Nucleation behavior of melted Bi films at cooling rates from 101 to 104K/s studied by combining scanning AC and DC nano-calorimetry techniques

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Crystal nucleation behavior of melted Bi films encapsulated in silicon nitride at cooling rates from $10^1$ to $10^4$ K/s

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Abstract:

We have studied the nucleation behavior of undercooled liquid Bi at cooling rates ranging from $10^1$ to $10^4$ K/s using a combination of scanning DC and AC nano-calorimetry techniques. Upon initial melting, the Bi thin-film sample breaks up into isolated islands. The number of islands in a typical sample is sufficiently large that highly repeatable nucleation behavior is observed, despite the stochastic nature of the nucleation process. We establish a model based on classical nucleation theory to evaluate the nucleation rate from DC and AC calorimetry results. The results show that the nucleation behavior of melted Bi is well described by classical nucleation theory over a wide range of cooling rates. The proposed technique provides a unique and efficient way to examine nucleation kinetics with cooling rates over several orders of magnitude. The technique is quite general and can be used to evaluate nucleation kinetics in other materials.

Keywords: crystal nucleation; nano-calorimetry; AC calorimetry

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I. Introduction

The undercooling of liquid metals and alloys below their thermodynamic freezing temperature has been a topic of interest for many years. The degree of undercooling and the nucleation process that initiates the liquid-to-solid phase transformation greatly influence the ensuing microstructure and properties of a material. Due to the stochastic nature of the nucleation process, a single measurement of the undercooling response of an individual droplet does not provide sufficient information to determine the kinetic parameters. Instead, the kinetics of solidification is studied by measuring a large number of independent nucleation events in dispersions of similar individual droplets, or by measuring nucleation in a single droplet multiple times using the same temperature trace. While the single droplet method provides a direct observation of individual nucleation events, the droplet dispersion method guarantees identical thermal histories for all droplets and is more efficient, especially when the numbers of droplets in the dispersion is large (>10^3). The nucleation rate can then be determined from the distribution of undercooling values obtained for a fixed cooling rate, or by measuring the undercooling as a function of cooling rate.

Recent developments in nano-calorimetry have enabled very fast scanning measurements at cooling rates that are not accessible with traditional differential scanning calorimeters or differential thermal analyzers. For instance, Schick et al performed measurements on single droplets of Sn over a wide range of cooling rates (100 to 14,000 K/s) using a chip-calorimeter. Because these measurements are performed on single droplets, they require many replicas at each cooling rate to ensure statistical significance. Here we combine chip-calorimetry with thin-film deposition techniques to fabricate the samples. When a very thin metal film is deposited on a substrate with high interfacial energy and then melted, the film breaks up into a large number of very small isolated islands to minimize the interfacial energy between metal and substrate. The film thus forms a dispersion of individual droplets that is ideal for nucleation studies. This approach has the advantage of being able to measure a large set of nearly identical droplets in a single scan. We perform calorimetry measurements using a nanocalorimeter sensor derived from an original design by Allen and coworkers, which has negligible thermal lag between sample and temperature sensor thus enabling accurate temperature measurement at very high scanning rates. This nanocalorimeter sensor combined with the appropriate AC-technique is also capable of making accurate measurements at slow scan rates where heat loss to the environment makes DC measurements not practical, even allowing in-situ XRD measurements during the scans. By combining AC and DC techniques we have performed measurements on undercooled Bi samples at cooling rates from 10^1 to 10^4 K/s and use classical nucleation theory to interpret the experimental results.

The main text of this paper is organized into four sections. In Sec. II, we introduce the nanocalorimetry chip that was used for the measurements and describe the measurement setup.
In Sec. III, we briefly review classical nucleation theory and we provide models that enable quantitative interpretation of the DC and AC results. Results from nucleation experiments on thin-film samples of Bi are discussed in Secs. IV and V.

II. Experimental detail

The calorimetry measurements in this study were performed using a micromachined nanocalorimetry sensor that has been described in detail elsewhere. Briefly, the sensor consists of a tungsten four-point electrical probe that serves both as a heating element and a resistance thermometer. The tungsten probe is completely encapsulated in silicon nitride and is supported by a freestanding silicon nitride membrane. Figure 1 shows a schematic of the sensor.

