

UKAEA-CCFE-PR(19)63

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Increasing the accuracy of laser flash analysis using noise-robust numerical algorithms in *PULsE*

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(Dated: 14 October 2019)

The laser flash method is highly regarded due to its applicability to a wide temperature range, from cryogenic temperatures to the melting point of refractory metals, and to extreme environments involving radioactive or hazardous materials. Although instruments implementing this method are mostly produced on a commercial basis by major manufacturers, there is always room for improvement both in terms of experimental methods and data treatment procedures. The measurement noise, either due to the detector performance or electromagnetic interferences, presents a significant problem when accurate determination of thermal properties is desired. Noise resilience of the laser flash method is rarely mentioned in published literature; there are currently no data treatment procedures which could guarantee adequate performance under any operating conditions. In this paper, a computational framework combining finite-difference solutions of the heat conduction problem with nonlinear optimization techniques based on the use of quasi-Newton direction search and stochastic linear search with the Wolfe conditions is presented. The application of this framework to data with varying level of noise is considered. Finally, cross-verification and validation using an external standard, a commercial and an in-house built laser flash instrument are presented. The open-source software implementing the described computational method is benchmarked against its industrial counterpart.

I. INTRODUCTION

Nearly sixty years have passed since Parker *et al.*¹ first proposed the flash method for determination of thermal properties. Unlike other methods, e.g. the transient hot-strip method², the transient hot wire method³, and the recently revisited guarded hot plate method⁴⁻⁶, which suffer from an inherent thermal contact resistance between the heater and the sample, the flash method implements a scheme for contactless heating by a pulsed laser source. The latter induces a time-dependent temperature response measured typically at the rear-surface of a cylindrical sample (although other detection concepts have been considered by Pavlov *et al.*⁷ and previously by Ronchi *et al.*⁸) either by an infrared detector or by a thermocouple and used to infer the thermal properties from a mathematical model of the experiment. Due to its many advantages, such as requiring only small samples, reducing measurement time, and being extendable to very high temperatures (above 3000 K⁸⁻¹⁰), the flash method soon became a standard in its field. It is truly indispensable for studies of radioactive or hazardous materials (e.g., low-active proton-irradiated tungsten samples¹¹ and mildly-radioactive neutron-irradiated beryllides¹²), especially for a highly-radioactive material that requires remote access (Walker *et al.*¹³ on the thermal conductivity of a 100 MWd/kgHM spent oxide fuel from a commercial PWR nuclear reactor), due to the versatility of sample mounting required for a pre-programmed robotic arm, for the use of a manipulator or, more commonly, for a glovebox environment.

The ASTM standard E1461 – 13¹⁴ sets out the applicability of the laser flash method to ‘*essentially fully dense (preferably, but low porosity would be acceptable), homogeneous,*

and isotropic solid materials that are opaque to the applied energy pulse’ (Blumm and Lindemann¹⁵ have shown it may also be used on liquids and melts). Experimental uncertainties include (but are not limited to) that of the ‘*detector performance and of the data acquisition system*’, which should deliver a ‘*linear electrical output proportional to the temperature rise*’. These uncertainties are of systematic nature and thus cannot be corrected for by making repeat measurements. As pointed out by Baba and Ono¹⁶, the main experimental challenges lie in the synchronization of the laser pulse with the start of data acquisition by the detector, which should provide accurate time and temperature readings. Sheindlin *et al.*¹⁷ briefly mention that ‘*optical and electrical noise*’, as well as the baseline drift, may be an additional source of uncertainty during experiments. The effect of noise is very poorly detailed in published literature, with a notable exception of the work by Šrámková and Log¹⁸ who considered the effect of oscillations in the mains current (‘hum’) and a shift in the baseline when performing a Levenberg-Marquardt minimization procedure. Synthetic high-noise time-temperature profiles were considered by Carr¹⁹ and Carr and Wood²⁰ to show that the standard half-rise time procedure is not always applicable under otherwise ideal experimental condition. Perhaps one of the key reasons for this is that most laser flash instruments are produced commercially by major manufacturers – unfortunately, the ASTM standard does not list any requirement on the acceptable level of noise the manufacturers of these instruments should adhere to. Therefore, the operator may often be forced to deal with noisy data not always possible to easily interpret.

Almost immediately after publication of the original paper by Parker *et al.*¹, it was soon noticed that the idealized heat transfer model (adiabatic heating by an infinitely small laser pulse) used to calculate the thermal diffusivity value was often conflicting with the experimental conditions. The main point of concerns were: (a) the radiative heat losses limit

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the high-temperature applications of the method and (b) the finite pulse width makes results for thin samples inconsistent. More sophisticated heat transfer models were proposed by Cowan²¹, Cape and Lehman²², Clark III and Taylor²³, and Thermitus and Laurent²⁴ who focused on heat losses (linearised with respect to the temperature rise due to it being small), while Larson and Koyama²⁵, Azumi and Takahashi²⁶, and Lechner and Hahne²⁷ considered primarily the effect of finite pulse widths. Unfortunately, errors had been introduced when deriving the analytical solutions due to its complexity, which required additional corrections by Josell, Warren, and Cezairliyan²⁸ and Blumm and Opfermann²⁹. Baranov *et al.*³⁰ have applied finite-difference solvers implemented in MATLAB for the heat problem in combination with a nonlinear optimization procedure to evaluate the thermal diffusivity values of uranium dioxide from the laser flash experiment. More recently, Pavlov *et al.*⁷ used the FlexPDE software to process data from the laser flash experiments applying the standard Levenberg-Marquardt minimization technique. Due to the sheer number of available heat transfer models, correction for those models, and data treatment procedures for the laser flash method, and also owing to the general lack of extensive validation and cross-verification for each of them, there is no consensus as per the ASTM document on which is the ‘best correction’.

Therefore, the goal of this paper is to set out a universal and easily verifiable method of data analysis that would: (a) not use cumbersome analytic expressions; (b) be independent of general-purpose commercially distributed mathematical packages and software; (c) be highly resilient to low- and high-frequency noise due to the imperfect detector performance. This method would then be used to process data from a laser flash experiment in a commercial instrument using an external standard. Ultimately, the results would be benchmarked with the industrial software to assess its capabilities. The algorithm and procedures outlined in this work are part of the PULsE (Processing Unit for Laser Flash Experiments) software, which is an open-source, cross-platform Java code freely distributed under the Apache 2.0 license³¹.

II. GENERAL REMARKS ON EXPERIMENTAL DATA TREATMENT

A. Calculation of the objective function

In the reverse heat conduction problem, two enumerated collections are compared against each other: the experimental data sequence $\Delta T(\tilde{t}_i)$, $i = 0, 1, \dots, n_{\text{exp}}$, where $n_{\text{exp}} \simeq 1,000 - 5,000$ is the number of experimental data points; and the calculated dataset (containing only unique elements) representing the heating curve $\Delta \hat{T}(t_j)$, $j = 0, 1, \dots, n_s$, where an arbitrary $n_s \simeq 100$ is chosen. Here we assume fixed time sampling for the latter, so that $\exists \Delta t_s \in \mathbb{R}$, $\forall j = 0, \dots, n_s - 1 : t_{j+1} - t_j = \Delta t_s$. Note that generally $\tilde{t}_i \neq t_j$, i.e. the time values for the experimental and calculated data points may not overlap.

To define a computational algorithm for the objective function, it is thus necessary to implement an interpolation

procedure. Instead of interpolating over the *experimental* dataset $\Delta T(\tilde{t}_i)$, which is guaranteed to produce interpolation errors (especially in the case of noisy detector data), the idea is to interpolate over the *solution* values $\Delta \hat{T}(t_j)$ (Fig. 1). With linear interpolation using nearest adjacent points, the value of the solution at time $\Delta \hat{T}(\tilde{t}_i)$, $i = 1, \dots, n_s - 1$ can be calculated as:

$$\Delta \hat{T}(\tilde{t}_i) = \frac{t_{k+1} - \tilde{t}_i}{\Delta t_s} \times \Delta \hat{T}(t_k) + \frac{\tilde{t}_i - t_k}{\Delta t_s} \times \Delta \hat{T}(t_{k+1}), \quad k = \left\lceil \frac{\tilde{t}_i}{\Delta t_s} \right\rceil, \quad (1)$$

where square brackets denote integer division, i.e. the ceiling integer value closest to the result of division, and k is the nearest (ceiling) element to \tilde{t}_i in the t_j , $j \in [0, n_s] \cap \mathbb{Z}$ set.

The objective function f can then be calculated as the sum of squared residuals (SSR) as follows:

$$f = \sum_{i=a}^b \left(\Delta T(\tilde{t}_i) - \Delta \hat{T}(\tilde{t}_i) \right)^2, \quad (2)$$

where $a, b \in [0, n_{\text{exp}}] \cap \mathbb{Z}$ are the lower and higher sum limits, respectively, defining the time domain for calculation.

