In situ LIF temperature measurements in aqueous ammonium chloride solution during uni-directional solidification

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Abstract We present in situ whole-field measurements of the temperature field using laser-induced fluorescence in a study of bottom-chilled uni-directional solidification of aqueous ammonium chloride. We utilize a two-color, two-dye, ratiometric approach to address the significant spatial and temporal variations of laser sheet intensity field due to refractive index variations caused by the evolving concentration and temperature fields. In our work we take advantage of two temperature sensitive fluorescent dyes with opposite temperature sensitivities in order to increase the overall sensitivity and temperature resolution of the measurements. The resulting temperature sensitivity (about 4% K$^{-1}$) is more than a factor of two higher than the original work of Sakakibara and Adrian (Exp Fluids 26:7–15, 1999) with a sensitivity 1.7% K$^{-1}$. In situ measurements of the temperature field during solidification are presented, along with temperature characteristics of some of the complex flow features, such as plumes and fingers.

1 Introduction

A wide variety of products are now made of metal alloys such as automobile engine blocks and the compressor and turbine section of an aircraft engine. The major issues for these alloys are melt-related defects and inhomogeneities such as segregation defects and freckles formed during the solidification process. The solidification process of a binary melt is influenced by fluid motion in the liquid, whose flow pattern strongly depends on both thermal and solutal buoyancy forces. Studies of these multiphase transport phenomena include stability and numerical analyses of the coupled nonlinear governing equations based on simplifying assumptions, exemplified by works such as Heinrich et al. (1989), Worster (1991), Neilson and Incropera (1991), Worster (1992), Schneider and Beckermann (1995), Schulze and Worster (1998) and Feltham and Worster (1999).

An experimental approach to studying the solidification of metallic alloys has been the use of transparent analogs of metallic alloys. A popular analog is the binary aqueous ammonium chloride (NH$_4$Cl-H$_2$O) system which has proven to be useful for flow visualization and morphological studies and has been utilized by many researchers because of its convenient solidification temperature and similar behavior to metallic alloys (e.g., Chen and Chen 1991; Magirl and Incropera 1993; Beckerman and Wang 1996; Liu and Hellawell 1999). Previous studies indicate that convective phenomena associated with solidification of aqueous ammonium chloride solution cover a large range of length scales that evolve dynamically. These features include the vertical growth of a solid/liquid interface along with the development of numerous fine structures of salt fingers, followed by the appearance of a number of plumes ejecting water-rich fluid jets from channels in the mushy zone of the growing dendritic crystal mass.
The general features described above are illustrated in Fig. 1 for the specific geometry that is the subject of the current study. This figure depicts a shadowgraph visualization of the solidification process in a hypereutectic (26% by weight; 26% w) ammonium chloride (NH₄Cl) solution within a rectangular container at room temperature whose base plate is cooled to \(-14\,^\circ C\) to impose a vertical temperature gradient and initiate uni-directional solidification (Lum et al. 2001; Lum 2001). The details of the experimental setup will be provided later in this paper. The cooling of the base plate starts at time zero and small-scale features, termed “fingers”, begin to form at about 4 min. As the cooling of fluid continues, more ascending water-rich fingers develop due to a need to reject more solute during the crystallization process. This is accompanied by a stronger convection and the fingers are discernible all the way to the top of the test section (see image at 10 min). The large Lewis number of aqueous ammonium chloride helps in maintaining the identity of the water-rich fingers (Lewis number is defined by $Le = \frac{\alpha}{D}$, where $\alpha$ and $D$ are thermal and mass diffusivity, respectively). During the initial stages of cooling, rapid formation of ammonium chloride crystals occurs which settle to form the mushy layer. As time progresses, well-defined chimney-like structures begin to form which provide outlets from the mush for rejecting lighter fluid into the surroundings through ascending water-rich plumes. The small fingers in the earlier stages die down as more plumes develop.

