A New Parameter Estimation Method for DSC Thermodynamic Property Evaluation – Part I: Analytic Development

G. E. Osborne, Ph.D. Candidate
J. I. Frankel, Professor
Mechanical and Aerospace Engineering and Engineering Science Department
University of Tennessee
Knoxville, Tennessee (USA) 37996-2210
email: gosborne@utk.edu
A. S. Sabau, Research Staff Member
Oak Ridge National Laboratory
1 Bethel Valley Road
Oak Ridge, Tennessee (USA) 37831-6083

ABSTRACT
A lumped heat transfer model and parameter estimation technique are proposed for determining key parameters associated with a heat flux *Differential Scanning Calorimeter* (DSC). Part I of this two-part paper focuses on developing the mathematical model and describing the proposed parameter estimation technique. Part II presents the numerical implementation using a conventional Runge-Kutta method with results indicating the merit of the proposed parameter estimation method. In this part, the physical model is derived, and simplifying assumptions are presented. The resulting heat transfer model requires the simultaneous resolution of two conduction and two radiation parameters, and one time-dependent function using two concurrent temperature data streams emanating from the container plates in the device. The unknown functions of interest include the furnace temperature which is expanded into a finite series involving R predefined basis functions each having a corresponding unknown expansion coefficient. The resulting system of initial-value problems is linearized using quasilinearization. Each dependent variable is then decomposed into a series of baseline and sensitivity functions. A least-squares minimization method is introduced using the collected data streams to determine the $4 + R$ parameters at the updated iterate. The iterative process is continued until convergence takes place for all system parameters. This paper highlights the modeling and algorithm aspects associated with resolving these parameters.

KEY WORDS
Parameter estimation, inverse problems, Function Decomposition Method, DSC

1 Introduction

Differential Scanning Calorimetry is often used for characterizing thermophysical properties such as specific heat, and melting and solidification characteristics such as the onset temperatures of phase transformation, the enthalpy of fusion, and the solid fraction as a function of temperature [1–5]. In such devices, however, the collected temperature data are not necessarily representative of the sample temperature due to thermal lags, contact conductances and radiative interactions. As a result, any simplified attempt to attach the recorded thermocouple reading to the sample site leads to erroneous results. It is imperative, therefore, to develop a mathematical model that correctly accounts for the heat transfer mechanisms in the DSC chamber where the sample is placed. Results from such a simulation provide an accurate depiction of the sample temperature by incorporating thermal lags into the modeled system. This paper develops a framework based on detailed modeling and the incorporation of experimental data to simultaneously extract the desired physical parameters and the furnace wall temperature.

2 Physical Model

A generalized physical model for the heat flux DSC of interest may be described by the schematic diagram shown in Figure 1. The model consists of two cylindrical containers (or pans) resting on disk-shaped plates. One combination of container and plate is associated with the sample whose thermophysical properties are unknown, while the other combination is defined as a known reference. For the purpose of this investigation, the sample and reference containers and plates are considered to be symmetric. The supporting plates are, in turn, connected by thin wires to a larger container holder which is attached to a disk holder. The entire apparatus is surrounded by a uniform heating surface or furnace. Thermocouples embedded in the bottom surfaces of the sample and reference plates are utilized to obtain temperature data for both components.

Heat flow analysis of a similar heat flux DSC model has shown that the temperature gradients within a particu-

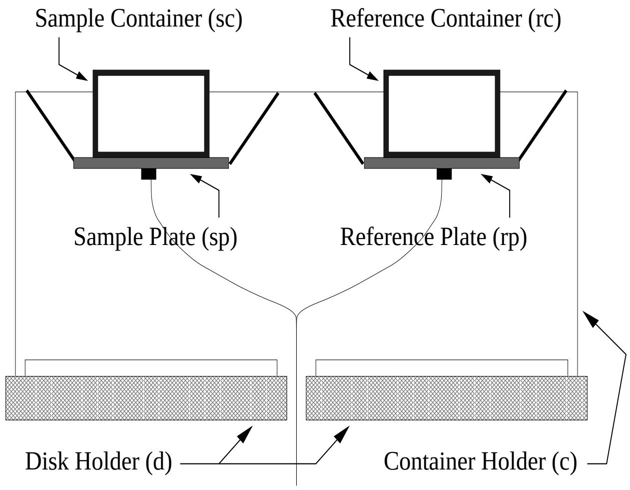

Figure 1. Schematic for typical heat flux DSC head system.

lar component are negligible when compared to the differences which occur at the boundaries between two separate regions of the calorimeter [6]. Therefore, it is possible to represent each component as a region possessing a spatially uniform temperature at any instant during the heating or cooling process. Heat transfer within the calorimeter may then be assumed to take place between the individual regions in the form of thermal resistances as suggested by [7] and [8].