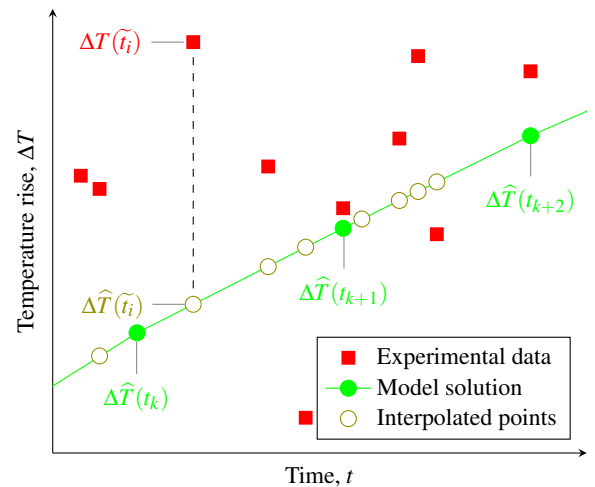


FIG. 1. An illustration of calculating the sum of squared residuals (SSR) using data from two enumerated collections of different size: the experimental data points $\Delta T(\tilde{t}_i)$ ($i = 0, 1, \dots, n_{\text{exp}}$) and the model solution $\Delta \hat{T}(t_j)$ ($j = 0, 1, \dots, n_s$). Eq. 1 is used to calculate the interpolated value $\Delta \hat{T}(\tilde{t}_i)$ at $t_k < \tilde{t}_i < t_{k+1}$ using the nearest points of the model solution $\Delta \hat{T}(t_k)$ and $\Delta \hat{T}(t_{k+1})$ and the experimental time \tilde{t}_i .

B. Conversion of the detector voltage to relative heating

The voltage $U(t)$ transmitted from the infrared detector (a liquid-nitrogen cooled InSb, mercury cadmium telluride (MCT), or an InGaAs detectors; in cheaper instruments – a PbSe Peltier-cooled detector) to the data acquisition module determines the spectral radiance [$\text{W} \times \text{sr}^{-1} \times \text{m}^{-3}$], which is used to estimate the temperature rise of the sample’s rear surface. Alternatively, the voltage $U(t)$ from a thermocouple

generated due to the Seebeck effect is converted to temperature via a characteristic function of the thermocouple. Whatever the tool used to measure the temperature, hereinafter it is referred to as *the detector*, and the voltage it measures is referred to as *the signal*.

A linear relation between the signal $U(t)$ and the heating $\Delta T(t) = T(t) - T_0$, where T_0 is the baseline test temperature measured by a separate detector, is assumed: $\Delta T(t)/C_2 = U(t) - C_1$, where the constant C_1 can be determined as the baseline level U_{\min} and C_2 – as the maximum relative heating $\Delta T_{\max} \propto \Delta U_{\max}$ (Fig. 2). To calculate the absolute temperature in degrees, a further conversion is necessary, e.g. for infrared detectors using Planck's equation and the emissivity $\varepsilon(T)$ of the sample. When a nonlinear dependence of temperature on the spectral radiance may be neglected, e.g. at high temperatures for infrared detectors (Baba and Ono¹⁶) or when using a thermocouple, thermal diffusivity may be calculated without introducing additional error utilizing just the heating values measured in arbitrary units.

It is important though to correctly estimate the baseline signal $U_b(t)$ and the maximum change of voltage ΔU_{\max} , assumed to be proportional to the maximum heating ΔT_{\max} . This becomes challenging for some experimental assemblies with noisy (see Fig. 2) and/or drifting signal (e.g. due to unstable detector current or imperfect temperature regulation). A linear baseline $\Delta T_b(t) = \Delta T_{\text{lin}} + k_{\text{lin}} \cdot t$ is usually enough to accommodate the drift, with ΔT_{lin} and k_{lin} determined using a simple linear regression for the detector signal acquired at $\tilde{t}_i < \tilde{t}_{i_0} := 0$, i.e. before the laser pulse:

$$\Delta T_{\text{lin}} = \langle T \rangle - k_{\text{lin}} \cdot \langle t \rangle, \quad (3a)$$

$$k_{\text{lin}} = \sum_{i=0}^{i_0-1} \frac{(\tilde{t}_i - \langle t \rangle) \cdot (T_b(\tilde{t}_i) - \langle T \rangle)}{(\tilde{t}_i - \langle t \rangle)^2} \quad (3b)$$

$$\langle T \rangle = \frac{1}{i_0} \sum_{i=0}^{i_0-1} T_b(\tilde{t}_i), \quad \langle t \rangle = \frac{1}{i_0} \sum_{i=0}^{i_0-1} \tilde{t}_i. \quad (3c)$$

As seen from Fig. 2, a constant-baseline approach ($k_{\text{lin}} = 0$) is sometimes preferred when fitting to a limited data sample with no obvious drift, as the random spread of data may be too large for an accurate estimation of the slope.

The outliers in Fig. 2 present measurement artefacts and prevent a simple estimation of the maximum heating ΔT_{\max} based on the absolute maximum value of the measured signal. An outlier-robust procedure based on data binning and coarsening (i.e., calculation of a running average of large chunks of data) has been implemented. Fig. 2 shows how effective this procedure is in terms of finding the peak in the probability density of the signal distribution with negligible drift of the measured signal, compared to simply finding the absolute maximum of the signal.

III. HEAT TRANSFER MODEL FOR THE LASER FLASH EXPERIMENT

When the sample thickness l is much smaller than its diameter d ($l/d \ll 1$, but usually $l/d \approx 0.1$), a one-dimensional

heat transfer model is sufficient to calculate the thermal diffusivity $a(T)$ with a good accuracy. Assuming that heating is small, so that $\lambda \neq \lambda(x)$ and $\Delta T/T_0 \ll 1$, the boundary problem may be linearised. Finally, it becomes possible to convert the heat equation and the boundary conditions to a dimensionless form by introducing the Biot (Bi) number, which determines the heat transfer resistance at sample's surface, and the Fourier (Fo) number, which characterizes transient heat conduction, as dimensionless quantities, thus allowing to simplify the solution by reducing the number of variables.

A. Boundary problem

A one-dimensional heat conduction problem for the laser flash experiment must include:

- (i) a heat source term $QP(t)$, where Q is the heat current and $P(t)$ is a time-dependent laser pulse function distributed over an area πd_{las}^2 , where d_{las} is the diameter of the laser spot at the front surface of the sample;
- (ii) heat sink terms at both the front $x = 0$ and the rear $x = l$ surfaces due to the radiation heat transfer $\varepsilon(T)\sigma_0(T^4(x,t) - T_0^4(x,t))$ from the sample to its surroundings in the furnace (assuming the latter are kept at a stable temperature T_0).

If $\Delta T/T_0 \ll 1$, it may be additionally assumed that $\varepsilon(T) \approx \varepsilon(T_0)$, so that the boundary problem is written as:

$$C_p \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[\lambda \frac{\partial T}{\partial x} \right], \quad 0 < x < l, \quad t > 0, \quad (4a)$$

$$\lambda \frac{\partial T}{\partial x} \Big|_{x=0} = -\frac{Q}{\pi d_{\text{las}}^2} P(t) + \varepsilon(T_0)\sigma_0 [T^4(0,t) - T_0^4], \quad (4b)$$

$$\lambda \frac{\partial T}{\partial (-x)} \Big|_{x=l} = \varepsilon(T_0)\sigma_0 [T^4(l,t) - T_0^4], \quad (4c)$$

$$T(0,x) = T_0. \quad (4d)$$

The dimensionless quantities are then introduced as follows:

$$\text{Fo} := at/l^2, \quad (5a)$$

$$\text{Bi} := 4\sigma_0 \varepsilon T_0^3 l / \lambda, \quad (5b)$$

$$\theta := (T - T_0) / \delta T_m, \quad (5c)$$

$$\delta T_m := Q / (C_p \pi d_{\text{las}}^2 l), \quad (5d)$$

$$y := x/l. \quad (5e)$$

Assuming that $\lambda \neq \lambda(x)$ and $(T - T_0)/T_0 \ll 1$, linearisation of Eqs. (4) results in an alternative boundary problem:

$$\frac{\partial \theta}{\partial \text{Fo}} = \frac{\partial^2 \theta}{\partial y^2}, \quad 0 < y < 1, \quad \text{Fo} > 0, \quad (6a)$$

$$\frac{\partial \theta}{\partial y} \Big|_{y=0} = \text{Bi} \cdot \theta - \Phi(\text{Fo}), \quad (6b)$$

$$\frac{\partial \theta}{\partial (-y)} \Big|_{y=1} = \text{Bi} \cdot \theta, \quad (6c)$$

