A Nucleation Progenitor Function approach to polycrystalline equiaxed solidification modelling with application to a microgravity transparent alloy experiment observed *in-situ*

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**Abstract**

A Nucleation Progenitor Function (NPF) approach that accounts for the interdependence between nucleation and growth during equiaxed solidification is proposed. An athermal nucleation density distribution, based on undercooling, is identified as a progenitor function. A Kolmogorov statistical approach is applied assuming continuous nucleation and growth conditions. The derived progeny functions describe the (supressed) distribution of actual nucleation events. The approach offers the significant advantage of generating progeny functions for volumetric (3D) data and projected image (2D) data. The main difference between 3D and 2D data in transparent alloy experiments is due to a stereological correction for over-projection. Progeny functions can be analysed to obtain statistical output information, e.g., nucleation counts, average nucleation undercooling and standard deviation. The statistical output data may be calculated in a formative (running) or a summative (final) mode. The NPF kinetics have been incorporated into a transient thermal model of equiaxed solidification. The model has been applied to characterise a microgravity solidification experiment with the transparent alloy system Neopentylgycol-30wt.%(d)Camphor. The model predicted thermal and observed nucleation and growth data with a good level of agreement.

Keywords: nucleation; equiaxed growth; solidification; microgravity.

# Introduction

Polycrystalline equiaxed solidification, leading to grain refinement in microstructure, is a significant topic for the metal processing industry. The advantages of fine-grained equiaxed structures in casting processes are well-known and include a reduction in defects and improvements in component strength. In wrought alloy processing, initial fine grain structures can improve recrystallization kinetics. A relevant industry standard [1], which outlines test procedures for grain-refined microstructure characterisation, exists. However, the standard does not attempt to predict cause-and-effect relationships in a detailed way. Nevertheless, much is known about the heterogeneous nucleation mechanisms that promote polycrystalline equiaxed grain structures. Such methods include inoculation of aluminium castings with TiB2 particles.

## Athermal nucleation distribution based on undercooling

Recently, Greer [2] and Easton et al. [3] reviewed grain refinement in castings. Indeed, Greer and co-workers [4] provided the much-needed physical explanation of how free-growth conditions are established on the inoculating grain refiner particles. The attainment of free-growth conditions on the particles was identified as the controlling factor in the grain refinement processes. The undercooling for free-growth conditions, , on any particle is related to the particle dimension, :

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Where is the solid-liquid interfacial energy and is the volumetric entropy of fusion. Applications of athermal nucleation distributions based on undercooling, originally proposed by Oldfield [5], have been commonplace in microstructure modelling. As reviewed in Rappaz [6] and more recently in Rappaz and Dantzig [7], nucleation distributions are often assumed to follow standard statistical probability density functions, such as Gaussian or log-normal. Quested and Greer [8] showed that the particle size distributions could be described using a standard statistical distribution (e.g., log-normal); therefore, after application of eq. (1), the suitability of athermal nucleation distributions based on undercooling has been clarified within the litrature.

## Predictive modelling of equiaxed solidification

A significant number of equiaxed solidification models have been developed to predict microstructure information at the macro scale subject to definitive processing conditions. Maxwell and Hellawell [9] were the first to provide a simplified model. They used Arrhenius-type nucleation kinetics and globular-to-dendritic growth kinetics to predict the suppression of nucleation rate due to latent heat release. They ignored any correction for impingement, which they justified because of low solid fraction.

Several modelling approaches have assumed free-growth nucleation conditions and athermal nucleation distributions [10–12]. Quested and Greer [10] developed an equiaxed solidification model based on an athermal nucleation distribution with both spherical and dendritic morphologies included in the analysis for comparison purposes. They used a standard Johnson-Mehl-Avrami-Kolmogorov correction for the impingement of grains, which caused the deactivation of seed particles in the latter stages of solidification due to the process of engulfment by previously nucleated grains.

Shu et al. [11] developed an equiaxed model that included the nucleation-supressing effects of solute rejection into the untransformed liquid phase. This model introduced a Solute Suppressed Nucleation (SSN) zone around each spherical envelope of dendritic mush. The effect of including the SSN zone was analysed and comparisons were made to experimental case studies. Plots of average grain size versus growth restriction factor were provided.

StJohn et al. [12] described the interdependence theory in which they examined the relationship between nucleation and growth. Their model included a nucleation free zone where nucleation is prohibited. The average radii of the spherical mushy envelopes plus the length of the solute affected zone around each envelope defines the nucleation free zone. The interdependence theory was used to predict average grain size and plots showed grain size as a function of the reciprocal of growth restriction factor.

