the crystallographic orientation and the growth velocity different growth morphologies are observed: dendrites or seaweed or nondendritic unsteady "degenerated" patterns. Transitions between morphological states can be initiated by changing growth velocity. In analogy to these experiments we enforced at low undercooling a morphological transitions from dendrite to seaweed during three-dimensional free growth by a cooling step, as suggested in the morphology diagram Fig. 1.1 for two-dimensional growth. We suppose that a similar morphology diagram as in Fig. 1.1 is valid for three-dimensional growth.

Hysteresis occurs, i.e. for very small perturbations in temperature no morphological transitions take place. But once seaweed patterns have been initiated by a sufficient strong perturbation they continue to grow as seaweed even in an environment where dendrites are preferred. Only after several minutes the crystal relaxes back to dendritic growth.

Our experiments indicate that the anisotropy of the surface tension of xenon is small. Otherwise no morphological transition would be possible at low undercooling. The assumption of small anisotropy is compatible with earlier studies we have performed [45]. There we have measured the surface tension $\gamma_{sl}$ of xenon by means of the grain boundary groove method. This led to $\gamma_{sl} = 9.43 \pm 0.37 \text{ mJ/m}^2$. Within
the precision of our measurements the anisotropy is too small to cause observable
effects.

4.2 Doublons

Doublons are predicted to be the basic building blocks of seaweed patterns in two
dimensions [39, 46]. A doublon consists of two fingers with a narrow inner groove
of liquid in between. Doublons in two dimensions have been found for vanishing
anisotropy in thin-film directional solidification experiments [41, 42, 43, 44]. In
analogy to these two-dimensional experiments we have observed doublon patterns
as building blocks of the seaweed patterns in three dimensions. When a morph¬
ological transition takes place or a doublon pattern is formed by tip-splitting
we found that the growth velocity decreases and the tip radius increases. Tip¬
splitting in three dimensions has been observed together with decreasing growth
velocity and increasing tip radius during tip-splitting in experiments under mi¬
crogravity conditions [47]. The undercooling in the cited work was of the order
of 0.01 in dimensionless units. Similar to our study, the competition between the
two doublon fingers and the relaxing back to dendritic grow was observed. No
occurrence of seaweed was reported in Ref. [47].

Similar to dendritic tip radii, Brener, Müller-Krumbhaar and Temkin [23] used
the tip radius \( \rho \) of the parabolic envelope of the double finger for scaling relations.
Based on our experimental results we concluded that the radius of the envelope
is not appropriate to describe doublon patterns in three dimensions. We find in
the experiments that the significant length scale of a doublon pattern is just the
tip radius of an unperturbed dendrite growing at the same nominal undercooling.
It is determined from the prime finger of the doublon.

Considering the tip radius of the surviving finger, the doublon pattern behaves
like an unperturbed dendrite at the same undercooling. Therefore we suggest that
the significant tip radius of a doublon pattern is the tip radius of the surviving
finger.

In Ref. [23] doublons in two dimensions are predicted to grow faster than
dendrites at the same parameters \( \Delta T \) and \( \epsilon \), but we have never observed a growth
velocity of a doublon faster than \( v_{\text{tip}} \) of the unperturbed dendrite. There are two
possible reasons for this difference:

- **Three-dimensional shape**: A growth rate smaller than the one predicted for
  fully developed doublons may be understood from the fact that more than
  the volume of one dendrite is solidified in three-dimensional growth: In the
4.3. *Fractal or compact growth?*

It is not obvious whether our crystals are compact or fractal in the sense of the morphology diagram Fig. 1.1.

Considering the morphology diagram Fig. 1.1 showing the morphologies in the plane undercooling $\Delta$ versus anisotropy $\epsilon$. The crystals in our experiments ([7, 28, 29] and present work) grow at low undercooling, $\Delta T \leq 220\,\text{mK}$ and $\Delta \leq 0.00372$ in dimensionless units. The anisotropy $\epsilon$ of the surface tension of xenon is small but no quantitative data are available (see Sec. 4.1). Furthermore, the location of the dotted line in Fig. 1.1 separating fractal (F) and compact (C) growth of dendrites depends on thermal noise and is not known quantitatively. For these reasons it is impossible to classify our crystals as fractal or compact by means of quantitative arguments in the morphology diagram in Fig. 1.1.

A definition used by the authors of the morphology diagram is based on the density of the crystal averaged over the embedding volume of the crystal [21, 24]. Compact growth means growth at a constant average density, irrespective of the value of this density, while in a fractal pattern the density varies with the length scale. As it is mentioned in Ref. [23] the classification as fractal or compact depends on the selected length scale. Possible length scales are the tip radius, the overall size of the pattern or the diffusion length. In Ref. [7] it is shown that our dendrites behave like a fractal when the tip radius is selected as length scale. The density, in the cited work called *filling factor*, increases linearly with increasing tip radius. But the density is found to be independent of the overall size of a dendrite or of the overall size of a cluster of dendrites as it is expected for a compact pattern.