$$\theta(0,y) = 0. \quad (6d)$$

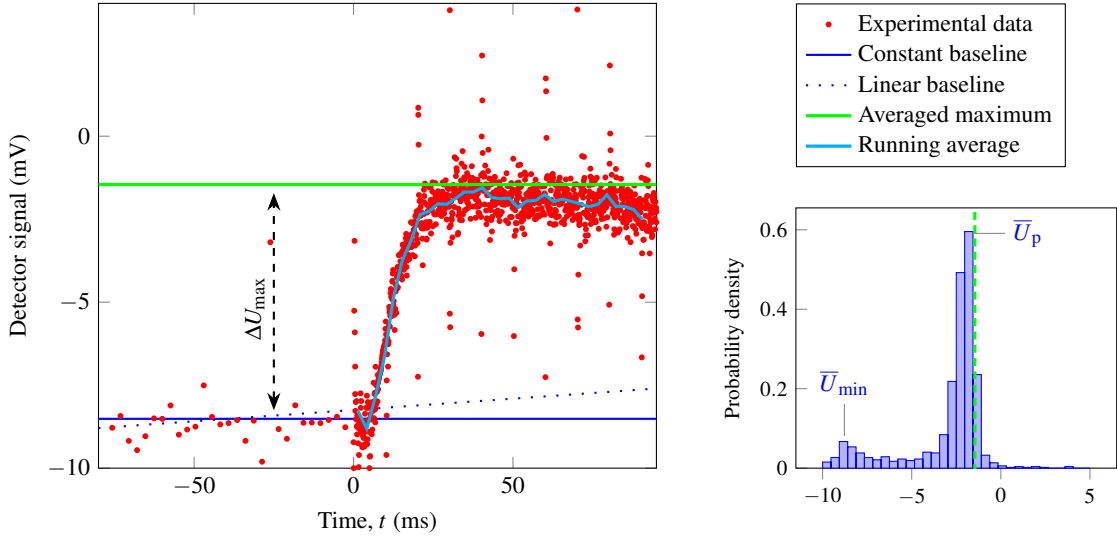


FIG. 2. An example pre-processing of the experimental data, showing: the baseline calculated by least-squares fitting to experimental data at $t < 0$; a running average curve generated by coarsening of experimental data using a default reduction factor of 32 and thus ensuring relative robustness to outliers; and the maximum \bar{U}_{\max} of the running average, which roughly corresponds to the \bar{U}_p peak in the probability density function.

B. Laser pulse function

The laser pulse functions can be changed programmatically during the experiment and can take various forms, including the following as example (a rectangular, a triangular, and a Gaussian pulse functions – previously considered by Baranov *et al.*³⁰):

$$P_1(t) = \begin{cases} t_{\text{las}}^{-1}, & t \leq t_{\text{las}}, \\ 0, & t > t_{\text{las}}, \end{cases} \quad (7a)$$

$$P_2(t) = \frac{2}{t_{\text{las}}} \cdot \begin{cases} 2t/t_{\text{las}}, & t \leq t_{\text{las}}/2 \\ 2(t - t_{\text{las}})/t_{\text{las}}, & t_{\text{las}}/2 < t < t_{\text{las}}, \end{cases} \quad (7b)$$

$$P_3(t) = \frac{5}{\sqrt{\pi}t_{\text{las}}} \cdot \exp\left(-25[t/t_{\text{las}} - 0.5]^2\right) \quad (7c)$$

After changing the variables to dimensionless numbers and introducing a computationally efficient sign function $\text{sgn}(x)$, a quantity $\Phi(\text{Fo}) := P(\text{Fo}) \cdot l^2/a$ may be defined, and Eqs. (7) can then be re-written:

$$\Phi_1(\text{Fo}) = \frac{1}{2\text{Fo}} \cdot [1 + \text{sgn}(\text{Fo}_{\text{las}} - \text{Fo})] \quad (8a)$$

$$\Phi_2(\text{Fo}) = \frac{1}{\text{Fo}_{\text{las}}} \cdot [1 + \text{sgn}(\text{Fo}_{\text{las}} - \text{Fo})] \cdot \left[1 - \frac{|\text{Fo}_{\text{las}} - 2\text{Fo}|}{\text{Fo}_{\text{las}}}\right] \quad (8b)$$

$$\Phi_3(\text{Fo}) = \frac{5}{\sqrt{\pi}\text{Fo}_{\text{las}}} \cdot \left(-25[\text{Fo}/\text{Fo}_{\text{las}} - 0.5]^2\right) \quad (8c)$$

C. Spatial and temporal domains

The spatial domain of Eqs. (6) is simply $y = [0, 1]$; the temporal domain depends on the actual data acquisition time t_{max} ,

which is chosen by an algorithm implemented in the instrument software or – when the latter fails – by the operator manually. A bad choice of t_{max} can not only result in additional computational costs, but may also lead to a biased estimate of the thermal properties if the accumulated experimental data points are too few, or if the statistics for the temperature rise region of the experimental $T(\hat{t})$ profile are under-represented. In addition, the signal registered at the sample's rear surface often shows a brief excursion during the pulse $0 \leq t \leq t_{\text{las}}$ – an event which cannot be described by a simple model such as that introduced in Sect. III A. These two aspects can be partially addressed by implementing a data truncation procedure, which would help in establishing a temporal domain suitable for solving the reverse heat conduction problem. The $\theta(y = 1, \text{Fo})$ solution of Eqs. 6 and the subsequent conversion of that function to a $\hat{T}(t_j)$ dataset (see Sect. II A) need to be defined at a temporal domain $0 \leq t \leq \hat{t}_{\text{max}}$, where \hat{t}_{max} ensures adequately represented statistics. The \hat{t}_{max} value may be chosen based on the characteristic thermal transfer time $\hat{t}_{\text{max}} \simeq l^2/a$ (this corresponds to $\text{Fo} = 1$ in Eq. (5a)), which in turn can be defined in terms of the half-rise time $t_{1/2} = 1.370l^2/(\pi^2a)$ (Heckman³²) first introduced by Parker *et al.*¹. This yields $\hat{t}_{\text{max}} \simeq \pi^2/1.370t_{1/2} \approx 7.2t_{1/2}$. Thus, the rectangular domain of Eqs. (4) is defined as: $D = (0 \leq x \leq l, 0 \leq t \leq \hat{t}_{\text{max}})$, and the domain of Eqs. (6) – as $\bar{D} = (0 \leq y \leq 1, 0 \leq \text{Fo} \leq 1)$.

IV. FINITE-DIFFERENCE SCHEMES FOR THE HEAT CONDUCTION PROBLEM

The domain \bar{D} (Sect. III C) is divided into a uniform grid by introducing the coordinate step size $h = 1/(N - 1)$, where N

is the number of individual coordinate points on the grid, and the discrete time step $\tau = \tau_F h^2$, $\tau_F \in \mathbb{R}$. The grid is used to discretize $\theta(y, \text{Fo})$, which becomes $\theta(\xi_j, \widehat{\text{Fo}}_m) = \theta_j^m$, $j = 0, \dots, N-1$, $m = 0, \dots, m_0$, called the grid function. This section shows different ways to calculate θ_j^m , which can later be converted to $\widehat{T}(t_j)$ (see Sect. II B).

A. Application to the boundary problem (Eq. (6))

Following Samarskii³³, consider a differential operator $\partial^2/\partial x^2$ acting on a function $f(x)$ of the differentiability class C^2 . Substituting $f(x)$ by the grid function $\phi(\xi_\alpha) := \phi_\alpha$, its second derivative on the grid then becomes $\Lambda\phi(\xi_\alpha)\Lambda\phi_\alpha = (\phi_{\alpha-1} - 2\phi_\alpha + \phi_{\alpha+1})/h^2 + O(h^2)$, where h is the grid step. If $\sigma \in \mathbb{R}$, the finite-difference representation of Eq. (6a) on a six-point pattern may be written as:

$$\frac{\theta_j^{m+1} - \theta_j^m}{\tau} = \Lambda \left(\sigma \theta_j^{m+1} + (1 - \sigma) \theta_j^m \right), \quad 1 \leq j < N-1, \quad 0 \leq m \leq m_0. \quad (9)$$

Three special cases of Eq. (9) will be considered: (a) the fully implicit scheme ($\sigma = 1$), (b) the forward-time central-space (FTCS) scheme ($\sigma = 0$), and (c) the Crank-Nicolson scheme ($\sigma = 0.5$). When $\sigma = 0$, Eqs. 9 can be explicitly solved against θ_j^{m+1} . The solution is straightforward and will be skipped here. If $\sigma \neq 0$, a sweep algorithm³³ may be used to solve the tridiagonal set of linear equations (9):

$$a_j \theta_{j-1}^{m+1} - b_j \theta_j^{m+1} + c_j \theta_{j+1}^{m+1} = F_j, \quad (10)$$

where $a_j = c_j = 1/h^2$. For the fully implicit scheme: $b_j = 1/\tau + 2/h^2$, $F_j = -\theta_j^m/\tau$. For the Crank-Nicolson scheme: $b_j = 2/\tau + 2/h^2$, $F_j = -2\theta_j^m/\tau - \Lambda\theta_j^m$.