Du and Li [13] extended an established precipitation model, the Kampmann-Wagner model, to include an SSN zone and multi-component growth kinetics by incorporating a CALPHAD approach. The model was applied to both uniform temperature-fixed cooling and direct casting scenarios.

## In-situ experimental monitoring of equiaxed nucleation and growth

Traditionally, in the case of metal alloys, experimental characterisation is performed *ex-situ*, also known as post-mortem analysis. In *ex-situ* analysis, metal samples are prepared by cutting, polishing, and etching along recommended guidelines so that grain structures are revealed.

Alternatively, *in-situ* experimental observation provides information on solidification processes in real time. Metals are opaque at visible wavelengths, hence *in-situ* analysis of metals has relied on the application of real-time x-ray radiography techniques. Several dedicated *in-situ* experimental apparatuses have been developed to investigate equiaxed solidification [14–17]

Recently, Xu *et al.* [18] applied their model of equiaxed solidification from reference [13] to an *in-situ* x-ray experiment involving Al-10wt.%Cu alloy inoculated with Al-5wt.%Ti-1wt.%B grain refiner master alloy. They investigated nucleation and growth conditions at different cooling rates. They showed predictions of final grain size versus cooling rate. Their results compared favourably with experimental observations in the case of well-refined alloy systems.

The analysis of transparent alloy systems using optical methods pre-dates real-time x-ray radiography by several decades. Jackson and Hunt [19] were the first to propose transparent alloy systems as being analogous model systems of metallic solidification. Indeed, *in-situ* optical analysis of transparent alloys has been used extensively to investigate time-dependent solidification behaviour in cellular [20], dendritic [21], and eutectic [22] systems. Transparent alloy *in-situ* observation has provided insights previously unobtainable through *ex-situ* characterisation. For example, dendrite arm fragmentation was first observed in a transparent alloy system [23] and later confirmed in metallic alloys by application of *in-situ* x-ray radiography [24]. However, there are several distinctions between transparent alloy and metal alloy *in-situ* processing worth pointing out. Firstly, transparent alloy systems typically have much lower melting temperatures than most metal alloys. Secondly, suitable metal alloy systems for x-ray observation require sufficient density difference between solute and solvent to provide improved x-ray absorption and image contrast between the phases. Thirdly, *in-situ* metal samples are prepared in thin foil format (typically some 100 µm in thickness), whereas, transparent alloy samples are typically thick samples to avoid boundary effects. This final point raises the issue of stereology effects on the image data from bulky samples. These stereology effects will be investigated in this manuscript.

## The Multiple Equiaxed Dendrite Interaction (MEDI) experiment.

In 2015, an *in-situ* transparent alloy experiment into polycrystalline equiaxed solidification was conducted under microgravity conditions (reported in reference [25]). The MEDI experiment was launched on-board the MASER-13 sounding rocket. The sample contained the transparent material, Neopentylgycol-30wt.%(d)Camphor, which is a hypoeutectic alloy with face-centred cubic lattice structure in the primary dendritic phase. The sequence of events during the launch led to in-situ observation of polycrystalline equiaxed nucleation and growth under high-quality microgravity conditions. A controller allowed fixed cooling conditions to be set under a low temperature gradient. Three thermocouples recorded temperatures within the sample. Observations of equiaxed dendritic solidification (nucleation, growth, and interaction) were made *in-situ* and in real-time using optical magnification methods at both the macro and micro length scales. This MEDI campaign was conducted as part of the European space agency CETSOL (Columnar-to-Equiaxed Transition in SOLidification Processing) programme [25].

## Aims and objectives

This manuscript proposes a Nucleation Progenitor Function (NPF) modelling approach for polycrystalline equiaxed solidification. The starting position for this approach is to define an athermal nucleation distribution as a progenitor function. Through application of the approach, different instances of continuous nucleation outputs (progeny functions) arise. Hence, an aim of this study is to define progenitor-progeny relationships. These progeny functions are then processed to give detailed information, e.g., average nucleation undercooling, standard deviation of nucleation undercooling, etc. Uniquely, by deriving alternative progeny functions, the NPF method can account for output data in 3D and 2D (taking into account 2D stereology effects in the data).

Specific aims and objectives of this work are:

1. Introduce the NPF approach for polycrystalline equiaxed solidification.
2. Develop a transient thermal model of solidification by incorporating the NPF method into the energy equation.
3. Summarise the experimental details of the MEDI experimental campaign and report on details of experimental data related to the nucleation and growth phenomenon.
4. Apply the thermal model and relate experimental observations of solidification from MEDI to the model predictions.

