# Modelling of Nucleation in Impulse Atomized Undercooled Droplets

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Numerous previous researchers have used nucleation models as part of their simulation of droplet solidification. None of these have verified the nucleation portion of these models with experimental results. In this work, a heterogeneous nucleation model based on the classical nucleation theory was coupled with a thermal model of a falling droplet through a stagnant gas. The pre-exponential factor, which is usually unknown, was determined to obtain an undercooling similar to experimental results for a 196 µm droplet solidified in helium. A stochastic element was added by using a cumulative density probability function, leading to a range of possible nucleation undercoolings and nucleation points. The primary and eutectic undercoolings as well as the number of nucleation points were then compared with additional experimental results of Al-Cu alloy droplets. Good agreement was found between the calculated and the experimental undercoolings. Modeling results also suggest the presence of one nucleation point in the majority of cases and are in agreement with experimental observations.

Keywords: nucleation; undercooling; Impulse Atomization; Al-Cu alloys

## Introduction

One of the most crucial characteristics of an alloy are often its mechanical properties. These properties can be improved by using controlled processes, such as rapid solidification. According to Jacobson and McKittrick [1], the primary aim of rapid solidification processing (RSP) is to obtain a material with a desirable microstructural feature that cannot be achieved by conventional solidification processing. Using RSP techniques, it is possible to refine the structures of the rapidly solidified alloy [2]. Alloys created using RSP processes can also show an extended solute solubility compared to conventional methods as well as the formation of non-equilibrium phases [3]. Rapidly solidified structures oft lead to improved properties, such as toughness, hardness, wear resistance, fatigue resistance and corrosion resistance [3].

The RSP simulated in this work is the Impulse Atomization (IA) process, which was developed by Yuan *et al.* [4] at the University of Alberta. It uses repetitive impulses to move small amounts of melt through orifices. Interactions between the particles can be neglected by creating only a few particles at a time. This process allows the creation of very narrow and monodisperse particle size distributions with a lower limit of 1-100 µm. The upper limit is only bound to the requirement of not forming a continuous jet from the liquid. The work of Henein shows that particles produced under Impulse Atomization conditions show a finer microstructure and higher cooling rates than those generated using gas atomization [5]. His work shows that Impulse Atomization is a very flexible technique and that the process is able to solidify a wide range of materials, from Pb to steel. The droplets produced using this technique show a controlled and narrow size distribution and it is possible to achieve mass flows similar to those in gas atomization. Furthermore, the process does not have complex elements, such as electric charges, making it therefore easier to investigate.

Wiskel *et al.* [6] [7] developed a heat transfer model for an IA droplet. A modified Whitaker correlation for the effective heat transfer coefficient provided the best agreement with experimental data. Furthermore, they attempted to find a correlation between microstructure and solidification time. The experimentally determined relations between solidification time and microstructure showed good agreement in comparison with the relation between secondary dendritic arm spacing and theoretical models of coarsening.

Gandin *et al.* [8] compared segregation measurements of droplets solidified under Electromagnetic Levitation with modelling results of equiaxed dendritic solidification. The atmosphere for the experiments carried out by Gandin *et al.* was low pressure Helium and the cooling rates were controllable by the power of the current flowing through the levitation coil. In the molten state the sample was approximately spherical and showed a diameter of about 5.3 mm. Their solidification model is based on a mushy zone inside the droplet and assumes that there is no mass exchange with its surrounding, ergo the mass of the droplet is constant throughout solidification. For each time step a new zone inside the droplet is created. This zone represents the expansion of the solidification inside the droplet.

Prasad et al. [9] extended the microsegregation model from Gandin *et al.* for an individual IA droplet falling through a stagnant gas during the atomization process. Their microsegregation model was compared to measurements carried out using stereology and neutron diffraction and showed good agreement with the mathematical model as described in [10].

