Nucleation behavior of melted Bi films at cooling rates from $10^1$ to $10^4$ K/s studied by combining scanning AC and DC nano-calorimetry techniques

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**ABSTRACT**

We study 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 silicon nitride-coated 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 data reduction technique to evaluate the nucleation rate from DC and AC calorimetry results. The results show that the driving force for the nucleation 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 reaction kinetics in other materials.

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1. Introduction

The undercooling of liquid metals and alloys below their thermodynamic freezing temperature has been a topic of interest for many years [1–8]. 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 [3,4,9–13], or by measuring nucleation in a single droplet multiple times using the same temperature trace [6,7,14–16]. 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 [6,7,17], or by measuring the undercooling as a function of cooling rate [3,13].

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 (100–14,000 K/s) using a chip-calorimeter [15,18]. 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 similar droplets in a single scan. We perform calorimetry measurements using a nanocalorimeter sensor derived from an original design by Allen and co-workers [19,20], 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 [21] is also capable of making accurate measurements at medium to slow scan rates where heat loss to the environment makes DC measurements not practical [22], even allowing in-situ XRD measurements during the scans [23,24]. 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 Section 2, we introduce the nanocalorimetry chip that was used for the measurements and describe the measurement setup. In Section 3, we describe a data reduction technique that combines DC and AC calorimetry results to study reaction kinetics. We then apply this technique to classical nucleation theory in Section 4. Results from the nucleation experiments on thin-film samples of Bi are discussed in Sections 5 and 6.

2. Experimental details

The calorimetry measurements in this study were performed using a micromachined nano-calorimetry sensor that has been described in detail elsewhere [21,25,26]. 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, which in turn is supported by a silicon frame. Fig. 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 using a standard procedure described in detail in Refs. [21,23].

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 $10^3$ 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 Ref. [21]. 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 Ref. [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. During 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 radius of the droplets was approximately 2.0 µm. During melting, the silicon

![Fig. 1. Schematic of the calorimetry sensor. The sample deposition region shown in yellow is the same as the calorimeter measurement area. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)](image)

![Fig. 2. (a) Optical micrograph of Bi thin film after initial melting; (b) Bi islands size distribution.](image)
nitride capping layer remained on top of the Bi droplets and aided 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].

3. Analysis of reaction kinetics by combining DC and scanning AC measurement results

3.1. DC calorimetry measurements

For a single-step reaction, it is common to assume that the rate of reaction follows [28]:

\[ \frac{dH}{dt} = k(T)r(x), \]

where \( H \) is the enthalpy of reaction, \( Q \) is the total enthalpy of reaction, and \( x \) is the extent of conversion ranging from 0 to 1. The enthalpy flow \( H \) is taken positive for an exothermic process. For a DC calorimetry measurement, the energy balance for the sensor can be written as

\[ P + H = C \frac{dT}{dt} + L, \]

where \( P \) is the input power, \( C \) is the total heat capacity of sample and addendum, and \( L \) is the rate of heat loss to the environment. 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 A. Once these quantities are known, the enthalpy flow \( H \) can be calculated as a function of temperature using Eq. (2). The conversion fraction \( x \) at an instance of time \( t \) is then determined as the fraction of the total enthalpy of reaction released at that time [28], given by

\[ x(t) = \frac{\int_0^t \frac{Hdt}{Q}}{\int_0^\infty \frac{Hdt}{Q}} \]

3.2. Scanning AC calorimetry measurements

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

\[ T = T_d + \theta, \]

where \( T_d(t) \) 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]:

\[ P_d + P_o + H(T_d + \theta, x) = C \frac{dT_d}{dt} + L(T_d + \theta), \]

where \( P_d \) and \( P_o \) represent the DC and AC components of the input power, respectively. If \( \theta \) is small and the angular frequency is large enough that the change in \( x \) during a single oscillation period is negligible, we can linearize \( L \) and \( H \) within one oscillation period so that

\[ L(T_d + \theta) = L_d + \frac{dL}{dT} \theta = L_d + \alpha \theta, \]

\[ H = \hat{H} + \frac{dH}{dT} \theta \]

where \( L_d \) and \( H_d \) are the rate of heat loss and the enthalpy flow for the nucleation process at temperature \( T_d \), respectively. Substituting Eqs. (6) and (7) into Eq. (5) and separating the DC and AC terms, leads to the following two equations

\[ P_d = C \frac{dT_d}{dt} + (L_d - \hat{H}_d) = C \frac{dT_d}{dt} + L', \]

\[ P_o = C \frac{d\theta}{dt} + (\alpha - \alpha_H) \theta = C \frac{d\theta}{dt} + \alpha' \theta \]

