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Initial transient behavior in directional solidification of a bulk transparent model alloy in a cylinder

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Abstract

To characterize the dynamical formation of three-dimensional (3D) arrays of cells and dendrites under diffusive growth conditions, *in situ* monitoring of a series of experiments on a transparent *succinonitrile* – 0.24 wt% *camphor* model alloy was carried out under low gravity in the DECLIC Directional Solidification Insert onboard the International Space Station (ISS). The present article focuses on the study of the transient solid-liquid interface recoil. Numerical thermal modeling led us to identify two thermal contributions to the interface recoil that increase with the pulling rate and add to the classical recoil associated with the solute boundary layer formation. As a consequence of those additional contributions, the characteristic front recoil is characterized by a fast initial transient followed by stabilization to a plateau whose location depends on pulling rate. The analysis of comparative experiments carried out on ground shows the absence of stabilization of the interface position, attributed to longitudinal macrosegregation of solute induced by convection. This behavior is surprisingly also observed in space experiments for low pulling rates. An order of magnitude analysis of the mode of solute transport reveals that for these conditions, the effective level of reduced gravity onboard the ISS is not sufficiently low to suppress convection so that the interface recoils with longitudinal macrosegregation in a similar way as in ground experiments.

Keywords

Directional solidification, In situ observation, Transparent systems, Interface dynamics, Initial transient

1. Introduction

The study of solidification microstructure formation is very important in the design and processing of new materials as the interface patterns formed by solidification largely govern mechanical and physical properties of materials. For example, the properties and the reliability of materials processed by all important commercial solidification techniques, such as continuous casting and laser welding, are governed by the microstructural characteristics of cells and dendrites. Directional solidification is one of the key techniques to precisely study the fundamental aspects of solidification. The melt in the crucible is solidified by pulling through a thermal gradient. For a binary alloy of given solute concentration, an experiment is controlled by the thermal gradient and the growth velocity. Fixing the thermal gradient, the planar solid-liquid interface can be destabilized by increasing the velocity, thus giving rise to cellular or dendritic microstructures. The critical velocity leading to the transition from a planar to a cellular front can be calculated by using the Mullins-Sekerka linear stability analysis [1].

The vertical Bridgman method is one of the most widely used since it has the advantage of steady temperature fields and controllable temperature gradient. In such experiments, the studies are in general focused on solidification under steady-state growth conditions. However, a transient period is always present as the first stage of the evolution of the solid-liquid interface from rest to a steady-state characterized by a growth velocity equal to the applied pulling rate. At rest, it is generally assumed in theoretical models that the smooth interface is initially located on the *liquidus* isotherm, at a fixed position determined by the thermal profile in the adiabatic area. The motion from the initial interface position (*liquidus* isotherm) to its steady-state one (*solidus* isotherm) is called front recoil, whose duration also defines the initial transient [2-5]. In our vertical Bridgman system, during steady-state the crucible moves downwards at the imposed pulling rate whereas the interface moves upwards in the crucible frame with the same imposed velocity. That means that in

the experiments the solid-liquid interface is fixed in the laboratory frame during steady-state growth. Therefore, in the laboratory frame, the front recoil corresponds to the downward motion of the interface between two fixed positions: the rest one and the steady-state one.

For a phase diagram in which the solute is more soluble in the melt than in the crystal, solute is rejected into the liquid and a solute boundary layer is progressively built up ahead of the solidification front. This solute build up at the interface diffuses into the liquid at a rate proportional to the concentration gradient. If the criteria for morphological instability is not fulfilled, the interface remains planar until the stationary state is reached; otherwise, the interface becomes unstable in the transient time [6].

Early theories on directional solidification were based on the hypothesis that the solid-liquid interface velocity immediately reaches the pulling velocity at the very beginning and remains constant until the end. Tiller et al.[4] calculated the time evolution of the interface concentration neglecting the time variation of the interface velocity and assuming an exponential profile of the solute concentration in the liquid during the initial transient, proportional to that of the steady-state; Smith et al.[3] extended the previous work by solving the transient diffusion equation. However, experimental results showed that the interface velocity rises progressively to reach the imposed velocity [6, 7]. In the limit of frozen temperature approximation and under diffusive growth conditions, Warren and Langer [5] (WL) developed an approach to describe the acceleration of the interface and the simultaneous build up of the solutal boundary layer during the initial transient based on the assumption of an exponential transient concentration profile in the liquid, similar to the one obtained in steady-state but with time-dependent solutal length and solute concentration at the interface. As a result, their model predicts the instantaneous solutal length, interface velocity, solute concentration at the interface and interface position. The WL model has been compared to experimental results [2, 8, 9] as well as to full numerical integration results [10].

The wide use of transparent organic analogs that behave like metallic alloys regarding solidification is related to their transparency to visible light, so that *in situ* and real time observation of the interface can be made by classical optical techniques [11, 12]. Ground-based studies, both in metallic and organic alloys, clearly showed that the fluid convection on Earth modifies the structure of the solute boundary layer causing non-uniform morphological instability, resulting in a non-uniform microstructure [13, 14]. Fluid flow elimination on Earth can be obtained by reducing the size of samples and many experiments on transparent systems have for example been conducted in thin samples (quasi-2D shape) [15-18]. Even if such configuration has led to significant progresses in understanding the dynamics of solidification, it does not perfectly represent 3D samples and quantitative data extracted from thin samples cannot be extrapolated to 3D [19-21]. Fluid flow elimination in 3D samples requires the reduced gravity environment of space. The study presented here was conducted onboard the International Space Station (ISS) in the framework of the CNES project MISOL3D (Microstructures de Solidification 3D) and NASA project DSIP (Dynamical Selection of 3D Interface Patterns). Experiments were realized using the Directional Solidification Insert (DSI) of the Device for the study of Critical Liquids and Crystallization (DECLIC) developed by the French Space Agency (CNES), which is dedicated to *in situ* and real-time characterization of the dynamical selection of the solid-liquid interface morphology on bulk samples of transparent materials [19, 22, 23]. Results are also compared to identical experiments performed on ground after the return on Earth of the DSI to assess the effects of convection.

One important point to note is that the growth microstructure usually develops during the initial solidification transient, while the solute boundary layer is still growing, when the criterion for morphological instability is fulfilled. Analyzing the dynamics of this initial transient is thus critical for the understanding of the final steady-state microstructure.

In this article, experiments will be analyzed in terms of their solidification front recoil. The experimental procedure as well as the numerical simulations used to model the thermal field of the

furnace will first be described. Experimental results of front recoils and interface curvatures in microgravity experiments will then be presented. Significant differences between the theoretical situation described by a frozen thermal field with planar isotherms and the actual situation of a cylindrical furnace where control temperatures are not directly applied to the material will be stressed; several contributions will be described and their dependence on growth rate will be analyzed. The final part will be dedicated to the effect of convection on the front recoil comparing microgravity and ground experiments. It will be shown that convection may also be present in space experiments under specific range of growth parameters.