Neglecting the effects of convection, which are small when compared with the other modes of heat transfer, and ignoring the minimal conduction which occurs along the wires supporting the sample and reference plates, a heat balance between the components of the model described above produces the system of governing equations

$$\begin{aligned} m_{sc}C_{sc}\frac{dT_{sc}}{dt} =& K_{sp}(T_{sp}-T_{sc}) - K_{sc}(T_{sc}-T_s) \\ &+ E_{fc}(T_f^4 - T_{sc}^4) + E_s(T_s^4 - T_{sc}^4) \\ &+ E_c(T_c^4 - T_{sc}^4), \end{aligned} \tag{1a}$$

$$\begin{aligned} m_{rc}C_{rc}\frac{dT_{rc}}{dt} =& K_{rp}(T_{rp}-T_{rc}) - K_{rc}(T_{rc}-T_r) \\ &+ E_{fc}(T_f^4 - T_{rc}^4) + E_r(T_r^4 - T_{rc}^4) \\ &+ E_c(T_c^4 - T_{rc}^4), \end{aligned} \tag{1b}$$

$$m_s\frac{dH_s}{dt} = K_{sc}(T_{sc}-T_s) - E_s(T_s^4 - T_{sc}^4), \tag{1c}$$

$$m_r\frac{dH_r}{dt} = K_{rc}(T_{rc}-T_r) - E_r(T_r^4 - T_{rc}^4), \tag{1d}$$

$$m_{sp}C_{sp}\frac{dT_{sp}}{dt} = -K_{sp}(T_{sp}-T_{sc}) - E_p(T_c^4 - T_{sp}^4), \tag{1e}$$

$$m_{rp}C_{rp}\frac{dT_{rp}}{dt} = -K_{rp}(T_{rp}-T_{rc}) - E_p(T_c^4 - T_{rp}^4), \tag{1f}$$

$$\begin{aligned} m_cC_c\frac{dT_c}{dt} =& E_{fc}(T_f^4 - T_c^4) + E_d(T_d^4 - T_c^4) \\ &- E_p(T_c^4 - T_{sp}^4) - E_p(T_c^4 - T_{rp}^4) \\ &- E_c(T_c^4 - T_{sc}^4) - E_c(T_c^4 - T_{rc}^4), \end{aligned} \tag{1g}$$

$$m_dC_d\frac{dT_d}{dt} = E_d(T_f^4 - T_d^4) - E_d(T_d^4 - T_c^4), \quad t \geq 0, \tag{1h}$$

where m is the component mass, C is the component specific heat, K is the component-specific conduction parameter, and E is the component-specific radiation parameter. Equations (1a – h) apply to the sample container (sc), reference container (rc), sample (s), reference (r), sample plate (sp), reference plate (rp), container holder (c), and disk holder (d), respectively. It can readily be seen that this model requires the determination of nine unknown temperature functions as well as the estimation of eleven unknown parameters – four conduction-related parameters and seven radiation-related parameters – using only the data gathered by the thermocouples on the sample and reference plates. It would therefore be beneficial, as a first approximation, to construct a simplified version of the above model.

3 System Simplification and Mathematical Formulation

A simplified model for the two-pan heat flux DSC system described in the previous section may be constructed based on the following assumptions:

- No reference sample is used in the reference container; as a result, the need for its contribution to the model is eliminated.
- The sample and sample container are considered to have the same instantaneous temperature; hence, only one equation is needed to analytically model both components.
- The container holder and disk holder are considered to have the same instantaneous temperature as the furnace wall; therefore, these two components may be neglected in the model.

Heat flux DSC experiments are often conducted without the use of a reference sample, validating the first assumption. The other assumptions may be justified based on the small mass of the components and the advantageous thermophysical properties associated with the alloys of which they are made.

Considering only single phase heating and cooling, the above assumptions lead to a set of governing equations for the remaining components as given by

$$\alpha_s\frac{dT_s}{dt} = K_{sp}(T_{sp}-T_s) + E_{fc}(T_f^4 - T_s^4), \tag{2a}$$

$$\alpha_r \frac{dT_r}{dt} = K_{rp}(T_{rp} - T_r) + E_{fc}(T_f^4 - T_r^4), \qquad (2b)$$

$$\alpha_{sp} \frac{dT_{sp}}{dt} = -K_{sp}(T_{sp} - T_s) + E_{fp}(T_f^4 - T_{sp}^4), \qquad (2c)$$

$$\alpha_{rp} \frac{dT_{rp}}{dt} = -K_{rp}(T_{rp} - T_r) + E_{fp}(T_f^4 - T_{rp}^4), \quad t \geq 0, \qquad (2d)$$

where

$$\alpha_s = m_{sc}C_{sc} + m_s C_s, \qquad (2e)$$

$$\alpha_r = m_r C_r, \qquad (2f)$$

$$\alpha_{sp} = m_{sp} C_{sp}, \qquad (2g)$$

$$\alpha_{rp} = m_{rp} C_{rp}, \qquad (2h)$$

with the initial conditions

$$T_s(0) = T_{sp}(0) = T_r(0) = T_{rp}(0) = T_o. \qquad (2i)$$

Furthermore, it is assumed that temperature data are available at both the sample plate and reference plate, i.e.,

$$\{T_{sp,i}\}_{i=0}^{M} \quad \longrightarrow \quad T_{sp}(t_i) = T_{sp,i}, \qquad (3a)$$

$$\{T_{rp,i}\}_{i=0}^{M} \quad \longrightarrow \quad T_{rp}(t_i) = T_{rp,i}. \qquad (3b)$$

Hence, the problem may be described as having four unknown system parameters – $K_{sp}, K_{rp}, E_{fc}, E_{fp}$ – as well as the unknown temperature functions. The two conduction-related parameters are associated with heat flow between the sample (or reference) plate and sample (or reference) container, while the two radiation-related parameters are associated with heat flow between the furnace wall and the plates (E_{fp}) or containers (E_{fc}).