Nucleation undercooling is a key parameter in RSP. Indeed, the velocity of the solid-liquid interface depends on the undercooling $\Delta T$. In the work of Gandin *et al* [8], the undercooling

temperatures of primary phase and of eutectic were measured in-situ. For the model validation of IA powders presented in [9] and [10], the primary phase nucleation temperature was estimated by determining the nucleation temperature that would yield a solidified volume fraction of alpha phase during recalescence in agreement with measured values obtained from microtomography data. The eutectic undercooling values used for the IA droplets were those measured and reported from the electromagnetic levitation experiments [8]. Recently Bogno *et al.* [11] developed a model to estimate droplet undercooling temperatures for primary phase and for eutectic. Based on neutron scattering measurements of the fraction of $Al_2Cu$ in Al-4.5wt.%Cu IA powders, the eutectic undercooling was determined using extensions of the liquidus and solidus lines of the corresponding phase diagram. A coarsening model using the secondary dendrite arm spacing was then used to estimate the primary phase undercooling of the droplets.

While all of these approaches discussed above have yielded validated results using quantified microstructures in 3D, solid solubility and phase fractions, all of them require post mortem analysis for solidified powders. It would be of value to determine if models of nucleation could be applied to predict *a priori* the nucleation temperatures of these droplets. Mathur *et al.* [12] and Bergmann *et al.* [13] established mathematical models for the rapid solidification of Ni-20wt%Cr and Fe-20wt%Mn and low carbon steels droplets under spray forming conditions. Using the classical nucleation theory, they first assumed homogeneous nucleation with a single nucleation site. To account for heterogeneous nucleation, they correlated the homogeneous undercooling temperature with an empirical factor taking into account the volume of the droplets. The trend in their experimental data suggests that nucleation occurs under nearly homogeneous conditions in small droplets (<50 $\mu$m). Lee and Ahn [14] developed a model for the solidification progress and the heat transfer analysis of Al-4.5wt.%Cu gas-atomized droplets during spray forming. Their model uses the Ranz-Marshall correlation to calculate the heat transfer coefficient of the droplet, as well as heterogeneous nucleation and spherical growth of the solidification front. The nucleation temperature is defined as the temperature where one stable nucleus is formed within the liquid droplet, i.e. a single nucleation event is assumed. Furthermore, the wetting angle for the nucleation of the primary Al-$\alpha$ is varied between 0 and 180 degrees. Their work shows that the degree of primary undercooling is controlled by the wetting angle and the effect of droplet size and cooling rate is negligible. However, the order of magnitude of their pre-exponential factor for the nucleation rate is akin to common values expected for homogeneous nucleation [15] and no nucleation undercooling for the eutectic phase was considered.

In this work, a numerical model based on classical nucleation theory is established to predict the primary undercooling of Al-4.5wt.%Cu IA powders using an extended version of the thermal model developed by Wiskel. It focuses on the Impulse Atomization process and uses a modified

Whitaker correlation to calculate the effective heat transfer coefficient. Heterogeneous nucleation is assumed and the wetting angle for the primary phase is determined to fit undercoolings determined experimentally from neutron scattering measurements and secondary dendritic arm spacing [11]. The pre-exponential is determined to be several orders of magnitude lower and therefore closer to the value suggested by Dantzig and Rappaz for heterogeneous nucleation [15].

**Thermal Model**

The thermal model used in this work has been adapted from Wiskel *et al.* [6] and is briefly presented below. The governing equation for the cooling of a droplet in free fall through a stagnant gas is:

$$\frac{dT}{dt} = -\frac{6\,h_{eff}}{\rho_d . c_{p,d} . d_d}\left(T - T_g\right) \qquad (1)$$