The manuscript introduces the NPF approach for a simplified case of constant cooling and uniform temperature (where temperature is initially assumed *a priori*); but, then develops to provide details of the full transient thermal model, where the presence of a temperature gradient can be accounted for. The MEDI experiment is summarised and observed output solidification data is provided. The NPF-adapted thermal model has been applied to the MEDI experiment. Detailed analyses and discussion are provided herein.

# Modelling

## The Nucleation Progenitor Function (NPF) approach

To demonstrate the framework for the NPF approach, we initially assume uniform temperature and a fixed cooling rate *a priori*; however, a transient thermal model is developed later (section 2.2).

### Progenitor function definition

The starting point for the NPF is to define a progenitor function that describes the collective nucleation potency of all inoculant particles. A general description of the progenitor distribution is

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where is an athermal nucleation density distribution based on undercooling, Δ*T*; is the volumetric nucleation density of all possible nucleation sites; and is a Probability Density Function (PDF). The undercooling is defined as Δ*T=TL­–T* where *TL* is the equilibrium liquidus temperature for the alloy composition*.* The progenitor function is best described as a seed activation function – all seeds activate but not all active seeds will form real crystals. This feature will become apparent later in the manuscript when the concept of phantom nucleation is described.

Application of various PDFs are cited in literature, typically either Gaussian or log-normal [7]. Providing an improved physical explanation, Greer assumed a log-normal distribution for particle size and showed that a PDF may be developed after application of eq. (1) (see reference [10]). For the purposes of demonstration, we assume a Gaussian distribution, , where the progenitor function is given as,

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where Δ*To* is the overall average nucleation undercooling for all potential seeds and Δ*Tσ* is the standard deviation. Hence, assuming a normal distribution, the overall condition of the inoculant particles is described by three statistical parameters, , Δ*To*, and Δ*Tσ*. Figure 1 shows a typical progenitor function plotted against undercooling (where *No=*1×1010 m˗3, Δ*To*=8 K and Δ*Tσ* =1 K).

A co-ordinate transformation is applied to change the progenitor function from the undercooling domain, Δ*T*, to the time domain, *t*. This transformation is achieved by multiplying equation (3) by the instantaneous time rate of change of temperature or,

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(The negative sign is required for mathematical consistency.) Equation (4) provides an instance of the progenitor function in the time domain that is now dependent on the original progenitor function and the process cooling conditions.

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| *Figure 1 The progenitor function – an athermal nucleation distribution based on undercooling.* |

### Kolmogorov statistical approach

Initially, all potential inoculating particles in a superheated liquid are described as *passive.* However, upon cooling, once the free-growth undercooling for any seed particles is reached, those particles start growing and are labelled as *active.* The density of active particles at any given time, *t*, is obtained by integrating equation (4) with respect to independent nucleation time, *tn*.

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The number of active nuclei at any time, *t*, is given by,

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and, if conditions are uniform, . The remaining passive seeds at any time will have a density given by

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Equation (5) describes the cumulative distribution function of all *active* seeds as a function of time. Over time, with cooling, all seeds transition from *passive* to *active* regardless of whether they nucleate or not. Only a subset of the *active* nuclei will go on to form actual nucleation events. To establish the proportion of *active* nuclei that actually nucleate, we use a Kolmogorov approach [26] (as presented in [27,28]) which applies Poisson statistics to distinguish between real and phantom nucleation events. Real events are those nucleation events that occur in untransformed regions. Phantom events are those that occur within (consumed by) the transformed volume.

Each active nuclei is assumed to grow with spherical geometry, hence the volume of any given grain,, at a given time (neglecting its initial size at the moment of initiation) is given by

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where the is the radius of that grain at time *t* where it nucleated at time *tn*. The radius of any grain is calculated by integrating the growth rate

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where is growth rate and is an intermediate time variable required for integration. If the seeds are spatially distributed without bias then the Possion statistical process holds. The probability that any remaining passive seed is excluded from the transformed volume (i.e., within untransformed regions) is

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where is the nucleation density of active seeds at the time of nucleation of that seed *i*. The probability that any passive seed does not belong to any previously grown, transformed volume is

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This probability *P* is also the volume fraction of untransformed region; hence, the volume fraction of transformed regions is given as

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The probability *Po* is recognised as the transformed volume fraction, , and the summation term in equation (11) is known as the extended volume fraction, . The equation is presented eloquently as the John-Mehl-Avrami-Kologorov (JMAK) equation,

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In the continuum limit, the extended volume fraction is given as

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This probability analysis allows us to determine the nucleation rate for real nucleation events,

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and, over time, the nucleation density of real nuclei is obtained by integrating,

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In the current framework of NPF, equation (15) describes a specific time-domain instance of a progeny function descended from the progenitor in equation (2).