Since the thermal buoyancy force is one of the main forces that plays an essential role in uni-directional solidification, it is important to characterize the in situ temperature distribution during the solidification process. Unfortunately, there exist very little non-intrusive quantitative experimental data on the in situ temperature field during the solidification process of ammonium chloride. Previous measurements include thermocouple measurements of temperature histories in the test container (Magirl and Incropera 1993) and at the container side wall (Wirtz et al. 1998). Non-intrusive measurements with thermochromic liquid crystal paints (TLC) have also been reported on the surface of a Hele-Shaw test cell (Solomon and Hartley 1998). Any inference on the temperature in the interior was indirect and based on the assumption of rapid diffusion of heat across the narrow gap of the test cell. The use of encapsulated TLC particles (10–15 μm in diameter) has been reported by Nishimura et al. (1992) and Nishimura and Wakamatsu (2000) for generating qualitative temperature maps based on the color change of TLC; the quantitative temperature distributions were measured by thermocouples, however. We also note that TLC tends to give a high temperature resolution, but over a rather narrow temperature range, e.g., 2.5°C range in Nishimura et al. (1992).

Motivated by the discussion above, we present here in situ whole-field measurements of the temperature field using laser-induced fluorescence (LIF) in a study of bottom-chilled uni-directional solidification process of aqueous ammonium chloride. This work was first reported briefly by Shafii and Koochesfahani (2003) and extensive details can be found in Shafii (2005). In our work we have employed a two-color, two-dye, ratiometric approach to address the significant spatial and temporal variations of laser sheet intensity field due to refractive index variations.

Fig. 1 Shadowgraph visualization of the unidirectional cooling of ammonium chloride at different times during the solidification process (Lum 2001). The entire test section is shown. Cooling is from the bottom and the growth of the solidification front is highlighted by the increasing thickness of the (black) mushy zone.
caused by the evolving concentration and temperature fields. The traditional approach uses a temperature sensitive dye along with another with little temperature sensitivity (e.g., see Sakakibara and Adrian 1999). In our work, however, we take advantage of two temperature sensitive fluorescent dyes, with opposite temperature sensitivities (Fluorescein and Kiton Red, at 514.5 nm excitation), in order to increase the overall sensitivity and temperature resolution of our measurements. An approach of this type has also been recently reported by Sutton et al. (2008) using other dye pairs for the 532-nm excitation of Nd-YAG laser. Another distinction in our study is that we focus on a “cold” application of LIF with temperatures below ambient, whereas most previous studies have addressed heated fluid measurements with temperatures above ambient.

In the following sections the LIF technique for measuring temperature is briefly described, along with a discussion of our dye selection, calibration, and further details of implementation. The experimental test facility and the procedure for creating the uni-directional solidification of ammonium chloride are given next. Finally, sample measurement results are provided in terms of in situ quantitative temperature maps at different times during the solidification process, along with characterization of temperature profiles at selected locations in the test section.

2 Temperature measurement using laser induced fluorescence (LIF)

The use of LIF in fluid flows takes advantage of the fact that, for dilute solutions and unsaturated laser excitation energies, the fluorescence emission intensity at a given point is given by $I = AI_i C \varepsilon \Phi$, where $A$ is a parameter representing the detection collection efficiency, $I_i$ the local incident laser intensity, $C$ the concentration of the dye, $\varepsilon$ the absorption coefficient, and $\Phi$ the photoluminescence quantum efficiency. For some molecules, the absorption coefficient $\varepsilon$ and/or the quantum efficiency $\Phi$ are temperature dependant, allowing the measurement of the emission intensity of tracer molecules to be used to quantify the temperature field in a fluid flow. The temperature sensitive fluorescent dye, Rhodamine B, has been one of the most common tracers used in various applications (see e.g., Sakakibara et al. 1993; Sato et al. 1997; Coppeta and Rogers 1998; Sakakibara and Adrian 1999, 2004; Lemoine et al. 1999; Coolen et al. 1999; Kim and Kihm 2001; Lavieille et al. 2001; Saeki and Hart 2001; Kim et al. 2003). Comparative studies of commonly used fluorescent dyes in liquids can be found in Coppeta and Rogers (1998) and Saeki and Hart (2001).

In its simplest form of implementation, the emission from a single fluorescent dye, over a single spectral band, can be used to measure the temperature field (e.g., Lemoine et al. 1999). The difficulty in this case is that any spatial and temporal variations in the local incident laser intensity need to be separately accounted for, something that is impossible to do if the variations are caused by the flow itself. A good example is the solidification process which is the focus of our investigation. This flow is characterized by variable temperature and concentration fields that cause a variable index of refraction field within the flow, causing the incident laser intensity field within the flow to vary in time and space. Figure 2 illustrates the recorded fluorescence intensity, before and during solidification, from a region in the test section that is illuminated by a laser sheet. The smoothly varying intensity field before the start of solidification, which is characteristic of the spatial intensity distribution of the laser sheet, develops significant “streaks” after the start of the solidification process. The strengths and positions of these streaks change with time.