Where $h_{eff}$ is the effective heat transfer coefficient, $\rho_d$ , $c_{p,d}$ and $d_d$ are the droplet density, heat capacity and diameter, respectively, and $T_g$ is the surrounding gas temperature. $h_{eff}$ consists of the additive contributions of convection, conduction and radiation heat transfer mechanisms. For alloys such as aluminum, the effective heat transfer for a moving droplet is dominated by convection and conduction. Radiation heat transfer can be significant for higher temperature alloy systems (iron based alloys). The effective heat transfer coefficient is defined here as:

$$h_{eff} = h_c + h_{rad} \qquad (2)$$

With $h_{rad}$ the radiative, and $h_c$ the convective and conductive components of the heat transfer coefficient. $h_{rad}$ is readily obtained as:

$$h_{rad} = \varepsilon\sigma \cdot (T^2 + T_g^2)(T + T_g) \qquad (3)$$

Where $\varepsilon$ is the droplet emissivity and $\sigma$ the Stefan-Boltzmann constant. The convective/conductive component $h_c$ is obtained with a semi-empirical equation where the Nusselt number (Nu) is averaged over the entire droplet surface [6]. As per Wiskel *et al.*, a modified Whitaker correlation is used:

$$\mathrm{Nu} = \frac{h_c d_d}{k_s} = 2\left(\frac{\beta}{k_s(\alpha+1)}\frac{T_s^{\alpha+1} - T_g^{\alpha+1}}{T_s - T_g}\right) + \left(0.4\,\mathrm{Re}^{1/2} + 0.06\,\mathrm{Re}^{2/3}\right)\mathrm{Pr}^{0.4}\left(\frac{\mu_g}{\mu_S}\right)^{1/4} \qquad (4)$$

With $\mathrm{Re} = \frac{\rho_g v d_d}{\mu_g}$ the Reynolds number and $\mathrm{Pr} = \frac{c_{p,g}\mu_g}{k_g}$ the Prandtl number. $k_g$, $c_{p,g}$, $\rho_g$ and $\mu_g$ are the conductivity, heat capacity, density and viscosity of the gas, respectively. $k_s$ is the gas conductivity at the droplet surface temperature $T_s$. $\alpha$ and $\beta$ are coefficients in the variation of the gas thermal conductivity with temperature, $k = \beta \cdot T^{\alpha}$. $\frac{\mu_g}{\mu_s}$ is the ratio between the viscosity of the gas at the free stream gas temperature and at the droplet surface temperature. Equation (1) is then solved using a fourth order Runge-Kutta method.

**Nucleation Model**

To determine the nucleation temperature (and thus undercooling), a classical heterogeneous nucleation approach is used in this model. Once the temperature of the droplet is below the liquidus temperature, the critical free energy is calculated:

$$\Delta G_n = \frac{16\pi\gamma_{sl}^3 T_L^2}{3\Delta H_f^2 \Delta T^2} f(\theta) \qquad (5)$$

with $\gamma_{sl}$ the solid-liquid interfacial energy, $T_L$ the liquidus temperature, $\Delta H_f$ the latent heat of fusion, $\Delta T$ the undercooling and $\theta$ the wetting angle. The geometrical factor $f(\theta)$ is defined as:

$$f(\theta) = \frac{(1-\cos(\theta))^2 . (\cos(\theta)+2)}{4} \qquad (6)$$

Using the critical free energy, the nucleation rate is calculated as follows:

$$I_f(T) = I_{f,0} \cdot \exp\left(\frac{-\Delta G_n}{k_b T}\right) \qquad (7)$$

The pre-exponential factor $I_{f,0}$ takes into account the atomic vibration frequency, the probability of capturing an atom at the interface and the density of nucleation sites in the melt that provide heterogeneous nucleation conditions with a wetting angle $\theta$.