In the sweep algorithm, the following recurrent expression is introduced:

$$\theta_j = \bar{\alpha}_{j+1} \theta_{j+1} + \bar{\beta}_{j+1}. \quad (11)$$

Let $L\phi(\xi_\alpha) = (\phi_{\alpha+1} - \phi_{\alpha-1})/2h$. The order of approximation for Eq. (9) is $O(\tau + h^2)$ for either $\sigma = 0$ or $\sigma = 1$ and $O(\tau^2 + h^2)$ for e.g. $\sigma = 0.5$. On the other hand, the following finite-difference representation of the boundary conditions (Eqs. (6b) and (6c)) has an order of approximation $O(h)$:

$$L\theta_0 = \text{Bi} \cdot \theta_0 - \Xi, \quad (12a)$$

$$L\theta_{N-1} = -\text{Bi} \cdot \theta_{N-1}, \quad (12b)$$

where $\Xi = \Xi^{m+1}$ is the discretized pulse function defined by substituting Fo_{las} , e.g. in Eqs. (8), with the discrete pulse width $\widehat{\text{Fo}}_{\text{las}} = \left[\frac{\text{Fo}_{\text{las}}}{\tau} \{l^2 a^{-1}\} \right] \cdot \tau$ (square brackets denote integer division). Note this effectively changes the magnitude of the heat source term in Eq. (12a) by $\sim O(\tau)$, which only slightly affects the maximum heating (Eq. (5d)); this is compensated automatically when re-scaling the solution to match

the experimental heating ΔT_{max} value (see Sect. II B). Additionally, the numerical solution described here is valid for any type of the $\Xi(\widehat{\text{Fo}}_{m+1})$ function, which can be given either in analytic (e.g. Eqs. (8)) or tabular form (i.e., directly measured using a laser power sensor) – without having to select a fitting function for the pulse shape (e.g. as done by Blumm and Opfermann²⁹).

To obtain the same order of approximation for the boundary conditions as for Eq. (9), a Taylor expansion in the h -vicinity of $\xi = \xi_0$ and $\xi = \xi_{N-1}$ may be used to define virtual nodes $\xi = \xi_{-1}$ and $\xi = \xi_N$:

$$\theta_{-1} \simeq \theta_0 - L\theta_0 \cdot h + \Lambda\theta_0 \cdot h^2/2, \quad (13a)$$

$$\theta_N \simeq \theta_{N-1} + L\theta_{N-1} \cdot h + \Lambda\theta_{N-1} \cdot h^2/2. \quad (13b)$$

Noticing that $\Lambda\theta_j^{m+1} = (\theta_j^{m+1} - \theta_j^m)/\tau\sigma - \Lambda\theta_j^m(1 - \sigma)/\sigma$ and combining Eqs. (12)–(13) yields the $\bar{\alpha}_1$ and $\bar{\beta}_1$ values for Eq. 11 as well as the grid function value at ξ_{N-1} .

(i) *Fully implicit scheme* ($\sigma = 1$):

$$\bar{\alpha}_1 = \frac{2\tau}{h^2 + 2\tau(1 + h\text{Bi})}, \quad (14a)$$

$$\bar{\beta}_1 = \frac{h^2\theta_0^m + 2h\tau\Xi^{m+1}}{h^2 + 2\tau(1 + h\text{Bi})}, \quad (14b)$$

$$\theta_{N-1}^{m+1} = \frac{h^2\theta_{N-1}^m + 2\tau\bar{\beta}_{N-1}}{h^2 + 2h\tau\text{Bi} + 2\tau(1 - \bar{\alpha}_{N-1})} \quad (14c)$$

(ii) *Crank-Nicolson scheme* ($\sigma = 0.5$):

$$\bar{\alpha}_1 = \frac{\tau}{h^2 + \tau(1 + h\text{Bi})}, \quad (15a)$$

$$\bar{\beta}_1 = \frac{(\Xi^{m+1} + \Xi^m) - (\theta_0^m - \theta_1^m)/h + (h/\tau - \text{Bi})\theta_0^m}{h\tau(h^2 + 2\tau[1 + h\text{Bi}])}, \quad (15b)$$

$$\theta_{N-1}^{m+1} = -\frac{h\theta_{N-1}^m(\tau\text{Bi} - h) - \tau\bar{\beta}_{N-1} + \tau(\theta_{N-1}^m - \theta_{N-2}^m)}{h^2 + h\tau\text{Bi} + \tau(1 - \bar{\alpha}_{N-1})}. \quad (15c)$$

Eqs. (14c) and (15c) are used to initiate the calculation of θ_j , $j = N-2, \dots, 1$ with the recurrent expression (Eq. (11)), in which the $\bar{\alpha}_j$ and $\bar{\beta}_j$ values are calculated as: $\bar{\alpha}_{j+1} = c_j/(b_j - a_j \cdot \bar{\alpha}_j)$ and $\bar{\beta}_{j+1} = (F_j - a_j \cdot \bar{\beta}_j)/(a_j \cdot \bar{\alpha}_j - b_j)$ for $j = 1, \dots, N-2$ (in addition to the $\bar{\alpha}_1$ and $\bar{\beta}_1$ values given by Eqs. 14a, 14b, 15a, and 15b). When the grid function θ_j^{m+1} has been fully calculated for $j = 0, \dots, N-1$, the above-described process repeats at the next time step $m+2$, $m+3$, etc. – until just above the time limit $m_{\text{max}} = \text{Fo}_{\text{max}}/\tau$ (so that the calculated solution is always defined on a slightly wider temporal domain than the experimental data – this helps the correct operation of the interpolation procedure as described in Sect. II A). Further, the number of computed θ^m data points is reduced to a pre-set value n_s with equal spacing between points; hence, only every $\lceil \text{Fo}_{\text{max}}/(n_s \cdot \tau) \rceil$ point form up the calculated heating curve stored in memory (square brackets denote integer division). Finally, the calculated curve is scaled by a factor of $T_{\text{max}}/\max(\theta_N^m)$ (see Sect. II B).

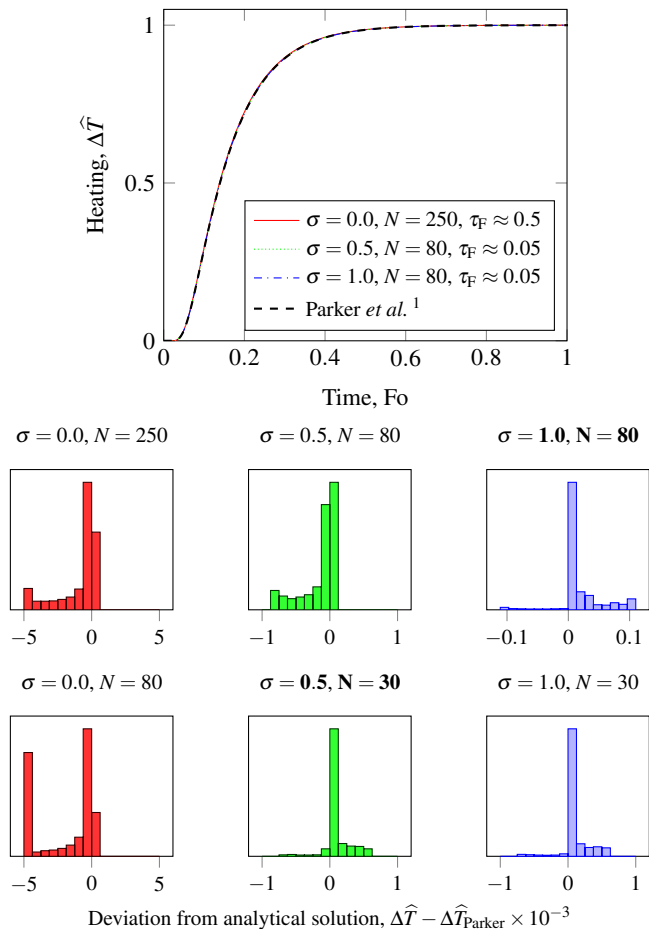


FIG. 3. Comparison of the finite-difference solution of the boundary problem in Eq. (6) using various different schemes (FTCS, fully implicit and Crank-Nicolson) with the analytic solution by Parker *et al.*¹, which describes the laser heating of a thermally-insulated wide, thin sample by an infinitely small laser pulse ($Bi = 0.0$). For the numeric solution, the pulse shape has been chosen as rectangular with the pulse duration $Fo_{\text{las}} \approx 1.41 \times 10^{-5}$. The deviation from the analytical solution is shown using probability density histograms of the residuals, plotted for different grid parameters.

B. Cross-verification

To verify whether the finite-difference scheme (Sect. IV A) and the boundary problem (Sect. III A) have been composed correctly, the numerical solution $\theta(y = 1, Fo)$ calculated using the described procedure is compared to the previously published analytical solutions by Parker *et al.*¹, Cape and Lehman²² and Josell, Warren, and Cezairliyan²⁸ for two extreme cases. In both cases the heating of a thin, wide cylinder by an infinitely short laser pulse is considered. The sample is either (a) thermally-insulated ($Bi = 0$) or (b) cooled down by the radiative heat transfer with an efficiency $Bi = 0.5$. The results of this comparison are shown in Figs. 3 and 4.