A common method to eliminate the effect of in situ variations of incident laser intensity is to use a ratiometric approach. In the two-color, single-dye, approach, emission from two different spectral bands with different temperature sensitivities are utilized (see Lavieille et al. 2001). A three-color approach, using emission from three different spectral

Fig. 2 Fluorescence intensity over an imaged area, a before solidification and b during solidification
bands, has also been reported for measurements with large optical paths (Lavieille et al. 2004). The most popular method, however, has been the two-color, two-dye, approach where two dyes with different temperature sensitivities are employed (e.g., Coppeta and Rogers 1998; Sakakibara and Adrian 1999, 2004; Kim and Kihm 2001; Kim et al. 2003). The details of this approach are given in the cited references and will not be repeated here. Briefly, however, for fixed concentrations of a mixture of two fluorescent dyes the fluorescence intensity ratio \( R \) of the two dyes is cast in the form \( R \equiv I_1/I_2 = K \cdot F(T) \). In this expression, \( I_1 \) and \( I_2 \) are the fluorescence intensities emitted by the two dyes, \( K \) is a constant that contains information about the specific experimental setup (i.e., dye concentrations and optical detection parameters), and \( F(T) \) represents the overall temperature response function that is connected to the temperature dependence of the absorption coefficients and quantum efficiencies of the two dyes. An experimental calibration is used to establish the fluorescence intensity ratio referenced to its value at a reference temperature \( T_o \), i.e., \( R(T)/R(T_o) \), as the primary calibration curve that is used to measure the fluid temperature. The following section provides details on the selection of the fluorescent dyes used in this study and the calibration of the temperature response curve.

### 2.1 Dye selection and calibration

The most common fluorescent dyes used in the two-color, two-dye, ratiometric method are the temperature sensitive Rhodamine B and the nearly temperature insensitive Rhodamine 110. The overall temperature sensitivity of this dye pair is 1.6–1.7% K\(^{-1}\) (Sakakibara and Adrian 1999). In our investigation, the vertical temperature variation in the liquid melt is about 20°C, but the transverse temperature variation across fingers and plumes is expected to be much smaller and on the order 2°C. It is, therefore, desirable to improve the temperature sensitivity of the fluorescent dye pair. To accomplish this, we take advantage of two temperature sensitive dyes, one with positive and the other with negative temperature sensitivities. Most fluorescent molecules, however, have a negative temperature sensitivity, i.e., fluorescence intensity decreases with increasing temperature. Fluorescein (disodium fluorescein), on the other hand, has a positive temperature sensitivity when excited at 514.5 nm (green line of argon-ion laser) due to the increase with temperature of its absorption at this wavelength (Coppeta and Rogers 1998). The second dye was selected to be Kiton Red because its absorption and emission spectra are red-shifted in comparison with Rhodamine B and this reduces the spectral conflicts in the two-dye approach.

The relative absorption and emission spectra of Fluorescein and Kiton Red are depicted in Fig. 3. To minimize spectral conflicts during detection, appropriate spectral bands were selected using two optical filters (Edmond Optics). Fluorescein’s fluorescence was captured over the wavelength range 535–545 nm (optical filter with full-width half-maximum FWHM of 10, 540 nm center wavelength), with minimal influence from Kiton Red’s emission. The fluorescence emission of Kiton Red was captured by a long pass filter over wavelengths greater than 600 nm, little affected by fluorescein’s emission. The negligible leakage through the filters was confirmed by preparing the Fluorescein solution and measuring its emission by the fluorescein camera, followed by introducing the Kiton Red dye into the solution and measuring the emission intensity again. The results showed the intensity change was about 0.1%, indicating there was negligible leakage through the fluorescein filter. The same experiment was carried out by preparing the solution with Kiton Red and then adding Fluorescein into the solution, resulting in the same conclusion as before, i.e., leakage through the kiton red filter was negligible. Note, in Fig. 3, that the Fluorescein emission over the selected spectral band is partially absorbed by Kiton Red, a spectral conflict that is difficult to avoid in the two-color, two-dye approach. To reduce this conflict, the molar concentrations of Fluorescein and Kiton red were minimized at 5 \times 10\(^{-7}\) M. The practical implication of this spectral conflict, and possible additional self-absorption, is that the detected emission intensity can become dependent on the optical path length \( L \) within the liquid (i.e., the distance between laser sheet illumination and the viewed test section wall). This influence is negligible in our study, as will be quantified later through calibration experiments.