2. Experimental procedure

2.1. Experimental and observation mode

The DECLIC-Directional Solidification Insert (DSI) mainly contains two elements: the Bridgman furnace and the experimental cartridge. Complete descriptions of DECLIC and of its inserts can be found elsewhere [22, 23]. The experimental cartridge includes a quartz crucible and a system of volume compensation. The cylindrical crucible has an inner diameter of 10mm and a length that enables about 10cm of solidification, thus allowing the study of the whole development of extended 3D patterns from the initial stage to the steady state.

In this study, a succinonitrile (SCN)-0.24wt% camphor alloy is studied whose properties are presented in Table 1. The alloy is prepared using SCN purified by NASA by both distillation and zone melting. All procedures for sample preparation and cartridge filling are carefully realized under vacuum to avoid humidity contamination. Once sealed, the cartridge is inserted in the Bridgman furnace. The thermal gradient G is imposed by regulating hot and cold zones, located above and below the adiabatic zone where the interface is positioned. A booster heater is located at the top of the cold zone. This booster heater is a thin local heater dedicated to the monitoring of the interface curvature [19, 24] but it affects the thermal gradient and can be considered a control area. Two

different sets of control temperatures have been used, associated with two different temperature gradients G_1 and G_2 ; their values will be discussed in the next part. After the thermal regulation, partial melting is performed (a solid seed of $\approx 20\text{mm}$ is always kept to preserve the oriented single crystal) and the sample is then homogenized for at least 24h (waiting time) before performing solidification. Directional solidification is carried out by pulling the crucible into the cold zone at a constant rate for a length of 60mm. Experiments with pulling rates ranging from 0.25 to 8 $\mu\text{m/s}$ will be considered in this study. At the end of the solidification, the procedure is repeated for another pulling rate.

The crucible is equipped with a flat glass window at the bottom and a lens immersed in the melt at the top. The main observation mode (Axial observation) takes advantage of the complete axial transparency of the cartridge provided by these two elements: the light coming from LEDs passes through the cartridge from the bottom to the top, therefore crossing the interface. The optical system formed by the immersed lens and a following relay lens produces the image of the interface on a CCD camera. This observation mode provides microstructure images and is used to study its dynamics and characteristics [25]. On the same cartridge axis, an interferometer is also set but it will not be detailed here (more information on its use can be found in [25]). The interface can also be observed from the side (Side view observation) thus imaging the motion of the interface as well as its macroscopic shape (Figure 1); we will detail these aspects in the following part as this observation mode is the major tool for the study of front recoils.

Throughout the sequence of directional solidifications, macroscopic shape and motion of the interface have been investigated by side view observation. Three examples of position measurements are illustrated in Figure 1. When the interface is convex, without (Figure 1a) or with (Figure 1b) microstructure, the position of the left (L) and right (R) borders, as well as that of the center (C), are easily measured; it is worth noting that in the case of Figure 1b, positions therefore correspond to the cell/dendrite tip positions. When the interface is concave (Figure 1c), the tip

positions in the center cannot be determined anymore as they are hidden by microstructures located on the border of the crucible. Image software is used to enhance the local contrast and observe the shape of the interface. The dark line underlined with a grey dashed line is taken as the interface shape even if it neither corresponds to the exact tip positions nor the *solidus* line, both out of reach. The instantaneous growth rate throughout the experiment is derived from measurements of interface position between two successive images.

2.2. Alloy physical characteristics

As previously mentioned, the alloy used is a SCN–0.24wt% camphor. The physical characteristics of this alloy are listed in Table 1. Considering that the alloy is extremely dilute, some physical properties of pure succinonitrile are used for the alloy.

There are several versions of the SCN-camphor phase diagram [26-30]: all of them agree concerning the *liquidus*, but there are large differences in the *solidus* and the solubility limit. To clarify these points and determine the solubility limit, Witusiewicz et al.[31] recently analyzed stable phase equilibria during isothermal annealing. A succinonitrile-camphor was annealed at 36°C for 2h and then successively at 38, 39, 41, 43, 47, 50, 52, 55 and 56°C for 1h each. In these experiments, they assumed that a complete equilibrium in the sample is established within 1h of isothermal annealing. A new phase diagram was then obtained that gives a low limit of solubility of camphor in solid succinonitrile (estimated at 0.3 wt%), in contradiction with the value of 7.1wt% reported by Teng and Liu[28]. In Witusiewicz et al.[31] paper, liquid fractions at different temperatures are given for a SCN-1.1wt% camphor alloy. This data can be used to re-estimate the *solidus* line and extract the partition coefficient. Indeed, taking the *liquidus* as linear with slope m_L , the concentration of the liquid (C_L) can be estimated as a function of temperature T :

$$C_L = \frac{T-T_m}{m_L} \quad (1)$$

where T_m is the melting temperature of succinonitrile (58.08°C). Assuming that phase equilibrium is obtained during experiments, the lever rule is used to determine the concentration in the solid (C_S) from the liquid fraction f_L of the alloy of concentration C_0 ($C_0 = 1.1\text{wt}\%$):

$$C_S = \frac{C_0 - f_L C_L}{1 - f_L} \quad (2)$$

This allows determining a new *solidus* line shown in Figure 2. The zoom of Figure 2 on small concentrations clearly shows that the *solidus* line cannot be fitted by a linear function, as it would not intersect the *liquidus* at T_m . As a consequence, the solute partition coefficient $k = \frac{C_S}{C_L}$ cannot be constant. The variation of the partition coefficient with the liquid concentration (C_L) is therefore extracted by fitting Witusiewicz data (using LAB fit software):

$$k = 1.4 \exp(-2.174 C_L^{0.257}) + 0.024 \quad (3)$$

In practice we are thus facing a dilemma. On one hand, according to Witusiewicz et al.[31], the variation of k with solute concentration would mean that in this work, for which the nominal concentration (C_0) of the alloy is 0.24wt%, the partition coefficient will vary in the range 0.138 (*solidus* with a corresponding temperature of 55.7°C) and 0.334 (*liquidus* corresponding to 57.8°C). On the other hand, Teng et al.[28] found a constant k for low camphor concentration ($k=0.20$ for $C_0=0.35\text{wt}\%$) and their temperature measurements of the steady-state planar front during pulling are also reliable. The discrepancy between the *solidus* lines in the two different phase diagrams is still a critical issue, and work is currently in progress to fully clarify this point. For the composition used in this study, we use equation (3) to analyze current results.