The number of nuclei at each computation step is then obtained by multiplying the nucleation density by the volume of the droplet $V_d$:

$$n(T) = V_d \int_{T_l}^{T} \frac{I_f(T)}{\dot{T}} dT \quad (8)$$

It is important to note that while nucleation depends on temperature, the model is stepped in time. Temperature and time are linked through the initial droplet temperature and the evolving thermal history of the droplet as described by equation (1). At each step, the thermal model provides a new temperature, which is in turn used in the nucleation model. A converging solution is found for a time step of $10^{-4}$ s. However, due to the high cooling rates involved in Impulse Atomization (up to $10^5$ K/s), a time step of $10^{-6}$ s is chosen.

An extensive micro-tomography study on Al-4.5wt%Cu alloy droplets with sizes ranging from 100 to 355 µm atomized under helium and argon showed that in the vast majority of cases, one single nucleation point is primarily observed [16].

In order to add a statistical element to the nucleation event and therefore influence the undercooling temperatures, a cumulative probability function is calculated using the following equation as per Morton *et al.* [17]:

$$F_i(T) = 1 - \exp(-n(T)) \quad (9)$$

Where the index $i$ represents the primary or eutectic nucleation. As the cumulative probability function can achieve values between 0 and 1, a random number between 0 and 1 is calculated for each step. This number is then compared to the cumulative probability function. If the cumulative probability function is greater or equal to the random number and n(T) ≥ 1, nucleation is triggered. As the computed undercooling temperature increases, the possibility of creating additional nucleation sites increases as well. In this work, the random number generator is used to show a possible range of predicted undercooling temperatures.

**Model setup**

Most of the thermophysical properties defined above can be found in the literature for Al-4.5wt%Cu and are listed in Table 1. However, values of the wetting angle and pre-exponential factor sometimes have to be treated as unknowns as it not always clear what the impurity causing nucleation is. For the wetting angle, literature values can show a range of about 10° to 70°, the pre-exponential factor varies from $10^{22}$ $\mathrm{m^{-3}s^{-1}}$ for heterogeneous nucleation to factors of a magnitude of about $10^{40}$ $\mathrm{m^{-3}s^{-1}}$ for homogeneous nucleation [15].

In case of the eutectic nucleation, it is safe to assume that $Al_2Cu$ will nucleate on the primary Al. The corresponding wetting angle $\theta_e$ has been determined by Kim and Cantor [18]; only the the

pre-exponential factor, $I_{f,\theta}$ remains unknown. In order to determine the appropriate value of $I_{f,\theta}$ for this alloy, experimental data from Bogno *et al.* [11] was used. In their work, a eutectic undercooling of 20.9 K was found for droplets with a diameter between 180 and 212 µm solidified in Helium atmosphere. It is important to note that this experimental undercooling was obtained using phase fraction results from neutron diffraction and secondary dendrite arm spacing measurements that were performed on a whole population of droplets solidified in similar conditions. Thus the value of 20.9 K represents an average of the undercoolings experienced by droplets with an average diameter of 196 µm. To determine the pre-exponential factor $I_{f,\theta}$, the model was run with values of $I_{f,\theta}$ ranging from $10^{16}$ to $10^{50}$ $\mathrm{m^3\ s^{-1}}$ with an integer increment of the exponent. Figure 1 shows the effect of $I_{f,\theta}$ on the predicted eutectic undercooling for a 196 µm IA droplet solidified in He; the value of $I_{f,\theta}$ greatly influences the undercooling temperature. For the studied composition, a pre-exponential factor of $10^{20}$ $\mathrm{m^3\ s^{-1}}$ was found to be in reasonable agreement with the experimental data, with a predicted undercooling of 18.9 K (Figure 1).