### Stereology correction for projected data

In transparent alloy systems where the sample is bulky (i.e., where the sample thickness is greater than the average crystal size), equiaxed nucleation events take place at varying depths in the sample. As growth proceeds, projected image data observed from a fixed viewpoint will suffer from the problem of over-projection. Non-contacting crystals may appear to overlap and late-stage nucleation events may be obstructed from view due to established crystals being present along the line of sight. This is a well-known stereology problem [29, 30] and corrections are provided to account for the unwanted data artefacts that arise. Underwood [29] reviewed the stereology correction for projection in bulk samples as,

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where is the total projection (the area fraction of all projected surfaces on all transformed regions) and is projected (or apparent) area fraction on the projection plane.

Mooney and McFadden [31] have presented a theoretical framework for analysing 2D image data arising from 3D equiaxed nucleation and growth. They showed that, assuming Poisson statistical assumptions, projected image data may also be analysed using a Kolmogorov approach but on the 2D observation plane. This leads to a derivation of the 2D JMAK equation,

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where is the observed area fraction with is the extended area fraction (which is analogous to the extended volume fraction but based on area calculations). Through application of the supporting theory for equation (18), a new progeny function is possible for the observed nucleation rate,

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With an associated observed nucleation density,

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The parameter *D* is the overall depth (or thickness) of the sample under observation. The observed nucleation rate and observed nucleation density are examples of areal density data (units of [mm-2s-1] and [mm-2] respectively). Mooney and McFadden showed equivalence between the current analysis and the correction factor presented in equation (17) given that, and .

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| *Figure 2 Progenitor-progeny relationships. An instance of the progenitor in the time domain with two progeny functions: Real (volumetric) nucleation rate and Observed (areal) nucleation rate.* |

Figure 2 show the progenitor-progeny relationships for a case with uniform temperature and constant cooling rate of 0.75 K/min. The progenitor function shown in Figure 1 is adapted to give an instance of the progenitor in the time domain. Two progeny functions are shown: real nucleation rate and the observed nucleation rate. Note that the progenitor nucleation rate and the real nucleation rate functions have volumetric units [mm-3s-1], whereas, the observed nucleation rate function is has areal units [mm-2s-1]. A detailed analysis of the exchange processes for all potent seeds as they progress from *passive* to *active* and from *active* to the various categories of real, phantom, and observable is provided in detail in reference [31].

### Statistical analyses of progeny functions

Analysis of the progeny functions will yield further information on the nucleation events. In order to establish the number of nucleated crystals during the course of solidification at time *t*, we integrate the volumetric grain density over the volume of interest.

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With uniform conditions, the relation simplifies to. Similarly, we can calculate the number of observed nucleation events (which is lower due to stereology effects) by integrating over the area, *A*, of the projection plane.

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Again, with uniform conditions, the relation simplifies to. Figure 3 shows a demonstrative set of results for nucleation counting based on data from Figure 2.

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| *Figure 3 Nucleation count (as a continuous function) over time for active, real, and observable events* |

In order to perform further statistical analysis in detail, equation (15) is subjected to the reverse coordinate transformation from the time domain back into the undercooling domain,

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And by applying a normalisation constant,, we get a PDF with respect to undercooling,

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The normalisation constant is required to ensure that the overall integral of the PDF is unity (a strict mathematical requirement). Similarly, we get a PDF for the observed nucleation distribution after applying a coordinate transformation on equation (20) to obtain, normalising with,

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The expected value equation is used to calculate the mean undercooling,, from a known continuous PDF, , as follows,

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Usually, for a two-sided distribution the integration limits are from to +, but in our case we can typically assume that the limits range from zero to infinity with negligible consequences. (However, one should exercise caution when using a two-sided distribution such as a Gaussian by checking that Δ*To >*3Δ*Tσ*).

The associated standard deviation of nucleation undercooling in this distribution,, is obtained through application of the expected value equation as follows,

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Hence, equations (26) and (27) can be applied to and to gather statistical measures for real and observable events, respectively.