For convenience, the radiative contribution from the furnace wall, T_f^4, can be represented as a series expansion of the form

$$T_f^4(t) = \sum_{j=0}^{R} a_j \Omega_j(t), \qquad t \geq 0, \qquad (4)$$

where the expansion coefficients, $\{a_j\}_{j=0}^{R}$, become additional unknown parameters which are determined in the minimization process. For an initial furnace wall temperature condition given by $T_f(0) = T_o$, the expansion at $t = 0$ may be written as

$$T_f^4(0) = T_o^4 = \sum_{j=0}^{R} a_j \Omega_j(0). \qquad (5)$$

Releasing the a_0 coefficient in the expansion leads to the expression

$$T_o^4 = a_0 \Omega_0(0) + \sum_{j=1}^{R} a_j \Omega_j(0). \qquad (6)$$

If $\Omega_j(t)$ is chosen such that $\Omega_0(0) \neq 0$, algebraic manipulation of Eq. (6) yields

$$a_0 = \frac{T_o^4}{\Omega_0(0)} - \sum_{j=1}^{R} a_j \left(\frac{\Omega_j(0)}{\Omega_0(0)} \right), \qquad (7)$$

and so, substituting Eq. (7) into the general expansion in Eq. (4) provides

$$T_f^4(t) = T_o^4 \left(\frac{\Omega_0(t)}{\Omega_0(0)} \right) + \sum_{j=1}^{R} a_j \left[\Omega_j(t) - \left(\frac{\Omega_j(0)\Omega_0(t)}{\Omega_0(0)} \right) \right]. \qquad (8)$$

Making the definitions

$$\omega_j(t) \triangleq \left[\Omega_j(t) - \left(\frac{\Omega_j(0)\Omega_0(t)}{\Omega_0(0)} \right) \right], \quad j = 1, ..., R, \qquad (9a)$$

$$\gamma(t) \triangleq T_o^4 \left(\frac{\Omega_0(t)}{\Omega_0(0)} \right), \qquad (9b)$$

where

$\Omega_j(t) \equiv$ Set of basis functions,

$\omega_j(t) \equiv$ Set of trial functions,

the series expansion for the radiative contribution due to the furnace wall can be written as

$$T_f^4(t) = \gamma(t) + \sum_{j=1}^{R} a_j \omega_j(t), \qquad t \geq 0. \qquad (10)$$

Inserting Eq. (10) into Eqs. (2a – d) produces the modified governing equations

$$\alpha_s \frac{dT_s}{dt} = K_{sp}(T_{sp} - T_s) + E_{fc}\left[\left(\gamma(t) + \sum_{j=1}^{R} a_j \omega_j(t) \right) - T_s^4 \right], \qquad (11a)$$

$$\alpha_r \frac{dT_r}{dt} = K_{rp}(T_{rp} - T_r) + E_{fc}\left[\left(\gamma(t) + \sum_{j=1}^{R} a_j \omega_j(t) \right) - T_r^4 \right], \qquad (11b)$$

$$\alpha_{sp} \frac{dT_{sp}}{dt} = -K_{sp}(T_{sp} - T_s) + E_{fp}\left[\left(\gamma(t) + \sum_{j=1}^{R} a_j \omega_j(t) \right) - T_{sp}^4 \right], \qquad (11c)$$

$$\alpha_{rp} \frac{dT_{rp}}{dt} = -K_{rp}(T_{rp} - T_r) + E_{fp}\left[\left(\gamma(t) + \sum_{j=1}^{R} a_j \omega_j(t) \right) - T_{rp}^4 \right], \quad t \geq 0, \qquad (11d)$$

subject to the initial conditions displayed in Eq. (2i).

3.1 Quasilinearization

In order to apply the Function Decomposition Method (FDM) to the set of simultaneous nonlinear ordinary differential equations which govern the system, it is first necessary to employ Bellman's quasilinearization technique [9]. Based in part upon the Newton–Raphson method, quasilinearization provides a powerful and rapidly converging means for solving nonlinear equations. As an initial step, Eq. (11a – d) may be recast in the form

$$\begin{aligned}\Psi_1 =&\alpha_s \frac{dT_s}{dt} - K_{sp}(T_{sp} - T_s)\\ &- E_{fc}\left[\left(\gamma(t) + \sum_{j=1}^{R} a_j\omega_j(t)\right) - T_s^4\right] = 0, \quad \text{(12a)}\end{aligned}$$

$$\begin{aligned}\Psi_2 =&\alpha_r \frac{dT_r}{dt} - K_{rp}(T_{rp} - T_r)\\ &- E_{fc}\left[\left(\gamma(t) + \sum_{j=1}^{R} a_j\omega_j(t)\right) - T_r^4\right] = 0, \quad \text{(12b)}\end{aligned}$$

$$\begin{aligned}\Psi_3 =&\alpha_{sp} \frac{dT_{sp}}{dt} + K_{sp}(T_{sp} - T_s)\\ &- E_{fp}\left[\left(\gamma(t) + \sum_{j=1}^{R} a_j\omega_j(t)\right) - T_{sp}^4\right] = 0, \quad \text{(12c)}\end{aligned}$$