Table 1: Thermophysical properties used in the model.

| Symbol | Value | Unit | Reference |
|---|---|---|---|
| $\varepsilon$ | $0.1$ | – | – |
| $\gamma_{sl,1}$ | $0.16340 \pm 0.02124$ | $\mathrm{J\ m^{-2}}$ | [19] |
| $\gamma_{sl,2}$ | $0.08777 \pm 0.01141$ | $\mathrm{J\ m^{-2}}$ | [19] |
| $\Delta H_{f,a}$ | $381773.5$ | $\mathrm{J\ kg^{-1}}$ | Extrapolation from [20] |
| $\Delta H_{f,\theta}$ | $365298.2$ | $\mathrm{J\ kg^{-1}}$ | Calculated |
| $I_{f,\theta}$ | $10^{20}$ | $\mathrm{m^{-3}\ s^{-1}}$ | This work |
| $k_b$ | $1.38064852 \times 10^{-23}$ | $\mathrm{m^2\ kg\ s^{-2}\ K^{-1}}$ | – |
| $T_e$ | $821$ | K | Thermo-Calc |
| $T_f$ | $933$ | K | Thermo-Calc |
| $T_l$ | $921$ | K | Thermo-Calc |
| $\theta_p$ | $12.6$ | ° | This work |
| $\theta_e$ | $24.6$ | ° | [20] |

For the primary phase however, both the wetting angle and the pre-exponential factor are unknown. In this work, it is assumed that both the primary and eutectic pre-exponential factor are the same, as both nucleation events are considered to be heterogeneous. Using this assumption, the wetting angle for the primary nucleation was determined using a trial and error approach. The model was run multiple times with different wetting angles until a match was found between the experimental and predicted primary undercooling values. A wetting angle $\theta_p$ of 12.6° allowed to retrieve the experimental undercooling of 14.4 K found by Bogno *et al.*

According to equation (8), only one nucleus forms in the droplet volume at this undercooling, which is in good agreement with the microtomography work of Bedel *et al.* [16]. The values obtained for the pre-exponential factors and the wetting angle of the primary phase are then used to predict the primary and eutectic undercoolings for three different droplet populations. The results are subsequently compared to the experimental values. In order to assess the number of nuclei that form once nucleation is triggered, the model was run 150,000 times with the random number approach for droplets of 196 µm solidified in both helium and nitrogen. For each nucleation undercooling, the number of nuclei given by equation 8 is recorded and compared to the analysis of Bedel *et al.* [16].