### Summative and formative outputs

As mentioned, the normalisation constants, and, are required to ensure that the integral equals unity. The normalisation process plays a key role in the interpretation of the preceding statistical analysis. Summative or final output data is provided by integrating to infinity. Practically speaking, we need only integrate until solid fraction is approximately unity or when the nucleation rate is almost zero. Hence to obtain overall or summative statistical data, we calculate the normalisation constants as follows

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However, if formative or running statistical data is required, then the normalisation process must use the current value density as follows,

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When applying equations (26) and (27) in the formative case, we use normalization constant equations (30) or (31).

## Thermal model

The heat equation for a solidification process under diffusive conditions is

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where, ** is density, *cp* is the specific heat capacity, *k* is the thermal conductivity, *L* is the latent heat of fusion per unit mass, and *fs* is the solid fraction.



Figure 4: Equiaxed mushy envelope growing within a control volume VCV.

In a CV formulation the solid fraction is, where is the local solid fraction within the mush. Figure 4 shows the scenario for a single equiaxed envelope within a control volume where and the volumetric fraction of mush is, . is the volume of solid formed within the mushy volume , and is the volume of the Control Volume (CV) and is the equiaxed tip velocity. The concept extends to multiple envelopes within a CV. Substituting and expanding the latent heat term in equation (32) gives

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The second term on the right hand side represents the latent heat due to thickening of the mushy zone, while the last term represents the latent heat due to growth of the mushy volumes in the CV.

Extensive details of the thermal model and its application for the full thermal characterisation of the MEDI experiment are presented by the authors elsewhere [32]. Two established approaches to solid fraction evolution (namely, a Scheil-based approach [33] and a Rappaz-Thevoz approach [34]) were reported in [32]. In the specific case of selected alloy, the differences between the two approaches were found to be minimal. Hence, in this manuscript, the local solid fraction (within the mush) is reported using the Scheil microsegregation equation for hypoeutectic alloys, as described in [33],

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where *TM* melting point of the solvent, *TE* is the equilibrium eutectic temperature, *kpart* is the partition coefficient.

The NPF approach is applied to obtain the volume fraction of mush through application of equation (13). Hence all of the output information associated with NPF approach and described in Section 2.1 is obtainable from the transient thermal model both in formative and summative formats.

The equiaxed dendrite tip growth rate is required for the calculation of extended volume fraction, in equation (14); the growth rate is assumed to be a function of undercooling, as follows,

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Finally, thermophysical properties are permitted to vary as a function of temperature, and for mush-containing CVs properties are estimated as per reference [33].

# Experimental materials and methods

## Physical apparatus and procedures

The physical apparatus and outline operation procedures for the MEDI experiment are presented elsewhere [25], but a summary is provided.



Figure 5: Schematic diagram of the MEDI experiment test cell.

Figure 5 provides an isometric view and sectional detail of the test cell that contained the alloy Neopentylgycol-30wt.%(d)Camphor. The alloy was contained in a central chamber and was viewed through a quartz window. This allowed for image recording at the macroscale of the sample window. The nominal dimensions of the cell chamber were 10 mm in the *x*-direction, 13 mm in the *z*-direction, and 3 mm in depth in the *y*-direction. The optical arrangement had a sufficient depth of field to capture nucleation events at all depths in the central chamber. A Peltier Element (PE) device, or heating element, was installed at the top (hot side) and bottom (cold side) of the test cell creating a temperature gradient in the *x*-direction. A controlled temperature difference was maintained between the two PE devices that gave a thermal gradient of approximately, *Gx*=0.3 0.1 K/mm. Three Ni-CrNi thermocouples with diameter 0.25 mm were installed in the *x-z* median plane of the cell at positions *x*=1.4 mm, 4.9 mm, and 8.2 mm relative to the bottom of the cell chamber (*x=*0 mm) and were directly in contact with the sample alloy material. The PE devices were cooled at a controlled rate of 0.75 K/min starting at approximately *t=*220 s before rocket lift-off (defined as *t* = 0 s) which was maintained throughout the microgravity phase of the flight. The microgravity period lasted approximately 6 minutes, from *t=*89 s to *t=*468 s. The first nucleation event was observed shortly after the beginning of the microgravity period.

## Image data post-processing and characterisation

The overview digital images were captured with a field of view (FoV) 13.6 mm wide by 10.9 mm high (1280 × 1024 pixels in size, giving an optical resolution of 10.625 m/pixel). Images were recorded in 8-bit grayscale and at 10 frames per second. The optical arrangement had a sufficient depth-of-field to capture nucleation events at all depths (3mm) in the central chamber. A second optical arrangement was installed to provide higher magnification *in-situ* microscopic detail at the scale of individual dendrites. Specific outputs from this higher magnification arrangement are reported in reference [25].