In a typical measurement, a thin-film sample is deposited in the shaded area between the two voltage sensing leads and an electric current is applied to the tungsten heating element, which, in turn, heats the sample. The measured values of current and voltage are used to determine the power supplied to the sample, while the temperature of the sample is determined from the resistance of the heating element, which is calibrated to temperature by measuring the resistance as a function of temperature in a vacuum furnace at an Ar pressure of 1 Atm.

![Schematic of the calorimetry sensor. The sample deposition region shown in yellow is the same as the calorimeter measurement area.](image)

The nanocalorimetry sensor is installed in a probe card that is mounted inside a high vacuum furnace, with a base pressure of 10⁻⁷ Torr. The furnace provides a chemically inert ambient for the sensor, enabling measurements in both vacuum and inert gas environments. In this work, the furnace was filled with helium to promote heat loss from the sample and thus maximize cooling rates. Measurements with cooling rates greater than 10³ K/s were performed at a pressure of 1 Atm of helium, while all other scans were performed at a pressure of 700 mTorr.

All nanocalorimetry measurements were performed using a custom low-noise data acquisition system described in detail in reference. Typical noise levels in the measurements were less than 0.1%. DC measurements were performed by applying current profiles that were designed to carefully control the cooling rates. AC measurements were performed at an angular frequency of 3209 rad/s using AC and DC current components in accordance with the selection.
criteria in reference 21. For the DC measurements, both the temperature of the sample and the power supplied to it were determined directly from the sensor as described earlier. For the AC measurements, the in-phase and out-of-phase response of the sample was determined by dividing measured voltage and current signals into segments consisting of an integer number of AC oscillation periods, and applying a discrete Fourier transform (DFT) to every segment as described elsewhere 21,23.

The Bi sample was prepared by means of thermal evaporation in a vacuum chamber with a base pressure of $6 \times 10^{-7}$ Torr. A 200 nm film of Bi was deposited directly onto the silicon nitride surface of a nanocalorimetry sensor by thermal evaporation from a 99.999% pure Bi source. Immediately after deposition, the Bi film was coated with a 30 nm layer of silicon nitride by RF sputtering. After initial melting, the Bi film broke up into a stable dispersion of small, individual islands, as expected for a liquid film that does not wet the substrate 23. Optical micrographs of the sample (Fig. 2a) were analyzed using digital image processing tools to yield the size distribution of the droplets (Fig. 2b), which was well represented by a Gaussian. The total number of droplets in the sample was estimated at 6600 over an area of 1.92 mm$^2$; the average diameter of the droplets was approximately 2.0 µm. The silicon nitride capping layer aids with the formation of a uniform dispersion. Experiments without silicon nitride resulted in the formation of a small number of much larger droplets. Note that the size of the droplets is not small enough to cause any significant melting point depression 27.

Fig. 2. a) Optical micrograph of Bi thin film after initial melting; b) Bi islands size
distribution.

III. Modelling

A. Nucleation model for thin-film material

According to classic nucleation theory, the nucleation rate for a spherical nucleus is given as a function of temperature by the following expression $^3$:

$$J = A \exp\left(-\frac{\Delta G^* f(\theta)}{k_B T}\right),$$  \hspace{1cm} (1)

where the activation barrier to nucleation $\Delta G^*$ is given by

$$\Delta G^* = \frac{16\pi \gamma_{SL} T_m^2}{3L_v\Delta T^2},$$  \hspace{1cm} (2)

and where $A$ is a kinetic pre-factor that is practically insensitive to small changes of temperature, $k_B$ denotes the Boltzmann constant, $\gamma_{SL}$ is the solid-liquid interfacial energy, $T_m$ is the melting temperature, $\Delta T = T_m - T$ is the degree of undercooling, and $L_v$ is the enthalpy of melting. The function $f(\theta)$ is the catalytic potency factor for heterogeneous nucleation and is defined as the ratio of the activation energies for heterogeneous and homogeneous nucleation, respectively. This factor can be written in terms of the wetting angle $\theta$ of the nucleus

$$f(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2 / 4.$$  \hspace{1cm} (3)