In each case, cross-verification of the different schemes ($\sigma = 0.0$, $\sigma = 0.5$, $\sigma = 1.0$) was performed. The probability density of residuals $\Delta\hat{T} - \Delta\hat{T}_{\text{Parker}}$ in Fig. 3

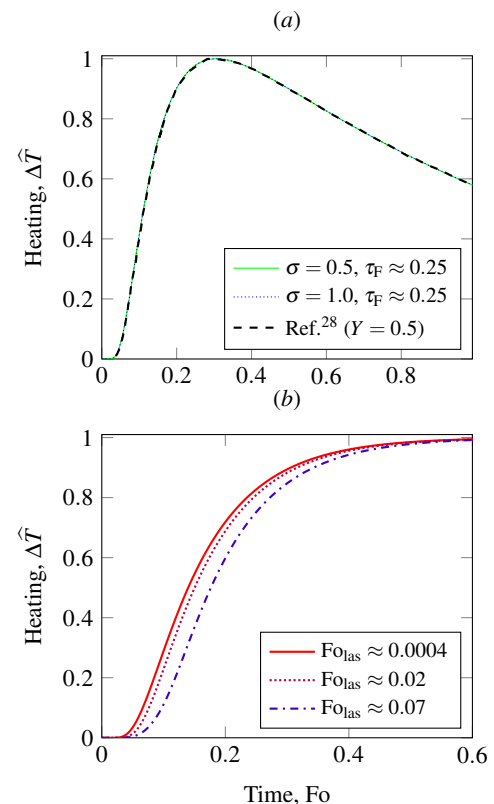


FIG. 4. The effect of (a) heat losses and (b) finite pulse width of a rectangular wave ($\sigma = 1.0$, $N = 30$). Comparison of the finite-difference solution of the boundary problem in Eq. (6) using various different schemes (FTCS, fully implicit and Crank-Nicolson) with the model by Cape and Lehman²² corrected by Josell, Warren, and Cezairliyan²⁸, which describes the laser heating of a wide, thin sample by an infinitely small laser pulse, following heat dissipation from front and rear surfaces with an efficiency $Y = 0.5$. For the numeric solution, the pulse shape has been chosen as rectangular with the pulse duration $Fo_{\text{las}} \approx 4 \times 10^{-4}$.

has been plotted for different grid parameters N and τ_F . The highest accuracy for a very short laser pulse is achieved with the fully implicit scheme ($\sigma = 1.0$) on a dense ($N = 80$, $\tau_F = 0.05$) grid, where the maximum deviation from the analytical solution (Fig. 3) is less than 0.01%, and with the Crank-Nicolson scheme ($\sigma = 0.5$) on a loose grid ($N = 30$, $\tau_F = 6.25 \times 10^{-3}$). Overall, both $\sigma = 0.0$ and $\sigma = 1.0$ schemes with an increased order of approximation $O(\tau + h^2)$ show good numeric stability and high accuracy down to $N = 15$ and even lower – compared to a conditionally-stable FTCS scheme with an $O(h)$ approximation of the boundary conditions. For the second comparison ($Bi = 0.5$) a very close agreement to the corrected Cape-Lehman model (Josell, Warren, and Cezairliyan²⁸) is shown in Fig. 4 (a). Fig. 4 (b) shows the solutions for different pulse widths Fo_{las} .

V. REVERSE-ENGINEERING OF THE TIME-TEMPERATURE PROFILES TO INFER THERMAL PROPERTIES

Thermal properties in a laser flash experiment are determined from the minimum of the objective function $f(\mathbf{S})$ calculated using Eq. (2) on a curve-to-curve basis. The argument \mathbf{S} is defined as a variable-size search vector, the components of which are formed by including the material-dependant thermal properties (a/l^2 , Bi and ΔT_{\max}), and, as an option for fine tuning of noisy data, either or both of the baseline parameters, k_{lin} and T_{lin} . In cases when noise is large and heat losses are expected to be negligible, to avoid situations where Bi may turn negative, it may be explicitly excluded from the search. Thus, the dimension of \mathbf{S} may vary from two (a/l^2 and T_{\max}) to five.

A. Nonlinear optimization algorithms

To find \mathbf{S} , a nonlinear optimization algorithm is used to determine the minimum direction \mathbf{S}_{min} . Once it is found, a linear search determines the optimal magnitude of the step in the \mathbf{S} direction. These actions are repeated iteratively. If proper algorithms are chosen, with each iteration the objective function $f(\mathbf{S})$ is brought closer to the global minimum. If the model (Eqs. 6) is adequate, an unbiased estimate of thermal properties is produced at the global minimum of $f(\mathbf{S})$.

1. Quasi-Newton method with approximated Hessian

The calculation of the objective function gradient takes one of the central parts in the direction search routine. If ΔS_i is a small variation of the i -th component of the search vector, the associated component of the gradient is $\Delta f(S_i + \Delta S_i) / \Delta S_i$, or more precisely (Gill, Murray, and Wright³⁴):

$$g_i = \frac{f(S_i + \Delta S_i) - f(S_i - \Delta S_i)}{2\Delta S_i}, \quad (16)$$

where a central-difference approximation is used; $f(S_i + \Delta S_i)$ is the value of the objective function calculated at a new search vector $\bar{\mathbf{S}}$, all components of which are identical to \mathbf{S} except for the i -th component, which is defined as $\bar{S}_i = S_i + \Delta S_i$. Eq. (16) introduces a calculation error $\sim O(\Delta S_i)$.

Consider the following Taylor expansion to the second order of $f(\mathbf{x}_k)$ in the $\gamma \mathbf{p}$ vicinity of $\mathbf{x}_k = \mathbf{S}_k$: $f(\mathbf{S}_k + \gamma \mathbf{p}_k) \simeq f(\mathbf{S}_k) + \gamma \mathbf{g}_k^T \mathbf{p}_k + \frac{1}{2} \gamma^2 \mathbf{p}_k^T \mathbf{G}_k \mathbf{p}_k$. The minimum of this quadratic form then corresponds to the Newtonian condition: $\mathbf{p}_k = -\mathbf{G}_k^{-1} \mathbf{g}_k$. If the Hessian matrix \mathbf{G}_k is approximated by \mathbf{H}_k , the direction to minimum is then defined as:

$$\mathbf{p}_k \approx -\mathbf{H}_k^{-1} \mathbf{g}_k, \quad (17)$$

where \mathbf{H}_k is a positive definite matrix containing the curvature information for the objective function.

A Broyden–Fletcher–Goldfarb–Shanno (BFGS) (Gill, Murray, and Wright³⁴) algorithm is used to calculate \mathbf{H}_{k+1} at the next iteration $k+1$ using the gradient value \mathbf{g}_k and the increment $\mathbf{u}_k = \mathbf{g}_{k+1} - \mathbf{g}_k$:

$$\mathbf{H}_{k+1} = \mathbf{H}_k + \frac{1}{\mathbf{g}_k^T \mathbf{p}_k} \mathbf{g}_k \mathbf{g}_k^T + \frac{1}{\gamma_k \mathbf{u}_k^T \mathbf{p}_k} \mathbf{u}_k \mathbf{u}_k^T, \quad (18a)$$

$$\mathbf{H}_0 = \mathbf{I}, \quad (18b)$$

where \mathbf{I} is a $r \times r$ identity matrix, r is the dimension of the search vector. Thus, the direction to the minimum at the first iteration coincides with the inverted gradient, same as in the gradient descent algorithm, which searches for a stationary point of the $f(\mathbf{S})$. The inverse of the approximated Hessian matrix \mathbf{H}_k is computed using a recursive procedure based on the Laplace expansion.

Note Eq. (18) is extremely sensitive to the selection of γ_k , which is chosen via a linear search algorithm.

2. Inexact stochastic linear search based on the Wolfe conditions

After the vector \mathbf{p}_k is calculated, the search vector \mathbf{S}_{k+1} at the next iteration may be expressed as $\mathbf{S}_{k+1} = \mathbf{S}_k + \gamma_k \mathbf{p}_k$. If $\gamma_k \in [0, \gamma_{\max}]$, a linear search may be applied to calculate γ_k , which minimizes the objective function $f(\mathbf{S}_k + \gamma_k \mathbf{p}_k)$. In practice, it is convenient to choose $\gamma_{\max} = 0.5 \times S_{\omega_0} / p_{\omega_0}$, where ω_0 is the index of the thermal diffusivity component of \mathbf{S}_k . If ω_1 is the index of the heat losses in \mathbf{S}_k and $S_{k, \omega_1} + \gamma_{\max} p_{k, \omega_1} > \Delta \text{Bi}_{\max}$, the value γ_{\max} is decreased so that the maximum changes of Bi are less than $\Delta \text{Bi}_{\max} \approx 1$.

The Wolfe conditions are used to assess whether \mathbf{S}_{k+1} is likely to be the minimum point. Here the strong Wolfe conditions are considered (Wolfe³⁵, Wolfe³⁶):

$$f(\mathbf{S}_{k+1}) - f(\mathbf{S}_k) \leq c_1 \gamma_k \mathbf{p}_k^T \mathbf{g}_k, \quad (19a)$$

$$|\mathbf{p}_k^T \mathbf{g}_{k+1}| \leq c_2 |\mathbf{p}_k^T \mathbf{g}_k|, \quad (19b)$$

where $c_1 = 0.05$, $c_2 = 0.8$.