Figure 6: Polycrystalline Equiaxed nucleation at 270 s, 370 s and 460 s after lift-off, from left-to-right, respectively.

Figure 6 shows three images recorded at different times during in the microgravity phase of the experimental flight. Polycrystalline equiaxed nucleation and growth was observed, starting at the cold end and progressing towards the hot end of the sample in the *x*-direction. The solid black items to the right of each image are the thermocouples. No thermocouple data on the lateral temperature gradient *Gz* was obtainable; however, the images showed uniform nucleation progressing in the *x*-direction. Hence, it was assumed that *Gz* was negligible and could be ignored.

The times and locations of the appearance (i.e., the observed nucleation event) of each equiaxed crystal were recorded. The temperature for each nucleation event, *Tevent*, was estimated by linear interpolation (or extrapolation) of the temperatures measured at the two nearest thermocouples to the event location; either TC1 and TC2 for events occurring in the upper half of the window, or TC2 and TC3 for events occurring in the lower half of the window. The corresponding nucleation undercooling was given by: *Tnuc*=*TL*–*Tevent*.



Figure 7: Colour mapped image in preparation for threshold analysis and area fraction calculation.

Projected area of the crystal growth was determined in frame-by-frame post-processing of recorded images. Thresholding image analysis was used to determine the area fraction; all observed equiaxed crystals were included in the area estimation. The viewing window frame and thermocouples features were excluded from this estimation. The global projected area of equiaxed mush, i.e., the total area of mush divided by the entire observation window area, was then calculated as an area fraction and plotted against time. Figure 7 shows an example of a frame image used in the threshold operation. Untransformed region is easily identified by its grey colour. The issue of over-projection is apparent at the colder, lower region of the sample where, collectively, individual crystals present themselves as a coherent entity on the projected image.

## Thermal model application

As mentioned, a full thermal characterisation of the MEDI experiment with detailed numerical scheme verification was reported in [32]. In summary, equation (33) was applied to the sample domain in two dimensions (*x* and *y*). This allowed the temperature to vary in these directions, thereby permitting temperature gradients in the initial analysis. Type I (Dirichlet) boundary conditions were determined for the top (*x=H*) and bottom (*x=*0) of the sample domain and Type III (Robin) boundary conditions were determined for the domain interface with the quartz-glass window (*y=D*/2). Assuming symmetry of the sample in the median *x-z* plane, an adiabatic boundary condition was applied at the cell centre (*y=*0). Heat loss through the viewing pane was shown to cause temperature gradients in the *y-*direction, *Gy*. The gradient *Gy* was zero on the *x-y* median plane but reached 0.3 K/mm at the glass interface with the sample. However, as reported in [32] due to the dimensions of the sample, the overall temperature difference across the sample in the *y-*direction did not exceed 0.22 K at any time in the simulation. Hence, in this study, temperature variation in the *y-*direction is assumed negligible. The simulated temperatures on the median plane are taken as being representative of the sample temperatures along the *x-*axis. Because the thermocouples (TC1, TC2, and TC3) were situated on the median plane, the experimental interpolation procedure for estimating nucleation undercooling was also based the assumption of negligible lateral gradients. Hence, direct comparisons between simulated and experimental data are permissible.



Figure 8 Sample domain divided into discrete volumes in the x-direction.

Figure 8 shows the entire sample domain (through the full depth of the sample) divided into elemental volumes.

The imposed temperature gradient, *Gx*, of 0.3 K/mm caused significant temperature variation in the *x-*direction. This had to be accounted for in the thermal analysis and in the presentation of overall global data (i.e., for the entire sample cell). Each elemental volume is considered as having independent statistical output data locally within the cell, for example, cell ‘j’ has a local mean undercooling value of and a local standard deviation of , as given by equations (26) and (27), respectively. But, to get the overall (global) statistical data for cases with a temperature gradient, i.e., across the entire sample, we applied the combined mean and variance equations as follows,

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Equations (36) and (37) are shown based on volumetric (3D) information; however, areal or 2D observed information is obtained by suitably replacing volumetric information with areal information (replace subscript ‘*REAL*’ with ‘*OBS*’ throughout). Equations (36) and (37) can be used in a formative or summative mode as defined previously.

The overall PDF of nucleation undercooling across the entire domain at a given time (accounting for temperature gradient) is obtained through the convolution of individual PDFs from all CVs that are undercooled. Assuming that control volumes from *j* =1, *n* are undercooled, then

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Where the operator represents the standard convolution process. Since the convolution process is both commutative and associative, the PDF for the entire domain (*pglobal*) may be calculated by convolving the PDF from the first CV to the PDF of the second CV and then convolving that result with PDF of the third CV and so on, until all *n* undercooled CVs are accounted for. Again, the subscript *global* is a generic term, specifically, the analysis may be applied to the 3D or 2D cases by consistently replacing the subscript *global* with the appropriate subscripts *REAL* or *OBS*.