The rate-determining step in the solidification of a very small metal droplet is the formation of a nucleus because the time to form a critical nucleus is typically much longer than the time it takes the nucleus to consume the droplet $^{28}$. Consequently, we assume that a droplet solidifies instantly upon formation of a nucleus. If we assign all droplets with volume $v_i$ (and thus a surface area of $s_i$) in the distribution to group $i$ and if we denote the number of droplets in that group by $n_i$, then

$$\sum_{i=1}^{m} n_i v_i = V,$$  \hspace{1cm} (4)

where $m$ is the total number of groups in the distribution and $V$ is the total volume of droplets at a given time. Let $I_i$ be the nucleation frequency per droplet for group $i$. The rate of nucleation then follows the law of radioactive decay $^3$,

$$\frac{dn_i}{dt} = -n_i I_i,$$  \hspace{1cm} (5)

provided the number of droplets is sufficiently large. Integrating this equation, it then follows that

$$n_i = n_{i0} \exp\left(-\int_0^t I_i dt\right),$$  \hspace{1cm} (6)
and
\[ \frac{dV}{dt} = \sum_{i=1}^{m} \frac{dn_i}{dt} v_i = - \sum_{i=1}^{m} n_{i0} v_i I_i \exp(-\int_{0}^{t} I_i dt), \tag{7} \]

where \( n_{i0} \) is the initial number of droplets in group \( i \). Equation (7) is very general and holds for any temperature history. For homogeneous nucleation, the expected nucleation frequency is given by
\[ I_i = J v_i, \tag{8} \]
while for the case of heterogeneous nucleation
\[ I_i = J s_i. \tag{9} \]

Equation (7) is not very useful in the analysis of experimental data because it is difficult to resolve the nucleation frequency for islands of different size. If the size distribution is sufficiently tight, however, the equation can be reformulated in terms of the average volume or surface area of the droplets:
\[ V = \left( \sum_{i=1}^{m} n_{i0} v_i \right) \exp(-\int_{0}^{t} I dt) = V_0 \exp(-\int_{0}^{t} I dt) \tag{10} \]
\[ \frac{dV}{dt} = -\left( \sum_{i=1}^{m} n_{i0} v_i I \right) \exp(-\int_{0}^{t} I dt) = -V_0 I \exp(-\int_{0}^{t} I dt), \tag{11} \]

where \( V_0 \) is the initial total volume of all liquid droplets and \( I \) is the nucleation frequency determined from the average volume \( v \) or surface area \( s \) of the droplets, depending on whether the nucleation process occurs homogeneously or heterogeneously. In Appendix I, we demonstrate that this approach works well for the distribution of droplet sizes in this study. Equation (11) provides the volumetric rate of solidification of a sample, which is directly related to the instantaneous heat flow \( H \) during solidification
\[ H = -L_v \frac{dV}{dt} = Q I \exp(-\int_{0}^{t} I dt), \tag{12} \]
where \( Q=L_v V_0 \) is the total enthalpy released during solidification and \( H \) is taken positive for an exothermic process. Equation (12) shows that the solidification of a dispersion of droplets can be described using a deterministic rule, even though individual nucleation events are stochastic.

B. Analysis of the nucleation kinetics for DC measurements

For a DC calorimetry measurement, the energy balance for the sensor can be written as
\[ P + H = C \frac{dT}{dt} + L, \tag{13} \]
where $P$ is the input power, $C$ is the total heat capacity of sample and addendum, $L$ is the rate of heat loss to the environment, and $H$ is the heat flow associated with the phase transformation. The power and temperature can be obtained directly from the sensor as described earlier; $C$ and $L$ can be determined as a function of temperature from a series of measurements at different cooling rates employing the procedure described in Appendix II. Once these quantities are known, the heat flow $H$ can be calculated as a function of temperature using Eq. (13). The nucleation rate can then be determined by fitting Eq. (12) to the experimental results. A more robust method of evaluating the nucleation rate uses information from measurements performed at different cooling rates following a Kissinger-type of analysis \(^{29}\). To this effect, it is instructive to take the natural logarithm of Eq. (12)

$$\ln H = \ln(A^\prime Q) - \frac{B}{T \Delta T^2} - \int_0^t I dt,$$

(14)

where $A^\prime = A^\nu$ or $A^s$ for homogeneous or heterogeneous nucleation, respectively, and $B$ is the kinetic factor

$$B = \frac{16\pi \gamma_{Sl}^2 T_m^2}{3L^2 k_B} f(\theta).$$

(15)