An important issue that needs consideration is the pH of the solution. The working fluid in our study, Aqueous
ammonium chloride solution, is acidic and its pH is measured to be as low as 4.3 for a 26% w solution (Shafii 2005). There is also a slight variation of solution pH with temperature (about 6% change over about 10°C; see Shafii 2005). It is known that fluorescence of Fluorescein is pH dependent, increases significantly over the pH range 3–7 and becomes insensitive to it above pH of about 7. On the other hand, Kiton Red does not exhibit a pH dependent fluorescence over the pH range 3–10 (Coppeta and Rogers 2005). In order to operate in the pH-insensitive range of Fluorescein, the pH of ammonium chloride solution was always raised to about 7.8 by adding Sodium Hydroxide (NaOH).

The calibration of the overall temperature response of the two-color, Fluorescein-Kiton Red, system was carried out in the same test section, and with the same optical and detection configuration as the actual solidification experiments; see Fig. 4. The test section was filled with the aqueous solution (Ammonium Chloride 19% wt., 5 × 10⁻⁷ M Fluorescein, and 5 × 10⁻⁷ M Kiton Red) at room temperature. This particular concentration of NH₄Cl was selected based on the phase diagram of ammonium chloride (Shafii 2005) to avoid solidification of the liquid solution down to −15°C. The calibration was carried out over the (4–20°C) range, however, because previous experimental results of Wirtz et al. (1998) suggested that the temperature of mush/melt interface was always above 4°C. The temperature of the fluid was lowered by lowering the temperature of the base plate, whose temperature was controlled by a recirculating constant-temperature bath (see Section 3 for further details). The solution was stirred continuously to ensure a uniform temperature over the imaged area in the test section. The temperature of the solution was independently monitored with a thermocouple. The fluid was illuminated with a laser sheet (argon-ion laser at 514.5 nm) and fluorescence images of Fluorescein and Kiton Red were recorded by two aligned 8-bit, 640 × 480 pixel Pulnix cameras (TM-9701) at 30 frames s⁻¹. Each camera was fitted with appropriate optical filter (see earlier description) to capture the emission from one dye. Calibration intensity data were averaged over 30 images and over a 32 × 32 pixel region of the image.

Figure 5 shows the measured intensity variation of both dyes with temperature for two different optical path lengths L. Measurements are also included for water solution (i.e., without NH₄Cl) to assess the influence ammonium chloride on the temperature response of these dyes. Intensity data of each dye are normalized by their respective intensity at reference temperature of 20°C. As expected for 514.5 nm excitation, the fluorescence intensity of Fluorescein decreases with decreasing temperature, whereas the emission of Kiton Red increases, instead. The normalized intensity ratio, \( R(T)/R(20°C) \), was calculated from the data in Fig. 5 and the results are illustrated in Fig. 6. Several observations are noteworthy in this figure. First, the presence of ammonium chloride has a very minor affect on the temperature response (i.e., calibration curve) compared to that for the native aqueous solution. Second, the effect of spectral conflict is small, but observable when we compare the calibration curve for the two optical path lengths \( L = 1 \) cm and 7 cm. Our studies of solidification typically used optical path lengths in the range 1–3 cm (Shafii 2005) and the results reported here are for \( L ≈ 1 \) cm. Generally speaking, before each experiment the appropriate calibration curve corresponding to its optical path length was first determined. The final observation from Fig. 6 is that the temperature sensitivity of the two-color, Fluorescein-Kiton Red, system is about 4% per °C, significantly higher than the 1.7% for the original Rhodamine B-Rhodamine 110 pair (Sakakibara and Adrian 1999). As mentioned earlier, the approach of using two dyes with positive and negative
temperature sensitivities has also been recently reported by Sutton et al. (2008) using other dye pairs with the 532-nm excitation of Nd-YAG laser.

Figure 7 depicts the results from a preliminary test to assess the effectiveness of the radiometric approach, described above, for in situ mapping of the temperature field in the uni-directional solidification problem under investigation. Shown are the inferred temperature fields if each dye (Fluorescein or Kiton Red) is used by itself using its own single-dye calibration curve. The non-uniform illumination field and “streaking” due to the index of refraction variations render the results unreliable. The temperature map using the ratiometric method does not suffer from the artifacts caused by the streaks and the nonuniform laser intensity field. The remaining oblique streak on the upper portion of the image was a consequence of the very low intensities of less than 20 counts in that region (see the laser sheet intensity distribution in Fig. 2), which make it difficult for the radiometric approach to remove the high intensity gradients in the streak. The temperature field illustrated in Fig. 7 shows evidence of a spanwise set of cold fingers protruding into the ambient ammonium chloride solution. Section 4 provides more specific examples of the evolution of the temperature field.

3 Experimental setup

The solidification system utilized is similar to the one described in Magirl and Incropera (1993). The schematic of the test section is shown in Fig. 8 and is identical to the one described in Wirtz et al. (1998), Lum (2001, and Lum et al.
Images were obtained with two CCD cameras (Pulnix sheet (thickness about 0.3 mm) using appropriate optics. A line (514.5 nm) and 1.5 W, was manipulated into a laser beam of an argon-ion laser, operating at single line, was confirmed by comparing the temperature measured by a thermocouple at specific locations in the test section. The base plate was kept constant. Eleven nucleators of size 1.59 mm × 1.59 mm × 3.18 mm were embedded in the base plate on a regular pattern to induce finite disturbances and create convective plumes in geometrically regular locations. The fluid used in these studies was a 26% wt aqueous solution of ammonium chloride (i.e., a hyper-eutectic ammonium chloride solution according to its phase diagram) mixed with 5 × 10⁻³ M Flourescein, and 5 × 10⁻⁷ M Kiton Red. The fluid in the test was initially at room temperature (about 23°C) and the solidification process was initiated by lowering the temperature of the base plate to −14°C. The two-color, two-dye, approach requires the dye concentrations in the solution to remain fixed. According to the phase diagram of the hyper-eutectic ammonium chloride solution used here, cooling of the fluid results in the phase change (crystallization) of ammonium chloride; the water itself does not freeze. As a result, we do not expect variations of dye concentration to develop. This was confirmed by comparing the temperature measured by LIF against that from a thermocouple at specific locations in the solution. The results agreed to better than 0.2°C.

The optical arrangement was discussed previously; see Fig. 4. The beam of an argon-ion laser, operating at single line (514.5 nm) and 1.5 W, was manipulated into a laser sheet (thickness about 0.3 mm) using appropriate optics. Images were obtained with two CCD cameras (Pulnix TM9701, 8-bit, 640 × 480 pixel, 30 frames s⁻¹), each fitted with the appropriate optical filter (see Sect. 2.1). The cameras viewed the same field of view through a cube beamsplitter and were aligned to one pixel accuracy. The framing rate of the camera used here is much faster than needed. The convective flow generated in this uni-directional solidification process is very slow (Lum 2001; Lum et al. 2001) and it can be considered “frozen” over several consecutive images. For example, the plumes shown in Fig. 1 ascend at about 2 mm s⁻¹. Therefore, temporal averaging of data over consecutive frames could be used for reducing the random error in the instantaneous temperature measurements. These issues will be discussed more fully when measurements of temperature distributions are presented in Sect. 4. In the early stages of the solidification process (approximately the first 8 min) the flow convection is exceedingly small in the liquid melt and possible photobleaching of the fluorescent dyes needs to be considered. It was observed that the intensity of Flourescein would drop about 1% upon two-seconds of continuous exposure to laser. Therefore, a shutter was used to limit the exposure of the solution to the laser to 0.5 s at a time. The bleaching rate of Kiton Red was measured to be about one tenth of Flourescein’s and was not a factor. The effect of dye bleaching in the worst case (i.e., roughly the initial 8 min of the solidification process) would correspond to a temperature error of about 0.06°C, based on the temperature sensitivity of current approach.