### Simulation input data

All of the thermophysical and simulation data used in this analysis are summarised here in Table 1 and Table 2.

Table 1: Thermophysical properties of Neopentylgycol-30wt.%(d)Camphor (after [32])

|  |  |  |  |
| --- | --- | --- | --- |
| Property | Symbol | Value | Units |
| Thermal conductivity of liquid | *k* | 0.12 | [W/mK] |
| Thermal conductivity of solid | *k* | 0.27 | [W/mK] |
| Density of liquid or solid | ** | 960 | [kg/m3] |
| Specific heat capacity of liquid | *cp* | 211[J/kgK]+6.4[J/kgK2]*T* | |
| Specific heat capacity of solid | *cp* | 940[J/kgK]+4.2[J/kgK2]*T* | |
| Latent heat of fusion | *L* | 23900 | [J/kg] |
| Equilibrium liquidus temperature | *TL* | 352.45 | [K] |
| Equilibrium eutectic temperature | *TE* | 326.05 | [K] |
| Melting temperature of pure NPG | *TM* | 404.71 | [K] |
| Partition coefficient | *kpart* | 0.072 | [–] |
| Diffusivity of solute in liquid | *Dl* | 97 | [m2/s] |
| Dendrite growth coefficient | *Ct* | 6.54469×10-10 | [m/s/K4] |
| Dendrite growth exponent | *b* | 4 | [–] |

Table 2: Simulation input data – all times are provided relative to lift-off at t=0s (after [32])

|  |  |  |  |
| --- | --- | --- | --- |
| Input | Symbol | Value | Units |
| Simulation start time | *t*start | –300 | [s] |
| Simulation end time | *t*end | 550 | [s] |
| Nominal cooling rate (from *t*= –235 s) |  | –0.75 | [K/min] |
| Grid size in *x* (ncols=33) | *x* | 0.3125 | [mm] |
| Grid size in *y* (nrows=9) | *y* | 0.1875 | [mm] |
| Numerical time step | *t* | 0.05 | [s] |
| Heat transfer coefficient at *y*=*D*/2 | *hloss* | 0.85 | [W/m2K] |
| Ambient environment temperature | *T∞* | 303.15 | [K] |
| Nuclei density | *N*o | 9×109 | [/m3] |
| Mean nucleation undercooling | *T*o | 9.5 | [K] |
| Standard deviation of nuc. undercooling | *T* | 0.55 | [K] |

# Results

## Thermal results

Figure 9 shows the simulated temperature data (dashed lines) against the measured data (solid lines) at the thermocouples TC1, TC2 and TC3, and at the hot side (TH) and cool side (TC). The simulated data is taken from the median plane at the locations of the thermocouples in each case. The agreement between the simulated and the measured data is within a Root Mean Square of 0.2 K which is deemed to be good agreement. As mentioned, detailed discussion on the thermal characterisation is provided elsewhere [32].

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Figure 9: Thermal data for the MEDI experiment: Simulated data (dashed lines) versus measured data from the thermocouples (solid lines).

## Microstructural data and results

Figure 10 provides experimental and modelling information related to the nucleation and growth during the microgravity stage of the experiment. Experimental measurements included the counting of nucleation events over time, , and the evolution of area fraction, . These measurements were observed on the projection plane and are therefore defined as being 2D (areal) information. For comparison, the model’s prediction of observable nucleation events, , and area fraction, , are shown. Area fraction shows good agreement, whereas the nucleation account shows reasonable agreement.

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Figure 10: Nucleation and growth data (observed experimental data versus modelling data)

For information, Figure 10 also gives the model’s prediction of real nucleation events in the 3D volume, , and the prediction of volume fraction of mush, . It is clear that the qualitative trends cited in reference [31] are displayed, that is, the area fraction is an overestimate of volume fraction and observed nucleation count in 2D is an underestimate of the real number of nucleation events.



Figure 11: Formative statistical data for mean and standard deviation of undercooling.

Figure 11 shows the formative (or running) statistical data for mean and standard deviation of observed nucleation events. The formative data from the model simulation are also shown. The progressive nature of the mean undercooling (due to the cooling rate and temperature gradient) is observable. Mean undercooling is shown to increase and reach a steady-state value over time. Standard deviation is reasonably constant over the time period. This behaviour is shown in the measured and the simulated outputs with reasonably good agreement.