$$\begin{aligned}\Psi_4 =&\alpha_{rp} \frac{dT_{rp}}{dt} + K_{rp}(T_{rp} - T_r)\\ &- E_{fp}\left[\left(\gamma(t) + \sum_{j=1}^{R} a_j\omega_j(t)\right) - T_{rp}^4\right] = 0, \quad \text{(12d)}\end{aligned}$$

where $\{\Psi_k\}_{k=1}^4$ is considered to be functionally dependent on all unknown variables and parameters, i.e.,

$$\{\Psi_k\}_{k=1}^4 = f(\vec{x_1}, \vec{x_2}, \vec{x_3}), \quad \text{(13a)}$$

$$\begin{aligned}\vec{x}_1 &= \left\{\frac{dT_s}{dt}, \frac{dT_r}{dt}, \frac{dT_{sp}}{dt}, \frac{dT_{rp}}{dt}\right\},\\ \vec{x}_2 &= \{T_s, T_r, T_{sp}, T_{rp}\}, \quad \text{(13b)}\\ \vec{x}_3 &= \left\{K_{sp}, K_{rp}, E_{fc}, E_{fp}, \{a_j\}_{j=1}^R\right\}.\end{aligned}$$

Developing a multivariable Taylor series about iterate p, a recurrence relation between iterates p and $p+1$ may be obtained in the form

$$\begin{aligned}\Psi_k^{(p+1)} = \Psi_k^{(p)} &+ \left.\frac{\partial \Psi_k}{\partial \vec{x}_1}\right)_p \left(\vec{x}_1^{(p+1)} - \vec{x}_1^{(p)}\right)\\ &+ \left.\frac{\partial \Psi_k}{\partial \vec{x}_2}\right)_p \left(\vec{x}_2^{(p+1)} - \vec{x}_2^{(p)}\right)\\ &+ \left.\frac{\partial \Psi_k}{\partial \vec{x}_3}\right)_p \left(\vec{x}_3^{(p+1)} - \vec{x}_3^{(p)}\right)\\ &+ H.O.T., \qquad k = 1, ..., 4. \quad \text{(14)}\end{aligned}$$

Upon truncation of the higher order terms and enforcement of the condition $\Psi_k^{(p+1)} = \Psi_k^{(p)} = 0$, substitution of the required partial derivatives produces the series of iterative equations:

$$\begin{aligned}0 = 0 &+ \alpha_s \left(\frac{dT_s}{dt}^{(p+1)} - \frac{dT_s}{dt}\right)\\ &+ \left(K_{sp} + 4E_{fc}T_s^3\right)\left(T_s^{(p+1)} - T_s\right)\\ &- K_{sp}\left(T_{sp}^{(p+1)} - T_{sp}\right) - (T_{sp} - T_s)\left(K_{sp}^{(p+1)} - K_{sp}\right)\\ &- \left[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_s^4\right]\left(E_{fc}^{(p+1)} - E_{fc}\right)\\ &- E_{fc}\sum_{j=1}^{R}\omega_j\left(a_j^{(p+1)} - a_j\right), \qquad (k=1), \quad \text{(15a)}\end{aligned}$$

$$\begin{aligned}0 = 0 &+ \alpha_r \left(\frac{dT_r}{dt}^{(p+1)} - \frac{dT_r}{dt}\right)\\ &+ \left(K_{rp} + 4E_{fc}T_r^3\right)\left(T_r^{(p+1)} - T_r\right)\\ &- K_{rp}\left(T_{rp}^{(p+1)} - T_{rp}\right) - (T_{rp} - T_r)\left(K_{rp}^{(p+1)} - K_{rp}\right)\\ &- \left[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_r^4\right]\left(E_{fc}^{(p+1)} - E_{fc}\right)\\ &- E_{fc}\sum_{j=1}^{R}\omega_j\left(a_j^{(p+1)} - a_j\right), \qquad (k=2), \quad \text{(15b)}\end{aligned}$$

$$\begin{aligned}0 = 0 &+ \alpha_{sp} \left(\frac{dT_{sp}}{dt}^{(p+1)} - \frac{dT_{sp}}{dt}\right)\\ &+ \left(K_{sp} + 4E_{fp}T_{sp}^3\right)\left(T_{sp}^{(p+1)} - T_{sp}\right)\\ &- K_{sp}\left(T_s^{(p+1)} - T_s\right) + (T_{sp} - T_s)\left(K_{sp}^{(p+1)} - K_{sp}\right)\\ &- \left[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_{sp}^4\right]\left(E_{fp}^{(p+1)} - E_{fp}\right)\\ &- E_{fp}\sum_{j=1}^{R}\omega_j\left(a_j^{(p+1)} - a_j\right), \qquad (k=3), \quad \text{(15c)}\end{aligned}$$