The computational procedure utilizing inequalities (19) starts by generating a random point $\alpha_k = z$ internal to the $[a, b]$ segment. The objective function is then calculated at this point, and if inequality (19a) is not satisfied, the segment is then reduced to $[a, z]$. If it is satisfied, then the second condition (inequality (19b)) is evaluated. If the latter is satisfied, then z is considered to be the minimum point, otherwise the computational domain is reduced to $[z, b]$. The procedure continues while the segment length is greater than E_{lin} .

The algorithm described above works particularly well with the quasi-Newton direction solver.

B. Initial conditions and stopping criteria

An initial value \mathbf{S}_0 is required and allows to reduce the computational costs if chosen reasonably. Fortunately, this

is easy to do once the half-rise time (Sect. II B) has been estimated from the experimental data. The initial thermal diffusivity value is determined using the classic solution by Parker *et al.*¹ with the corrected coefficient reported by Heckman³², Josell, Warren, and Cezairliyan²⁸ and Carr¹⁹: $a_0 = 1.370 \times l^2 / \pi^2 t_{1/2}$. The maximum heating and initial baseline values are determined as described in Sect. II B, the initial value of the Biot number is set to zero.

After starting the search, a fixed-size buffer (the default is eight entries) is filled successively with S_k values at each new iteration k ; this is complemented by the SSR value (Eq. (2)). When the buffer is full, the standard deviation of those values δS_ω is calculated for each ω -th component plus for the SSR. The relative error, calculated as $\delta S_\omega / \langle S_\omega \rangle$ is then compared to a constant E_{gen} . If $\forall \omega \in \mathbb{Z} : \delta S_\omega / \langle S_\omega \rangle \leq E_{\text{gen}}$, the search completes normally. Otherwise, the buffer is cleared and the search continues until the criterion is finally satisfied or if the iteration limit is reached.

C. Example applications and convergence tests

Three previously measured time-temperature profiles were selected to represent a gradual deviation from the perfect experimental conditions. These deviations are introduced by unknown experimental factors, which affect either the perceived temperature rise or the actual heat transfer in the sample. The pre-selected data is then reverse-engineered following the procedure described above to produce an optimal S_k . The performance of this procedure under real-world conditions is judged and the convergence is tested.

The raw data was collected using two experimental installations:

- (a) the Kvant laser flash analyser designed at the Moscow Engineering Physics Institute equipped with two temperature detection capabilities: (i) a thermocouple (pre-welded onto the rear surface of the sample coated with platinum black prior to each experiment) connected to a scalable amplifier with automatic constant-voltage subtraction providing rapid detection of heating with an error of less than 2.5×10^{-3} K and (ii) an in-house designed InGaAs pyrometer (a detector sight diameter $d_{\text{av}} = 6$ mm). A combination of a rotary pump and a diffusion pump ensure high vacuum (0.01 Pa or 10^{-4} mbar). An additional capability of controlling the oxygen partial pressure is realized by means of a solid-electrolyte galvanic cell; the oxygen partial pressure can be changed on-the-fly. The laser delivers 1.5 ms fixed-width pulses with an energy of 5 – 7 J per pulse using a ruby laser;
- (b) the Linseis Culham LFA, a prototype based on the Linseis LFA 1600 instrument, modified by the manufacturer to allow integration in a research room in the Materials Research Facility (MRF) at UKAEA for testing of mildly-radioactive samples. The furnace ambient temperature is measured using a low-resolution pyrometer, while a PbSe-based Peltier-cooled detector is

used to register the rear-surface heating of the sample. A simple rotary pump is capable of pumping the chamber down to 0.1 – 0.01 mbar. The pulse width, pulse energy (up to 31 J), the detector gain and aperture can be changed by the operator during the experimental run.

The materials under study were the following: a sintered sample of nearly-stoichiometric uranium dioxide ($l = 1.7118$, $d = 10.061$) with a porosity of about 8.5 % and two 10-mm Zr-1%Nb E110 alloy discs cut by electrical discharge machining ($l = 0.414$ mm and $l = 0.199$ mm). The raw heating curve analysed here for the uranium dioxide pellet was reported previously (e.g., Baranov *et al.*³⁷). The measurements of the E110 alloy samples were conducted with the Linseis Culham LFA, graphite-spraying both surfaces of the samples prior to tests with a Graphit 33 Contact ChemieTM coating.

Thermal properties are reverse-engineered from experimental data using the heat transfer model given by Eqs. (6). A quasi-Newton direction search (Sect. V A 1) with a linear stochastic search algorithm based on the Wolfe conditions (Sect. V A 2) was applied to reach the minimum of the objective function (gradient resolution $\Delta S_i / S_i = 10^{-4}$, linear search error $E_{\text{lin}} = 10^{-7}$, overall search error $E_{\text{gen}} = 10^{-3}$). The model solution was calculated using a fully implicit ($\sigma = 1.0$) difference scheme (Eq. (9)) with the default grid settings $N = 30$, $\tau_F = 0.25$ (total number of points for the model curve $n_s = 100$).

1. Uniform low noise

Fig. 5 shows a heating curve for a nearly-stoichiometric UO_2 sample at a test temperature $T_0 = 1829.7$ K. Due to a poor thermal conductivity, which is especially low at high temperatures, the characteristic heat conduction time is high. Conversely, the heat losses due to radiation are huge. The heat transfer model (Eqs. (6)) perfectly describes the experimental data, except for the initial segment, which can be attributed to the long-distance bipolar diffusion induced by the absorption of the incident laser beam by the semi-conducting material (Baranov *et al.*³⁷). Since the baseline was accurately determined by the instrument software, only the thermal diffusivity a , the Biot number Bi , and the maximum temperature ΔT_{max} were included in the search vector. Excellent convergence is obtained already after 16 iterations, with the mean deviation per point $|\Delta \hat{T}_i - T_i| \approx 1.5 \times 10^{-2}$ K. Interestingly, the first iteration (same as for the gradient descent method) results in a shift of the search vector to a different local minimum, but the numerical procedure quickly escapes it and gets to the right track to the global minimum.

2. Non-uniform high noise

Fig. 6 shows a heating curve for a $l = 0.414$ mm E110 alloy sample at a test temperature $T_0 = 1024$ K. The material tested with the Linseis Culham LFA is a fair thermal conductor and the sample is sufficiently thin so that the heat wave

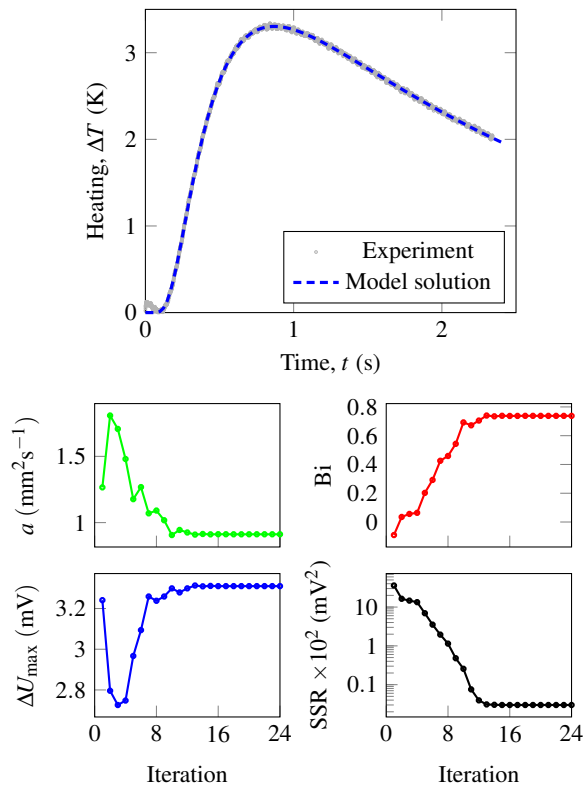


FIG. 5. An example run of the reverse-engineering procedure for an experimental time-temperature profile measured with the Kvant laser flash analyser (total number of data points $n_{\text{exp}} = 4,800$) of a 91.5 % dense UO_2 sample at $T_0 = 1829$ K, showing the final heating curve corresponding to the optimized set of model parameters and the components of the search vector, fully converged after 24 iterations. Note the small plateau on the SSR plot, which is likely attributed to a local minimum of the objective function.

reaches the rear surface of the sample relatively fast. Because of this, the heat losses are negligible at this and even higher temperature, hence they can be excluded from the search vector. On the other hand, the baseline (initially defined at $k_{\text{lin}} = 0$ as explained in Sect. II B) needs to be adjusted due to the inaccurate baseline estimation based on the under-represented statistics at $t < 0$ from noisy data. Same as previously, full convergence is obtained after 24 iterations, with the average data spread of ≈ 0.25 mV. The search for the optimal baseline slope seems to be taking the longest time.