The first term on the right hand side of Eq. (14) is constant. If the enthalpy flow is evaluated at a fixed conversion fraction, the last term is constant also. Equation (14) then shows that the logarithm of the enthalpy flow is linearly related to $1/T \Delta T^2$. Thus a graph of the enthalpy flow at a fixed conversion fraction measured as a function of $1/T \Delta T^2$ for different cooling rates yields a straight line with the kinetic factor as slope. The derivation of Eq. (14) is quite general and there is no need for a constant cooling rate during the experiment.

C. Analysis of the nucleation kinetics for AC measurements

For a scanning AC measurement, the power supplied to the calorimeter consists of a DC component and an AC components with angular frequency $\omega$. The resulting temperature response can be written as

$$T = T_a + \theta,$$

(16)

where $T_a(t)$ is the average temperature over one oscillation period and $\theta(t)$ represents the oscillating part of the temperature. The energy balance for the sensor can then be written as \(^{21}\):

$$P_a + P_\omega + H(T_a + \theta, t) = C \frac{d(T_a + \theta)}{dt} + L(T_a + \theta),$$

(17)

where $P_a$ and $P_\omega$ represent the DC and AC components of the input power, respectively. If $\theta$ is small and the angular frequency is large so that the number of nucleation events that occur
during a single oscillation period is negligible, we can linearize $L$ and $H$ within one oscillation period so that

$$L = L_a + \frac{\delta L}{\delta T} |_{T_a} \theta = L_a + \alpha \theta, \quad (18)$$

$$H = H_a + \frac{\delta H}{\delta T} |_{T_a} \theta = H_a + \alpha_H \theta, \quad (19)$$

where $L_a$ and $H_a$ are the rate of heat loss and the enthalpy flow for the nucleation process at temperature $T_a$, respectively. Substituting Eq. (12) into Eq. (19) leads to the following expressions for $H_a$ and $\alpha_H$ at a fixed time $t$

$$H_a = I(T_a) Q \exp\left(\int_0^t 1 dt\right), \quad (20)$$

$$\alpha_H = \frac{\delta I}{\delta T} |_{T_a} Q \exp\left(\int_0^t 1 dt\right) = B g(T) H_a, \quad (21)$$

where

$$g(T) = \frac{(\Delta T - 2T)}{T^2 \Delta T^2}. \quad (22)$$

Substituting Eqs. (18) and (19) into Eq. (17) and separating the DC and AC terms, leads to the following two equations

$$P_a = C \frac{dT_a}{dt} + (L_a - H_a) = C \frac{dT_a}{dt} + L', \quad (23)$$

$$P_w = C \frac{d\theta}{dt} + (\alpha - \alpha_H) \theta = C \frac{d\theta}{dt} + \alpha' \theta. \quad (24)$$

Both the heat capacity $C$ and the coefficient $\alpha'$ can be determined from experimental calorimetry data using established methods $^{21, 23}$. The quantity of interest, $\alpha_H = - (\alpha' - \alpha)$, is non-zero only during the nucleation process. Thus $\alpha_H$ can be obtained by fitting the base line in a graph of $\alpha'$ as a function of temperature and by subtracting the baseline from the $\alpha'$ curve. If we take the natural logarithm of Eq. (21), we obtain an expression that is very similar to the enthalpy equation in the DC case (Eq. 15)

$$\ln(\frac{\alpha_H}{g}) - \ln B = \ln(\alpha' Q) - \frac{B}{T \Delta T^2} - \int_0^t 1 dt. \quad (25)$$