$$
\begin{aligned}
0 = 0 &+ \alpha_{rp}\left(\frac{dT_{rp}}{dt}^{(p+1)} - \frac{dT_{rp}}{dt}\right) \\
&+ \left(K_{rp} + 4E_{fp}T_{rp}^3\right)\left(T_{rp}^{(p+1)} - T_{rp}\right) \\
&- K_{rp}\left(T_r^{(p+1)} - T_r\right) + \left(T_{rp} - T_r\right)\left(K_{rp}^{(p+1)} - K_{rp}\right) \\
&- \left[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_{rp}^4\right]\left(E_{fp}^{(p+1)} - E_{fp}\right) \\
&- E_{fp}\sum_{j=1}^{R}\omega_j\left(a_j^{(p+1)} - a_j\right), \qquad (k=4), \quad t \geq 0.
\end{aligned} \tag{15d}
$$

where for convenience, superscripts for the previous iterate, p, have been dropped. Collecting all unknown variable terms corresponding to the most recent iterate, $p+1$, onto the left-hand side gives the recurrence relations

$$
\begin{aligned}
\alpha_s \frac{dT_s}{dt}^{(p+1)} &+ \left(K_{sp} + 4E_{fc}T_s^3\right)T_s^{(p+1)} - K_{sp}T_{sp}^{(p+1)} \\
&= \Big\{\alpha_s\frac{dT_s}{dt} - K_{sp}\left(T_{sp} - T_s\right) \\
&- E_{fc}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_s^4\Big]\Big\} - K_{sp}\left(T_{sp} - T_s\right) \\
&+ K_{sp}^{(p+1)}\left(T_{sp} - T_s\right) + 4E_{fc}T_s^4 \\
&+ E_{fc}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_s^4\Big] \\
&+ E_{fc}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fc}\sum_{j=1}^{R} a_j\omega_j,
\end{aligned} \tag{16a}
$$

$$
\begin{aligned}
\alpha_r \frac{dT_r}{dt}^{(p+1)} &+ \left(K_{rp} + 4E_{fc}T_r^3\right)T_r^{(p+1)} - K_{rp}T_{rp}^{(p+1)} \\
&= \Big\{\alpha_r\frac{dT_r}{dt} - K_{rp}\left(T_{rp} - T_r\right) \\
&- E_{fc}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_r^4\Big]\Big\} - K_{rp}\left(T_{rp} - T_r\right) \\
&+ K_{rp}^{(p+1)}\left(T_{rp} - T_r\right) + 4E_{fc}T_r^4 \\
&+ E_{fc}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_r^4\Big] \\
&+ E_{fc}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fc}\sum_{j=1}^{R} a_j\omega_j,
\end{aligned} \tag{16b}
$$

$$
\begin{aligned}
\alpha_{sp} \frac{dT_{sp}}{dt}^{(p+1)} &+ \left(K_{sp} + 4E_{fp}T_{sp}^3\right)T_{sp}^{(p+1)} - K_{sp}T_s^{(p+1)} \\
&= \Big\{\alpha_{sp}\frac{dT_{sp}}{dt} + K_{sp}\left(T_{sp} - T_s\right) \\
&- E_{fp}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_{sp}^4\Big]\Big\} + K_{sp}\left(T_{sp} - T_s\right) \\
&- K_{sp}^{(p+1)}\left(T_{sp} - T_s\right) + 4E_{fp}T_{sp}^4 \\
&+ E_{fp}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_{sp}^4\Big] \\
&+ E_{fp}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fp}\sum_{j=1}^{R} a_j\omega_j,
\end{aligned} \tag{16c}
$$

$$
\begin{aligned}
\alpha_{rp} \frac{dT_{rp}}{dt}^{(p+1)} &+ \left(K_{rp} + 4E_{fp}T_{rp}^3\right)T_{rp}^{(p+1)} - K_{rp}T_r^{(p+1)} \\
&= \Big\{\alpha_{rp}\frac{dT_{rp}}{dt} + K_{rp}\left(T_{rp} - T_r\right) \\
&- E_{fp}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_{rp}^4\Big]\Big\} + K_{rp}\left(T_{rp} - T_r\right) \\
&- K_{rp}^{(p+1)}\left(T_{rp} - T_r\right) + 4E_{fp}T_{rp}^4 \\
&+ E_{fp}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_{sp}^4\Big] \\
&+ E_{fp}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fp}\sum_{j=1}^{R} a_j\omega_j, \quad t \geq 0.
\end{aligned} \tag{16d}
$$

It can readily be seen that the expressions inside the brackets in Eq. (16a – d) are equal to Ψ_k, i.e., $\{\cdots\} = \Psi_k = 0$, and so these equations become

$$
\begin{aligned}
\alpha_s \frac{dT_s}{dt}^{(p+1)} &+ \left(K_{sp} + 4E_{fc}T_s^3\right)T_s^{(p+1)} - K_{sp}T_{sp}^{(p+1)} \\
&= -K_{sp}\left(T_{sp} - T_s\right) + K_{sp}^{(p+1)}\left(T_{sp} - T_s\right) + 4E_{fc}T_s^4 \\
&+ E_{fc}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_s^4\Big] \\
&+ E_{fc}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fc}\sum_{j=1}^{R} a_j\omega_j,
\end{aligned} \tag{17a}
$$

$$
\begin{aligned}
\alpha_r \frac{dT_r}{dt}^{(p+1)} &+ \left(K_{rp} + 4E_{fc}T_r^3\right)T_r^{(p+1)} - K_{rp}T_{rp}^{(p+1)} \\
&= -K_{rp}\left(T_{rp} - T_r\right) + K_{rp}^{(p+1)}\left(T_{rp} - T_r\right) + 4E_{fc}T_r^4 \\
&+ E_{fc}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_r^4\Big] \\
&+ E_{fc}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fc}\sum_{j=1}^{R} a_j\omega_j,
\end{aligned} \tag{17b}
$$

$$\alpha_{sp}\frac{dT_{sp}}{dt}^{(p+1)} + \left(K_{sp}+4E_{fp}T_{sp}^3\right)T_{sp}^{(p+1)} - K_{sp}T_s^{(p+1)}$$
$$= K_{sp}\left(T_{sp}-T_s\right) - K_{sp}^{(p+1)}\left(T_{sp}-T_s\right) + 4E_{fp}T_{sp}^4$$
$$+ E_{fp}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_{sp}^4\Big]$$
$$+ E_{fp}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fp}\sum_{j=1}^{R} a_j\omega_j, \qquad (17c)$$

$$\alpha_{rp}\frac{dT_{rp}}{dt}^{(p+1)} + \left(K_{rp}+4E_{fp}T_{rp}^3\right)T_{rp}^{(p+1)} - K_{rp}T_r^{(p+1)}$$
$$= K_{rp}\left(T_{rp}-T_r\right) - K_{rp}^{(p+1)}\left(T_{rp}-T_r\right) + 4E_{fp}T_{rp}^4$$
$$+ E_{fp}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_{sp}^4\Big]$$
$$+ E_{fp}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fp}\sum_{j=1}^{R} a_j\omega_j, \quad t \geq 0. \qquad (17d)$$

Eq. (17a – d) can be confirmed by checking the limit as $p \to \infty$, in which case the governing equations are returned.

3.2 Function Decomposition

With the iterative, linearized recurrence relations defined, functional decomposition of the unknown temperature variables may now be applied. The process begins by expressing these variables at iterate $p+1$ as functional expansions of the form

$$y_i^{(p+1)}(t) = \hat{z}^i(t) + \sum_{m=1}^{NP+R} b_m^{(p+1)} z_m^i(t), \quad i = 1, ..., NV, \qquad (18)$$

where $\hat{z}^i(t)$ is the baseline function for $y_i^{(p+1)}(t)$, $\left\{z_m^i(t)\right\}_{m=1}^{NP+R}$ is the set of sensitivity functions for $y_i^{(p+1)}(t)$, $\{b_m\}_{m=1}^{NP+R}$ is the set of unknown system parameters and coefficients, $NP+R$ is the number of unknown system parameters plus unknown coefficients for the series expansion describing $T_f^4(t)$, and NV is the number of unknown variables. For the simplified two-pan DSC model described, expansions for the unknown temperatures can be given by

$$T_s^{(p+1)}(t) = \hat{z}^{(s)}(t) + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(s)}(t), \qquad (19a)$$

$$T_r^{(p+1)}(t) = \hat{z}^{(r)}(t) + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(r)}(t), \qquad (19b)$$

$$T_{sp}^{(p+1)}(t) = \hat{z}^{(sp)}(t) + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(sp)}(t), \qquad (19c)$$

$$T_{rp}^{(p+1)}(t) = \hat{z}^{(rp)}(t) + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(rp)}(t), \qquad (19d)$$

where

$$\left\{b_m^{(p+1)}\right\}_{m=1}^{R+4} = \left\{K_{sp}, K_{rp}, E_{fc}, E_{fp}, a_1, \ldots, a_R\right\}^{(p+1)}. \qquad (19e)$$

Substituting the appropriate expansions into Eq. (17a – d) generates:

$$\alpha_s\Big(\frac{d\hat{z}}{dt}^{(s)} + \sum_{m=1}^{R+4} b_m^{(p+1)}\frac{dz_m^{(s)}}{dt}\Big)$$
$$+ \left(K_{sp}+4E_{fc}T_s^3\right)\left(\hat{z}^{(s)} + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(s)}\right)$$
$$- K_{sp}\left(\hat{z}^{(sp)} + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(sp)}\right)$$
$$= -K_{sp}\left(T_{sp}-T_s\right) + K_{sp}^{(p+1)}\left(T_{sp}-T_s\right) + 4E_{fc}T_s^4$$
$$+ E_{fc}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_s^4\Big]$$
$$+ E_{fc}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fc}\sum_{j=1}^{R} a_j\omega_j, \qquad (20a)$$

$$\alpha_r\Big(\frac{d\hat{z}}{dt}^{(r)} + \sum_{m=1}^{R+4} b_m^{(p+1)}\frac{dz_m^{(r)}}{dt}\Big)$$
$$+ \left(K_{rp}+4E_{fc}T_r^3\right)\left(\hat{z}^{(r)} + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(r)}\right)$$
$$- K_{rp}\left(\hat{z}^{(rp)} + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(rp)}\right)$$
$$= -K_{rp}\left(T_{rp}-T_r\right) + K_{rp}^{(p+1)}\left(T_{rp}-T_r\right) + 4E_{fc}T_r^4$$
$$+ E_{fc}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_r^4\Big]$$
$$+ E_{fc}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fc}\sum_{j=1}^{R} a_j\omega_j, \qquad (20b)$$

$$\alpha_{sp}\Big(\frac{d\hat{z}}{dt}^{(sp)} + \sum_{m=1}^{R+4} b_m^{(p+1)} \frac{dz_m^{(sp)}}{dt}\Big)$$
$$+ \left(K_{sp} + 4E_{fp}T_{sp}^3\right) \left(\hat{z}^{(sp)} + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(sp)}\right)$$
$$- K_{sp}\left(\hat{z}^{(s)} + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(s)}\right)$$
$$= K_{sp}\left(T_{sp} - T_s\right) - K_{sp}^{(p+1)}\left(T_{sp} - T_s\right) + 4E_{fp}T_{sp}^4$$
$$+ E_{fp}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_{sp}^4\Big]$$
$$+ E_{fp}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fp}\sum_{j=1}^{R} a_j\omega_j, \tag{20c}$$

$$\alpha_{rp}\Big(\frac{d\hat{z}}{dt}^{(rp)} + \sum_{m=1}^{R+4} b_m^{(p+1)} \frac{dz_m^{(rp)}}{dt}\Big)$$
$$+ \left(K_{rp} + 4E_{fp}T_{rp}^3\right) \left(\hat{z}^{(rp)} + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(rp)}\right)$$
$$- K_{rp}\left(\hat{z}^{(rp)} + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(rp)}\right)$$
$$= K_{rp}\left(T_{rp} - T_r\right) - K_{rp}^{(p+1)}\left(T_{rp} - T_r\right) + 4E_{fp}T_{rp}^4$$
$$+ E_{fp}^{(p+1)}\Big[(\gamma + \sum_{j=1}^{R} a_j\omega_j) - T_{sp}^4\Big]$$
$$+ E_{fp}\sum_{j=1}^{R} a_j^{(p+1)}\omega_j - E_{fp}\sum_{j=1}^{R} a_j\omega_j, \quad t \geq 0. \tag{20d}$$

Based on Eq. (20a – d), a linear system of ordinary differential equations for the baseline and sensitivity functions may be produced by equating terms containing like coefficients from the set $\{1, b_1, \ldots, b_{R+4}\}$. Therefore, for example, the baseline functions are given by

$$\frac{d\hat{z}}{dt}^{(s)} = \frac{1}{\alpha_s}\Big\{\Big[-(K_{sp} + 4E_{fc}T_s^3)\hat{z}^{(s)} + K_{sp}\hat{z}^{(sp)}\Big] - K_{sp}(T_{sp} - T_s) + 4E_{fc}T_s^4 - E_{fc}\sum_{j=1}^{R} a_j\omega_j\Big\}, \tag{21a}$$

$$\frac{d\hat{z}}{dt}^{(sp)} = \frac{1}{\alpha_{sp}}\Big\{\Big[-(K_{sp} + 4E_{fp}T_{sp}^3)\hat{z}^{(sp)} + K_{sp}\hat{z}^{(s)}\Big] + K_{sp}(T_{sp} - T_s) + 4E_{fp}T_{sp}^4 - E_{fp}\sum_{j=1}^{R} a_j\omega_j\Big\}, \tag{21b}$$

$$\frac{d\hat{z}}{dt}^{(r)} = \frac{1}{\alpha_r}\Big\{\Big[-(K_{rp} + 4E_{fc}T_r^3)\hat{z}^{(r)} + K_{rp}\hat{z}^{(rp)}\Big] - K_{rp}(T_{rp} - T_r) + 4E_{fc}T_r^4 - E_{fc}\sum_{j=1}^{R} a_j\omega_j\Big\}, \tag{21c}$$

$$\frac{d\hat{z}}{dt}^{(rp)} = \frac{1}{\alpha_{rp}}\Big\{\Big[-(K_{rp} + 4E_{fp}T_{rp}^3)\hat{z}^{(rp)} + K_{rp}\hat{z}^{(r)}\Big] + K_{sp}(T_{rp} - T_r) + 4E_{fp}T_{rp}^4 - E_{fp}\sum_{j=1}^{R} a_j\omega_j\Big\}, \quad t \geq 0, \tag{21d}$$

with the initial conditions

$$\hat{z}^{(s)}(0) = \hat{z}^{(sp)}(0) = \hat{z}^{(r)}(0) = \hat{z}^{(rp)}(0) = T_o. \tag{21e}$$

A similar series of equations can be formed for each of the sensitivity functions, $z_1, \ldots, z_{R+4}$, where the initial conditions are all equal to zero. The resulting systems of coupled equations may be solved by using conventional time-stepping routines or by treating time elliptically and employing a weighted residuals method [10].

3.3 Minimization

The final step which must be performed for each iteration is the determination of the sensitivity coefficients, $\{b_m^{(p+1)}\}_{m=1}^{R+4}$, which correspond to the unknown system parameters. This calculation is accomplished by means of a discrete least-squares minimization using the measured temperature data sets described in Eq. (3a) and Eq. (3b). Reconstructing the temperature functions for both the sample and reference plates, residual functions may be written as

$$R_1^{(p+1)}(T_{sp}^{(p+1)}(t_i)) = \hat{z}^{(sp)}(t_i) + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(sp)}(t_i) - T_{sp,i}, \quad i = 0, 1, \ldots, M, \tag{22a}$$

$$R_2^{(p+1)}(T_{rp}^{(p+1)}(t_i)) = \hat{z}^{(rp)}(t_i) + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(rp)}(t_i) - T_{rp,i}, \quad i = 0, 1, \ldots, M. \tag{22b}$$

Implementation of the discrete least-squares method leads to the total least-squares error for the above residuals in the form

$$S(\{b_m^{(p+1)}\}_{m=1}^{R+4})$$
$$= \sum_{i=0}^{M} \left(\hat{z}^{(sp)}(t_i) + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(sp)}(t_i) - T_{sp,i} \right)^2$$
$$+ \sum_{i=0}^{M} \left(\hat{z}^{(rp)}(t_i) + \sum_{m=1}^{R+4} b_m^{(p+1)} z_m^{(rp)}(t_i) - T_{rp,i} \right)^2. \quad (23)$$

The minimization condition is enforced with respect to the sensitivity coefficients, that is,

$$\frac{\partial S(\{b_m^{(p+1)}\}_{m=1}^{R+4})}{\partial b_k^{(p+1)}} = 0, \qquad k = 1, 2, \ldots, R+4. \quad (24)$$

Applying Eq. (24) to the error expression given by Eq. (23) generates a new system of linear equations for the sensitivity coefficients which can be written as

$$\sum_{i=0}^{M} \sum_{m=1}^{R+4} b_m^{(p+1)} \left(z_m^{(sp)}(t_i) z_k^{(sp)}(t_i) + z_m^{(rp)}(t_i) z_k^{(rp)}(t_i) \right)$$
$$= \sum_{i=0}^{M} \Big[\left(T_{sp,i} - \hat{z}^{(sp)}(t_i) \right) z_k^{(sp)}(t_i)$$
$$+ \left(T_{rp,i} - \hat{z}^{(rp)}(t_i) \right) z_k^{(rp)}(t_i) \Big],$$
$$k = 1, 2, \ldots, R+4. \quad (25)$$

Solution of this system yields updated values for the unknown system parameters which are then used to reconstruct updated temperature profiles for all components of the model. The iterative process described in this section is repeated until satisfactory convergence of the parameters is achieved.

4 Conclusions

A mathematical-inverse methodology is proposed for acquiring important DSC parameter information. The described approach is general and applicable to larger systems. In practice, a progressive set of experiments/simulations is planned to isolate unchanging parameters from the experimental runs containing the unknown sample. The modeled system, given by Eqs. (21a-d) and subject to Eq. (21e), can be solved by conventional doctrine involving an initial-value solver. However, in cases involving large data sets (say > 8000 points/set), a less conventional method of weighted-residuals involving time-collocation will require less memory, increase stability, and compute faster than by using a conventional time marching scheme. The accompanying paper details the numerical implementation of the developed algorithm and presents numerical results indicating the merit of the proposed parameter estimation technique.

Acknowledgments

This work was supported under a DOE grant provided to the University of Tennessee under the Industrial Materials for the Future Program (DE-FC07-01ID14249).

References

[1] M. J. Richardson. Application of differential scanning calorimetry to the measurement of specific heat. In K. D. Maglic, A. Cezairliyan, and V. E. Peletsky, editors, *Compendium of Thermophysical Property Measurement Methods, Vol. I*, pages 669 – 685. Plenum Press, New York, 1984.

[2] I. Moon, R. Androsch, and B. Wunderlich. A calibration of the various heat-conduction paths for a heat-flux-type temperature-modulated DSC. *Thermochimica Acta*, 357–358:285–291, 2000.

[3] S-C. Jeng and S-W. Chen. The solidification characteristics of 6061 and A356 aluminum alloys and their ceramic particle-reinforced composites. *Acta Mater.*, 45(12):4887–4899, 1997.

[4] S-W. Chen, C-C. Huang, and J-C. Lin. The relationship between the peak shape of a DTA curve and the shape of a phase diagram. *Chemical Engineering Science*, 50(3):417–431, 1995.

[5] C-C. Huang and Y-P. Chen. Measurements and model prediction of the solid-liquid equilibria of organic binary mixtures. *Chemical Engineering Science*, 55:3175–3185, 2000.

[6] H. B. Dong and J. D. Hunt. A numerical model of a two-pan heat flux DSC. *Journal of Thermal Analysis and Calorimetry*, 64:167–176, 2001.

[7] R. Ciach, W. Kapturkiewicz, W. Wolczynski, and A. M. Zahra. Computer simulation of thermal analysis in heat-flux DSC applied to metal solidification. *Journal of Thermal Analysis*, 38:1949–1957, 1992.

[8] G. Hohne, W. Hemminger, and H.-J. Flammershein. *Differential Scanning Calorimetry*. Springer, Berlin, 1996.

[9] R. E. Bellman and R. E. Kalaba. *Quasilinearization and Nonlinear Boundary Value Problems*. Elsevier, New York, 1965.

[10] G. E. Osborne, J. I. Frankel, and M. Keyhani. The Function Decomposition Method and its application in thermal inverse analysis. In *International Mechanical Engineering Congress and Exhibition*, Anaheim, California, November 15–20 1998.

[11] M. Abramowitz and I. A. Stegun. *Handbook of Mathematical Functions*. Dover, New York, 1972.