Both the heat capacity \( C \) and the coefficient \( \alpha' \) can be determined from experimental calorimetry data using established methods [21,23]. In Eq. (9), \( \alpha_H = (\alpha' - \alpha) \) is non-zero only during the nucleation process. Thus \( \alpha_H \) can be obtained by first performing a least square fit of the \( \alpha' \) signal as a function of temperature in the region outside the reaction to determine the baseline, and then subtracting the baseline from the \( \alpha' \) curve. The quantity \( \alpha_H \) is of interest because it is directly related to the kinetics of the reaction. Indeed, substituting Eq. (1) into Eq. (7) leads to the following expressions for \( \alpha_H \)

\[ \frac{\partial}{\partial T} \ln \left( \frac{k(T)}{\alpha_H} \right) = Q \frac{\partial k(T)}{\partial T} \frac{r(x)}{H}, \]

It is evident from this equation that

\[ \frac{\partial}{\partial T} \ln \left( \frac{k(T)}{\alpha_H} \right) = Q \frac{\partial k(T)}{\partial T} \frac{r(x)}{H}, \]

i.e., the quantity on the left hand side of this equation is equal to the enthalpy flow. Depending on the precise form of \( k(T) \), this expression may be used in Eq. (3) to determine the extent of reaction during an AC measurement.

3.3. Combining both DC and AC measurement results

If we take the natural logarithm of Eqs. (1) and (11), we obtain expressions for DC and AC measurements

\[ \ln \frac{H}{Q} + \ln k(T) + \ln r(x), \]

\[ \ln \alpha_H - \ln \left( \frac{\partial}{\partial T} \ln k(T) \right) = \ln Q + \ln k(T) + \ln r(x), \]

Eqs. (12) and (13) can be applied to a series of DC and AC measurements with varying scanning rate for the analysis of reaction kinetics. For instance, for an Arrhenius type of reaction, we have:

\[ k(T) = A \exp \left( \frac{-E_a}{k_B T} \right) \]

where \( A \) is the pre-factor, \( E_a \) is the activation energy, and \( k_B \) the Boltzmann constant. Substituting Eq. (14) into (12) and (13) yields

\[ \ln H = \ln(AQ) + \ln r(x) - \frac{E_a}{k_B T} \]

\[ \ln(\alpha_H T^2) - \ln \left( \frac{E_a}{k_B T} \right) = \ln(AQ) + \ln r(x) - \frac{E_a}{k_B T} \]

If the pre-factor is temperature independent, the first term on the right hand side of Eq. (15) is constant. If the enthalpy flow is evaluated at a fixed conversion fraction, the second term is constant also. Eq. (15) then shows that the logarithm of the enthalpy flow is linearly related to \( 1/T \). Thus a graph of the enthalpy flow at a fixed conversion fraction as a function of \( 1/T \) yields a straight line with \( E_a/k_B \) as slope. Eq. (16) is a special case of Eq. (11) and shows that \( \alpha_H T^2 \) is proportional to the enthalpy flow. The conversion fraction for the AC measurement can then be calculated from Eq. (3) where \( \alpha_H T^2 \) takes the place of \( H \) as the integrand. Similar to Eq. (15), Eq. (16) provides a linear relationship between \( \ln(\alpha_H T^2) \) and \( 1/T \) with the same slope \( E_a/k_B \), as long as \( \alpha_H T^2 \) is evaluated at a fixed conversion fraction. Since the right hand sides of Eqs. (15) and (16) are identical, it is possible to combine data points obtained from both DC and AC measurements into one linear fitting, provided that the...
\[ \ln(a_{T}T^{2}) \text{ data points are shifted by } -\ln(E_{a}/k_{B}). \text{ As the parameter } E_{a} \text{ is not known a priori, it is necessary to perform the fit using a recursive approach.} \]

The combination of DC and AC results enables kinetic analysis of the reaction over a wide range of scanning rates. It should be noted that neither Eq. (12) nor (13) requires a constant scanning rate, but rather the direct measurements of \( H \) and \( \alpha_{H} \). 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. We will show in the next section that the same technique can also be applied to non-Arrhenius type processes such as nucleation.

4. Application to nucleation theory

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

\[ J = A \exp\left[ -\frac{\Delta G^{*}(T)}{k_{B}T} \right] \]

(17)

where the activation barrier to nucleation \( \Delta G^{*} \) is given by

\[ \Delta G^{*} = \frac{16\pi r_{SL}^{2}T_{m}^{2}}{3} \frac{1}{L_{o}^{2} \Delta T^{2}} \]

(18)

and where \( k_{B} \) denotes the Boltzmann constant, \( r_{SL} \) is the solid–liquid interfacial energy, \( T_{m} \) is the melting temperature, \( \Delta T = T_{m} - T \) is the degree of undercooling, and \( L_{o} \) is the enthalpy of melting. \( A \) is a kinetic pre-factor that depends exponentially on temperature [8]. The temperature dependence of the pre-factor is, however, much weaker than that of the exponential factor in Eq. (17), because of the strong dependence of \( \Delta G^{*} \) on the undercooling. Consequently, \( A \) is treated as practically insensitive to temperature in the analysis of nucleation kinetics [3,6,7,10]. 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 contact angle \( \theta \) of the nucleus,

\[ f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)}{4} \]

(19)

and is equal to unity for an angle of \( \pi \). If the size of the droplets in the dispersion is small (<10 \( \mu \)m), as is the case in our study, the majority of the droplets should be free from catalytic nucleation sites within their volume [5,12,29]. Thus nucleation will either proceed homogeneously in the bulk of the droplets or be catalyzed by the interface with the silicon nitride. In the latter case, we assume that all droplets have the same contact angle \( \theta \), and thus the same catalytic potency factor \( f(\theta) \). 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 [30]. 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 or interfacial area of \( s_{i} \)) in the distribution to group \( i \), and if we denote the number of droplets and the nucleation frequency per droplet in that group by \( n_{i} \) and \( i_{i} \), respectively, the rate of nucleation then follows the law of radioactive decay [3]

\[ \frac{dn_{i}}{dt} = -n_{i}i_{i} \]

(20)

provided the number of droplets is sufficiently large. For bulk nucleation, the expected nucleation frequency is given by

\[ i_{i} = jv_{i} \]

(21)

while for interface nucleation:

\[ i_{i} = js_{i} \]

(22)

Integrating Eq. (20) over time, it then follows that

\[ n_{i} = n_{i0} \exp\left( -\int_{0}^{t} i_{i}(T(t))dt \right) \]

(23)

where \( n_{i0} \) is the initial number of droplets in group \( i \), and where the nucleation frequency \( i_{i} \) varies with time via the temperature history of the sample. The total volume of unsolidified droplets and the volumetric rate of solidification can then be calculated as

\[ V = \sum_{i=1}^{m} n_{i}v_{i} = \sum_{i=1}^{m} v_{i}n_{i0} \exp\left( -\int_{0}^{t} i_{i}(T(t))dt \right) \]

(24)

\[ \frac{dV}{dt} = \sum_{i=1}^{m} \frac{dn_{i}}{dt}v_{i} = -\sum_{i=1}^{m} n_{i0}v_{i} \exp\left( -\int_{0}^{t} i_{i}(T(t))dt \right) \]

(25)

where \( m \) is the total number of groups in the distribution and \( V \) is the total volume of droplets at a given time. Eqs. (24) and (25) are very general and hold for any temperature history, but they are 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 equations can be reformulated in terms of the average volume or interfacial area of the droplets,

\[ V = \left( \sum_{i=1}^{m} n_{i0}v_{i} \right) \exp\left( -\int_{0}^{t} l_{i}(T(t))dt \right) = V_{0} \exp\left( -\int_{0}^{t} l_{i}(T(t))dt \right) \]

(26)

\[ \frac{dV}{dt} = -\left( \sum_{i=1}^{m} n_{i0}v_{i} \right) l_{i} \exp\left( -\int_{0}^{t} l_{i}(T(t))dt \right) = -V_{0} l_{i} \exp\left( -\int_{0}^{t} l_{i}(T(t))dt \right) \]

(27)

where \( V_{0} \) is the initial total volume of all liquid droplets and \( l_{i} \) is the nucleation frequency determined from the average volume \( v \) or interfacial area \( s \) of the droplets, depending on whether the nucleation process occurs in the bulk or at the interface. In Appendix B, we analyze the error associated with this simplification and demonstrate that this approach works well for the distribution of droplet sizes in this study. Eq. (27) provides the volumetric rate of solidification of a sample, which is directly related to the instantaneous enthalpy flow \( H \) during solidification

\[ H = -L_{v} \frac{dV}{dt} = QI \frac{V}{V_{0}} = QI(1 - x) \]

(28)

where \( Q = L_{v}V_{0} \) is the total enthalpy released during solidification and the conversion fraction is given by \( x = 1 - V/V_{0} \). Eq. (28) shows that the solidification of a dispersion of droplets can be described using a deterministic rule, even though individual nucleation events are stochastic. Comparing Eq. (28) with Eq. (1), the nucleation model can be cast into the general formalism by letting

\[ k(T) = l = A^{*} \exp\left( -\frac{B}{T \Delta T^{2}} \right) \]

(29)

\[ r(x) = 1 - x \]

(30)

where \( A^{*} = A v \) or \( A s \) for bulk or interface nucleation, respectively, and \( B \) is the kinetic factor

\[ B = \frac{16\pi r_{SL}^{2}T_{m}^{2}}{3L_{v}k_{B}} f(\theta) \]

(31)

Substituting Eqs. (29) and (30) into Eqs. (12) and (13) yields the following equations for DC and AC measurements

\[ \ln I = \ln H - \ln[1 - x]Q = \ln A^{*} - \frac{B}{T \Delta T^{2}} \]

(32)
\[ \ln I = \ln \left( \frac{\Delta H}{g} \right) - \ln[(1 - x)Q] - \ln B = \ln A^\ast - \frac{B}{\Gamma \Delta T^2}, \]  

where
\[ g = \frac{\Delta T - 2T}{T^2 \Delta T^3} \]

For a given conversion fraction, both \((1 - x)\) and \(Q\) are known constants. Thus, Eq. (32) provides a way to calculate the nucleation frequency \(I\) from the enthalpy flow in a DC measurement. Eq. (32) also shows that the logarithm of the enthalpy flow is linearly related to \(1/\Gamma \Delta T^2\), with the kinetic factor \(B\) as the slope. Similar to Eq. (32), Eq. (33) provides a linear relationship between \(\ln(\Delta H/g)\) and \(1/\Gamma \Delta T^2\) with the same slope \(B\), as long as \(\Delta H/g\) is evaluated at the same fixed conversion fraction. The conversion rate can be calculated from Eq. (3), where \(\alpha(t)\) replaces \(H\) as the integrand. As the right hand sides of Eqs. (32) and (33) are identical, it is possible to combine data points obtained from both DC and AC measurements into one linear fit, provided that the \(\ln(\Delta H/g)\) data points are shifted by \(-\ln B\), which can be done with a recursive approach.

5. Results

Fig. 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 \(-2 \times 10^3\) 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.

Fig. 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. (20) is valid.

Using the energy balance, Eq. (2), 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 \(\alpha(t)g\) curves for the AC scans (Fig. 4b), which is expected given that \(\alpha(t)g\) is proportional to \(H\) according to Eqs. (32) and (33). The duration of the solidification process changes from several milliseconds for the fastest DC scan to several seconds for the slowest AC scan. In both cases, we calculate the nucleation frequency at 50% conversion to minimize any errors introduced by the baseline subtraction, using either Eq. (32) or (33).

Fig. 5a shows the undercooling at 50% conversion as a function of cooling rate, where the cooling rate at 450 K was used as the nominal cooling rate. As 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 100 K. Fig. 5b shows a combined plot of \(\ln(I)\) for all DC and AC cooling scans as a function of \(1/\Gamma \Delta T^2\). In this graph, the AC data were shifted in the y-direction by an amount \(-\ln(B)\) as seen in Eq. (33), 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. (32) or (33). The catalytic potency factor \(f(\theta)\) and the contact angle \(\gamma\) can be calculated from Eqs. (31) and (19) using literature values for the physical properties of Bi: \(T_m = 544.7\) K, \(\rho_v = 5.288 \times 10^3\) J/m\(^3\), and \(\gamma_{sa} = 0.0544\) J/m\(^2\) [8]. The results are summarized in Table 1. In the analysis, the interfacial area was calculated as the total surface area of the droplets because the droplets were completely encapsulated in silicon nitride.

6. 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

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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 [28]. 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 interface 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.

The technique described in Section 3 makes it possible to combine both DC and AC measurement results in the analysis of reaction kinetics. The technique can be applied to general single-step reactions, and depending on the specific reaction model, may require a recursive approach in order to combine both DC and AC data points into one single curve. This approach is valid only if the reaction of

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Table 1

Summary of results.

<table>
<thead>
<tr>
<th>( Q ) ((J))</th>
<th>Intercept ((\ln(s^{-1})))</th>
<th>( A' ) ((s^{-1}))</th>
<th>( A\times A' ) ((m^2 \cdot s))</th>
<th>( B ) ((K^\circ))</th>
<th>( f(\theta))</th>
<th>( \theta (%))</th>
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</thead>
<tbody>
<tr>
<td>((5.15 \pm 0.27) \times 10^{-5})</td>
<td>21.31 ± 1.4</td>
<td>(1.8 \times 10^{0.68})</td>
<td>(3.58 \times 10^{19.68})</td>
<td>((9.04 \pm 0.76) \times 10^7)</td>
<td>0.436</td>
<td>85.1</td>
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</tbody>
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![Fig. 4](image1.png)  
(a) Reaction enthalpy flow as function of time for nucleation in DC cooling scan. (b) \( \alpha \)-/\( \gamma \)-curves as a function of time for nucleation in AC cooling scans. The origin of time corresponds to 500 K for each cooling scan, and the corresponding cooling rates are shown in Fig. 3a.

![Fig. 5](image2.png)  
(a) Undercooling at 50% conversion as a function of the nominal cooling rate at 450 K. (b) Graph of the logarithm of the nucleation frequency at 50% conversion as a function of \( 1/T\Delta T^2 \).

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interest follows the same reaction model over the entire range of scanning rates.

Eqs. (32) and (33) are derived through a straightforward application of classical nucleation theory to a collection of droplets. The equations provide a convenient means of analyzing nucleation results as illustrated by the results for Bi in Fig. 5b. The straight line in the log(\(f(T)\)) vs. \(\Delta T^2\) plot demonstrates that the nucleation rate is well described by classical nucleation theory. It also indicates a single nucleation mechanism is active over three orders of magnitude of cooling rate [6]. As noted before, the droplets are too small for bulk heterogeneous nucleation [12,29], leaving the possibilities of either homogenous nucleation or heterogeneous nucleation catalyzed by the interface with the silicon nitride. This is further supported by the fact that nucleation does not usually follow the classical rate Eq. (17) if bulk heterogeneous nucleation is dominant, because accidental catalysts of varying degrees of effectiveness (i.e. different \(f(\theta)\) values) are liable to be present in different droplets [8]. The value of \(f(\theta)\) is found to be less than unity, indicating that the Bi/SiN\(_x\) interface catalyzes the nucleation process. Considering the large interface-volume ratio for the droplets, it is not surprising that interface heterogeneous nucleation is preferred. We further note that the value of \(A\) in our measurement is much smaller than the theoretical estimate of 10\(^{29.5}\) m\(^{-2}\) s\(^{-1}\) by Turnbull [8]. Such a difference is not uncommon and can be accounted for by a modest temperature-dependence of the interfacial energy, to which \(A\) is extremely sensitive [3,31]. For example, Turnbull measured a value of \(A\) that is 7 orders of magnitude larger than the theoretical estimate, which can be accounted for by a temperature-dependence of approximately 0.1%/K of the interfacial energy [3]. In fact, Sapaev has exploited this discrepancy between the experimental and theoretical values of \(A\) to study the temperature-dependence of the interfacial energy [31].

The Bi nucleation behavior we observed is similar to a previous study by Chaubey et al. [13] on the nucleation of Bi droplets entrapped in a Zn-matrix, where the main nucleation mechanism was found to be interface heterogeneous nucleation catalyzed by the interface with the solid Zn. This is to be expected as the droplet size in their study averaged around 6 nm, making the presence of catalytic sites inside the droplets highly unlikely. The cooling rate used by Chaubey’s was 2.5 K/min, resulting in an undercooling of 132 K. This undercooling is larger than the undercooling observed in this study and can be attributed to the smaller droplet size and the less catalytic interface with solid Zn. Perea-Pezek [5,32] has reported an even larger undercooling of 227 K in a study of Bi dispersions with a 10–20 \(\mu\)m droplet size. The Bi droplets were suspended in a polyphenyl ether carrier fluid and maintained independent through use of thin surface coatings produced by a chemical reaction [4]. The large undercooling indicates that the surface coatings used in their study are even less catalytic. Our observation stands in contrast with measurements over a wide range of cooling rates on a single 10 \(\mu\)m droplet of tin by Yang et al. [15], where nanocalorimetry uncovered two different nucleation mechanisms, i.e., interface and bulk heterogeneous nucleation.

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 Eqs. (6) and (7) is acceptable.

7. 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 and encapsulated in silicon nitride. 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 for a wide range of cooling rates. The results indicate that nucleation of solid Bi occurs heterogeneously catalyzed by the interface with the silicon nitride and that a single nucleation mechanism is active over three orders of magnitude of cooling rate.

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Appendix A. 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

\[
P_1 = C \left( \frac{dT}{dt} \right)_1 + L;
\]

\[
P_2 = C \left( \frac{dT}{dt} \right)_2 + L;
\]

\[
\vdots
\]

\[
P_n = C \left( \frac{dT}{dt} \right)_n + L,
\]

where \(P, C\) and \(L\) have the same physical meaning as in Eq. (2), 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, Eq. (35) 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 \(P\) as a function of \((dT/dt)\), 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. Fig. 6 depicts the results obtained for the various DC scans in a 1 atm helium environment. Fig. 6a shows the linear relationship between applied power and scan rate for three representative temperatures, while Figs. 6b and 6c 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 supercooled 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. 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.

Appendix B. Effect of size distribution on the nucleation rate

First consider the case of bulk nucleation, where Eq. (21) holds true. When the number of droplets is large enough, Eqs. (24) and (25) can be written in integral form:

\[
V = \sum_{i=1}^{n} n_0 v_i \exp \left( -\int_{0}^{t} l_i \, dt \right) = \int_{0}^{+\infty} ve^{-\int_{0}^{l} dt} \frac{dv}{dv} \, n_0 dv = \int_{0}^{+\infty} ve^{-M(t)} \frac{dv}{dv} \, n_0 dv,
\]

\[
\frac{dV}{dt} = -\sum_{i=1}^{n} n_0 v_i l_i \exp \left( -\int_{0}^{t} l_i \, dt \right) = \int_{0}^{+\infty} v^2 e^{-\int_{0}^{l} dt} \frac{dv}{dv} \, n_0 dv
= -\int_{0}^{+\infty} J^2 \frac{dM(t)}{dt} \frac{dv}{dv} \, n_0 dv.
\]

where

\[M(t) = \int_{0}^{t} j dt,\]

and where \(dn_0/dv\) is the probability density function of the droplet volume at \(t=0\) (before any nucleation events). For simplicity, we assume \(dn_0/dv\) is described by a Gaussian distribution,

\[
\frac{dn_0}{dv} = \frac{N_0}{\sqrt{2\pi}\sigma} e^{-(v-v_0)^2/2\sigma^2},
\]

where \(N_0\) is the total number of droplets, \(v_0\) is the average volume and \(\sigma\) the standard deviation at time \(t=0\). Substituting Eq. (39) into (36) and (37), we obtain

\[
V = \frac{N_0}{\sqrt{2\pi}\sigma} \int_{0}^{+\infty} v e^{-M(t)} e^{-(v-v_0)^2/2\sigma^2} dv
\]

\[
\approx \frac{N_0}{\sqrt{2\pi}\sigma} \int_{-\infty}^{+\infty} v e^{-M(t)} e^{-(v-v_0)^2/2\sigma^2} dv
\]

\[
\frac{dV}{dt} = -\frac{JN_0}{\sqrt{2\pi}\sigma} \int_{-\infty}^{+\infty} v^2 e^{-M(t)} e^{-(v-v_0)^2/2\sigma^2} dv
\]

\[
\approx -\frac{JN_0}{\sqrt{2\pi}\sigma} \int_{-\infty}^{+\infty} v^2 e^{-M(t)} e^{-(v-v_0)^2/2\sigma^2} dv.
\]
The last approximation is accurate as long as \( \nu_0 > 3\sigma \). The integrals in Eqs. (40) and (41) can be evaluated analytically

\[
V = \frac{N_0}{\sqrt{2\pi} \sigma} \int_{-\infty}^{+\infty} v e^{-M_r \nu_0^2/2\sigma^2} dv = N_0(\nu_0 - \sigma^2 M) e^{-M_r
\]
\[
= (1/2)M^2 \sigma^2 = V_0 (1 - \sigma^2 M / \nu_0^2) e^{-M_r + (1/2)M^2 \sigma^2} \tag{42}
\]

\[
dV/dt = -\frac{N_0}{\sqrt{2\pi} \sigma} \int_{-\infty}^{+\infty} v^2 e^{-M_r \nu_0^2/2\sigma^2} dv
\]

\[
= -N_0 e^{-M_r \nu_0^2 + (1/2)M^2 \sigma^2} \left[ \sigma^2 + (\nu_0^2 - \sigma^2 M)^2 \right] \tag{43}
\]

Note that if \( \sigma = 0 \), then Eqs. (42) and (43) are identical to Eqs. (26) and (27). We can thus calculate the ratio between the volume rates \( dV/dt \) calculated from the full size distribution and from the average size:

\[
\eta = \frac{dV/dt}{dV/dt}_{\sigma=0} = e^{(1/2)M^2 \sigma^2} \left[ \frac{\sigma^2}{\nu_0^2} + \left( 1 - \frac{\sigma^2 M}{\nu_0^2} \right)^2 \right] \tag{44}
\]

For simplicity, we take \( M = 0.7/\nu_0 \) for a conversion rate of approximately 50%, which is used in the analysis of the experiments

\[
1 - \frac{V}{V_0} = 1 - \left( 1 - \frac{\sigma^2}{\nu_0^2} \right) e^{-0.7 \cdot 2.45 \sigma^2 / \nu_0^2} \approx 1 - e^{-0.7} \approx 50\% \tag{45}
\]

Substituting this value of \( M \) into Eq. (44) yields

\[
\eta = e^{0.245(\sigma/\nu_0)^2} \left[ (\sigma/\nu_0)^2 + (1 - 0.7(\sigma/\nu_0)^2)^2 \right] \tag{46}
\]

where \( \beta = (\sigma/\nu_0)^2 \) is a parameter describing the width of the volume distribution relative to its mean. A smaller value of \( \beta \) indicates a tighter distribution. Eq. (46) provides the error associated with using the average instead of the full size distribution. Fig. 7 shows a plot \( \eta \) as a function of \( \beta \). In general, \( \eta \) is larger than 0.98, i.e., using the average droplet size causes an error of less than 2% in the nucleation rate. In this study, \( \beta \approx 0.1 \).

For the case of interface nucleation, the ratio between the volume rates for groups and \( j \) is (assume \( \nu_i > \nu_j \)):

\[
\frac{(dN/dt)_{\nu_i}}{(dN/dt)_{\nu_j}} = \frac{\nu_i}{\nu_j} \left( \frac{\nu_j}{\nu_i} \right)^2 \tag{47}
\]

The right hand side is the ratio of the volume rates in the case of bulk nucleation. This indicates that the distribution of the volume rates in the case of interface nucleation is tighter than for bulk nucleation. Thus, in the case of interface nucleation, \( \eta \) should be closer to unity than the value given by Eq. (44).

This analysis shows that the effect of the droplet size distribution on the analysis is small as long as the ratio of the standard deviation of the distribution to its mean is small. Furthermore, it is evident from Eqs. (42) and (44) that the value of \( \eta \) at a given conversion fraction \((1 - V/V_0)\) is only a function of \( \nu_0 \) and \( \sigma \), and is independent of the temperature history. This implies that for a given size distribution, all measurements need to be corrected by the same factor if the average size model is used. Thus the slope of the data in Fig. 5b is unaffected, while the intersect needs to be corrected by a corresponding amount.

To demonstrate how well the above analysis work in our specific case, we compare the solidification rates of two sets of Bi droplets using the data in Table 1; a set of droplets that follow the experimental size distribution (Fig. 2b) where the solidification rate is given by Eq. (25), and a set of droplets of uniform size where the solidification rate is given by Eq. (27). The results are depicted in Fig. 8. It is obvious from the figure that the effect of the precise size distribution is comparable to the analysis result from Eq. (46), and is indeed neglectable: a 0.5 K difference in peak temperature and a 2% difference in peak height.

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