3. Pathological data

Fig. 7 shows a heating curve for a $l = 0.199$ mm E110 alloy sample at a test temperature $T_0 = 1024$ K measured with the Linseis Culham LFA. The low thickness of the sample leads to rapid heat conduction, with the acquisition time less than 5 ms. At this time the baseline intercept estimated at $t < 0$ seemed to be sufficiently accurate as it was measured over a longer time interval than the actual heating curve. On the other hand, the data obviously showed either a detector sig-

nal drift or an ambient temperature instability, which needed to be corrected for by adjusting the baseline slope. Additionally, the data in Fig. 7 shows anomalies with pronounced low-frequency, high-amplitude noise, which distorts the heating curve so that it becomes nearly impossible to assess its true shape. However, applying the nonlinear optimization procedure described in this section allows reaching a global minimum of the objective function in less than 24 iterations, with an average data spread of ≈ 0.45 mV.

VI. CROSS-VALIDATION WITH EXTERNAL REFERENCE AND COMMERCIAL SOFTWARE

An attested reference tungsten sample ($l = 2.034$ mm, $d = 9.88$ mm) was purchased from Netzsch to conduct an independent validation study. The sample arrived with a printed copy of a reference table listing the pre-measured thermal diffusivity values in accordance with the ASTM standard¹⁴. The sample was then prepared for laser flash measurements following the manufacturer and ASTM recommendations by coating both sides with a thin layer of high-emissivity carbon. As previously, a Graphit 33 Contact ChemieTM spray was used on the sample pre-heated at 100 °C. The coated tungsten sample had its thickness measured with a micrometer and then was placed in a graphite sample holder on top of a graphite thermal shield of the Linseis Culham LFA. The system was evacuated to a pressure below 10^{-1} mbar and filled with a Grade Zero argon gas. This process was repeated three times, after which the gas flow was set to 8 l/h. The heating curves were measured in a range of temperatures $T_0 = 473 - 2273$ K (heating and cooling rates were $20^\circ\text{C}/\text{min}$) with a PbSe detector. At each temperature, the detector parameters (gain, iris, and acquisition time), as well as the laser power and pulse duration, were changed manually by the operator to deliver the best signal-to-noise ratio and recorded in a metadata file separately. Measurements and data processing using the ‘‘Combined model’’ and constant-baseline subtraction were controlled from the commercial Linseis Aprosoft software adapted specifically for the Linseis Culham LFA. Default settings were used for the temperature and detector current stability controls, and a constant delay of 90 s was used between shots. The resulting thermal diffusivity data is plotted in Fig. 8.

The recorded detector signal exported in ASCII-format and metadata files prepared by the operator were used as input when running PULsE. Again, as previously, a quasi-Newton direction search (Sect. V A 1) with a linear stochastic search algorithm based on the Wolfe conditions (Sect. V A 2) were adopted for data treatment (a gradient resolution $\Delta S_i/S_i = 10^{-4}$, a linear search error $E_{\text{lin}} = 10^{-7}$ and a global search error $E_{\text{gen}} = 10^{-3}$). A fully implicit ($\sigma = 1.0$) difference scheme was used to calculate $\hat{T}(t)$ (Eq. (9)) with the default grid settings $N = 30$, $\tau_F = 0.25$ (total number of points for the model curve $n_s = 100$).

Experimental data was processed individually for each curve, adjusting the time range only when such intervention was necessary (an example of this is shown in Fig. 9 (a), and a standard truncation routine was applied automatically (see

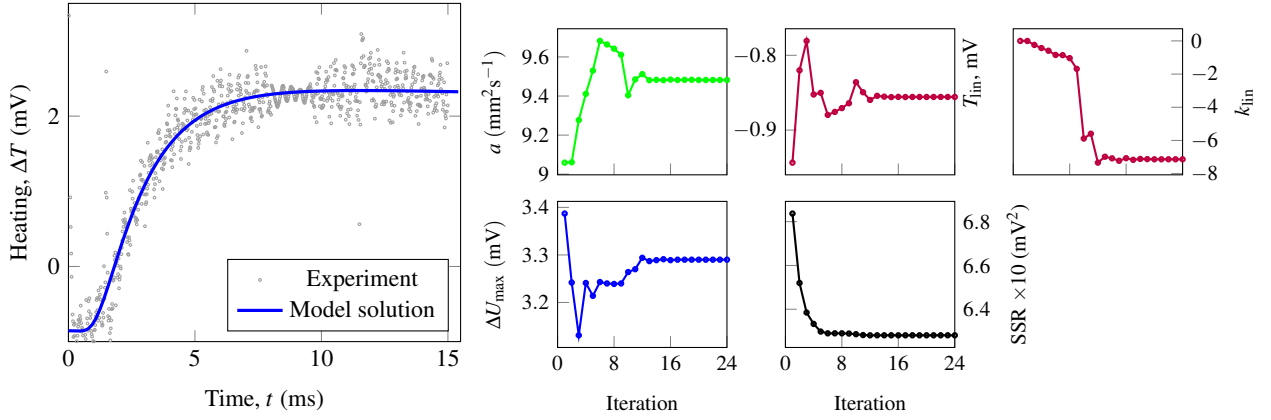


FIG. 6. An example run of the reverse-engineering procedure for an experimental time-temperature profile with a high non-uniform noise (likely consisting of several noise harmonics) measured with the Linseis Culham LFA (total number of data points $n_{\text{exp}} = 864$) of a graphite-coated $l = 0.414$ mm E110 alloy sample at $T_0 = 1024$ K, showing the final heating curve corresponding to the optimized set of model parameters and the components of the search vector, fully converged after 24 iterations.

Sect. III C).

The default search variables were: the thermal diffusivity a , the maximum heating ΔU_{max} , and the baseline intercept T_{in} . A linear negative drift of the detector signal could be observed at $T_0 = 473$ K (see e.g. Fig. 9 (a)), which required including the baseline slope as a search variable at that temperature. Obviously, this drift (to be discussed in more detail in a future paper) could not originate from the radiation heat losses due to a rapid heat transfer, low detection times, and low test temperature – all contributing to a low Bi value (as from Eq. (5b)). If included in the search vector, the latter would have been poorly estimated due to a low signal-to-noise ratio (Fig. 10 (a)). At $T_0 \leq 1073$ K and $T_0 > 1873$ K the heat losses were indistinguishable from the detector noise (e.g. Fig. 9 (b)). Likewise, at medium temperatures ($1273 \leq T_0 \leq 1873$ K) the accuracy of detector measurements was sufficiently high and the temperature-dependent heat losses pronounced. All of these factors had to be taken into account manually when performing the final calculations (see supplementary material). Unfortunately, PULsE still requires manual input based on the recommendations above to produce the most accurate results. Work is currently undergoing to deliver a fully-automatic procedure for determining the most important independent variables based on a statistical data analysis.

Finally, a residual analysis was conducted for the thermal diffusivity datasets from the Linseis Aprozsoft and PULsE software (Fig. 10 (b)). A large number of outliers characteristic to the Aprozsoft results (Fig. 8) was due to an intermittent detector failure, with the signal saturating at either the lower (-10 mV) or higher ($+10$ mV) detection limits (this could have also been due to an operator error when selecting the detector gain). PULsE, on the other hand, was able to reconstruct the heating curve based on these incomplete measurements by limiting the search range, hence the error distribution is localized near zero for PULsE data (Fig. 10). Quite importantly, even though the commercial software was able to deliver meaningful values in many cases, the associated error distribution had a median

at $0.867 \text{ mm}^2\text{s}^{-1}$, meaning that an uncompensated systematic error was present. The median error for the PULsE data was significantly lower ($-0.18 \text{ mm}^2\text{s}^{-1}$), suggesting a better quality of the search procedure, a better thermal transfer model or both.

VII. CURRENT LIMITATIONS OF THE COMPUTATIONAL METHOD

The following list of problems will be addressed in future publications.

- A source of uncertainty associated with non-uniform heating has not been considered in the present study, but is listed in the ASTM document¹⁴. If the diameter of the laser spot d_{las} is smaller than the diameter of the sample d , radial heat fluxes will induce a change to the heating curve (e.g. as shown by Baba and Ono¹⁶). Hence, a fully two-dimensional heat conduction problem should be used instead;
- An automated procedure for selecting an optimal number of variables to achieve the least influence of the systematic experimental errors on the values of thermal properties is currently lacking; instead, some parameters are selected manually. A better procedure will likely involve a constrained version of nonlinear optimization (to limit $\text{Bi} \geq 0$) and a variable time domain. The latter will need to rely on a different statistic than the χ^2 – a possible solution would be using a Bayesian information criterion, which has proven to be effective for a different problem considered recently by Fulton and Lunev³⁸;
- Additional data filtering, e.g. using fast-fourier transform filters (Pavlov *et al.*⁷) or with an additional sinusoidal wave function (Šrámková and Log¹⁸) to mimic

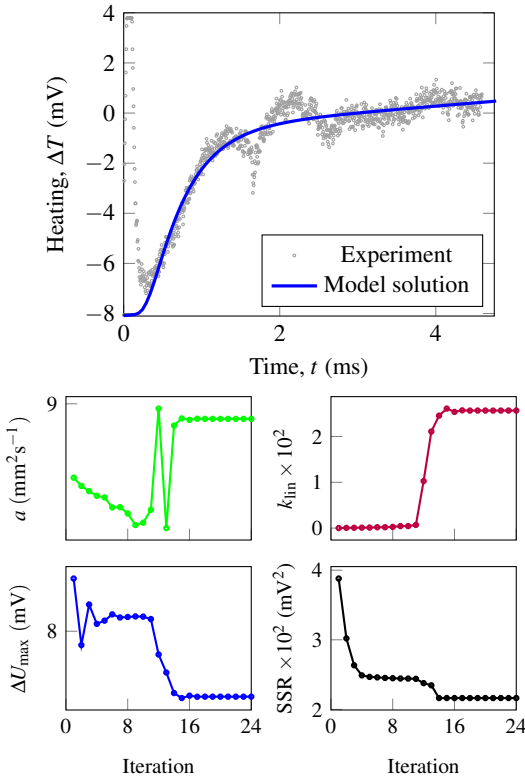


FIG. 7. An example run of the reverse-engineering procedure for an experimental time-temperature profile with a highly-inaccurate temperature measurement combined with a detector signal drift measured with the Linseis Culham LFA (total number of data points $n_{\text{exp}} = 1,050$) of a graphite-coated $l = 0.199$ mm E110 alloy sample at $T_0 = 674$ K, showing the final heating curve corresponding to the optimized set of model parameters and the components of the search vector, fully converged after 24 iterations.