2.3. Thermal modeling

No direct *in situ* measurement of the thermal gradient is available in the DSI as no thermocouple is inserted inside the sample to avoid thermal perturbations. Control temperatures are imposed to the regulating areas but these areas do not touch the cartridge as a gap of 1mm was necessary for cartridge manipulations. These elements, added to the cylindrical geometry and the difference of

conductivity between the quartz crucible and the alloy, lead to a thermal field which is difficult to characterize analytically.

An attempt to *in situ* determine the thermal gradient at the interface at rest was done during experiments for the studied gradients. The method, detailed in [25], is to measure the displacement of the interface associated to a small shift of the control temperatures. All the changes are supposed to be small enough so that the interface stands in the same area of the thermal field. The control areas are the hot zone and the booster heater so that the thermal shift was applied to these areas. With this method, G_1 and G_2 have respectively been evaluated to 28 K/cm and 12 K/cm.

The software packages CrysVUn® and CrysMAS® are designed for the global modeling of solidification processes in complex furnaces with axial or translational symmetry [32], CrysMAS being an improved and more powerful version of CrysVUn; those software have been developed by the Crystal Growth Laboratory (Fraunhofer Institute IISB, Erlangen, Germany). Calculations are based on a method of finite volumes on unstructured grids that enables tackling the entire growth setup on the basis of a geometrical model of the furnace, crucible and sample. Simulations are used here to compute the thermal field and study the interface position and shape. The temperatures applied to the different elements of the furnace, pulling rate, and the physical properties of all materials involved, are the input parameters for the numerical simulations.

A calibration step is needed to adjust the numerical model with respect to material thermal properties. This calibration was done using *in situ* measured data under microgravity. They correspond to the measurement of the variation of the interface position at rest between four sets of control temperatures: the ones corresponding to each gradient (G_1 and G_2), and the ones corresponding to a shift of 2°C applied to the hot zone and to the booster heater for each gradient. The interface position and shape at rest correspond to the *liquidus* isotherm position and shape, respectively. The best results obtained are compared to experimental data in Figure 3. The numerical model leads to $G_1=19$ K/cm and $G_2=12$ K/cm. The difference between the values obtained by the

direct experimental method and the numerical simulation may come from the incorrect assumption that the thermal zones are equally efficient with the thermal shift, meaning that they should react linearly just inducing a shift of the thermal field without distortion.

Based on the calibrated model, simulations for the two gradients have been performed at pulling velocities varying from 0.25 $\mu\text{m/s}$ to 8 $\mu\text{m/s}$, similar to experimental conditions. It is worth noting that in these purely thermal simulations, the microstructure is not taken into account and the interface is located on the *solidus* isotherm, as in a planar front growth. To analyze the different contributions to recoil and change of curvature of the interface, additional simulations are also performed fixing the latent heat of fusion, ΔH , to zero. An example of the results for $G_2=12\text{ K/cm}$ and $V_p=4\text{ }\mu\text{m/s}$ is given in Figure 4 Three different contributions to the recoil are therefore highlighted:

- An isotherm shift due to pulling that is deduced from the comparison of the *liquidus* isotherms positions at rest and during pulling for $\Delta H=0$; this shift of isotherms can be seen as the “instrumental recoil”, mentioned for example by Akamatsu et al.[33], which is due to the evolution of thermal exchanges induced by pulling;
- The solutal recoil that corresponds to the interface temperature change from the *liquidus* to the *solidus* (taken during pulling for $\Delta H=0$);
- An isotherm shift due to latent heat release measured from the comparison of the *solidus* isotherms positions during pulling for $\Delta H=0$ and the normal value of ΔH .

Those different contributions on recoil and interface curvature will be discussed in the following parts.

3. Results and discussion

The interface recoil is investigated by measuring the motion of the interface in the adiabatic area using transverse observation. Figure 5a-c shows a step by step evolution of the whole experiment starting from rest for respectively, 0.25, 4 and 8 $\mu\text{m/s}$ ($G_2=12\text{K/cm}$) and Figure 6 shows

the interface at the end of solidification for different pulling rates. Front recoil with time at two locations along the interface (border and center) has been measured to study the interface amplitude (difference of location between the interface center and border). It should be noticed that at the beginning of microgravity experiments (December 2009), there was a bubble in the solid seed that could be due to solid shrinkage (it can be seen in Figure 3 and Figure 5b-c). It could be seen at rest for small solidification lengths, for example at $V_p=4$ and $8\mu\text{m/s}$ done in October 2010. However, it disappeared after a few sequences of solidification and melting, even if the solid seed has never been melted. For the experiment at $V_p=0.25\mu\text{m/s}$ (November 2010), it had disappeared.

3.1. Interface shape

The macroscopic interface shape is a consequence of the isotherms shape that is usually curved in 3D configurations. It is an important parameter to take into account to correctly analyze pattern formation as it affects the whole pattern dynamics, inducing for example advection as observed in 3D samples [34] or in 2D samples for artificially curved interface [35].

At rest, the interface position depends on the thermal field assuming that it is located on the *liquidus* isotherm for the nominal concentration. This is a classical assumption but no temperature measurement is available to check it. The macroscopic interface shape is therefore imposed by the shape of the isotherms. For a convex interface, the crucible receives heat from outside (surrounding temperature higher than melting point), which corresponds to an interface located closer to the hot zone [36]. Thus, the interface position and its shape may be adjusted changing the hot and cold zone temperatures, and this is illustrated by the CrysMAS simulations of Figure 3. In Figure 5a, the interface at rest is convex and it becomes more and more convex until the end of solidification for $V_p=0.25\mu\text{m/s}$; at $V_p=4\mu\text{m/s}$, the interface initially convex becomes flat; and for $V_p=8\mu\text{m/s}$, the initially convex interface, becomes flat and at the end is slightly concave. Figure 5d schematically shows the evolution of the interface for three different pulling rates from rest until the end of solidification. The

behavior is similar for both thermal gradients. The interface shape at the end of solidification for all pulling rates is shown in Figure 6 and the interface amplitudes A (difference between the interface positions measured in the center and on the border of the crucible) are presented in Table 2 (the negative values mean that the interface becomes concave). The increase of interface concavity with pulling rate for pulling rates higher than $1\mu\text{m/s}$ is consistent with the expected effect of pulling described for example by Chang and Wilcox [36]. The interface shape is indeed related to its position in the thermal field, so that the interface adapts to the concave isotherms as it moves closer to the cold zone. Moreover, due to the low thermal conductivity of the alloy compared to the quartz crucible, evacuation of latent heat generated during growth mainly occurs through the crucible, thus inducing a thermal radial gradient from the border (colder) to the center (hotter) of the crucible. The interface then progressively becomes more concave as its velocity increases. Lastly, isotherms are shifted downwards by heat transport in the ampoule also leading to an increase in concavity. For $V_p=0.25$ and $0.5\mu\text{m/s}$, an atypical behavior was found as the interface becomes more and more convex during solidification.