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Figure 12: Overall distribution of the observed nucleation events on undercooling, and the probability density function of nucleation undercooling for the entire domain.

Figure 12 shows the final frequency table, that is, the summative nucleation data for the measured undercooling values recorded during the entire microgravity experiment. For comparison, Figure 12 shows the simulated global PDF for the observed nucleation density prediction over the entire domain. The final summative values for the mean and standard deviation of nucleation events are provided for both the measured and the simulated cases. The observed mean undercooling measured during the experiment was 8.4 K compared with 8.7 K for the simulation. The measured standard deviation was 0.6 K and the corresponding simulated value was 0.3 K. We can see that the global PDF, *p­OBS*, is in good agreement with the frequency distribution, qualitatively, we see that the PDF is showing skewness in agreement with the frequency data.

# Discussion

A new method called the Nucleation Progenitor Function approach to equiaxed solidification is proposed and applied to a set of experimental data from a microgravity experiment. The NPF approach highlights a so-called progenitor-progeny relationship between nucleation potency distribution and the actual, or suppressed, nucleation rate. This progenitor-progeny relationship is presented elsewhere in literature but without explicit reference (for example, see Quested and Greer [10] or Mooney and McFadden [31]). Nevertheless, this manuscript is the first to clearly define the relationship and propose its statistical interrogation for practical usage. Hence, it is claimed that the NPF approach is a new interpretation of equiaxed solidification modelling based on established theory. One of the practical advantages of the NPF approach is the ability to account for a stereology correction with ease, such as that which is required for bulky transparent alloy experiments that operate on the principle of opacity and transmission of light. Another advantage is the ability to combine PDF data (using convolution) in order to take account of temperature gradients in the sample.

This research predicts that the stereology correction is a significant factor in the presentation of the results. Figure 10 showed significant deviation between 2D observed outputs and 3D (real) outputs coming from the simulation. Due to the nature of the experimental setup it was only possible to compare simulation results with observed experimental data taken from the projection plane. Nevertheless, the 3D volume fraction was used to determine the latent heat evolution in the model and good thermal agreement was found between the simulation and experiment thermal datasets in Figure (9).

The NPF approach presented here does not account for solute suppression or nucleation free zones as proposed in other modelling approaches [11–13]. This omission is argued for in the case of this material because of low solutal diffusivity in liquid. The diffusivity of solute in liquid for Neopentylgycol-30wt.%(d)Camphor is *Dl* = 97 m2/s, which is typically two orders of magnitude lower than for the corresponding metal alloys in [11–13]. Hence, dimensions of the Solute Suppressed Nucleation (SSN) zone, related to the length of the solutal field, were assumed negligible. Hence, the nucleation suppression, accounted for in the progeny functions, are due only to engulfment of non-active seeds by the growth of previously nucleated seeds.

# Conclusion

A new approach to modelling polycrystalline equiaxed nucleation and growth is proposed. This approach begins by defining a starting function called the Nucleation Progenitor Function (NPF), which is also the well-established nucleation density distribution based on undercooling: . The NPF defines the overall potency of all nucleation sites. A coordinate transformation is applied to create an instance of the progenitor function in the time domain. Kolmogorov statistics are then applied which leads to the establishment of instances of progeny functions in the time domain that describe the actual (supressed) nucleation. An coordinate transformation is applied to the progeny functions to return to the undercooling domain. After normalisation, the progeny functions can be interrogated in detail using the expected value equation for statistical outputs in both formative (running) and summative (overall) statistical evaluations. Progeny functions can be derived for volumetric output or in 2D which takes stereological corrections into account.

In this manuscript, the NPF approach was incorporated into the latent heat term of the heat equation, which allowed for a fully transient thermal and material characterisation analysis of the microgravity MEDI experiment to take place.

The model showed good agreement with thermal, nucleation, and growth data and was able to predict both areal (observed) and volumetric output information. The stereological correction was shown to be significant in the case of the MEDI experiment. A further advantage of the NPF thermal model was demonstrated by its ability to deal with a thermal gradient along the length of the sample. The model was able to predict the statistical results on a local, cell-by-cell basis and on an overall, global basis. Formative statistical analysis was provided over the full course of the microgravity stage of the experiment.

The NPF approach, which highlights progenitor-progeny relationships between seed activation and nucleation, is formally presented here for the first time and has been demonstrated by application to equiaxed solidification in a transparent analogue material. It is intended that the NPF approach be extended to include metal alloy systems, among other topics, in future studies.

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