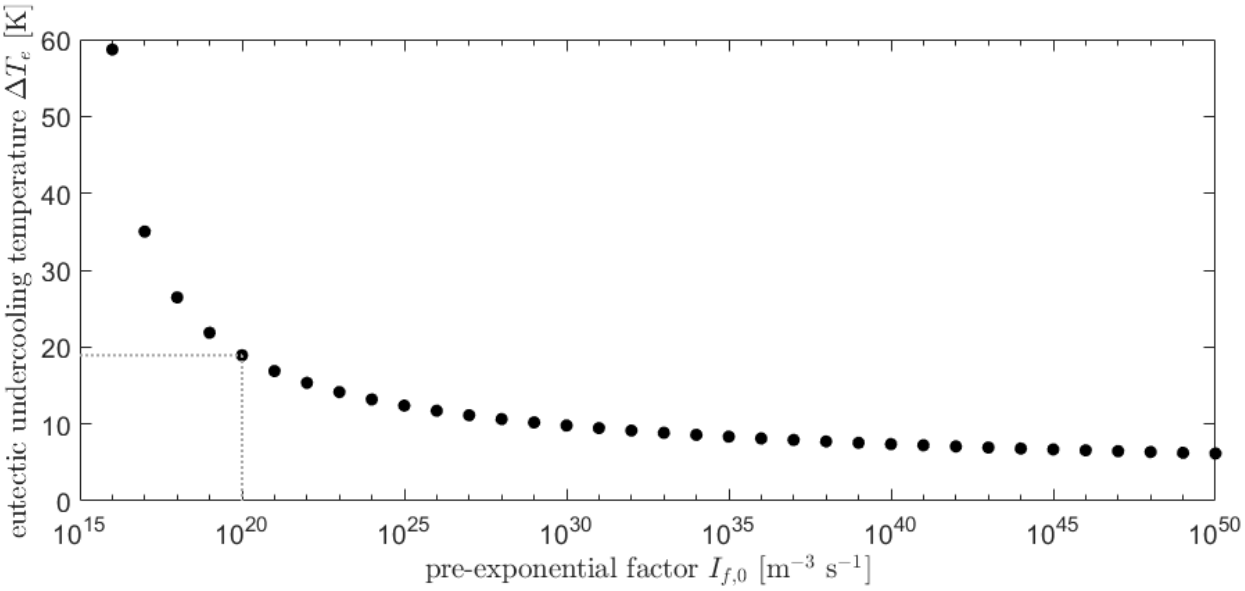


Figure 1: Effect of the pre-exponential factor on the predicted eutectic undercooling for a 196 µm IA droplet solidified in He.

**Results and discussion**

Using the values listed in Table 1 as well as the $I_{f,\theta}$ value of $10^{20}$ as shown in Figure 1 and the wetting angle for the primary phase nucleation of 12.6°, the undercooling values were determined for additional particle sizes atomized in both He and $N_2$ gases. The results shown in Table 2 were obtained with the numerical models of the droplet heat loss combined with the nucleation model. The predicted undercooling values are compared with the estimated values determined by Bogno *et al.* [11] using post portem data also listed in Table 2. Figure 2 is a graphical view the predicted and experimental undercoolings for 196 and 925 µm droplets solidified in helium and nitrogen atomospheres. The markers indicate the undercoolings at which

one stable nucleus forms according to equation (8), i.e. the minimum required undercoolings for nucleation. The bars represent the range of undercoolings obtainable with the use of the cumulative probability density function (equation 9) and the random number generator. The agreement between the model prediction of undercooling temperatures and the estimated values is fairly good, with a maximum deviation of 6 K.

Table 2: Experimental and predicted primary and eutectic undercoolings of 196 and 925 µm droplets solidified in He and $N_2$.

| $d$ [µm] | Gas | $\Delta T_p^{exp}$ [K] | $\Delta T_p^{model}$ [K] | $\Delta T_p^{model}$ Range [K] | $\Delta T_e^{exp}$ [K] | $\Delta T_e^{model}$ [K] | $\Delta T_e^{model}$ Range [K] |
|---|---|---|---|---|---|---|---|
| **196** | *He* | 14.4 | 14.4 | 14.4 – 17.4 | 20.9 | 18.9 | 18.9 – 24.2 |
| **925** | *He* | 14.3 | 11.1 | 11.1 – 12.4 | 20.0 | 14.0 | 14.0 – 16.0 |
| **196** | $N_2$ | 14.0 | 13.6 | 13.6 – 16.1 | 17.3 | 17.7 | 17.7 – 21.9 |
| **925** | $N_2$ | 14.0 | 10.8 | 10.8 – 12.0 | 17.6 | 13.7 | 13.7 – 15.5 |