CrysMAS numerical simulations have been analyzed to extract curvatures (namely the interface amplitude) and are compared to the experimental values in Figure 7a. A good agreement is obtained except for the case of $V_p=0.25\mu\text{m/s}$ for which the numerical curvature is lower compared to the experimental one. A detailed analysis of the different contributions to curvature change between rest and pulling leads to the conclusion that the major effect on curvature is due to the latent heat release (Figure 7b). The effects of instrumental recoil and latent heat release are both roughly proportional to pulling rate, and they both increase concavity. The physical change of isotherm from *liquidus* to *solidus* leads to a *quasi*-constant value of interface amplitude change which is positive, so that it corresponds to an increase of convexity. Those results justify a slight increase of convexity for low pulling rates, when latent heat and instrumental recoil contributions may be negligible. However, this does not explain the anomaly obtained for $V_p=0.25\mu\text{m/s}$.

3.2. Interface motion: global front recoil

Figure 8 shows the interface position at the center as a function of the solidified length L , or more precisely the pulled length, equivalent to time ($L = V_p t$), for a set of different pulling rates and a fixed thermal gradient ($G_2 = 12$ K/cm). The measured interface recoils at the steady state are given in Table 2 for both thermal gradients. The rates 0.25 and 0.5 $\mu\text{m/s}$ (Figure 8a) are separated because they have a different behavior: for this range of pulling rates, the interface position keeps decreasing with time whereas it stabilizes for pulling rates of 1 $\mu\text{m/s}$ and higher. Moreover, for pulling rates higher than 1 $\mu\text{m/s}$, the recoil increases with pulling rate which is not the case below 1 $\mu\text{m/s}$. Above $V_p=1$ $\mu\text{m/s}$, the recoil curves are then characterized by two stages: a transient stage, roughly contained in the first 15 mm of growth, and a steady-state stage characterized by a fixed position of the interface in the adiabatic zone. Let us focus on the analysis of this typical behavior, while the analysis of pulling rates below 1 $\mu\text{m/s}$ will be done in the §3.4 that is dedicated to the influence of convection.

The build up of the solute boundary layer during growth leads to a change of the interface temperature that, for a planar front growth, should reach the *solidus* temperature for the nominal concentration C_0 ; the recoil associated is named “solutal recoil” and its amplitude therefore corresponds to the transition of the interface from the *liquidus* to the *solidus* isotherms, namely to the thermal length l_T :

$$l_T = \frac{m_L C_0}{G} \frac{k-1}{k} \quad (4)$$

where m_L is the *liquidus* slope and k the partition coefficient for $C_S=C_0$ (i.e. $k=0.138$). For $C_0=0.24\text{wt}\%$, this displacement is 1.08 mm for $G_1=19$ K/cm and 1.71 mm for $G_2=12$ K/cm and is independent of pulling rate.

If there is microstructure development, tips grow in the undercooled area towards the *liquidus*. Measurements are as much as possible performed at the tips level, as the *solidus* position is

unknown. In steady state, the tips are located at a distance Δ_t of the *solidus* given by the expression of Bower, Brody and Flemings (BBF) [37]:

$$\Delta_{t,BBF} = \frac{D_L}{V_p} \left(\frac{V_p}{V_c} - 1 \right) = l_T - \frac{D_L}{V_p} \text{ with } V_c = \frac{kG D_L}{(k-1)m_L C_0} \quad (5)$$

where D_L is the solute diffusion coefficient in the liquid, V_c is the critical velocity and is equal to 0.251 $\mu\text{m/s}$ for $G_1=19$ K/cm and 0.158 $\mu\text{m/s}$ for $G_2=12$ K/cm, considering the k at the *solidus* temperature (0.138) as tips start to grow from the *solidus* isotherm. The position of the *solidus* can then be deduced from the experimental steady-state recoils (Figure 9) and the distance between the *liquidus* at rest and the *solidus* during pulling, is named “experimental corrected recoil” $\Delta z_{c,exp}$:

$$\Delta z_{c,exp} = \Delta z_{exp} + \Delta_{t,BBF} \quad (6)$$

where Δz_{exp} is the measured recoil from the interface position at rest to the cell tips position during steady-state growth. Results are presented in Table 2. Whatever the pulling rate is, $\Delta z_{c,exp}$ is always larger than the theoretical value obtained using eq. (4). Moreover, once more besides the particular cases of 0.25 and 0.5 $\mu\text{m/s}$, $\Delta z_{c,exp}$ increases linearly with pulling rate. The difference between theoretical and experimental values comes from the theoretical assumption of a frozen thermal field, meaning that the thermal field is neither shifted nor disturbed by pulling. CrysMAS simulations clearly show, for example on Figure 4, that the instrumental recoil and the effect of latent heat release are far from being negligible on the thermal field and the interface motion.

CrysMAS results are then analyzed to determine the sensitivity to pulling rate of the different contributions to recoil detailed in §2.3. Results are compared to the experimental values of “experimental corrected recoil” $\Delta z_{c,exp}$ in Figure 10. Numerically, the solutal contribution to recoil is roughly insensitive to pulling rate, whereas instrumental recoil and latent heat contribution increase linearly with pulling rate. The total numerical ($\Delta z_{c,num}$) and experimental ($\Delta z_{c,exp}$) recoils display the same variation with pulling rate (same slope), thus explaining the relative positions of the interface for different pulling rates observed in Figure 6. However, experimentally corrected recoils are larger than numerical ones, with an intercept at $V=0$ approximately 800 μm larger in experiments. In order

to explain that discrepancy, the first hypothesis is that it is due to an underestimation of the thermal length l_T . But **increasing l_T to increase** $\Delta z_{c,num}$ induces a similar increase of $\Delta_{t,BBF}$ so that $\Delta z_{c,exp}$ automatically also increases: the gap can never disappear. The other source of discrepancy could be an underestimation of the diffusion coefficient D_L in eq. (5), but matching the measured values would require an unrealistic $D_L = 1100 \mu\text{m}^2/\text{s}$ yielding a stable planar growth up to $V_c = 0.645 \mu\text{m}/\text{s}$ for $G_2 = 12 \text{ K}/\text{cm}$ and $V_c = 1.02 \mu\text{m}/\text{s}$ for $G_1 = 19 \text{ K}/\text{cm}$, whereas structures are observed for a pulling rate as low as $0.25 \mu\text{m}/\text{s}$ and $0.5 \mu\text{m}/\text{s}$ respectively for these two gradients.