Similar to Eq. (15), Eq. (25) provides a linear relationship between $\ln(\alpha'/g)$ and $1/T \Delta T^2$, with the slope being the kinetic factor $B$ of interest, as long as $\alpha'/g$ is evaluated at a fixed conversion fraction. Since the right hand sides of Eqs. (15) and (25) are identical, it is possible to combine data points obtained from both DC and AC measurements into one linear fitting, provided that
the \( \ln(\alpha_f/g) \) data points are shifted by \(-\ln B\). As the parameter \( B \) is not known a priori, it is necessary to perform the fit using a recursive approach.

It should be noted that neither Eq. (14) nor (25) requires a constant scanning rate unlike most other Kissinger-type measurements \(^{29}\). This is an especially useful property for nano-calorimetric measurements, where the latent heat can easily change the scanning rate, and a feedback control of the temperature is not always feasible.

**IV. Results**

Figure 3a displays cooling rate traces for a total of 22 scans of the Bi sample. The solid curves represent DC scans with cooling rates ranging from \(-2 \times 10^4\) K/s to \(-1 \times 10^3\) K/s, while the dashed curves represent AC scans with cooling rates from \(-1 \times 10^3\) K/s to \(-30\) K/s. During solidification, the cooling rate first decreases as the latent heat is released. This drop is followed by an increase in cooling rate, sometimes overshooting the original cooling rate especially at smaller cooling rates. This overshooting is not the result of any phase transition, but is caused by a temporary increase in heat loss from the sample as discussed elsewhere \(^{21,23}\). It is evident from the figure that solidification takes place at ever-lower temperatures as the cooling rate increases.

Figure 3b shows ten DC cooling scans obtained under identical experimental conditions. It is evident that the cooling trace is extremely reproducible. The solidification process starts at approximately 450 K and ends around 400 K, spread out over more than 50 K. This result stands in contrast with experiments on single droplets, where the stochastic nature of the nucleation event causes the trace to vary significantly from measurement to measurement. This reproducibility is in line with previous measurements on similar samples \(^{21,23}\) and provides direct evidence that the number of isolated Bi droplets is sufficiently large that Eq. (5) is valid.
Using the energy balance, Eq. (13), the enthalpy flow $H$ can be determined as a function of time from the DC data in Fig. 3a. The results are shown in Fig. 4a. As the cooling rate decreases, the maximum amplitude of enthalpy peak decreases and the solidification process takes a longer period of time to complete. The same trends appear in the $\alpha H/g$ curves for AC scans (Fig. 4b), which is as expected given that $\alpha H/g$ is proportional to $H_a$ according to Eq. (21). The duration of the solidification process changes from several milliseconds for the fastest DC scan to several seconds for the slowest AC scan. The conversion fraction is determined as a fraction of the total heat released during the nucleation process $^{29}$, which can be calculated for the DC scans by integrating the enthalpy flow $H$ over time. The procedure for the AC results is similar, but now $\alpha H/g(T)$ is integrated instead of $H$. In both cases, we used the temperature at 50% conversion to determine the undercooling to minimize any errors introduced by the baseline subtraction.
Fig. 4. a) Reaction heat flow as function of time for nucleation in DC cooling scans. The origin of time corresponds to 480 K for each cooling scan. 

b) $\alpha H/g$ curves as a function of time for nucleation in AC cooling scans. The origin of time corresponds to 460 K for each cooling scan.