The estimation of temperature requires calculation of the intensity ratio at the same spatial location. To accomplish this, a reference target (1 mm grid pattern) placed in the image plane was used to establish the relative displacement between the pixels of one camera relative to those of the other. This was done to sub-pixel accuracy (better than 0.1 pixel) using the spatial correlation procedure described by Gendrich and Koochesfahani (1996). The resulting displacement field was used to define a third order two-dimensional polynomial mapping function by a least-squares procedure. A bi-linear interpolation scheme was used to estimate intensities at sub-pixel locations.

### 4 Results and discussion

Before carrying out quantitative temperature measurements, it would be prudent to establish that the presence of fluorescent dyes in the liquid melt did not influence the solidification process. Experiments were carried out with and without the addition of fluorescent dyes at four times the nominal concentration and shadowgraph image time series, similar to Fig. 1, were analyzed. It was noted that the timing of various events (e.g., fingers, plumes), the wavelength of plumes and the rise speed of plumes all remained unchanged. The growth of the mushy zone, calculated from the shadowgraph images and shown in Fig. 9, also confirmed that the low concentration of the dyes used here did not influence the solidification process under investigation.

We now discuss representative temperature measurements. The image area selected was 25 × 19 mm² in size and was chosen to be located on the first row nucleators approximately 2.25 cm above the cooling base plate. See Fig. 10 for a schematic of the imaged region. The spatial resolution of the measurement in the imaged plane was about 40 μm per pixel. The measured temperature maps at different times during the solidification process are shown Fig. 11. The approximate location of the imaged area...
relative to the mushy zone is indicated by the red box on the shadowgraph images that are included in the figure.

Temperature maps in Fig. 11 are shown in three different ways corresponding to different temperature accuracy levels. The data in the left column represent the instantaneous map, calculated from a single image pair of the two CCD detectors corresponding to a temporal averaging time of 30 ms. The noise characteristics of the CCD cameras, measured using a highly stable light source, corresponded to a rms intensity fluctuation of about 2.5% of the mean intensity for the conditions of these experiments (Shafii 2005). Assuming the noise of the two detectors are uncorrelated, the temperature sensitivity of current two-dye approach would suggest a temperature measurement rms uncertainty of 0.8°C based on a single image pair. This accuracy is comparable to the 1.4 K 95% confidence level reported in Sakakibara and Adrian (1999).

As mentioned earlier, the convective flow generated in our uni-directional solidification problem is very slow (Lum 2001; Lum et al. 2001) and it can be considered “frozen” over several consecutive images. Therefore, we take advantage of temporal averaging over 10 consecutive frames (i.e., 300 ms temporal averaging) in order to reduce the random error in the temperature measurement to about 0.25°C. These results are shown in the temperature maps in the middle column of Fig. 11. Comparison of temperature maps in the left and middle columns clearly show the justification of “frozen” flow state over the 300 ms integration period and the resulting reduction of the temperature measurement noise. The temperature maps in the right column represent a further spatial filtering (8 x 8 pixel area), using the Wiener method in Matlab, in order to reduce the remaining striations in the spatial maps and a further improvement in temperature accuracy by a factor of eight, estimated at 0.03°C. As can be seen in Fig. 11, because of the high resolution of the original images the corresponding degradation of spatial resolution by spatial filtering does not impact the ability to clearly resolve the essential thermal features in this problem.

The temperature maps of Fig. 11 reveal the presence of four fingers in the imaged area at time $t = 17$ min and one of them has a lower temperature than the rest (i.e., the third finger from the left located at $X = 1.5$ cm). This finger is right above a nucleator and later becomes a plume, while the adjacent fingers weaken and decline in number. We note that the number of fingers visible in the temperature map is significantly less that those in the shadowgraph images. This is because the shadowgraph technique shows a field of view that is integrated across the depth of the test section, whereas the LIF temperature maps are obtained over a single plane illuminated by a thin laser sheet. Generally speaking, at each time the temperatures are cooler at the bottom of the image than the top, as expected from the mean vertical temperature gradient that is imposed. Also, as time progresses the temperature field over the imaged plane becomes cooler over the entire plane as the mushy zone grows and gets close to the bottom of the images area. We note that at $t = 40$ min three of the four fingers subside and only one finger survives as a plume. At this time, the mushy zone height is about 1.8 cm, 0.45 cm below the imaged area. The missing portion of the plume

![Fig. 9](image-url) Growth of the mushy region with time. Kiton Red and Fluorescein concentrations are $2 \times 10^{-6}$ M; pH $\approx 7.8$

![Fig. 10](image-url) Location and size of the imaged area for the temperature maps in Fig. 11
on the top of the temperature map is likely due to the helical motion of the plume, causing the center of plume to move out of the illuminated laser sheet. At time $t = 60$ min, the mushy zone has reached the bottom of the imaged area and one distinct plume is clearly observed. The feature on the right side of the plume is speculated to be a finger that is about to form. At this time the mush interface has a temperature of 8.4°C, whereas the temperature of the plume at the exit of the mush is cooler and is about 7.8°C.

Temperature profiles along a horizontal line at selected times are extracted from the temperature maps of Fig. 11 in
order to quantify the temperature profiles across the finger and plumes. Results are shown in Fig. 12 across a line at \( Y \approx 0.3 \) cm in the temperature maps (about 2.6 cm above the cooling plate). Data are shown for both 300 ms temporal averaging and those after 8 \( \times \) 8 pixel spatial filtering. When compared with the spatially smoothed profiles, the un-smoothed data indicate about 0.3\(^\circ\)C rms fluctuation, consistent with the previous estimate of temperature accuracy for data with 300 ms temporal averaging. Temperature profiles in Fig. 12 clearly show that the location of the finger that later becomes the plume change very little during the solidification process (minimum peak always remains at \( X \approx 1.5 \) cm). We also note that the minimum temperature in the center of the finger and the plume illustrated in Fig. 12 is typically two degrees cooler than the surroundings.

It is also instructive to examine the vertical variation of temperature differential \( \Delta T \) between the ambient and the finger and plume. Figure 13 shows the measured difference between the two indicated vertical lines at \( t = 17 \) min and \( t = 60 \) min. The temperature difference right at the exit of the mushy zone (\( Y = 0 \) cm and \( t = 60 \) min) is about 0.8\(^\circ\)C. The maximum temperature difference reaches about 2.7\(^\circ\)C and occurs when the plume is formed.

5 Conclusions

A two-color, two-dye, ratiometric laser induced fluorescence method was implemented for carrying out in situ whole-field measurements of the temperature field in a study of bottom-chilled uni-directional solidification of aqueous ammonium chloride. The traditional approach uses a temperature sensitive dye along with another with little temperature sensitivity. In our work, however, we took advantage of two temperature sensitive fluorescent dyes, with opposite temperature sensitivities, in order to increase the overall sensitivity and temperature resolution of our measurements. The resulting temperature sensitivity was more than a factor of two higher than the original work of Sakakibara and Adrian (1999).

Initial measurements of the in situ temperature field during solidification of ammonium chloride solution were presented for the first time. Many interesting characteristics of the process were quantified, including formation and evolution of fingers and plumes and the temperature distributions within them. It was shown that as the plume moves upward the maximum temperature difference between the center of the plume and the surroundings reaches about 2.7\(^\circ\)C.

We note that even though the locations of the pixels of one CCD camera relative to the pixels of the second camera were determined with sub-pixel accuracy (better than 0.1 pixel), some streaks and striations still remained in the final temperature maps. The reasons for the remaining streaks have been discussed by Sakakibara and
Adrian (2004) where they also suggest a blurring method for improvement. Subsequent to the results we presented here, improvements were achieved in terms of both removing the streaks and also temperature accuracy by using higher resolution CCD cameras with better dynamic range (Cooke Corp. Pixelfly, 12-bit, 1,024 × 1,392 pixel). Combination of better detection signal-to-noise ratio and higher pixel density led to an increase in temperature accuracy by a factor of four compared to those presented higher pixel density led to an increase in temperature accuracy by a factor of four compared to those presented here (see Shafii 2005). Sample of a temperature map acquired with improved detection is shown in Fig. 14. This figure illustrates the temperature map of ammonium chloride solution at t = 9 min over an imaged area 30 × 22 mm² located above the second nucleator on the second row. The spatial resolution of the measurement in the plane of illumination is about 21 μm per pixel, a factor of two better than before. Temperature variations within fingers are shown in great detail and clarity, with little evidence of streaks.

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Fig. 14 Temperature map of imaged area (30 × 22 mm²) using 1,024 × 1,392 pixel, 12-bit CCD cameras (300 ms temporal average, 8 × 8 pixel spatial average). Gray region indicates the area below the laser sheet where no data is available.