An alternative relation to estimate the tip undercooling was proposed by Karma and Pelcé (KP) [38]. This formula has recently been shown to provide a more accurate prediction of cell tip undercoolings in a three-dimensional phase-field simulation study [20]. This formula incorporates the dependence on the cell shape. Expressed as the distance between the tips and the solidus, it gives:

$$\Delta_{t,KP} = \frac{(1-f_s) \left(l_T - \frac{D_L}{V_p} \right)}{1-f_s(1-k)} \quad (7)$$

where f_s is the solid fraction in a region behind the tip where the cell width can be considered constant. f_s is defined as the ratio of the cell width to the primary spacing [20] for bidimensional geometries, while for 3D samples it is considered to be the square of that ratio. In our study, the exact shape of the structures is unclear but it is possible to roughly evaluate f_s from top observations considering that solid structures act as guides of light, thus appearing bright, while liquid grooves diffuse light, thus appearing dark. The primary spacing is the center to center distance between two neighbor structures and can be easily measured [25] while the cell width is the size of the bright area of the structure. Measurements have been realized for at least 100 microstructures, for each pulling rate and thermal gradient and the f_s values are presented in Table 2. The KP expression predicts larger undercooling compared to the BBF one, hence yielding a better agreement with the experimental results, especially for the highest pulling rates (see Table 2 and Figure 10). However, it

is worth remembering that KP tip undercooling calculation strongly depends on solid fraction, and the validity of our method to measure it experimentally may be questioned.

Our analyses are based on the assumption that the interface at rest is located on the *liquidus* isotherm, and that the concentration in the liquid is homogeneous (nominal concentration). Recent results of Xu et al.[39] question this assumption with their study of the temperature of the interface at rest in a thermal gradient. In their experiments they observe a variation of the interface position going first through a maximum in solute interface concentration in the liquid, then followed by a slow stabilization on a temperature lower than the *liquidus*. The first maximum of the interface recoil and concentration is attributed to the temperature gradient zone melting (TGZM) phenomenon occurring in the mushy zone already pointed out by Nguyen Thi et al.[40], which is not observed in our case as we see a monotonous return of the interface to its initial position after melting. In our case, the situation is different as we start from a homogeneous solid single phase so that no mushy zone is present. However, the numerical simulations in [39], starting from a uniform system, also show that the interface slowly tends to a location below the *liquidus* isotherm associated to a solutal boundary layer; this configuration is close to our experimental situation. The shift of the solute concentration at the interface is attributed to an effect of solute diffusion in the solid phase, and its amplitude is then related to the ratio D_S/D_L , with D_S , the solute diffusion coefficient in the solid. This effect may slightly modify the interface recoil but it is difficult to quantify it in our experiments; however, it is of minor importance regarding the large differences between numerical and experimental recoils.

3.3. Interface motion: initial transient

As mentioned in the introduction, first theoretical models considering that the interface velocity immediately reaches the external pulling rate have been now replaced by more accurate models taking into account the interface velocity transient [5] or even numerical simulation [10, 41-43]. The

WL model [5] is recognized to provide a good analytical approximation of the front recoil [10, 41-43] reproducing many experimental situations of planar front recoil. Experimentally, the most striking comparison of experimental data with the WL model has been done by Losert et al.[2] who studied the interface motion and solute concentration in thin samples of SCN-coumarin 152. A good agreement is obtained for pulling rates close to the critical velocity. These authors did not measure independently the *liquidus* temperature of the alloy, but considered that the temperature of the stationary interface in the gradient zone is the *liquidus* temperature. Thus, like in this work, these authors ignored a possible initial boundary layer. Bogno et al. [8] also used the WL model to compare to interface velocity profiles in thin samples of a metallic alloy *in situ* observed by X-ray radiography: a good agreement is obtained only for the early stages of growth as convection rapidly creates heterogeneities of concentration along the interface. One assumption of the WL model is that the thermal field is frozen so that the recoil is only of solutal origin. We have previously demonstrated that we are not in such a configuration so that the WL model cannot be directly used but has to be modified to include thermal effects previously identified. Let us note Δz_τ , the total isotherm shift at the steady state resulting from both latent heat release and instrumental recoil. Numerical studies have been conducted several years ago to evaluate the transient interface velocity for purely thermal effects after a velocity jump in a Bridgman furnace [44, 45]. In spite of little differences between the two studies, both concluded that the interface position $z_0(t)$ asymptotically approaches its steady-state position with a time dependent thermal shift $\Delta z_\tau [1 - \exp(-t/\tau)]$, where t is the time, and τ is a delay time dependent of the physical parameters of the alloy, the geometry of the furnace and crucible, the thermal gradient and the pulling rate. Analytical expressions obtained from the fit of numerical results have been successfully tested to reproduce experimental results [45-47] in metallic systems but the calculation of the delay time, especially using Fu and Wilcox expressions [45] implies the knowledge of experimental parameters such as heat transfer coefficients that are in our case unknown. Saitou et al.[45] proposed a simpler expression of the delay time $\tau = \frac{\rho \Delta H q_0}{2\lambda G}$, where ρ is

the mean density of solid and liquid, ΔH is the latent heat of fusion, q_0 is the length of the adiabatic area (16mm), and λ is the mean thermal conductivity of the solid and liquid. Using this expression, we obtain a τ of 867 s for $G_1=19\text{K/cm}$ and 1373 s for $G_2=12\text{K/cm}$. The drawback of this expression is its dependence on the latent heat only, meaning that it may describe the latent heat recoil but not the isotherm shift associated to the instrumental recoil. The order of magnitude of the delay time associated to the instrumental recoil may be estimated using the characteristic time for diffusion through the adiabatic area $q_0^2/D_{th} \approx 2226$ s, with D_{th} the thermal diffusion given in Table 1. Therefore, since both the delay time and the amplitude (see fig. 10) of the isotherm shifts due to latent heat release and due to instrumental recoil are of the same order, we decided to treat these two phenomena using a unique delay time τ and total isotherm shift Δz_T .