Figure 5a shows the undercooling as a function of cooling rate, where the cooling rate at 450 K was used as the nominal cooling rate. As is expected, larger cooling rates result in greater undercooling. The maximum undercooling exceeds 120 K at cooling rates greater than $2 \times 10^4$ K/s, while a cooling rate of 30 K/s still results in an undercooling larger than 100K. Figure 5(b) shows a combined plot of ln(H) for all DC cooling scans and ln($\alpha H/g$) as a function of $1/T\Delta T^2$. In this graph, the AC data was shifted in the y-direction by an amount -$\ln(B)$, where B was determined using recursive least squares regression. The figure clearly illustrates that the AC and DC data are in good agreement with each other and in particular that the slopes of both sets of data are the same. The linear relationship between the data indicates that a single nucleation mechanism is active over three orders of magnitude of cooling rate. The kinetic factor B and the pre-factor $A^\ast$ can be calculated from the slope and intercept of the linear fit using Eq. (14) or (25). The catalytic potency factor $f(\theta)$ and the contact angle can be calculated from Eq. (15) using literature values for the physical properties of Bi: $T_m=544.7$ K, $L_v=5.288e8$ J/m$^3$, and $\gamma_{SL}=0.0544$ J/m$^{2.8}$. The results are summarized in Table I.
Fig. 5. a) Degrees of undercooling as a function of cooling rate. b) Nucleation kinetics plot of the logarithm of the reaction power as function of $1/T\Delta T^2$ at 50% conversion.

Table I. Summary of results

<table>
<thead>
<tr>
<th>$Q$ (J)</th>
<th>Intercept (ln(W))</th>
<th>$B$ ($K^3$)</th>
<th>$A^*$ (s$^{-1}$)</th>
<th>$f(\theta)$</th>
<th>$\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(5.15\pm0.27)\times10^5$</td>
<td>10.70±1.35</td>
<td>$(9.01\pm0.74)\times10^7$</td>
<td>$1.72\times10^{(9\pm0.59)}$</td>
<td>0.435</td>
<td>85</td>
</tr>
</tbody>
</table>

V. Discussion

Nucleation of a solid phase in a melt is by nature a stochastic process. In the present case, the solidification peaks of a thin-film sample of Bi are highly reproducible, giving the appearance of a deterministic solidification process. The reproducibility in our experiments arises because the Bi film breaks up into a very large number of isolated islands and solidification of the sample is not the result of a single nucleation event, but that of a very large number of independent events. The calorimetry trace can be regarded as the cumulative superposition of the traces for all individual nucleation events and there is no need to perform a large number of measurements at a given cooling rate.

The nanocalorimetry measurements demonstrate significant undercooling before nucleation takes place, but the degree of undercooling varies less than 20 K as the cooling rate is changed
over three orders of magnitude. This result stands in contrast with typical chemical reactions, where changes in heating rate result in much larger shifts in reaction temperature \(^{29}\). Thus the ability to study nucleation over a wide range of cooling rates is essential for accurate measurement of the kinetic parameters. Scanning DC nanocalorimetry can be used to study the reaction at ultra-fast cooling rates, while scanning AC calorimetry works for medium and low rates. The maximum cooling rate is set by the heat loss from the sample to the environment. Considering the large surface to volume ratio of the thin-film sample, this heat loss occurs primarily by heat transport through the helium, and can be enhanced by increasing the pressure and by decreasing the distance between the sample and a nearby heat sink. The minimum cooling rate is set by the resolution of the \(\alpha\)-signal in the AC measurements. As the cooling rate decreases, the peak in the \(\alpha\)-curve decreases, resulting in a larger relative error following baseline subtraction. This constraint can be relaxed by amplifying the \(\alpha\)-signal using a lock-in amplifier.

Equations (14) and (25) are derived through a straightforward application of classical nucleation theory to a collection of droplets under the conditions of a DC or AC scanning calorimetry experiment. The equations provide a convenient means of analyzing nucleation results as illustrated by the results for Bi in Fig. 5b. The results demonstrate that a single nucleation mechanism is active over three orders of magnitude of cooling rate. The catalytic potency factor for heterogeneous nucleation is less than unity indicating that the Bi/SiNx interface catalyzes the nucleation process – the wetting angle of the nucleus is much smaller than 180°. Considering the large interface-volume ratio for the droplets, it is not surprising that heterogeneous nucleation is preferred. It is of course possible that some droplets contain nucleation sites of stronger potency, but their number is evidently not large enough to affect the results.