For these reasons we think that further discussions about the classification "fractal or compact" and about the dependence on the length scale are necessary.
4.4 Fractal dimension of seaweed patterns

We compared the optimized and the nonoptimized box dimension of the contour of a seaweed pattern. Depending on the box size the number of boxes to cover the contour was between 0 and 43 % smaller for the optimized method than for the nonoptimized one. The slope in the log-log-plot and hence the box dimension $d_f$ depends on the method to arrange the boxes. We decided to use the optimized method because it is closer to the definition of the box dimension given in Sec. 2.4.1.

To find out the range of box size $\varepsilon$ or correlation radius $r$ where the scaling relation Eq. (2.7) or Eq. (2.10) holds, we have determined the local slope $[36]$ in the log-log-plot and used it to select the range of box sizes or correlation radii to determine the fractal dimension. Averaging the fractal dimensions of the contours of several seaweed patterns we found $d_f = 1.48 \pm 0.07$ (box dimension) and $\nu = 1.47 \pm 0.07$ (correlation dimension).

Bisang and Bilgram [28] determined the fractal dimension of the contour of a projection of xenon dendrites. It was found that the fractal dimension is independent of undercooling and of the "age" of the specific dendrite. Averaging over data obtained at various undercoolings leads to $d_f = 1.42 \pm 0.05$ (box dimension) and $\nu = 1.51 \pm 0.08$ (correlation dimension). Taking into account the error estimate, dendrites and seaweed patterns have the same fractal dimension.

Ihle and Müller-Krumbhaar determined the fractal dimension of seaweed patterns in two dimensions obtained by numerical simulation [46] for isotropic surface tension. They also used the concept of the local slope to find the scaling range. In difference to our investigations where the contour is analyzed they calculated the box dimension of the area filled by the seaweed (area box dimension). This led to a fractal dimension of about 1.73.

Analyzing the fractal dimensions of contours of seaweed patterns we found that the data points in the log-log-plots do not exactly lie on an straight line. And the local slope in the log-log-plots depends on the box size and the correlation radius, respectively. It is difficult to find a scaling range which is at least one order of magnitude and where the local slope does not vary to much. Similar results can be seen in Ref. [46], where the local slope of a fractal seaweed pattern has been analyzed. For these reasons we think that further investigations are necessary to discuss, if fractal dimensions are really suitable to describe seaweed patterns. The area box dimension and the temperature dependence of the fractal dimensions have to be studied to allow a comparison with the fractal dimension of dendrites and with theoretical results.
4.5 Conclusions

It is possible to induce the three-dimensional growth of seaweed from liquid xenon. The transition from dendritic to seaweed-like growth is enforced by means of a cooling step.

The fractal dimension of the contour of a dendrite is a measure for the distance to the equilibrium shape of the crystal. The dimension of the contour of an equilibrium (sphere or plane) is 1. The typical length scale for a dendrite or seaweed pattern is the tip radius of the dendrite. The perturbation of the crystal growth does not change the tip radius and the fractal dimension but it changes the morphology of the solidification patterns.

In the experiments on solidification of thin samples, the surface tension $\gamma_{sl}$ can be changed by choosing the crystallographic orientation. Thus a transition to seaweed is initiated. In our three-dimensional experiments we do not change $\gamma_{sl}$. We initiate a transition by means of a perturbation. Due to a hysteresis effect in the temperature behavior of the morphology we observe seaweed at the same nominal undercooling where we also can observe dendrites. Therefore seaweed and dendrites are characterized by the same length scale and the same fractal dimension.
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### Table A.1: Selected properties of xenon

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<th>Property</th>
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<td>Molecular weight</td>
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<td>Capillary length</td>
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<td>Unit of supercooling</td>
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$^1$ ($\ell$) liquid; ($s$) solid


[h] Estimate according to Ref. [48]

** Materials with $\alpha < 2$ are usually not faceting in contact with the melt.
References


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# Curriculum Vitae

27th January 1970  Born in Geneva, Switzerland

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<tr>
<td>1976-1982</td>
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<td>1982-1984</td>
<td>Grammar school in Rikon im Tösstal, ZH</td>
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<td>1990-1995</td>
<td>Study of physics at the ETH Zürich</td>
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<td>1994</td>
<td>Industrial practica on electrostatic problems on textile machines, Maschinenfabrik Rieter, Winterthur</td>
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<td>Diploma work in experimental physics in the Medical Physics group of Prof. P. Rüeggsegger (ETH Zürich) on „Erweiterung des Auflösungsbereiches von Mikrotomogrammen mittels inverser Filter“ (&quot;Enhancement of resolution of micro tomograms using inverse filters&quot;)</td>
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<tr>
<td>1996-2000</td>
<td>Research and teaching assistant at the Laboratory for Solid State Physics (ETH Zürich) in the Freezing and Melting team of Prof. J. H. Bilgram within the group of Prof. H. R. Ott</td>
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<td>1998-2000</td>
<td>Post-graduate study on medical physics at the ETH Zürich</td>
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<td>Ph.D. thesis at the Laboratory of Solid States Physics (ETH Zürich) on “Morphology of Structures in Three-dimensional Diffusional Growth&quot;</td>
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