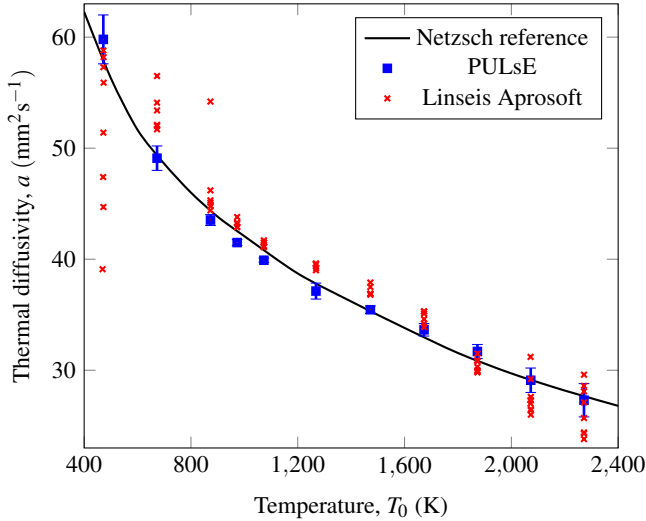


FIG. 8. Cross-validation results for PULsE (manual processing of each individual curve) and Linseis AproSoft (batch processing) using the data acquired with the Linseis Culham LFA on a standard tungsten sample from Netzsch, pre-coated with graphite. The solid line is plotted using the reference values provided by Netzsch.

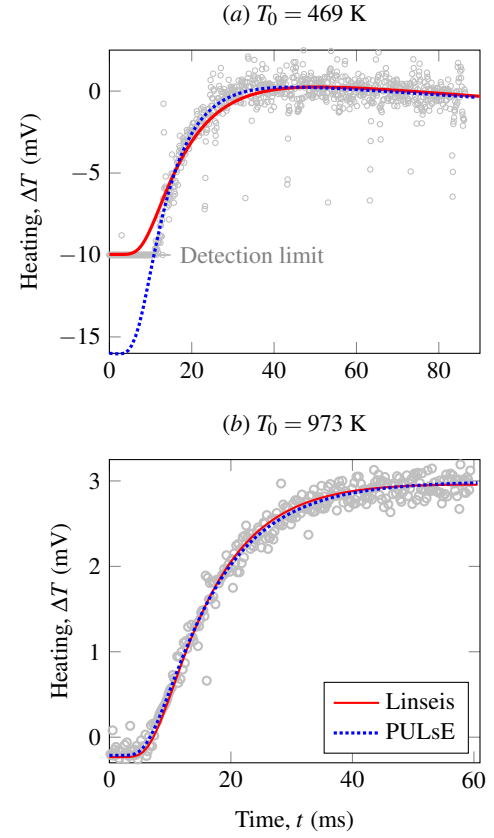


FIG. 9. Example benchmarking of PULsE on two datasets: (a) an experiment at $T_0 = 469$ K. Due to a detector failure, the signal saturated at -10 mV for the first ≈ 12 ms after the laser shot. PULsE was capable of correcting for that error after manually limiting the time range to exclude problematic values, resulting in a value of thermal diffusivity $a = 56.03$ mm^2s^{-1} , while Linseis Aprosoft ($a = 39.1$ mm^2s^{-1}) lacks that capability; (b) an experiment at $T_0 = 973$ K. Although the curves look similar, the model calculations in PULsE ($a = 41.1$ mm^2s^{-1}) are in closer agreement with the measured data compared to Linseis Aprosoft ($a = 43.2$ mm^2s^{-1}).

the electric noise of the mains power supply or other potential sources of electromagnetic interference such as the excessive cable length or the proximity to power cables, may add to the noise robustness of the numerical method;

- Parker *et al.*¹ have originally estimated that in the adiabatic case the maximum front surface temperature of the sample after a laser pulse is $T_{\text{max}}(x=0) = 38T_{\text{max}}(x=l) \cdot l/a^{1/2}$, where $[l] = \text{cm}$, $[a] = \text{cm}^2\text{s}^{-1}$. When heat dissipates by radiative transfer, the front-surface heating will be lower; however, it is clear that for sufficiently low test temperatures $\Delta T/T_0$ may no longer be considered small. The other side of the problem consists in the intrinsic nonlinear dependence of heating on the spectral radiance, which is especially pronounced when $\Delta T > 30 - 40$ K (Wang and Dinwiddie³⁹). This means that both the nonlinear detector output and the nonlinear heat losses need to be taken into

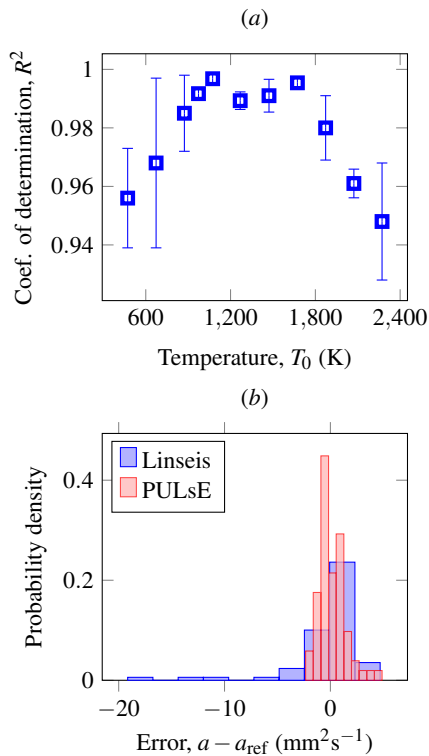


FIG. 10. Statistical analysis of the thermal diffusivity data: (a) the coefficient of determination R^2 calculated with PULsE and averaged at each test temperature, showing a correlation with the detector signal-to-noise ratio; (b) the probability density of error $a_i - a_{i,\text{ref}}$, where $a_{i,\text{ref}}$ are the Netzsch reference values, with the median values 0.867 and $-0.18 \text{ mm}^2 \text{ s}^{-1}$ for thermal diffusivity data obtained with the Linseis Aprosoft and PULsE software respectively.

account for some cases, e.g. for the twin detector design used by Pavlov *et al.*⁷ and Ronchi *et al.*⁸;

- A more computationally-efficient optimization technique may need to be considered for the two-dimensional and nonlinear problems;
- Current analysis does not cover: multi-layered heat transfer, a distributed heat source, and the twin-detector design.

It is hoped that some of the limitations may be resolved in collaboration with other researchers – particularly, the extension of the computational method to the twin-detector design.

VIII. CONCLUSIONS

A computational method based on the finite-difference solution of the heat conduction problem coupled with a nonlinear optimization procedure utilizing the BFGS algorithm and Wolfe conditions is reported. The results of finite-difference calculations have been verified against some extreme cases of the analytic models considered previously: (a) the adiabatic heating caused by an infinitely short laser pulse; (b) the

Cape-Lehman model corrected by Josell *et al.* ($Y = 0.5$) – demonstrating high accuracy and reliability. The optimization procedure was shown to effectively treat experimental data at different noise levels, including noise formed of several superimposed harmonics and varying baseline drift. A cross-validation study of the PULsE software implementing this computational method has been conducted with Linseis equipment at the Materials Research Facility on a Netzsch reference sample by benchmarking against the packaged Linseis software. Generally, PULsE outperforms Linseis Aprosoft due to wider data treatment capabilities and fine tuning. Future work will focus on extending its capabilities and improving batch-processing of data.

ACKNOWLEDGMENTS

This work was partially funded by the RCUK Energy Programme (Grant No. EP/T012250/1). The research used UKAEA’s Materials Research Facility, which has been funded by and is part of the UK’s National Nuclear User Facility and Henry Royce Institute for Advanced Materials.

SUPPLEMENTARY MATERIAL

See supplementary material for a complete set of experimental data and calculations results using PULsE and Linseis Aprosoft.

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