Finally we need to point out that there are two experimental factors that could potentially affect the results adversely: the temperature uniformity across the sample area and the temperature oscillations of the AC measurements. We have performed extensive finite element simulations of the temperature distributions in the nano-calorimetry sensor \(^{21}\). These simulations show that the temperature distribution is quite uniform across the sample area with \(\sim 2\%\) of variation and that it is nearly identical for all scans \(^{21}\). Thus the effect of temperature non-uniformity on the nucleation analysis is negligible. The scanning AC measurements were conducted following protocols established previously \(^{21}\) and the corresponding temperature oscillation were controlled to be \(\sim 3\) K at the solidification temperature. This temperature oscillation is small compared to the undercooling so that the linearization in Eq. (18) and (19) is acceptable.

VI. Conclusion

We have studied the nucleation behavior of Bi droplets over a wide range of cooling rates by combining both scanning DC and AC nano-calorimetry techniques. The Bi sample is fabricated using thermal evaporation. Upon initial melting, the Bi film breaks up into a large number of individual droplets that solidify independently. As a result the calorimetry trace samples a very
large number of nucleation events resulting in highly repeatable measurements in spite of the stochastic nature of nucleation. By applying classical nucleation theory to a collection of droplets under the conditions of a DC or AC scanning calorimetry experiment, simple equations are derived to analyze the calorimetry traces. The results indicate that nucleation of solid Bi occurs heterogeneously and that a single nucleation mechanism is active over three orders of magnitude of cooling rate.

VII. Acknowledgement

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Appendix I: Effect of size distribution on the nucleation rate.

Using the data in Table 1, we compare the solidification rates of two sets of Bi droplets: a set of droplets of uniform size where the solidification rate is given by Eq. (10), and a set of droplets that follow the experimental size distribution (Fig. 2b) where the solidification rate is given by Eq. (7). The results are depicted in Fig. 6. It is obvious from the figure that the effect of the precise size distribution is negligible: A 0.5 K difference in peak temperature and a 2% difference in peak height.

Fig. 6. Normalized solidification rate as a function of temperature for droplets that are uniform in size and for droplets that follow the experimental distribution. The time-temperature trace of the fastest DC scan is used in the calculation.

Appendix II: Data reduction scheme for DC measurements
For a series of $n$ DC calorimetry scans each performed at a different scan rate, the heat balance equations in the absence of any reaction or phase transformation are given by

\[
P_1 = C \left( \frac{dT}{dt} \right)_1 + L; \\
P_2 = C \left( \frac{dT}{dt} \right)_2 + L; \\
P_n = C \left( \frac{dT}{dt} \right)_n + L,
\]

where $P$, $C$ and $L$ have the same physical meaning as in Eq. (13), and the subscripts refer to individual scans. As pointed out previously, both the power supplied to each sensor and its temperature are readily determined as a function of time. Assume that $C$ and $L$ are functions of temperature only. Equation (26) can then be considered as a set of linear equations in $C$ and $L$. At each temperature, $C$ and $L$ can be evaluated from a linear fit of $P_i$ as a function of $(dT/dt)_i$, i.e., $C$ and $L$ can be determined as a function of temperature. During a reaction or phase transformation, this linear relationship does not hold. In this case, it may be possible to estimate $C$ and $L$ by interpolation. If heat loss occurs primarily by transient conduction, $L$ depends on the entire temperature history of the sensor and this approach fails.

Figure 7 depicts the results obtained for the various DC scans in a 1 atm Helium environment. Figure 7a shows the linear relationship between applied power and scan rate for three representative temperatures, while Figs. 7b and 7c show results for $C$ and $L$ over the entire temperature range, except during the phase transformation. It is evident from the figure that the heat capacity of the super-cooled liquid bismuth is slightly larger than that of solid bismuth, in agreement with previous AC nano-calorimetry measurements on thin-film samples $^{23}$ and with measurements on bulk samples $^{30}$. The heat loss curve is linear over the temperature range of the experiments, indicating that radiative heat loss is negligible. This result combined with the observation that the heat loss increases with helium pressure suggests convection through the helium as the main heat loss mechanism.
Fig. 7. a) Applied power as a function of scan rate for three representative temperatures; b) Heat capacity and c) heat loss obtained from a linear fitting of Eq. (26) at each temperature.
References:
