Thermal contact conductance at melting and crystallization of metal micro-droplets

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Abstract

To measure interfacial thermal contact conductance in fast thermal processes, ultrafast scanning calorimetry combined with high-resolution high-speed infrared thermography is applied. The dynamics of temperature distribution on the sample surface is measured by thermography during melting and crystallization of a tin particle of about 580 ng and 70 μm in diameter. The temperature difference on the sample/sensor interface is measured and used to determine the interfacial thermal contact conductance with acceptable accuracy on a millisecond time scale. It is shown that the temperature difference can be of the order of 100 K at melting and crystallization. This is very essential for applications with fast temperature changes like additive manufacturing and for calorimeter calibration. The method can be applied to different materials in fast thermal processes on a micro-scale. During crystallization, the effect of reheating (about 100 K) is observed.

Nomenclature

Greek Symbols

\( \alpha_g \) Coefficient of heat transfer through the surrounding gas, \( W \cdot m^{-2} \cdot K^{-1} \)

\( \alpha_C \) Convective component of heat transfer through gas, \( W \cdot m^{-2} \cdot K^{-1} \)

\( \alpha_r \) Contribution of thermal radiation to the heat loss, \( W \cdot m^{-2} \cdot K^{-1} \)

\( \Delta Q_S \) Heat required for the sample heating from \( T_j \) to \( T_{melt} \), \( \Delta Q_S = C_0(T_{melt} - T_j), J \)

\( \Delta Q_m \) Heat required for the membrane heating from \( T_m \) to \( T_{CR} \), \( \Delta Q_m = C_0(T_{CR} - T_m), J \)

\( \Delta t_{CR} \) Crystallization time interval, ms

\( \Delta t_m \) Melting time interval, ms

\( \Delta T_{mel} (t) \) Interfacial temperature difference \( \Delta T_{mel}(t) = T_m(t) - T_j(t), K \)

\( \Delta T_z \) Temperature difference along z-axis in the sample, K

\( \varepsilon(T) \) Emissivity, dimensionless

\( \varepsilon_0(T, \lambda_m) \) Spectral emissivity of polished tin sample at the wavelength \( \lambda_m \), dimensionless

\( \eta_n \) \( n \)-th eigenvalue \( \eta_n = \frac{\pi(2n + 1)}{2n}, m^{-1} \)

\( \lambda \) Thermal conductivity of the sample, \( W \cdot K^{-1} \cdot m^{-1} \)

\( \lambda_m \) Thermal conductivity of the membrane, \( W \cdot K^{-1} \cdot m^{-1} \)

\( \lambda_g \) Thermal conductivity of the surrounding gas, \( W \cdot K^{-1} \cdot m^{-1} \)
\( \lambda_w \) \hspace{1cm} \text{Wavelength, } \mu \text{m} \\
\( \rho \) \hspace{1cm} \text{Sample density, g cm}^{-3} \\
\( \rho_p \) \hspace{1cm} \text{Electrical resistivity, } \mu \text{Ohm} \cdot \text{m} \\
\( \rho_m \) \hspace{1cm} \text{Membrane density, g cm}^{-3} \\
\( \tau \) \hspace{1cm} \text{Characteristic time } \tau = d_m \rho_m c_m / 2 \alpha_g, \text{ ms} \\
\( \tau_{\text{in}} \) \hspace{1cm} \text{Time constant } \tau_{\text{in}} = 1 / D_m (\eta_i^{2} + \eta_i^{2}), \text{ ms} \\
\Phi_q(r) \hspace{1cm} \text{heat flow transmitted in the gas, } \mu \text{W} \\
\Phi(t, x, y) \hspace{1cm} \text{Reduced heat flux, K} \cdot \text{s}^{-1} \\
\text{Latin Symbols} \\
\( a_0 \) \hspace{1cm} \text{Size of the square heating zone of the membrane, } \mu \text{m} \\
\( b_m \) \hspace{1cm} \text{Distance from the membrane center to the frame, } \mu \text{m} \\
\( c_m \) \hspace{1cm} \text{Membrane specific heat capacity, J g}^{-1} \cdot \text{K}^{-1} \\
\( c_p \) \hspace{1cm} \text{Sample specific heat capacity, J g}^{-1} \cdot \text{K}^{-1} \\
\( C_0 \) \hspace{1cm} \text{Heat capacity of the membrane heating zone } C_0 = \rho_m c_m V_0, \text{ J K}^{-1} \\
\( C_A, C_S \) \hspace{1cm} \text{Addenda and sample heat capacity, J K}^{-1} \\
\( d_{m}, d_{S} \) \hspace{1cm} \text{Membrane and sample thickness, } \mu \text{m} \\
\( D_m, D_0 \) \hspace{1cm} \text{Membrane and sample thermal diffusivity, m}^{2} \cdot \text{s}^{-1} \\
\( D_S \) \hspace{1cm} \text{Sample diameter, } \mu \text{m} \\
\( G_{SS}, G_{SL} \) \hspace{1cm} \text{Thermal contact conductance of the solid/solid and solid/liquid interface, W m}^{-2} \cdot \text{K}^{-1} \\
\( h_S \) \hspace{1cm} \text{Thickness of the model sample, } \mu \text{m} \\
\( h_0 \) \hspace{1cm} \text{Specific enthalpy, J g}^{-1} \\
\( H_S \) \hspace{1cm} \text{Sample enthalpy, } \mu \text{J} \\
\( IRI(t, x, y) \) \hspace{1cm} \text{Infrared radiation intensity, relative units (r.u)} \\
\( IRI_{bg} \) \hspace{1cm} \text{Background level of } IRI, \text{ relative units (r.u)} \\
\( L \) \hspace{1cm} \text{Distance from the membrane to housing, mm} \\
\( m_S \) \hspace{1cm} \text{Sample mass, ng} \\
\( P_0, P_{\text{diff}} \) \hspace{1cm} \text{Heating and differential power, mW} \\
\( q_S \) \hspace{1cm} \text{Heat flow required for the sample heating } q_S = C_S R, \mu \text{W} \\
\( q_{S\delta} \) \hspace{1cm} \text{Heat flow from the sample to the gas } q_{S\delta} = \alpha_g (T_S(t) - T_i) S_S, \mu \text{W} \\
\( q_{\text{ns}} \) \hspace{1cm} \text{Membrane/sample interfacial heat flow } q_{\text{ns}} = G_C (T_m(t) - T_c(t))/S_C, \mu \text{W} \\
\( q_Z \) \hspace{1cm} \text{Heat flux through the sample during crystallization } q_Z = H_S / S_C \Delta T_m, \text{ W m}^{-2} \\
\( R \) \hspace{1cm} \text{Scanning rate, K s}^{-1} \\
\( r_0 \) \hspace{1cm} \text{Characteristic radius of the membrane heating zone, } \mu \text{m} \\
\( r_1 \) \hspace{1cm} \text{Distance from the center of the heating zone to the thermocouples, } \mu \text{m} \\
\( S_S \) \hspace{1cm} \text{Sample surface area, m}^{2} \\
\( S_C \) \hspace{1cm} \text{Thermal contact area, m}^{2} \\
\( t \) \hspace{1cm} \text{Time, s} \\
\( t_0 \) \hspace{1cm} \text{Time interval from the beginning to the end of the heating scan, s} \\
\( t_1, t_2 \) \hspace{1cm} \text{Melting start and melting end moments, s} \\
\( t_3 \) \hspace{1cm} \text{Crystallization start moment, s} \\
\( t_{\text{CR}} \) \hspace{1cm} \text{Time in the middle of crystallization process, s} \\
\( T_{\text{C}} \) \hspace{1cm} \text{Thermal contact conductance, W m}^{-2} \cdot \text{K}^{-1} \\
\( T_m \) \hspace{1cm} \text{Initial temperature of the scan, K} \\
\( T_{\text{max}} \) \hspace{1cm} \text{Maximum temperature of the scan, K} \\
\( T_{\text{melt}} \) \hspace{1cm} \text{Melting point, K} \\
\( T(t, x, y) \) \hspace{1cm} \text{Temperature distribution, K}
1. Introduction

The ability to cool and heat samples at extremely high rates using ultrafast scanning calorimetry opens up remarkable opportunities in materials science [1–3]. Over the past two decades, great progress has been made in the field of ultra-fast chip-calorimetry. The kinetics of fast melting, crystallization, structural reorganization, and glass transition can be studied [4–10]. However, the potential of ultrafast chip-calorimetry has not yet been fully realized. The temperature calibration of chip calorimetry still needs to be improved [11]. Often, the problem of temperature calibration of chip calorimeter is related to the uncertainty of thermal contact conductance (TCC) between the sample and the calorimeter membrane. This is not a problem in the case of polymer samples with excellent adhesion of the sample to the membrane, but the thermal contact is not so perfect in the case of metal samples. Thus, TCC between the sample and the calorimeter membrane still requires detailed investigation. TCC affects the temperature distribution in the membrane-sample system and the temperature calibration of the calorimeter [11].

TCC is a very important parameter for many industrial processes, such as additive manufacturing. TCC significantly affects the heat exchange in a system of melting particles during laser or electron-beam melting, sintering, cladding, and shaping, as well as in the process of fused-deposition involving a stream of molten droplets. Currently, additive manufacturing is a technology that is rapidly spreading to a number of industries. However, it is still limited by low productivity and due to the uncertainty of the mechanical properties of the finished product [12, 13]. In fact, microstructure and mechanical properties of the resulting materials strongly depend on its thermal history (heat treatment) [14–16]. Thus, heat transfer is one of the key factors affecting additive manufacturing [17–22]. TCC between the newly molten particle and the already sintered under-layer strongly affects the heat exchange in the system, which in turn affects the thermal history and mechanical properties of the deposited material. However, due to the lack of reliable data, TCC is still not taken into account when modeling heat transfer in additive manufacturing.

The purpose of this article is to draw attention to the importance of TCC and to show how TCC can be measured and taken into account when modeling heat transfer in various processes, including fast scanning calorimetry and additive manufacturing. We focus on measurements of interfacial TCC for micro-droplets in fast thermal processes on a millisecond time scale. To measure the interfacial TCC, it is necessary to obtain information about the heat flux across the interface and the temperature difference at the interface. The heat flux and temperature difference can be measured in a fast scanning calorimeter combined with high-speed high-resolution infrared thermography used as a non-contact thermal imaging tool [23–26]. The surface temperature of the sample $T_S(t, x, y)$ can be obtained from the intensity of infrared radiation $IRI(t, x, y)$, measured using thermography.

TCC can vary in a wide range depending on various factors. Usually, the interfacial TCC between polished solid materials depends on the applied pressure and can be in the range $10^3$–$10^4$ W m$^{-2}$ · K$^{-1}$ [27, 28]. The TCC at the solid/liquid interface is more stable and larger. It can be in the range from $10^3$ up to $10^7$ W m$^{-2}$ · K$^{-1}$. 

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**Greek letters**

- $\theta$: Membrane and sample temperature, K
- $\theta_T$: Thermostat temperature, K
- $V_0$: Volume of the membrane heating zone $V_0 = \pi d_m r^2_0$, m$^3$
- $V_S$: Sample volume, m$^3$
- $(x_0, y_0)$: Sample center coordinates, pixels
- $r, x, y, z$: Space variables, m

**Subscripts**

- $bg$: Background
- $CR$: Crystallization
- $g$: Gas parameter
- $in$: Initial temperature
- $l, n$: $l$-th and $n$-th Fourier components
- $lag$: Time lag
- $m$: Membrane
- $max$: Maximum temperature
- $melt$: Melting point
- $S$: Sample
- $t$: Thermostat
For instance, TCC at the mercury/silicon interface is about $10^7 \text{ W m}^{-2} \cdot \text{K}^{-1}$ [29]. Similar results were observed for water/solid interfaces with and without wettability [30].

In the first part of the paper, we consider the dynamics of the temperature of a metal microdroplet (a tin sample of about 580 ng) and the membrane of the commercial calorimetric sensor (XEN-39391 from Xensor Integration, NL [31]) during melting and crystallization of the sample. The origin of limitations on the accuracy of temperature measurements is analyzed. Next, we focus on TCC measurements. The heat exchange in the membrane/sample system and the surrounding gas is studied. We focus on the measurements during melting and crystallization of the tin micro-droplet near the melting point $T_{\text{melt}} = 505 \text{ K}$. A comparison and analysis of the results obtained with quasi-static and dynamic changes in the temperature of the sample-membrane system is carried out. Thus, it is shown that high-speed high-resolution infrared thermography in combination with ultrafast chip-calorimetry is a reliable tool for measuring TCC on a micro-scale and on a millisecond time scale.

In addition, the effect of reheating of a deeply supercooled liquid droplet is observed during crystallization. This effect is essential for the analysis of crystallization kinetics [32, 33] and the resulting microstructure [15–22]. Moreover, the effect is important for several applications, where solidification occurs at deep undercooling. In fact, the temperature of the particle can jump back to the melting point. The reheating of the supercooled material can be of the order of 100 K. Our goal is to draw attention to the effect of reheating of a deeply supercooled liquid during crystallization.

2. Chip sensor (XEN-39391) for ultra-fast calorimetry

The calorimetric sensor XEN-39391 consists of an amorphous silicon-nitride membrane with thermocouple junctions and a resistive heater located at the central region of the membrane, see figure 1.

Chip sensors for ultrafast calorimetry are commercially available from Xensor Integration, NL. The technical details for the sensors are available on the website of Xensor Integration [31]. The central heated zone of the membrane ($116 \times 116 \mu \text{m}^2$) with heater stripes and six thermocouple junctions is utilized as the calorimeter cell. The resistive heater located at the central part of the membrane consists of parallel (vertical) stripes about 116 $\mu \text{m}$ long, see figure 2(a). The thermocouple hot junctions are located between the heater strips and measure the temperature of the membrane around the center of the heated zone, see figure 2. The thermocouple junctions, heater strips, and electrical leaders are formed by p- and n-type polysilicon tracks with appropriate thermoelectric properties and resistivity. The electrical circuit is protected by a submicron amorphous silicon-nitride layer. The membrane thickness $d_m$ is equal to about 1 $\mu \text{m}$. The thermocouple cold junctions are positioned on the silicon frame, see figure 1. The square membrane is fixed on the silicon frame at a distance of $b_m = 350 \mu \text{m}$ from the center of the membrane. The temperature of the cold junctions is equal to the temperature of the silicon frame, which is close to the thermostat temperature $T_t$. The frame is mounted on a standard housing, see figure 1. For the combined infrared thermography—fast scanning calorimeter, the sensor...
is installed in ambient air with a stable temperature \( T_g \) and gas pressure. The distance from the membrane to the housing \( L \) is equal to 0.3 mm. The size of the heated zone \( a_0 = 116 \, \mu m \) (see figure 2) is less than the distance \( b_{air} \). Denote by \( r_0 \) the radius of the central heated zone of the membrane which is of the order of 100 \( \mu m \). Thus, \( r_0 \) is significantly smaller than \( b_{air} \). In this case, the heat supplied by the heater of the sensor is dissipated into the surrounding gas before this heat reaches the membrane periphery [11, 26]. Therefore, the heat transfer between the membrane and the frame is negligible. The main channel of heat transfer from the membrane hot-zone to the surrounding gas before this heat reaches the membrane periphery is heat convection, which is caused by the temperature dependence of the gas density and the dynamic viscosity of nitrogen gas at normal temperature and pressure are about 1.25 kg m\(^{-3}\) and 2·10\(^{-5}\) Pa·s, respectively, [34]. Therefore, \( Gr = 0.016 \) and \( (Gr)^{1/4} = 0.35 \) for \( T = T_{melt} = 505 \) K is the melting point of tin. Thus, the convective contribution to the heat loss from the membrane is equal to \( \alpha_C = 0.35 \nu_g \). When the membrane is horizontal, this contribution only acts on the upper side of the membrane. Then, the ratio of this convective component to the conductive heat loss from the two faces of the membrane is equal to \( \alpha_C/2\alpha_g = 0.18 \). Thus, the contribution of natural convection does not exceed the uncertainty of the \( \alpha_g \) estimate, which is about 20%. In addition, the effect of natural convection depends on the orientation of the membrane relative to the vertical axis. However, no difference was observed in the experiment when the orientation of the membrane changed from horizontal to vertical. Therefore, the convective contribution to heat transfer from the membrane to the surrounding gas is insignificant.

![Figure 2. Zoomed image of the central part of the membrane: top view of the sensor in normal light (a)—there are six thermocouple junctions between the heater stripes (shown by arrows). Photograph of the sensor with a tin sample during heating: black and white IR image (b) and color image (c) with a color code corresponding to the infrared radiation intensity (IRI) in relative units (r.u).](image)
The contribution of thermal radiation to the heat loss from the membrane is equal to 
\[ \alpha_r = \varepsilon \sigma (T^4 - T_m^4) / (T - T_r), \]
where the Stefan-Boltzmann constant \( \sigma = 5.67 \times 10^{-8} \text{ W/(m}^2\text{K}^4) \) and the emissivity of the silicon-nitride membrane \( \varepsilon \) does not exceed 0.2 [37, 38]. Thus, \( \alpha_r \) is about 9 W/(m\(^2\)K) at \( T = 800 \text{ K} \) and \( T_r = 300 \text{ K}. \)

Therefore, contribution of the thermal radiation to the heat loss from the membrane is about 3.5 \% which does not exceed the uncertainty of the \( \alpha_r \) estimate. Thus, the heat loss from the membrane due to the thermal conductivity of the surrounding gas significantly exceeds other contributions.

### 3. Differential ultra-fast scanning chip-calorimetry

In ultrafast chip-calorimetry, the sample is placed on the membrane in the middle of the heated zone of the sensor under an optical microscope as described in [2]. Usually, after first melting, the sample shape and position are stable due to adhesive forces acting between the sample and membrane [2]. The mass of the sample can be determined from the measured enthalpy of melting and crystallization. The result can be compared to the mass determined from the sample volume estimated from the sample size measured using a microscope. In this paper, a sample of pure tin was measured, provided by Shanghai University [39]. Particles from the same batch were already used in previous studies [40–42]. A special consumable electrode direct current arc (CDCA) technique was used to produce nearly spherical particles with very smooth surface [39]. The spherical shape is useful for modelling additive manufacturing and a smooth surface provides reliable thermography measurements. After the first melting, the spherical particle formed a stable micro-drop on the central region of the sensor and do not change after further melting, see figure 2. Next, we consider the results of the calorimetric measurements with and without power compensation.

In differential scanning calorimetry, the sensor loaded with the sample and the reference sensor are maintained at the same temperature, when the temperature of the membrane near the sample increases linearly with time. The difference in input power required to match the temperature of the loaded sensor with the temperature of the reference sensor is the amount of excess power absorbed or released by the sample [2].

In power compensation mode, the precise proportional integral derivative (PID) controller is used to control the temperature of the reference sensor [2, 4]. The PID controller makes the temperature of the reference sensor to follow the program temperature by applying a power \( P_0(t) \) to the heater of the sensor. The same power \( P_0(t) \) is applied to the sensor loaded with a sample. The difference between the temperatures of the sensors is minimized by the differential controller by applying the differential power \( P_{diff}(t) \) to the sample sensor. This allows to use an accurate but relatively slow PID controller for reference temperature control in combination with a fast proportional controller, for details see [4]. In this paper, we will compare the results for both measurements with and without power compensation.

The heat capacity of the sample, whether measured with or without power compensation, can be determined from the following calorimetric equation appropriate for a perfectly symmetric system:

\[
C_A \frac{\partial T}{\partial t} = P_0(t) - B(T - T_r),
\]

\[
(C_S + C_A) \frac{\partial T}{\partial t} = P_0(t) + P_{diff}(t) - B(T - T_r),
\]

where \( C_A \) and \( C_S \) are the heat capacities of the sample and addenda, \( P_0(t) \) is the heating power supplied by the resistive film-heater, \( T(t) \) is the temperature measured by the thermocouples located near the sample on the membrane, \( T_r \) is the temperature of the thermostat, \( B \) is the parameter that describes the heat transfer from the heating zone to the thermostat. Thus, the heat capacity of the sample is proportional to the differential power

\[
C_S \frac{\partial T}{\partial t} = P_{diff}(t).
\]

It is assumed that the difference \( T(t) - T_r(t) \) between the measured temperature \( T(t) \) and sample temperature \( T_r(t) \) is insignificant. However, the temperature gradients in the membrane/sample system can affect the accuracy of the measurements [11]. Temperature gradients in the membrane and temperature differences at the membrane/sample interface can be significant but are often not taken into account in fast calorimetry experiments.

### 4. Measurements of temperature and sample parameters

#### 4.1. Calorimetry and sample parameters

The temperature of the membrane \( T_m(t, x, y) \) is measured by six thermocouples located around the center of the heating zone of the calorimetric chip at six different points, see figure 2. Two thermocouples are placed at the points with coordinates \((x_1, y_1) = (\pm 30 \mu m, 0)\) and four at points \((x_2, y_2) = (\pm 16 \mu m, \pm 32 \mu m)\). Thus, the measured temperature \( T(t) \) is the average of the temperature values indicated by the letters A and B, see figure 3. The temperature \( T_m(t, 0, 0) \) in the center of the heating zone of the membrane is indicated by the letter C. The
Figure 3. Temperature distribution in unloaded (a) and loaded (b) sensor XEN-39391 at $R = 2000$ K s$^{-1}$ and $m_{\text{ng}} = 580$ ng. $T_{\text{f}}(t_{0}, x, 0)$ and $T_{\text{m}}(t_{0}, x, 32 \, \mu\text{m})$—triangles up and down, respectively; $T_{\text{f}}(t_{0}, +30 \, \mu\text{m}, 0)$, $T_{\text{f}}(t_{0}, +16 \, \mu\text{m}, 32 \, \mu\text{m})$, and $T_{\text{m}}(t_{0}, 0, 0)$—squares, circles, and diamond. The dashed line shows the measured temperature $T(t_{0})$, which is equal to the average value calculated from points A and B.

Table 1. Thermal parameters of tin near the melting point at normal pressure.

| Material | Density $\rho$ (g cm$^{-3}$) | Specific enthalpy of phase transition $h_{g}$ (J g$^{-1}$) | Specific heat capacity $c$ (J g$^{-1}$ K$^{-1}$) | Volumetric heat capacity $\rho c_{p}$ (J m$^{-3}$ K$^{-1}$) | Thermal conductivity $\lambda$ (W m$^{-1}$ K$^{-1}$) | Thermal diffusivity $D_{\text{th}}$ (m$^{2}$ s$^{-1}$) |
|----------|-------------------------------|----------------------------------|-----------------|-----------------------------|-----------------|-----------------|
| Tin      | 7.0                           | 60.4                             | 0.26            | 1.82$\times$10$^{6}$       | 32              | 1.8$\times$10$^{-3}$ |

time lag between the temperature change in the center of the heating zone and the temperature measured by thermocouples is equal to $t_{\text{lag}} = t_{0}^{2}/4D_{\text{m}}$, where $t_{0} = 36 \, \mu\text{m}$ is a distance from center of the heating zone to the thermocouples and $D_{\text{m}} = 1.3 \cdot 10^{-6}$ m$^{2}$ s$^{-1}$ is the thermal diffusivity of the membrane [31, 34]. Therefore, $t_{\text{lag}} = 0.25$ ms. Thus, the temperature lag $t_{\text{lag}} = R = 0.5$ K between the central zone and the thermocouples is insignificant at $R = 2000$ K s$^{-1}$. However, the difference $T(t_{0}) - T_{\text{m}}(t_{0}, 0, 0)$ between the measured temperature $T(t_{0})$ and the temperature in the center of the heating zone of the membrane is significant, see figure 3.

Consider the sensor XEN-39391 loaded with a sample of mass $m_{\text{ng}} = 580$ ng. Let the temperature $T(t_{0})$ measured by the thermocouples of the sensor change at a constant scanning rate $R$ from the initial value $T_{\text{i}} = 320$ K to the maximum $T_{\text{m}} = 650$ K at heating and back to 320 K at cooling. The thermostat temperature remains at $T_{\text{i}} = 300$ K. Denote by $t_{0}$ the time interval from the beginning to the end of the heating scan. Thus, $t_{0} = 165$ ms for $R = 2000$ K s$^{-1}$ and $T_{\text{m}} - T_{\text{i}} = 330$ K. The temperature distribution $T_{\text{m}}(t_{0}, x, y)$ calculated for an unloaded and a loaded sensor XEN-39391 at the end of the heating scan (at $t_{0}$) is shown in figure 3, for details of calculation see appendix. The difference $T(t_{0}) - T_{\text{m}}(t_{0}, 0, 0)$ varies during the temperature scan in the range of 0–8 K and 0–13 K at $R = 2000$ K s$^{-1}$ in the unloaded and the loaded sensor, respectively, see figure 3.

The temperature distribution $T_{\text{m}}(t_{0}, x, y)$ was calculated on the assumption that the thermal diffusivity of the sample is the same as that of the membrane. However, the thermal diffusivity of tin is an order of magnitude larger than that of the membrane [43], see table 1. Therefore, the lateral temperature gradients in the membrane/sample system are smoothed out due to the high thermal diffusivity of the sample. Thus, the temperature distribution $T_{\text{f}}(t_{0}, x, y)$ is much flatter than the distribution $T_{\text{m}}(t_{0}, x, y)$ shown in figure 3.

The temperature distribution $T_{\text{f}}(t_{0}, x, y)$ measured in a tin sample with $m_{\text{ng}} = 580$ ng is shown in figure 4. The temperature distribution $T_{\text{f}}(t_{0}, x, y)$ obtained from the radiation intensity $IRI(t_{0}, x, y)$, for details see below. The measurements were performed during crystallization near the center of the sample, which corresponds to the coordinates $(x_{0}, y_{0}) = (32 \, \text{pix}, 30 \, \text{pix})$. In fact, the actual temperature distribution $T_{\text{f}}(t_{0}, x, y)$ is even flatter than the distribution shown in figure 4.

$T_{\text{f}}(t_{0}, x, y)$ was obtained under the assumption that the emissivity of the sample is the same from different points. However, the emissivity of metals depends on the angle between the normal to the surface of the sample...
Figure 4. IR radiation intensity \( I(R, t, x, y) \) (a) and \( T_{tm}(t, x, y) \) (b) versus distance \( x \) for a sample of tin weighing \( m_s = 580 \text{ ng} \) at \( R = 2000 \text{ K s}^{-1} \) and \( y_s = 30 \text{ pix} \) during crystallization at \( t = 0.52 \text{ ms}, 0.79 \text{ ms}, \) and \( 1.8 \text{ ms} \) after the beginning of crystallization process – squares, circles, and triangles, respectively.

Table 2. The size parameters of the measured sample.

| Mass \( m_s \) | Enthalpy of phase transition \( H_k \) | Heat capacity \( C_s \) | Diameter \( D_s \) | Thickness \( d_s \) | Surface area \( S_s \) | Thermal contact area \( S_c \) |
|---------------|-----------------|-------------|--------|--------|------------|-----------------|
| ng            | \( \mu l \)     | \( \text{J K}^{-1} \) | \( \mu m \) | \( \mu m \) | \( \text{m}^2 \) | \( \text{m}^2 \) |
| 580           | 35              | 151         | 68     | 34     | 7.3 \(\times\) 10^{-9} | 3.65 \(\times\) 10^{-9} |

and the direction of the emitted radiation, as follows from the Fresnel equations [44–46]. Actually, the emissivity of a metal droplet from the periphery is higher than from the central region, see figure 2(c). Because of the uncertainty of the emissivity, we get the uncertainty of the surface temperature of the sample. This uncertainty can be estimated at about 10 K, see figure 4. In fact, the radiation intensity has a minimum in the middle of the sample surface. Subsequently, we focus the camera on the minimum radiation intensity at \((x_0, y_0) = (32 \text{ pix}, 30 \text{ pix}).\)

Consider the temperature gradient in the sample along the \( z \)-axis. This gradient is maximum during a sudden crystallization process, when the heat flux \( q_x \) through the sample is about \( H_k/C_s \Delta T_x = 1.6\times10^6 \text{ W m}^{-2} \), where the enthalpy of the phase transition of the sample \( H_k = 35 \mu l \), the cross sectional area of the sample \( S_c = 3.6\times10^{-9} \text{ m}^2 \), and the crystallization time interval \( \Delta T_x \) is 6 ms, see tables 1 and 2. Thus, the temperature difference \( \Delta T_x = q_x d_x / \lambda_0 \) along the \( z \)-axis during crystallization is about 2 K, where the sample thickness is equal to \( d_x = 34 \mu m \) and \( \lambda_0 \) is about 30 W m\(^{-1}\) K\(^{-1}\). Therefore, the temperature gradient along the \( z \)-axis of the sample is insignificant with respect to the measured interfacial temperature difference, see below.

For further discussion, we are interested in the temperature difference at the membrane/sample interface. Denote by \( T_{m}(t) \) and \( T_{t}(t) \) the average temperature of the membrane and sample at the interface. \( T_{m}(t) \) is between \( T_{m}(t, 0, 0) \) and \( T(t) \), see figure 3. Denote by \( \Delta T_{m}(t) \) the uncertainty of the measurement of the interfacial temperature \( T_{m}(t) \). The uncertainty \( \Delta T_{m}(t) \) is about 6 K in a loaded sensor for thermal processes near \( T_{m}(t) \) at \( R = 2000 \text{ K s}^{-1} \). However, the temperature difference \( \Delta T_{m}(t) = T_{m}(t) - T_{t}(t) \), measured in the experiment, is about 50 K, see below. Therefore, the interfacial temperature difference \( \Delta T_{m}(t) \) is measured with an error of about 10 %.

To determine the size parameters of the sample we use the calorimetric measurements of the enthalpy of phase transition, as well as the images obtained with the IR camera. The temperature \( T(t) \) measured by the thermocouples of the sensor was scanned with constant rates \( R = 200 \text{ K s}^{-1} \) and \( 2000 \text{ K s}^{-1} \). The lower and higher rate corresponds to the quasi-static and dynamic temperature scanning mode, respectively, for details see appendix. The sample mass can be determined from the enthalpy of crystallization. The absolute value of the differential power \( |P_{diff}(t)| \) during crystallization of the tin sample is shown in figure 5. The enthalpy of the phase transition \( H_k \) is the area under the curve \( |P_{diff}(t)| = \mu l \), where \( BL(t) \) is the base-line, see figure 5.

The enthalpy of the phase transition is equal to \( H_k = 32 \mu l \) and 38 \( \mu l \), measured at \( R = 200 \text{ K s}^{-1} \) and \( 2000 \text{ K s}^{-1} \), respectively. Thus, the measured enthalpy \( H_k = 35 \pm 3 \mu l \) does not depend on the rate (within 10 % accuracy) for quasi-static and dynamic temperature changes. The error of 10% can be explained by the
effect of the rate on the symmetry of the calorimetric differential system. In fact, the temperature of the membrane is affected by the sample during phase transitions, for details see below. This effect is less in power compensation mode than in the measurements without compensation. Subsequently, we use the results obtained with power compensation. The enthalpy of fusion measured in the melting process is the same as the enthalpy measured during crystallization within the accuracy 10\%. However, the melting process is more smeared than the crystallization process, and the base-line is not as obvious as in the case of crystallization. Thus, we obtain the mass of the sample \( m_S = \frac{H_S}{h_0} \) equal to 580 \( \pm \) 50 ng, where \( h_0 = 60.4 \text{ J g}^{-1} \) is the specific enthalpy of the phase transition\([34]\). The volume of the sample \( V_S = \frac{m_S}{\rho} \) equals 8.3 \( \cdot \) 10\(^{-14} \text{ m}^3\), where \( \rho = 7.0 \text{ g m}^{-3} \), see table 1.

The diameter of the sample \( D_S = 68 \pm 5 \mu\text{m} \) is obtained from the IR intensity measurements, see figures 2 and 4. The sample shape is close to a spherical segment, see figure 2. Thus, the thickness of the sample at the top \( d_S = 34 \mu\text{m} \) is obtained from the equation for spherical segmental volume \( V_S = \pi d_S (3D_S^2/4 + d_S^2)/6 \). In fact, the shape of the sample is close to the hemisphere. The surface area of the sample \( S_S = \pi D_S^2/2 \) facing the surrounding gas is 7.3 \( \cdot \) 10\(^{-9} \text{ m}^2\). The area of thermal contact at the membrane/sample interface \( S_C = \pi D_S^2/4 \) is 3.65 \( \cdot \) 10\(^{-9} \text{ m}^2\). The thermal parameters of tin used for further calculations are collected in table 1\([34, 43, 47]\), see figure 6. The size parameters of the sample used for further calculations are collected in table 2.

The temperature dependency of the electrical resistivity \( \rho_e(T) \) of tin, used to estimate the emissivity of the sample, is shown in figure 7. The points marked with squares and circles are calculated from the thermal conductivity \( \Lambda \) in accordance with the Wiedemann-Franz law \( \rho_e = \frac{LT}{\Lambda} \), where the Lorentz number is \( L = 2.445 \cdot 10^{-8} \text{ W} \cdot \text{Ohm} \cdot \text{K}^{-2} \)[48].
The spectral emissivity $\varepsilon_l(T, \lambda_w)$ at the wavelength $\lambda_w = 4 \, \mu m$ in the direction normal to the polished surface of a metal sample can be calculated from the semiempirical relation

$$\varepsilon_l(T, \lambda_w) = C_1 \rho_2 / \lambda_w - C_2 \rho_2 / \lambda_w,$$

where $C_1 = 0.365$, $C_2 = 0.0667$, $\rho_2$ in $\mu$Ohm-m, and $\lambda_w$ in $\mu m$ [45, 50], see figure 8. Usually, the emissivity of metals, as well as the electrical resistivity $\rho(T)$, has a step at the melting point [46]. The temperature dependency of the spectral emissivity $\varepsilon_l(T, \lambda_w)$ at the wavelength $\lambda_w = 4 \, \mu m$ in the direction normal to the polished surface of pure tin is shown in figure 8.

To investigate the dynamics of the temperature distribution on the sample surface, IR thermography as a tool of non-contact thermal imaging is applied in combination with ultrafast scanning calorimetry. A high-speed high-resolution IR camera with an array of InSb photodetectors is used in combination with a specially designed Si-Ge microscopic lens [23–25]. The spectral response of the IR system is at a wavelength of 3–5 $\mu m$. The thermal images of the IR camera are captured at 0.2 ms exposure time and an acquisition rate of 3800 Hz with the lateral size of 64 $\times$ 64 pixels at a spatial resolution of about 4 $\mu m$. A pure Sn micro-sized droplet of about 68 $\mu m$ diameter was placed on the center of the 116 $\times$ 116 $\mu m^2$ heating area of the chip sensor, see figure 2. The distribution of the infrared radiation intensity $IRI(t, x, y)$ from the central heated part of the sample was measured simultaneously with the temperature $T(t)$ measured by six thermocouples at the membrane, see figures 2 and 3. The differential power $P_{\text{diff}}(t)$, $T(t)$, and $IRI(t)$ shows a very sharp change at the beginning of the crystallization process, see figures 5 and 9–12. Thus, the calorimeter and IR camera can be synchronized by using the fast change of the measured parameters with an accuracy of $\pm 0.2$ ms.

The melting and crystallization processes measured in the experiments with and without power compensation are fully reproducible, see figure 9. The time dependence of the radiation intensity $IRI(t, x_0, y_0)$ measured at 3 neighboring points near the center of the sample is shown in figure 9(a). The camera focuses on
the lower surface of the sample at \( x = 32 \, \text{pix}, 31 \, \text{pix}, \) and \( 30 \, \text{pix} \) (at \( y_p = 30 \, \text{pix} \)). The radiation intensities measured in the neighboring points are the same and reproducible from scan to scan. The radiation intensity is reproducible, and it is the same when the camera is focused on the upper or lower surfaces of the sample, see figure 9(b). Thus, the shape of the sample is stable in the experiments, even in the molten state.

Consider the radiation intensity in the middle of the sample during melting and crystallization at \( R = 2000 \, \text{K s}^{-1} \) and \( 200 \, \text{K s}^{-1} \). In the case of \( R = 2000 \, \text{K s}^{-1} \), the melting time interval is equal to \( \Delta t_m = 27 \, \text{ms} \) and 32 ms, as well as the crystallization time interval is \( \Delta t_c = 6 \) and 8 ms, with and without power compensation, respectively, see figure 10. In the case of \( R = 200 \, \text{K s}^{-1} \), the melting time interval is equal to \( \Delta t_m = 90 \, \text{ms} \) and 115 ms, as well as the crystallization time interval is \( \Delta t_c = 6 \) and 8 ms, with and without power compensation, respectively, see figure 12.

It is noteworthy that the value of the radiation intensity during crystallization is fully reproducible and equals 13500 r.u. with a good accuracy of about 1%, see figures 9–12. This value does not depend on the rate \( R \) and the camera focus.

The value of the radiation intensity during melting is close to intensity during crystallization with good accuracy, see figures 9–12. In fact, this value \( IRI_{\text{melt}} = 13500 \) r.u. corresponds to the melting point of tin \( T_{\text{melt}} = 505 \, \text{K} \). The measurements were reproducible during many heating/cooling scans. In addition, the value of radiation intensity at the initial temperature is fully reproducible and is equal to \( IRI_i = 10250 \) r.u., see figures 9–12. Thus, we use the intensities \( IRI_i = 10250 \) r.u. and \( IRI_{\text{melt}} = 13500 \) r.u. corresponding to the temperatures 320 K and 505 K as reference points for estimating the sample temperature. The sample temperature can then be calculated from the measured radiation intensity.
4.2. Noncontact IR thermometry

To obtain interfacial thermal contact conductance, it is necessary to measure the temperature difference at the interface. In fact, measuring the temperature on both sides of the interface is not a trivial task, especially for a micro-sized droplet during fast melting and crystallization. This problem can be solved using contactless IR thermometry, combined with microcalorimetry.

The temperature \( T_{x_0 y_0} \) of the sample surface on the side opposite the membrane can be obtained from the thermal radiation intensity \( IRI(t, x_0, y_0) \) measured in a point \((x_0, y_0)\) since the sample temperature \( T_S \) is proportional to the ratio \( \varepsilon(T_S) / \varepsilon(T) \). Indeed, the intensity of the thermal radiation from the sample at the wavelength \( \lambda_w \) is equal to the product of the spectral emissivity \( \varepsilon(T_S, \lambda_w) \) of the sample surface and the intensity of the radiation of a blackbody, which is described by Planck’s law \[45\]. The thermal radiation measured by the optical system consisting of InSb photodetectors and Si-Ge microscope lens is in the spectral range 3–5 \( \mu \text{m} \) \[23–25\].

Denote by \( A(\nu) \) the response function of the measuring system, which is zero outside some frequency range \((\nu_1, \nu_2)\). Then the intensity measured by the photodetectors of the IR camera is proportional to the integral \[ \int_{\nu_1}^{\nu_2} \varepsilon(T_S, \nu) A(\nu) \nu^3 / (\exp(h \nu / kT_S) - 1) d\nu. \] Therefore, according to mean value theorem for definite integrals \[51\], this integral is equal to the product \( \varepsilon(T_S, \nu_0) A(\nu_0) T_S^4 B \), where \( B = \int_{\nu_1}^{\nu_2} x^3 [1 / (\exp(x) - 1)] dx \)
is a constant, \( x = \frac{h}{kT_0} \) and \( \nu_0 \) is the frequency inside the spectral range \((\nu_0, \nu_2)\). Thus, the intensity measured by the IR camera is proportional to \( \varepsilon(T, \lambda_{n0}) T_0^4 \), where \( \lambda_{n0} \) is a wavelength inside the range 3–5 \( \mu \text{m} \).

Let us consider the temperature dependence of the emissivity at \( \lambda_e = 4 \, \mu \text{m} \), see figure 8. The choice of the value of the variable \( \lambda_e \) inside the narrow spectral range is insignificant, since we are only interested in the ratio of the emissivity at different temperatures and a fixed wavelength, see equation (5). The variable \( \lambda_e \) of the function \( \varepsilon(T, \lambda_e) \) is further omitted because the wavelength is fixed.

Thus, the temperature of the sample surface \( T_s \) is proportional to the ratio \( \frac{\text{IRI}(T_s)}{\varepsilon(T_s)} \). The coefficient of proportionality can be calculated from the measured value of the intensity \( \text{IRI}_{\text{melt}} = 13500 \) r.u. corresponding to the melting point of tin \( T_{\text{melt}} = 505 \, \text{K} \), see figures 9 and 11. Next, consider the time dependence of the intensity \( \text{IRI}(t, x_0, y_0) \) and temperature \( T_t(t, x_0, y_0) \) for a certain point \((x_0, y_0) = (32 \, \text{pix}, 30 \, \text{pix})\) in the middle of the sample. The sample temperature \( T_t(t) \) can be obtained from the intensity \( \text{IRI}(t) \) according to the relation

\[
T_t(t) = T_{\text{melt}} \left( \frac{\text{IRI}(t)}{\varepsilon(T_{\text{melt}})} \right)^{1/4} \left( \frac{\text{IRI}_{\text{melt}}}{\text{IRI}(t)} \right)^{1/4},
\]

(5)

where \( \text{IRI}_{bg} \) is some background level that depends on the thermal noise and dark current of the photodetectors [26]. \( \text{IRI}_{bg} \) can be obtained from the intensity \( \text{IRI}_{\text{in}} = 10250 \) r.u. measured at known temperature \( T_{\text{in}} = 320 \, \text{K} \), see figures 9 and 11. Therefore, from equation (5) we get

\[
\frac{\text{IRI}_{bg}}{\text{IRI}_{\text{melt}}} = 1 - \alpha \cdot \frac{\text{IRI}_{\text{melt}}}{\text{IRI}_{\text{melt}}}/(1 - \alpha),
\]

(6)

where \( \alpha = \frac{\varepsilon(T_{\text{melt}})}{\varepsilon(T_{\text{in}})} \)\. Thus, equation (5) is satisfied identically for \( T_t = T_{\text{melt}} \), as well as for \( T_t = T_{\text{in}} \). We perform an iterative procedure to get \( T_t \) from equation (5). For the zero approximation of \( T_t \), we use equation (7), where the term \( \frac{\varepsilon(T_{\text{melt}})}{\varepsilon(T_s)} \) is neglected:

\[
T_t(t) = T_{\text{melt}} (\text{IRI}(t) - \text{IRI}_{bg})^{1/4}/(\text{IRI}_{\text{melt}} - \text{IRI}_{bg})^{1/4}.
\]

(7)

Thus, the temperature \( T_t \) estimated from equation (7) is used to calculate \( \varepsilon(T_t) \). After that, the corrected temperature \( T_t \) is obtained from equation (5) using \( \varepsilon(T_t) \) calculated with \( T_t \) from the previous iteration. This iterative process can be repeated several times to improve the accuracy of the sample temperature calculation. The iteration procedure converges fairly quickly. In fact, the calculated temperature \( T_t(t) \) changes insignificantly after 4 iterations.

Let’s calculate the temperature \( T_s(t) \) from equation (5) for \( \varepsilon(T) = \varepsilon_0(T, \lambda_e) \), see equation (4) and figure 8. Emissivity \( \varepsilon_0(T, \lambda_e) \), as well as the electrical resistivity \( \rho(T) \), has a step at the melting point, see equation (4), figures 7 and 8. The emissivity from the surface of liquid tin is greater than from the surface of solid tin. The sample surface facing the surrounding gas is colder than the surface facing the membrane. Thus, the melting process begins on the surface facing the membrane. On the contrary, the crystallization of the sample begins on the surface facing the surrounding gas. The surface of the sample is solid, except for a period of time when the sample is completely melted. Therefore, the value \( \varepsilon_0(T, \lambda_e) \) for \( T > T_{\text{melt}} \) is used to estimate the temperature \( T_s(t) \) for a fully molten sample. Accordingly, \( \varepsilon_0(T, \lambda_e) \) for \( T \leq T_{\text{melt}} \) is used to estimate the temperature \( T_s(t) \) until the end of the melting process and immediately after the beginning of crystallization, see figures 13 and 14.

Compare the experiments with and without power compensation. The effect of the sample on the temperature of the membrane is significant during melting and crystallization, when measurements are performed without power compensation. In this case, the rate \( \frac{dT_{\text{melt}}(t)}{dt} \) varies greatly during the melting and crystallization process, see figure 13. However, with power compensation, the effect of the sample on the membrane temperature is negligible, at least during the melting process, see figure 14.

Next, we will consider the measurements of TCC with power compensation when the effect of the sample on the sample temperature \( T_{\text{melt}}(t) \) is lowest. TCC can be derived from the interfacial heat flux and the temperature difference at the membrane/sample interface. We will focus on the thermal processes near \( T_{\text{melt}} \), where the temperature difference \( T_{\text{melt}}(t) - T_s(t) \) is about 50 K, see figure 14. The temperature \( T_t(t) \) measured by IR thermometry is close to the temperature of the sample at the interface. Thus, the temperature difference at the membrane/sample interface is equal to \( T_{\text{melt}}(t) - T_s(t) \) with insignificant uncertainty, because the temperature difference \( \Delta T_s \) in the sample along the z-axis is less than 2 K. Next, the interfacial thermal contact conductance can be obtained from the temperature difference \( T_{\text{melt}}(t) - T_s(t) \) and the heat flux across the interface.

\[
\frac{dT_{\text{melt}}}{dt} = \frac{1}{C_p} \left( \frac{\Delta T_{\text{melt}}}{\Delta \varepsilon} \right) \frac{d\varepsilon}{dt} + \frac{1}{A_{\text{int}}} \frac{d\varepsilon}{dt} \frac{q_{\text{int}}}{C_p}.
\]

(8)

5. Measurement of thermal contact conductance during melting and crystallization

The temperature difference at the membrane/sample interface \( T_{\text{melt}}(t) - T_s(t) \) depends on the interfacial TCC \( G_c(T) \), the area of the interfacial contact \( S_c \), and the heat flow \( q_{\text{int}} \) across the interface:

\[
q_{\text{int}} = G_c(T_{\text{melt}}(t) - T_s(t)) S_c.
\]
Determine the interfacial TCC \( G_{SS} \) and \( G_{SS} \) of the solid/solid and solid/liquid interface before and after the sample begins to melt, respectively. Consider the processes of melting and crystallization under quasi-static and dynamic temperature scanning at \( R = 200 \) K s\(^{-1}\) and \( 2000 \) K s\(^{-1}\). Enlarged fragments of figure 14 near the phase transitions are shown in figures 15 and 16.

Denote \( t_1, t_2 \), and \( t_f \) the moments of the beginning of melting, the end of melting and the beginning of crystallization, respectively, see figures 15 and 16. Determine the interfacial TCC \( G_{SS} \) before the beginning of the melting process from equation (9) for the interfacial temperature difference \( T_m(t_1) - T_S(t_1) \).

\[
q_{\text{ms}} = q_{\text{gs}} + q_S
\]

where \( q_{\text{ms}} = G_{SS}[T_m(t_1) - T_S(t_1)]S_C, \) \( q_{\text{gs}} = \alpha_g(T_S(t_1) - T_s)S_S, \) and \( q_S = C_sR. \) Thus, for the rate \( R = 2000 \) K s\(^{-1}\), we get \( T_m(t_1) = 532 \) K, \( T_S(t_1) = 471 \) K, \( q_{\text{gs}} = 0.32 \) mW, \( q_S = 0.3 \) mW, and \( T_m(t_1) - T_S(t_1) = 61 \) K, see figure 15(a), tables 3 and 4. Therefore, \( G_{SS} = 2.8 \times 10^3 \) W m\(^{-2}\) K\(^{-1}\).

Similarly, for the scanning rate \( R = 200 \) K s\(^{-1}\), we get \( T_m(t_1) = 525 \) K, \( T_S(t_1) = 470 \) K, \( q_{\text{gs}} = 0.32 \) mW, \( q_S = 0.03 \) mW, and \( T_m(t_1) - T_S(t_1) = 55 \) K, see figure 16(a), tables 3 and 4. Then, \( G_{SS} = 1.8 \times 10^3 \) W m\(^{-2}\) K\(^{-1}\).

Summarizing the measurements in the quasi-static and dynamic temperature scanning modes, we get \( G_{SS} = (2.3 \pm 0.5) \times 10^3 \) W m\(^{-2}\) K\(^{-1}\) as an average value obtained in both modes. The results obtained for \( G_{SS} \) in the quasi-static and dynamic temperature scanning modes coincide within 22\% inaccuracy occurring due to the uncertainty of \( n_0, T_S(t), T_m(t), \) and emissivity.
The melting process starts from the hot surfaces of the sample facing the membrane. The cold surfaces of the sample facing the gas remain solid during the melting process. Then the front of the molten material extends in the direction from the membrane to the cold surface. The thermal contact between the membrane and the sample during melting is described by TCC $G_{SL}$ of the solid/liquid interface. The sample temperature has a step at the beginning of melting due to a change in TCC from $G_{SS}$ to $G_{SL}$. The sample temperature jumps up to the melting point $T_{melt}$ in a short period of time of about a few ms, see figures 15(a) and 16(a). The energy $H_S = 35 \ \mu J$ is absorbed by the sample during the melting time interval $\Delta t_m = 27$ ms and 90 ms at $R = 2000$ K s$^{-1}$ and 200 K s$^{-1}$, respectively, see figures 10(a) and 12(a). The energy balance for the melting process is

$$ q_{mS} \Delta t_m = H_S + q_{gS} \Delta t_m + \Delta Q_S, $$

where $q_{mS}$ is the heat flux from the membrane to the sample, $q_{gS}$ is the heat flux from the gas to the sample, and $\Delta Q_S$ is the heat of fusion.

### Table 3. Temperature and heat flow in the membrane at different rates.

| Rate (K s$^{-1}$) | $T_m(t_0)$ (K) | $T_m(t_1)$ (K) | $T_m(t_2)$ (K) | $T_m(t_3)$ (K) | $\Delta Q_{mS}$ (\mu J) |
|-----------------|----------------|----------------|----------------|----------------|-------------------------|
| 2000            | 532            | 584            | 414            | 427            | 0.94                    |
| 200             | 525            | 544            | 426            | 435            | 0.65                    |

The melting process starts from the hot surfaces of the sample facing the membrane. The cold surfaces of the sample facing the gas remain solid during the melting process. Then the front of the molten material extends in the direction from the membrane to the cold surface. The thermal contact between the membrane and the sample during melting is described by TCC $G_{SL}$ of the solid/liquid interface. The sample temperature has a step at the beginning of melting due to a change in TCC from $G_{SS}$ to $G_{SL}$. The sample temperature jumps up to the melting point $T_{melt}$ in a short period of time of about a few ms, see figures 15(a) and 16(a). The energy $H_S = 35 \ \mu J$ is absorbed by the sample during the melting time interval $\Delta t_m = 27$ ms and 90 ms at $R = 2000$ K s$^{-1}$ and 200 K s$^{-1}$, respectively, see figures 10(a) and 12(a). The energy balance for the melting process is

$$ q_{mS} \Delta t_m = H_S + q_{gS} \Delta t_m + \Delta Q_S, $$

where $q_{mS}$ is the heat flux from the membrane to the sample, $q_{gS}$ is the heat flux from the gas to the sample, and $\Delta Q_S$ is the heat of fusion.
Table 4. Temperature and heat flow in the sample at different rates and emissivity.

| Emissivity | Rate | TtS(t1) | Ttm(t3) | \(\Delta Q_m\) | \(q_{gS}\Delta t_m\) | \(\Delta Q_s\) | \(q_{gS}\Delta t_r\) | \(q_s\) | \(q_{gS}\) |
|------------|------|---------|---------|----------------|-----------------|---------------|-----------------|------|-------|
| \(\varepsilon_0(T)\) | 2000 | 471 | 800 | 5.1 | 10.5 | 18.8 | 2.3 | 0.3 | 0.32 |
| \(\varepsilon_0(T)\) | 2000 | 700 | 384 | 5.3 | 35 | 18.2 | 2.3 | 0.3 | 0.32 |
| \(\varepsilon_0(T)\) | 2000 | 475 | 395 | 4.5 | 10.5 | 16.6 | 2.3 | 0.3 | 0.33 |
| \(\varepsilon_0(T)\) | 2000 | 473 | 398 | 4.8 | 35 | 16.1 | 2.3 | 0.3 | 0.33 |
| \(\varepsilon_0(T)\) | 2000 | 478 | 403 | 4.1 | 10.5 | 15.4 | 2.3 | 0.3 | 0.34 |
| \(\varepsilon_0(T)\) | 2000 | 474 | 403 | 4.7 | 35 | 15.4 | 2.3 | 0.3 | 0.33 |

where the heat loss from the sample during melting is \(q_{gS}\Delta t_m = \alpha_g(T_{melt} - T_t)S\Delta t_m\) and the heat required to increase the sample temperature from \(T_t(t_1)\) to \(T_{melt}\) is \(\Delta Q_m = C_g[(T_{melt} - T_t(t_1))]\). The interfacial heat flow from the membrane to the sample during melting is \(q_{mS} = G_{SL}SC_v[(T_t(t_1) + T_m(t_2))]/2 - T_{melt},\) where \(T_m(t_1)\) and \(T_m(t_2)\) are the membrane temperatures at the beginning and end of the melting process.

Thus, for the rate \(R = 2000\ K\ s^{-1}\), we get \(q_{gS}\Delta t_m = 10.5\ \mu J\) and \(\Delta Q_m = 5.1\ \mu J\) at \(T_t(t_1) = 471\ K,\) see table 4. Then, the sum in the right hand side of equation (10) is equal to 50.6 \(\mu J\). Therefore, \(G_{SL} = 9.7 \times 10^3\ \text{W m}^{-2}\text{K}^{-1}\) at \(T_m(t_1) = 532\ K,\) \(T_m(t_2) = 584\ K,\) and \([T_m(t_1) + T_m(t_2)]/2 - T_{melt} = 53\ K,\) see table 3.

Similarly, for the rate \(R = 200\ K\ s^{-1}\), we get \(q_{gS}\Delta t_m = 35\ \mu J\) and \(\Delta Q_m = 5.3\ \mu J\) at \(T_t(t_1) = 470\ K,\) see table 4. Then, the sum in the right hand side of equation (10) is equal to 75.2 \(\mu J\). Therefore, \(G_{SL}\) is about \(7.8 \times 10^3\ \text{W m}^{-2}\text{K}^{-1}\) at \(T_m(t_1) = 525\ K\) and \(T_m(t_2) = 544\ K,\) and \([T_m(t_1) + T_m(t_2)]/2 - T_{melt} = 29.5\ K,\) see table 3.

Summarizing the results obtained in the quasi-static and dynamic temperature scanning modes, we get \(G_{SL} = (8.7 \pm 0.9) \times 10^3\ \text{W m}^{-2}\text{K}^{-1}\).

The crystallization process starts from the cold surfaces of the sample facing the gas. Then the front of the crystallized material extends in the direction of the membrane. Thus, during the crystallization, \(TCC\) between the membrane and the sample is described by \(TCC\) of the solid crystallized material. Therefore, for the rate \(R = 2000\ K\ s^{-1}\), see figures 15(b) and 16(b). The crystallization time interval \(\Delta t_r = 6\ ms\) is the same for the rates \(R = 200\ K\ s^{-1}\) and \(2000\ K\ s^{-1}\), see figures 10(b) and 12(b). Thus, the energy \(H_S = 35\ \mu J\) released during the crystallization results in a power of about 5.8 mW. The energy required to heat the sample to the melting point \(T_{melt}\) from the temperature \(T_t(t_1)\) is equal to \(\Delta Q_S = C_g[T_{melt} - T_t(t_1)]\). The remaining part of the energy released during crystallization is transferred to the ambient gas and membrane.

The membrane temperature \(T_m(t_1)\) is less than \(T_{melt}\). Thus, the membrane is heated by the sample from \(T_m(t_2)\) to \(T_m(t_1)\), see figures 15(b) and 16(b). The temperature of the sample and membrane remains nearly constant during the crystallization process. The sample and membrane temperatures are close to \(T_{melt}\) and \(T_m(t_1)\), respectively. The temperature gradients in the sample are insignificant. Thus, the energy balance for the crystallization process is

\[
H_S = (q_{gS} + q_{mS})\Delta t_r + \Delta Q_S + \Delta Q_m
\]

where \(\Delta Q_m = C_0[T_m(t_1) - T_m(t_2)]]\) is the heat required to increase the temperature of the membrane from \(T_m(t_2)\) to \(T_m(t_1)\). The heat capacity of the membrane heating zone can be estimated as \(C_0 = \rho_m\varepsilon_m V_0\), where \(V_0 = \pi d_m r_0^2\) is the volume of this zone. Thus, \(C_0 = 72\ \text{nJ K}^{-1}\) at \(V_0 = 3.1 \times 10^{-14}\ \text{m}^3\) and \(\rho_m\varepsilon_m = 2.3 \times 10^8\ \text{J m}^{-3}\text{K}^{-1}\). The heat capacity of the sample is \(C_S = 151\ \text{nJ K}^{-1}\), see table 2. \(TCC\) at the membrane/sample interface can be calculated from equation (12):

\[
G_{SL} = [H_S - \Delta Q_S - \Delta Q_m - q_{gS}\Delta t_r] / [(T_{melt} - T_m(t_1))SC_t\Delta t_r]\text{.}
\]

Therefore, for \(R = 2000\ K\ s^{-1}\), we get \(T_t(t_1) = 380\ K,\) \(T_m(t_1) = 414\ K,\) and \(T_m(t_2) = 427\ K,\) see figure 15(b), tables 3 and 4. In fact, \(\Delta Q_S = 18.8\ \mu J,\) \(\Delta Q_m = 0.94\ \mu J,\) and \(q_{gS}\Delta t_r = 2.3\ \mu J\). Thus, \(G_{SL} = 7.6 \times 10^5\ \text{W m}^{-2}\text{K}^{-1}\) for the crystallization process.

Similarly, for \(R = 200\ K\ s^{-1}\), we get \(T_t(t_1) = 384\ K,\) \(T_m(t_1) = 426\ K,\) and \(T_m(t_2) = 435\ K,\) see figure 16(b), tables 3 and 4. Then, \(\Delta Q_S = 18.2\ \mu J,\) \(\Delta Q_m = 0.65\ \mu J,\) and \(q_{gS}\Delta t_r = 2.3\ \mu J\). Thus, \(G_{SL} = 9.0 \times 10^5\ \text{W m}^{-2}\text{K}^{-1}\) for the crystallization process.

Summarizing the results obtained for the crystallization process in the quasi-static and dynamic temperature scanning modes, we get \(G_{SL} = (8.3 \pm 0.7) \times 10^5\ \text{W m}^{-2}\text{K}^{-1}\). Nearly the same result \(G_{SL} = (8.7 \pm 0.9) \times 10^5\ \text{W m}^{-2}\text{K}^{-1}\) we get from the measurements during melting.
The emissivity of a metal strongly depends on the quality of its surface [52–54]. The surface of the measured sample was unpolished. Besides, the surface of the tin sample is known to oxidize after multiple melting experiments. Thus, the emissivity of the measured sample can be much greater than the spectral emissivity \( e(T) \) at the wavelength \( \lambda_w = 4 \mu m \) of a pure polished tin sample, see figure 8. Therefore, we should consider the influence of emissivity on the result of measuring of TCC. Since the actual emissivity is uncertain, we will use different emissivities \( e_1(T) \) and \( e_2(T) \) for further calculations and compare these results with the result obtained for a pure polished sample. \( e_1(T) \) is moderately larger than \( e_0(T, 4 \mu m) \), see figure 8. Time dependency \( T_m(t) \) determined from \( IRI(t) \) for the spectral emissivity \( e(T) \) is shown in figure 17. \( e_1(T) \) is as large as necessary to meet the requirement for \( (T_m(t) - T_m(t)) \) to be close to about \( T_m(t) \) during cooling at \( R = 2000 \text{ K s}^{-1} \), see figure 18. The uncertainty \( \delta T_m(t) \) of the measurement of the interfacial temperature \( T_m(t) \) varies in the range 0–13 K during the temperature scanning at \( R = 2000 \text{ K s}^{-1} \), see section 4. The reason for that requirement is as follows. In fact, during cooling at \( R = 2000 \text{ K s}^{-1} \), the heat flow required to cool the sample \( q_g = C_g R \) is equal to 0.3 mW, which is close to the heat flow from the sample to the surrounding gas \( q_{gS} = \alpha_S (T_g(t) - T_m(t)) \). Actually, \( q_{gS} = 0.39 \text{ mW} \) at \( T_g(t) = T_m(t) \). Thus, the heat flow between the membrane and the sample is insignificant during cooling at \( R = 2000 \text{ K s}^{-1} \). Therefore, the temperature difference \( T_m(t) - T_g(t) \) should be relatively small or close to zero during cooling at \( R = 2000 \text{ K s}^{-1} \). At the cooling rate

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure17}
\caption{Time dependency of \( T_m(t) \) and \( T_S(t) \) measured with power compensation at \( R = 2000 \text{ K s}^{-1} \) (a) and 200 K s\(^{-1}\) (b). \( T_m(t) \) and \( T_S(t) \) — squares and circles. \( (T_m(t) - \delta T_m(t)) \) — dash-dotted line shows the uncertainty of \( T_m(t) \). \( T_S(t) \) is determined from \( IRI(t) \) for the spectral emissivity \( e_1(T) \), see figure 8.}
\label{fig17}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure18}
\caption{Time dependency of \( T_m(t) \) and \( T_S(t) \) measured with power compensation at \( R = 2000 \text{ K s}^{-1} \) (a) and 200 K s\(^{-1}\) (b). \( T_m(t) \) and \( T_S(t) \) — squares and circles. \( (T_m(t) - \delta T_m(t)) \) — dash-dotted line shows the uncertainty of \( T_m(t) \). \( T_S(t) \) is determined from \( IRI(t) \) for the spectral emissivity \( e_2(T) \), see figure 8.}
\label{fig18}
\end{figure}
Table 5. Thermal contact conductance at different rates and emissivity.

| Emissivity | Rate in K s\(^{-1}\) | \(G_{\text{SL}}\) measured during melting in kW m\(^{-2}\) K\(^{-1}\) | \(G_{\text{SS}}\) measured during crystallization at \(t_1\) in kW m\(^{-2}\) K\(^{-1}\) |
|------------|-----------------|-----------------------------|-----------------------------|
| \(\varepsilon_0(T)\) | 2000 | 9.7 | 7.6 |
| | 200 | 7.8 | 9.0 |
| \(\varepsilon_1(T)\) | 2000 | 9.6 | 8.9 |
| | 200 | 7.7 | 10 |
| \(\varepsilon_2(T)\) | 2000 | 9.5 | 9.6 |
| | 200 | 7.7 | 11 |

2000 K s\(^{-1}\), the condition that \(T_\text{f}(t)\) equals about \(T_\text{m}(t) - \delta T_\text{m}(t)\) is met when the emissivity is equal to \(\varepsilon_2(T)\), see figure 18(a). Next, we will show that TCC derived for different emissivities is approximately the same with an accuracy of about 20%.

The results obtained for \(\varepsilon_1(T)\) and \(\varepsilon_2(T)\) are similar to that for \(\varepsilon_0(T, 4 \mu m)\), see tables 4 and 5. Thus, for different emissivities, we get \(G_{\text{SL}} = (8.7 \pm 1) \times 10^3\) W m\(^{-2}\) K\(^{-1}\) and \((9.4 \pm 1.7) \times 10^3\) W m\(^{-2}\) K\(^{-1}\) obtained from melting and crystallization, respectively. TCC for the solid/solid interface obtained at different emissivities is \(G_{\text{SS}} = (2.4 \pm 0.8) \times 10^3\) W m\(^{-2}\) K\(^{-1}\). The uncertainty of \(G_{\text{SL}}\) and \(G_{\text{SS}}\) is about 20 % and 30 %, respectively. This error is due to the uncertainty of \(\varepsilon_0, T_\text{f}(t), T_\text{m}(t),\) and \(\varepsilon(T)\).

Summarizing, it can be concluded that ultrafast scanning calorimetry combined with high-resolution high-speed infrared thermography can be used to measure TCC of a thermal contact on a micrometer scale and on a millisecond time scale with acceptable accuracy. The uncertainty of the emissivity of the sample does not have a very strong effect on the measurement of TCC during melting and crystallization, since \(T_\text{f}(t)\), obtained from the thermal radiation intensity \(IRI(t)\), depends on the ratio \(\varepsilon(T_{\text{melt}}) / \varepsilon(T_{\text{f}})\)\(^1/4\), see equation (5).

In addition, the effect of reheating of a deeply supercooled molten sample is observed at crystallization. This effect is essential for the analysis of crystallization kinetics \([32, 33]\). Furthermore, the effect is important for a number of applications, where solidification occurs at deep undercooling. The temperature of the supercooled particle returns within 0.2 ms to the melting point after the start of the crystallization process. The reheating of the supercooled tin sample observed in the experiment reaches as much as about 100 K, see figures 13 and 14.

6. Conclusions

Ultrafast scanning calorimetry combined with high-resolution high-speed infrared thermography can be used to measure TCC on a micrometer scale and millisecond time scale. The dynamics of the temperature distribution in the sample \(T_\text{f}(t, x, y)\) can be obtained from the dynamics of the infrared radiation intensity \(IRI(t, x, y)\) measured by the thermography. The temperature difference between the measured sample and the sensor membrane can be used to determine interfacial TCC. The accuracy of TCC measurement depends on the uncertainty of the emissivity of the measured sample and the temperature difference measured at the membrane/sample interface. Acceptable accuracy of about 20% and 30% for measurements of TCC at the solid/liquid and solid/solid interfaces, respectively, is obtained for a metal droplet at temperatures near melting and crystallization. TCC \(G_{\text{SS}} = 2.4 \times 10^3\) W m\(^{-2}\) K\(^{-1}\) and \(G_{\text{SL}} = 9 \times 10^3\) W m\(^{-2}\) K\(^{-1}\) obtained for the solid/solid and solid/liquid interfaces, is consistent with literature \([27–29]\). The uncertainty of the emissivity of the sample does not have a very strong effect on the measurement of TCC during melting and crystallization, since sample temperature \(T_\text{f}(t)\), obtained from the intensity \(IRI(t)\), depends on the ratio \(\varepsilon(T_{\text{melt}}) / \varepsilon(T_{\text{f}})\)\(^1/4\).

The method can be applied to measure different materials in fast thermal processes on a millisecond time scale. The results obtained in the quasi-static and dynamic modes of temperature scanning are in good agreement with each other.

TCC is an important parameter for various industrial processes including additive manufacturing. In addition, TCC is very important for temperature calibration of ultrafast calorimeters. According to DIN specification 91127, reference metal samples can be used for temperature calibration of calorimeters. The temperature difference between the measured sample and the sensor membrane can be about several tens of K even for particles with relatively large contact area such as in this work. At ultrafast measurements this difference can be of the order of 100 K during melting and crystallization, see figures 15 and 16. Therefore, it is very important to know the temperature difference at the membrane/sample interface for calibration of calorimeters. It should be noted that the temperature difference at the membrane/sample interface can be significant even when calibration is performed in quasi-static scanning mode.
Furthermore, during crystallization, the effect of reheating a deeply supercooled molten sample is observed. This effect is very important for several applications and for analysis of crystallization kinetics [32, 33] as well as resulting micro-structure [15–22]. The temperature of the supercooled particle returns to the melting point within 0.2 ms. The reheating of the supercooled sample measured in the experiment is about 100 K, see figures 13 and 14.

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Appendix. Temperature distribution in the unloaded and loaded sensor

Consider a spherical sample of radius \( r_0 \) placed in an ambient gas with thermal conductivity \( \lambda_g \). Let the distance \( L \) from the sample to the walls of the thermostat is significantly larger than \( r_0 \) and a constant heat flow is applied to the sample. Thus, we have a spherically symmetric problem for the temperature distribution \( T_s (r) \) in the gas around the sample. From the Laplace equation \( \Delta T_s (r) = 0 \) we get \( T_s (r) = T_0 \), where \( T_0 \) is the sample temperature. The heat flow transmitted in the gas due to its thermal conductivity is equal to

\[
\mathbf{F} = -4 \pi r^2 \lambda_g \frac{\partial T_g (r)}{\partial r},
\]

that is \( \Phi_2 = 4 \pi r_0 \lambda_g (T_s - T_0) \). Therefore, the heat flux transmitted from the unit area of the sample equals \( \lambda_g (T_s - T_0) / r_0 \). Thus, we get the coefficient \( \alpha_2 = \lambda_g / r_0 \) describing the heat loss per unit surface area of the sample. The same result is obtained for the dynamic heat transfer process, for details see [35].

The heat flow in the gas from the heated zone of the membrane can be described by equation (A1), because of nearly spherical temperature distribution around the central heated region in the gas. Thus, the heat loss per unit surface area of the membrane can be described by the coefficient \( \alpha_2 = \lambda_s / r_0 \), where \( r_0 \) is the radius of the central heated zone of the membrane. Parameter \( r_0 \) characterizing the size of the heating zone, is approximately equal to or larger than the size of the heater. In fact, \( r_0 = 5 a_0 / 6 \) with an accuracy of about 20% for a square heater of size \( a_0 \times a_0 \), for details see [26]. The size of the heating zone of the sensor XEN-39391 is equal to \( a_0 = 116 \text{ } \mu m \), see figure 2. Thus, \( r_0 \) is about 100 \( \mu m \). The heat loss from two faces of the heating zone of the membrane is equal to \( 2 \lambda_s / r_0 \). The heat loss per unit surface area of the sample and the membrane is approximately the same, since the heat loss parameter in both cases depends mainly on the thermal conductivity through the surrounding gas.

We assume that the temperature change in the sensor is small enough to consider the thermal parameters of the membrane and the thermal conductivity of the surrounding gas as independent of temperature. The influence of changes in thermal parameters on the temperature can be taken into account by iterative methods [56]. In fact, this effect does not change the qualitative behavior of the sensor dynamics, for details see [56]. Thus, we consider only the case of temperature-independent thermal parameters, when an analytical solution can be obtained for the dynamics of the temperature distribution in the sensor.

Denote by \( \rho_m, c_m, D_m, \text{ and } d_m \) the density, specific heat capacity, thermal diffusivity, and thickness of the membrane, respectively. The temperature distribution \( T(t, x, y) \) in a very thin membrane of the unloaded sensor can be described by equation (A2)

\[
\frac{\partial T}{\partial t} + \frac{(T - T_0)}{\tau} = D_m \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + \Phi(t, x, y),
\]

where \( \Phi(t, x, y) \) is the surface density of the heat flux from the heater divided by \( \rho_m c_m d_m \) — the heat capacity per unit area of the membrane, for details see [11, 56]. Thus, the reduced heat flux \( \Phi(t, x, y) \) is measured in K s\(^{-1}\). The solution of equation (A2) for the square domain \(-b_m \leq x \leq b_m; -b_m \leq y \leq b_m\) can be presented as a series expansion on the orthogonal eigenfunctions \( \cos(\eta_n x) \cos(\eta_n y) \) [57]:

\[
T(t, x, y) = \sum_{l=n=0} T_l = \sum_{l=n=0} \psi_{l,n}(t) \cos(\eta_n x) \cos(\eta_n y),
\]

with eigenvalues \( \eta_n = \pi (2n + 1) / 2b_m \) for \( T(t, x, b_m) - T_l = 0 \) and \( T(t, b_m, y) - T_l = 0 \). The exact analytical solution of equation (A3) is described by the function \( \psi_{l,n}(t) \) which can be obtained from
equation (A4), for details see [11, 56]:

$$\frac{\partial \psi_{r,n}(t)}{\partial t} + (\tau^{-1} + \tau_{r,n}) \psi_{r,n}(t) = B_{r,n}(t),$$

(A4)

where $B_{r,n}(t) = \frac{4}{\sigma g_{n}} \int_{0}^{h_{n}} \int_{0}^{h_{n}} \Phi(t, x, y) \cos(\eta_{x} x) \cos(\eta_{y} y) dx dy$. The function $\psi_{r,n}(t)$ depends on the relaxation time $\tau = \frac{\alpha_{r} c_{v,n}}{2 \alpha_{g}}$ and $\tau_{r,n} = \frac{1}{\alpha_{r} (\eta_{x}^{2} + \eta_{y}^{2})}$. The quasi-static dynamics of the temperature distribution $T(t, x, y)$ is observed at $\frac{\partial T}{\partial t} < (T - T_{0}) / \tau$, see equation (A2). The quasi-static dynamics for the unloaded sensor corresponds to rates below $2 \cdot 10^{4} \text{ K s}^{-1}$ at $\tau = 4.4$ ms and $(T - T_{0})$ of the order of 100 K. However, for the loaded sensor the quasi-static dynamics corresponds to rates below 1000 K s$^{-1}$, as follows from equation (A5).

The temperature distribution $T(t, x, y)$ can be approximated by the sum of the quasi-static and dynamic temperature scanning modes, respectively. The quasi-static dynamics calculated for unloaded sensor XEN-39391 is shown in figure 3(a).

Next, assume that a square sample $l_{x} \times l_{y}$ of thickness $h_{S}$ is placed at the middle of the heater, and the thermal diffusivity of the sample is the same as that of membrane. The sample volume $l_{x} l_{y} h_{S}$ and the interfacial area $l_{x} l_{y}$ is equal to $V_{S}$ and $S_{C}$, respectively. Therefore, $h_{S} = V_{S} / S_{C}$ ($h_{S} = 22.7$ $\mu$m). The effect of the sample can be modeled by the additional heat flux applied to the interfacial area from the sample [11]. The heat flux is proportional to the rate $\frac{\partial T}{\partial t}$ and the sample heat capacity $\rho_{c} V_{S}$ divided by the interfacial area $S_{C}$. Then the temperature distribution $T(t, x, y)$ in the membrane can be described by equation (A5) [11]:

$$\frac{\partial T}{\partial t} + \frac{(T - T_{0})}{\tau} = D_{m} \left( \frac{\partial^{2} T}{\partial x^{2}} + \frac{\partial^{2} T}{\partial y^{2}} \right) + \Phi(t, x, y) - \rho_{c} h_{S} F(x, y) \left( \frac{\partial T}{\partial t} \right) / \rho_{m} c_{m} d_{m},$$

(A5)

where $F(x, y) = 1$ in the domain $(-l_{x}/2 < x < l_{x}/2; -l_{y}/2 < y < l_{y}/2)$ and $F(x, y) = 0$ outside that domain.

The solution of equation (A5) for a constant rate $R$ is similar to the solution of equation (A3) with the normalized heat flux $(\Phi(t, x, y) - \rho_{c} h_{S} F(x, y) / \rho_{m} c_{m} d_{m})$. The temperature distribution calculated for the loaded sensor XEN-39391 with the sample $V_{S}, S_{C}, h_{S} = V_{S} / S_{C}, m_{S} = \rho_{V_{S}} C_{S} = \rho_{c} V_{S}$ and $D_{S} = D_{m}$ is shown in figure 3(b).

Denote by $\gamma_{c}$ the ratio $m_{S} / \rho_{c} h_{S}$ which is equal to 18 at $h_{S} = 22.7$ $\mu$m for a model sample of $m_{S} = 580$ ng. The quasi-static dynamics of the temperature distribution $T(t, x, y)$ in the sensor loaded with the sample is observed at $\frac{\partial T}{\partial t} < (T - T_{0}) / (1 + \gamma_{c})$, see equation (A5). Thus, the quasi-static dynamics for the loaded sensor corresponds to the rates below 1000 K s$^{-1}$ at $\tau = 4.4$ ms and $(T - T_{0})$ of the order of 100 K.

Thus, the measurements were performed at the rates $R = 200$ K s$^{-1}$ and 2000 K s$^{-1}$. The lower and higher rate corresponds to the quasi-static and dynamic temperature scanning modes, respectively.

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