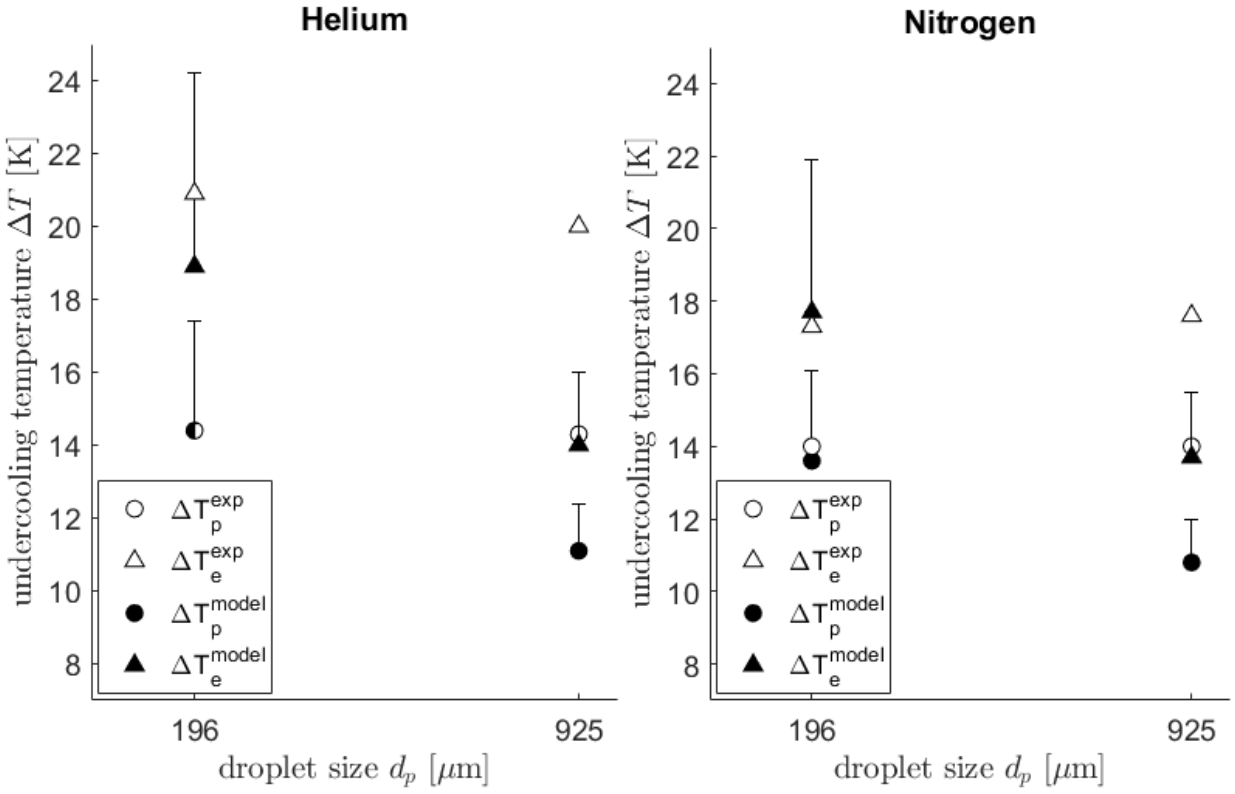


Figure 2: Predicted and experimental undercoolings of 196 and 925 µm droplets solidified in He (left) and $N_2$ (right). The bars represent the range of undercoolings obtainable with the use of the cumulative probability density function and the random number generator.

For 196 µm droplets in nitrogen atmosphere, a small derivation can be noticed. The primary undercooling temperature is predicted to be marginally lower than observed in the experiments. For the eutectic undercooling temperature a marginally greater undercooling temperature is predicted. Considering the possible undercooling range for the primary undercooling

temperature, the predicted undercooling temperature shows good agreement with the experimental results. The prediction for the eutectic undercooling remains greater than those obtained by Bogno *et al.*

The droplet size of 925 µm shows deviations from experimental results for both atmospheres. It can be seen that the undercooling temperatures are predicted to be lower. Furthermore, the predicted temperature range is narrower as compared to a droplet size of 196 µm for both the eutectic and the primary undercooling. From the model, this is not fully surprising as the volume of the droplet directly influences the number of nuclei at a given undercooling (equation 8). Futhermore, larger droplets experience a lower cooling rate, which also increases *n(T)*. The effect of cooling rate can also be seen when comparing droplets of the same size atomized in different gases. The thermal conductivity of helium being higher than that of nitrogen [21], droplets solidified in He experience higher cooling rates. Accordingly, the model predicts higher undercoolings for He-atomized particles. Finally, wetting angles are a function of the interfacial energies between the solid, liquid and the impurity [15], which in turn are a function of temperature. It is thus expected that the wetting angles change with the undercooling. However, no such temperature dependent data exists. A good fit of the experimental values can be obtained by modifying the wetting angles by less than 3°. Thus, the wetting angles used are considered reasonable.