Warren and Langer [5] formulated the problem in terms of two time-dependent variables: the solute boundary-layer thickness l and the interface position z_0 in a reference frame that is moving with a constant velocity V_p , whose origin is taken at the isotherm corresponding to the melting point of the pure solvent. A modified WL model is then developed which includes the isotherm shift by writing the temperature field in a frame translating at velocity V_p in the form:

$$T(z) = T_m + Gz + G\Delta z_T \left(1 - e^{-t/\tau}\right) \quad (8)$$

where T_m is the melting point of the pure substance. With this definition, a pure substance that would solidify at $z = 0$ without thermal drift now solidifies at a steady-state position $z = -\Delta z_T < 0$. Following WL, z_0 is the position of the solid-liquid interface in the moving frame and C_0 is the solute concentration on the liquid side of the interface. It follows from eq. (8) that:

$$C_0 = \frac{T_m - T(z_0)}{|m_L|} = -\frac{G}{|m_L|} \left[z_0 + \Delta z_T \left(1 - e^{-t/\tau}\right) \right] \quad (9)$$

The dynamical equations of the WL model that include the thermal drift are the same as the original dynamical equations (2.11) and (2.13) of [5]. However, these two equations have to be used jointly with the modified interface equilibrium condition (eq. (9)). To rewrite those equations in a convenient form, we define the initial position of the interface at rest z_∞ , which is fixed in time, as:

$$z_{\infty} = -\frac{|m_L|}{G} C_{\infty} \quad (10)$$

Eliminating C_0 and C_{∞} from equations (2.11) and (2.13) of [5], we obtain:

$$(V_P + \dot{z}_0) = \frac{2D_L}{l} \left[\frac{z_0 + \Delta z_T (1 - e^{-t/\tau}) - z_{\infty}}{(1-k)(z_0 + \Delta z_T (1 - e^{-t/\tau}))} \right] \quad (11)$$

$$\dot{l} = \frac{4D_L}{l} \left[\frac{z_{\infty} - k(z_0 + \Delta z_T (1 - e^{-t/\tau}))}{(1-k)(z_0 + \Delta z_T (1 - e^{-t/\tau}))} \right] - l \left[\frac{\dot{z}_0 + \Delta z_T e^{-t/\tau} / \tau}{z_0 + \Delta z_T (1 - e^{-t/\tau}) - z_{\infty}} \right] \quad (12)$$

where l is the instantaneous boundary layer thickness, C_{∞} is the fixed nominal concentration of the alloy that is not affected by the thermal drift, and \dot{l} and \dot{z}_0 denote first order time derivatives. We note that those equations reduce to the equations (2.14) and (2.15) of the WL model [5] in the limit $\Delta z_T \rightarrow 0$, as expected.

We applied this modified WL model to analyze our results, treating τ as an adjustable parameter. The total thermal shift Δz_T that is used as input into the model for each pulling rate and gradient is deduced from experiments using the relation:

$$\Delta z_{c,exp} = l_T + \Delta z_T \quad (13)$$

where $\Delta z_{c,exp}$, the ‘‘corrected experimental recoil’’ corresponding to the distance between the interface position at rest (= position of the *liquidus* isotherm) and the position of the *solidus* isotherm during steady-state growth, is given by eq. (6). The distance between the tips and the *solidus* Δ_t required in eq. (6) may be calculated using either the BBF or the KP model.

Results corresponding to the best fit are presented in Figure 11 for both thermal gradients and pulling rates equal to or higher than $1 \mu\text{m/s}$. The predictions from the WL model presented in Figure 11 result from a least square fit with τ against the experimental data at early time, namely $L = V_p t \leq 1.5 \text{ mm}$ for $G = 19 \text{ K/cm}$ (a) and $L \leq 2 \text{ mm}$ for $G = 12 \text{ K/cm}$ (b), *i.e.* while the solid-liquid interface is still planar before morphological destabilization. These simulations correspond to a KP undercooling model, but using the BBF undercooling model yields similar results with slightly different values of τ . The model results are superimposed to experimental data during the complete

solidification duration for pulling rates of 2 and 4 $\mu\text{m/s}$, with the dashed line corresponding to the final solidus position $\Delta z_{c,exp}$. The initial transient phases are zoomed for pulling rates of 1 and 8 $\mu\text{m/s}$, illustrating the good agreement obtained between the experimental and modeling results until microstructure appearance. τ . The fitted values of τ appear in Table 3. While the expression by Saitou et al. [45] provides an easy order of magnitude estimation of the time delay τ that takes into account its dependence on the temperature gradient, it lacks a dependence on the pulling velocity. The values in Table 3 show qualitative agreement with this dependence on G and also highlight the decrease of τ with V_p . Hence, the values from Saitou et al. (867 s for $G_1 = 19 \text{ K/cm}$ and 1373 s for $G_2 = 12 \text{ K/cm}$) are bounded by our *extremum* estimations of τ , namely from 342 to 1591 s for $G_1 = 19 \text{ K/cm}$ and from 396 to 1998 s for $G_2 = 12 \text{ K/cm}$. Additionally, the predictions of the original WL model (*i.e.* with $\Delta z_T = 0$) in dotted line in Figure 11 highlight the importance of the thermal drift contribution to reproduce accurately the experimental measurements.

3.4. Role of convection

As previously mentioned, similar experiments have been conducted on ground after the DSI return on Earth to analyze the effects of convection on pattern growth. Those ground experiments were carried out with the same control parameters, being the only difference the presence of convection. It is known that the presence of convection greatly affects the interface morphology [11]. Among the main effects, let us for example remind the shifting of the critical transition velocity from smooth to cellular/dendritic interface [48, 49] or the change in average value [50] and homogeneity [13, 51] of the primary spacing. Here, its influence on the initial transient and front recoil is addressed.

Interface recoil comparisons between results obtained on Earth (presence of convection, 1g) and onboard the ISS (μg environment) for different pulling rates and imposed thermal gradient of 12K/cm are presented in Figure 12. The fast motion observed at the beginning of the solidification is

similar on ground and in μg but the interface decelerates earlier on Earth. Whatever the pulling rate is, front recoils on ground are characterized by the absence of stabilization of the interface position, meaning that instead of reaching a plateau, the interface keeps moving downwards. An interesting point is that this kind of profile is also observed during space experiments for pulling rates lower than $1 \mu m/s$, that present atypical behavior regarding both the front recoil and the interface shape evolution.

In absence of isotherm shift, the interface motion is due to the evolution of the solute concentration at the interface and can be seen as the indication of the axial macrosegregation. Therefore, we used theories developed in this frame to analyze the front recoils obtained in presence of convection. In particular, Favier [52, 53] has developed an analysis of segregation during directional solidification that enables the determination of the axial solute profiles for different growth configurations (Bridgman, floating zone and Czochralski). He adopted the concept of a diffusive boundary layer approximation introduced by Burton, Prim and Slichter [54]: within this boundary layer δ close to the interface, the transport is purely diffusive, whereas convection is dominant beyond δ leading to a homogenous solute concentration in the liquid. Extending its use to both transient and steady-state regimes in horizontal solidification, Favier obtained segregation equations that describe the whole range of situations existing between a purely diffusive transport mode ($\delta \rightarrow \infty$) and the complete convective mixing described by Gulliver-Scheil equation ($\delta \rightarrow 0$). Various profiles can then be drawn as a function of the parameter $\Delta = \frac{\delta V_p}{D_L}$: for small values of Δ , the enrichment of the liquid by convection starts quite fast whereas for large values of Δ , a purely diffusive transient growth precedes the stage of liquid enrichment and leads to well-known S-shape curves of segregation profiles (see e.g. Fig. 4 of [53]). Camel and Favier [55, 56] extended this study by an order of magnitude analysis that enables predicting the macrosegregation regime as a function of characteristic dimensionless numbers of the system. In particular, they established a universal diagram (Fig. 4 of [56]), reproduced in Figure 13, that enables the determination of the

macrosegregation regime as a function of the dimensionless Peclet and Grashof-Schmidt numbers (Peclet number $Pe = \frac{RV_p}{D_L}$ characteristic of the solidification; Grashof-Schmidt $Gr = \frac{\beta_T |g| GR^4}{\nu^2}$ and $Sc = \frac{\nu}{D_L}$ characteristic of the convection). The characteristic length R is taken as the crucible radius and D_L is the solute diffusion coefficient in the melt, β_T the thermal expansion coefficient, g the gravity value and ν the kinematic viscosity.

For the experiments under study (succinonitrile-0.24wt% camphor, $G=12K/cm$) and considering the properties presented in Table 1, dashed lines are superimposed with the original diagram of Figure 13 for different Peclet numbers corresponding to V_p of 0.25, 0.5 and $1\mu m/s$, and for Grashof-Schmidt numbers calculated for different values of gravity $1g, 10^{-3}g, 10^{-4}g, \mu g$ (with $g=9.81 m^2/s$).

Considering the experimental recoil profiles obtained on Earth, it is clear that they are characteristic of the S-shape macrosegregation profile corresponding to a convecto-diffusive growth so that the continuous decrease of the front position is explained, even if the diagram cannot be directly used as we performed vertical solidification. More surprising are once more the profiles obtained for $V_p < 1 \mu m/s$ onboard the ISS: they also present the continuous decrease characteristic of a S-shape macrosegregation whereas the transport is supposed to be diffusive. The Camel and Favier diagram is then much more useful to understand these experiments as residual gravity may be perpendicular to the growth axis, which is equivalent to horizontal solidification and is also the most critical configuration in terms of convection. As shown in Figure 13, diffusive conditions would be obtained if the level of gravity in the Station was really $10^{-6}g$ but it is well known that the gravity level onboard is much closer to $10^{-4}g$. It is also worth reminding that the DECLIC device is not located in the center of the ISS but in the Japanese KIBO module at the extremity of a small arm, so that the gravity level is not optimal. Preliminary analyses of DECLIC accelerometers measurements reveal an average value of acceleration of about 0.5mg along the crucible axis and 0.9mg along the radial axis which is the most critical orientation in terms of convection (for frequencies of the order of 1Hz). Those results place the operating points for $V_p = 0.25 \mu m/s$ and $0.5 \mu m/s$ inside -or close to- the

convective domain of Figure 13, thus explaining the absence of *plateau* for these pulling rates and the atypical behavior generally observed.

4. Conclusion

In this article, results obtained with the DECLIC Directional Solidification Insert, dedicated to *in situ* and real time observation of the solid-liquid interface during directional solidification of bulk transparent alloys, are presented. The data presented in this study comes from the side view observation which enables the study of the shape and the motion of the interface during the whole experiment. Two main objectives motivated this study: first, a better knowledge of the sensitivity of the thermal field on pulling in such large bulk samples; secondly, a better understanding of the interface behavior in a not frozen thermal field. The DECLIC-DSI was installed onboard the International Space Station, under microgravity, thus avoiding fluid flow influence; after the spatial campaigns of experiments, it was brought back to Earth where similar experiments have been performed for comparison. The experiments analyzed have been carried out on a transparent organic alloy (succinonitrile-0.24wt% camphor).

The thermal analyses have been performed using the CrysVUn® and CrysMAS® software packages that are designed for the global modeling of solidification processes in complex furnaces, the first step being the drawing of the complete setup and the definition of all material properties. Simulation revealed two contributions to interface motion during pulling that add to the standard physical recoil that corresponds to the interface temperature change from the *liquidus* to the *solidus*, thus justifying the qualification of not frozen thermal field: an isotherm shift due to the evolution of thermal exchanges induced by pulling (“instrumental recoil”) and an isotherm shift due to latent heat release. Those contributions increase linearly with pulling rates.

Experimentally, the evolution of the interface position as a function of the solidification length has been measured for different pulling rates and thermal gradients. Except for low pulling rates discussed separately, the interface position stabilizes after a fast initial recoil. The global interface recoil increase with pulling rate is not compatible with a frozen thermal field condition, for which the planar front recoil is well described by the Warren and Langer model. Therefore, the Warren and Langer model was modified to take the isotherm shift contributions into account. A good agreement was obtained between experiments and the modified model.

Analyses of front recoils for ground experiments reveal a different behavior characterized by the absence of stabilization of the interface position after the fast initial motion: the interface position keeps moving towards the cold thermal area, meaning that the solute concentration at the interface keeps increasing. This behavior can be explained by the effect of convection using for example descriptions of Favier and coworkers, who considered a complete mixing of liquid ahead a diffusive boundary layer of finite length. In that case, longitudinal segregation takes place and the concentration at the interface evolves with an “S-shape” curve consistent with the absence of plateau observed in our experiments.

For experiments with the lowest pulling velocities in space, the interface does not stabilize after the initial transient, indicating a longitudinal solute segregation comparable to the one observed during ground experiments. The order of magnitude analysis of fluid flow versus solidification developed by Camel and Favier revealed that for the lowest pulling rates, the reduced gravity onboard the International Space Station exceeds the acceptable value for a diffusive transport regime so that a residual convection affects the results, thus explaining the recoils obtained.

The present study enabled a better understanding of the general front behavior for geometrical configurations not associated to a frozen thermal field, therefore addressing the more general case of large three-dimensional geometries. However, it also raises some questions that deserve to be deepened. It clearly appeared that thermal transients have to be taken into account for a complete

understanding of front dynamics for such bulk samples. A first approach that modifies the WL model has been proposed that needs to be further validated and extended to include microstructural development using the phase-field method previously applied to the same alloy [21]. With ground experiments in thin samples or in capillary tubes, an interesting point would be to analyze the effect of the convection on front recoils, varying for example the thickness of the samples. Another challenging task would be estimation of the tip undercooling, so far out of reach in our experiments with bulk samples.

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Nomenclature

A	interface amplitude
C	concentration
C_∞	initial concentration of the liquid
D_L	diffusion coefficient of solute in the liquid
D_s	diffusion coefficient of solute in the solid
D_{th}	thermal diffusion coefficient
f_L	liquid fraction
f_s	solid fraction
g	gravity
G	thermal gradient
Gr	Grashoff number
k	partition coefficient
l	length of the solute boundary layer (WL model)
L	solidification length
l_T	thermal length
m_L	<i>liquidus</i> slope
Pe	Peclet number
q_0	length of the adiabatic area
R	crucible radius
Sc	Schmidt number
t	time
T	temperature
V	interface velocity
V_p	pulling rate

z_0	interface position
z_{∞}	initial interface position at rest

Greek letters

β_T	thermal expansion coefficient
δ	diffusive boundary layer thickness
Δ	adimensional boundary layer thickness
ΔH	latent heat of fusion
Δz_{exp}	measured position of stationary interface
$\Delta z_{c,\text{exp}}$	experimental corrected recoil (<i>i.e.</i> final <i>liquidus</i> position)
$\Delta z_{c,\text{num}}$	total numerical recoil obtained by CrysMAS simulations
Δz_T	thermal drift
Δ_t	distance between tips and <i>solidus</i>
λ	thermal conductivity
ρ	density
τ	time delay
ν	kinetic viscosity

Subscripts

0	nominal
c	critical
exp	experimental
L	liquid
m	melting
num	numerical

S solid

Abbreviations

BBF	Bower, Brody and Flemings
CNES	French Space Agency (<i>Centre National d'études Spatiales</i>)
DECLIC	Device for the study of Critical Liquids and Crystallization
DSI	Directional Solidification Insert
DSIP	Dynamical Selection of 3D Interface Patterns
ISS	International Space Station
KP	Karma and Pelcé
MISOL3D	Microstructures de Solidification 3D
NASA	National Aeronautics and Space Administration
SCN	succinonitrile
TGZM	temperature gradient zone melting
WL	Warren and Langer model
μg	microgravity
1g	on Earth (presence of convection)

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Figure & Table captions

Table 1 – Properties of succinonitrile and succinonitrile-camphor alloy.

Table 2 – Interface amplitude at end of solidification (A), under microgravity (μg) and on Earth ($1g$); experimental interface recoil (Δz_{exp}); experimental corrected interface recoil ($\Delta z_{c,exp}$), using the BBF and KP approaches under microgravity (f_s is the measured solid fraction as defined in the KP model); and simulated recoils using CrysMAS thermal simulations ($\Delta z_{c,num}$). Each measurement has a standard deviation of $\pm 25\mu m$.

Table 3 – Δz_T values and fitted values of the delay time τ (s) used in the modified WL model considering a BBF and a KP tip undercooling. The Δz_T values are obtained using eq. (13) with the values of $\Delta z_{c,exp}$ listed in Table 2 for each model.

Figure 1 – Interface motion measurement method, for $G_2=12K/cm$: (a) convex without structures at rest; (b) convex with structures at $4\mu m/s$; and (c) concave at $8\mu m/s$.

Figure 2 – Phase diagram for the binary system succinonitrile-camphor: \bullet , *liquidus* and \circ , *solidus* lines estimated using fraction of liquid phase measured by Witusiewicz et al.[31]. (b) is a zoom of (a) close to the melting point of pure succinonitrile.

Figure 3 – Interface position and shape for different thermal conditions: experimental images on top are compared to CrysMAS simulations at bottom, with the temperature field as color map. G_1 and G_2 correspond to the nominal control temperatures for the 2 gradients; G_1

shifted and G_2 shifted correspond to the same control temperatures than respectively G_1 and G_2 , except that hot zone and booster heater temperatures have been decreased by 2°C.

Figure 4 – Position and shape of the *liquidus* and *solidus* isotherms at $G_2 = 12$ K/cm. In blue: at rest ($V_p=0$). In orange: at $V_p = 4$ $\mu\text{m/s}$ with a latent heat $\Delta H = 0$. In red: at $V_p = 4$ $\mu\text{m/s}$ with $\Delta H \neq 0$.

Figure 5 – Interface evolution from rest to steady state under microgravity at $G_2 = 12$ K/cm and $V_p =$ (a) 0.25, (b) 4 and (c) 8 $\mu\text{m/s}$; (d) Schematic representation of interface shape from rest until the end of solidification for three different pulling rates.

Figure 6 – Steady state interface for different pulling rates at $G_2=12\text{K/cm}$ under microgravity.

Figure 7 – Analysis of the interface shape with pulling rate ($G_2=12$ K/cm): a) Comparison of the experimental and numerical interface amplitudes as a function of pulling rate. b) Analysis of numerical data to identify the different contributions to the interface shape change between rest and pulling. Respectively, differences of interface amplitudes are measured between the isotherms shapes: Rest and *Liquidus* at V_p ($\Delta H=0$) for the “Instrumental recoil”; *Liquidus* and *Solidus* at V_p ($\Delta H=0$) for the “Solutal recoil”; *Solidus* at V_p , $\Delta H = 0$ and $\Delta H \neq 0$ for the “Latent heat contribution”.

Figure 8 – Interface position (z_0) as a function of solidified length ($L=V_p t$) at $G_2=12\text{K/cm}$ for different pulling rates ($\mu\text{m/s}$): (a) ●, 0.25; ○, 0.5; ▲, 1 (b) ▲, 1; △, 2; ■, 4; □, 8.

Figure 9 – Schematic representation of interface recoil for $V_p=0.5\mu\text{m/s}$ and $G_2=12\text{K/cm}$, and the corresponding positions of *liquidus* and estimated *solidus*.

Figure 10 – Analysis of the interface recoil with pulling rate ($G_2=12\text{ K/cm}$): experimental data is given in black, with the BBF and KP calculations for the tip undercooling, and compared to the different recoil contributions identified with numerical simulations.

Figure 11 – Interface position (z_0) as a function of solidified length (L) for different pulling rates: experimental points are superimposed with the modeling results using Warren and Langer [5] model modified to take into account the isotherm shift (full line) and the original model (dotted line), for (a) $G_1=19\text{K/cm}$ and (b) $G_2=12\text{K/cm}$. The dashed line corresponds to the estimated *solidus* line.

Figure 12 – Interface position (z_0) as a function of solidified length (L) at $G_2=12\text{K/cm}$ for different pulling rates onboard ISS (noted “ μg ”) and on ground (noted “ 1g ”).

Figure 13 – (Grashof-Schmidt, Peclet) diagram [55, 56] with different segregation profiles shown schematically.