A statistical analysis of the nucleation sites is shown in Figure 3. Using the density probabilty function with a random number generator adds a stochastical aspect to the nucleation model which is absent from the other models described in the introduction. This allows to reach a range of different undercoolings as shown in Table 2 and enables the formation of more than one stable nucleus. After running the program 150,000 times for each gas, it can be seen that in more than 85% of the simulations only one stable nucleus was created. In about 9.5% of the simulations, the nucleation was triggered by two nucleation sites. The possibilities for three nucleation sites to be formed is about 3.5%. More than three nucleation sites were rarely achieved. Using microtomography on a population of 0-212 µm diameter range droplets solidified in helium, Bedel *et al.* [16] found that 59 out of 62 droplets (95%) showed a single nucleation point while the remaining 3 (5%) had two nucleation events (Figure 3). Similar results were found for the 250-300 µm diameter range as well as for droplets solidified in argon. For the Al-4.5wt%Cu alloy, it is thus common to see only one nucleation site after solidification. Therefore the numerical results show a good agreement with experiments.

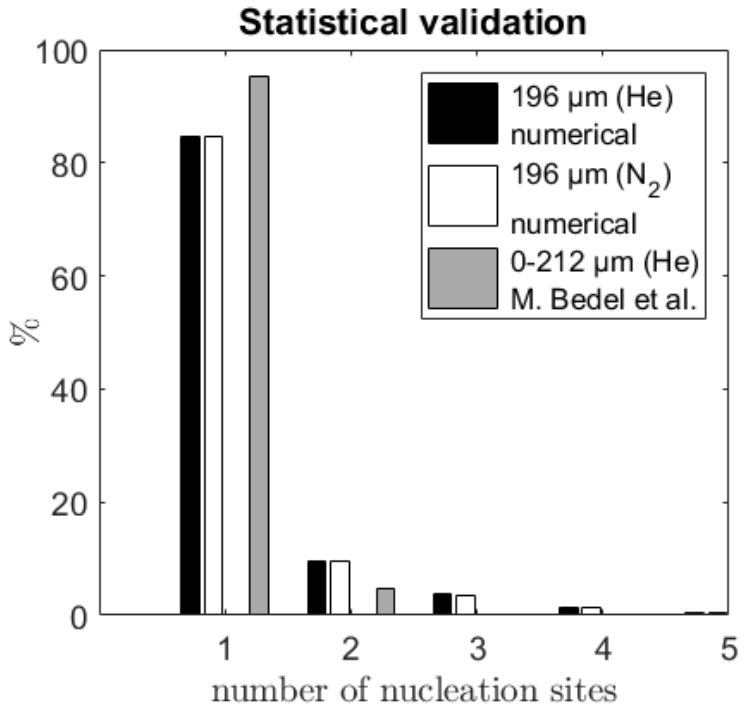


Figure 3: Histogram of the predicted number of stable nuclei and experimental observations from Bedel *et al.* [16]. The model was run 150,000 times for each atomizing gas.

**Conclusions**

A model for nucleation in undercooled droplets was successfully implemented for Impulse Atomization conditions. Both the primary and eutectic nucleation were predicted and show sensible results.

The wetting angle and the pre-exponential factor were successfully fitted to experimental data. The pre-exponential factor used in this work differs from other values found in literature and other work. Usually a value of about $10^{40}$ is used, akin to homogeneous. However, a pre-exponential factor of $10^{20}$ delivers reasonable results in regard to the primary and eutectic nucleation. For the wetting angle of the primary phase, a value of 12.6° shows good results.

The results from the simulation show good agreement with the experimental data. Primary and eutectic undercoolings for IA experiments were successfully validated and the number of nucleation points within a droplet agrees well with post-mortem microtomography investigations.

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