Title

Analysis of the influence of thermal gradients inside T-history samples on the method accuracy: theoretical approach

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Abstract

The present work analyses the effect of radial thermal gradients inside T-history samples on the enthalpy temperature curve measurement. A conduction heat transfer model has been utilized for this purpose. Some expressions have been obtained that relate the main dimensionless numbers of the experiments with the deviations in specific heat capacity, phase change enthalpy and phase change temperature estimations. Although these relations can only be strictly applied to solid materials (e.g. measurements of shape stabilized phase change materials, SSPCM), they can provide some useful and conservative bounds for the deviations of the T-history method. Biot numbers emerge as the most relevant dimensionless parameters in the accuracy of the specific heat capacity and phase change enthalpy estimation whereas this model predicts a negligible influence of the temperature levels used for the experiments or the Stefan number.

Keywords: T-history method, Phase Change Material, Enthalpy, Storage Capacity

Nomenclature

A	Time integral of T_∞-T_{sur} [K·s]	δT_m	Error in phase change temperature [°C]
$\hat{A}$	Measured time integral of T_∞-T_{sur} [K·s]	θ	Dimensionless temperature
Bi	Biot number	λ	Thermal conductivity [W/(m·K)]
C	Thermal capacity [J/K]	ξ	Eigenvalue of cond. heat transfer problem
$\hat{C}$	Measured thermal capacity [J/K]	ρ	Density [kg/m^3]
c_p	Specific heat capacity [J/(kg·K)]	**Abbreviations**	
e	Thickness of the tube [m]	DSC	Differential Scanning calorimetry
e_q	Relative error in surface temperature	PCM	Phase Change Material
$e_{\bar{T}}$	Error in the sample average temperature	SSPCM	Shape Stabilized Phase Change Material
f	Liquid fraction	**Subscripts**	
h	Enthalpy [kJ/(kg·K)], heat transfer coefficient [W/(m^2·K)]	0	Initial conditions
J_o	Zeroth order Bessel function	cn	Measured in the centreline of the sample
J_1	First order Bessel function	e	Relative to the T-history experiment
L_c	Characteristic length [m]	m	Relative to the melting process
m	Mass [kg]	ms	Relative to a measured temperature
R	Radius [m], thermal resistance [K·m^2/W]	r-c	Combined radiation and convection
r_e	Relation between temperature errors	ref	Relative to the reference sample
Ste	Stefan number	s	Relative to a T-history sample
T	Temperature [°C]	sur	Relative to the surface of the tube
t	Time [s]	t	Relative to the tube
Greek symbols		∞	Ambient temperature
ΔT_m	Phase change temperature range [°C]		

1. Introduction

The determination of the thermo-physical properties of phase change materials is essential both for the correct design of thermal energy storage systems and for their simulation. The

enthalpy versus temperature curve determination (h-T) is therefore crucial. Although the DSC technique is the most commonly used for this determination, the T-history method is currently attracting increasing attention due to its simplicity and its good results [1]. In light of the results of previous experimental works dealing with the evaluation of the accuracy of the T-history method, such as that of Lazaro et al. [2] on the empirical verification of a T-history set up, researchers [2-3] generally agree on the suitability of this methodology for measuring the enthalpy temperature curve in a typical PCM application.

The T-history method assumes a uniform temperature distribution inside the samples. In order to ensure this condition, the restriction for the lumped capacitance systems ($Bi=h\cdot L_c/\lambda<0.1$) has been used [4]. This restriction is based on the analysis of classical transient heat conduction problems, where the phase change process is not considered. In this restriction, different definitions can be used for the characteristic length: the ratio between volume and heat transfer area or the distance corresponding to the highest temperature gradient. Some researchers [5-7] have used the first expression ($Bi=h\cdot R/(2\cdot\lambda)$), whereas the second and more conservative one ($Bi=h\cdot R/\lambda$) has been utilized in [8-10].

Hong et al. [9] claimed that the classical condition for the Biot number was not sufficient for ensuring a uniform temperature distribution during the phase change process. They measured radial thermal gradients inside a sodium acetate sample (R=8mm) during its cooling process. Temperature differences during its solidification were higher than those corresponding to the sensible heat transfer stages. They found that more accurate calculations were obtained when the temperature of the centreline was used. However, since a qualitative explanation of this fact was not found, they suggested that an analytical investigation of the effect on h-T calculations of these thermal gradients would be interesting. The objective of the present study is to analyse the influence of radial thermal gradients inside the T-history samples on the deviations of the calculated h-T curve.

2. Methodology

For this purpose, the thermal gradients inside T-history samples resulting from conduction heat transfer are evaluated. Only radial temperature distribution is considered, since T-history tubes are usually designed with a large ratio between their length and diameter (L/D>10). Hong et al. [9] and Rady et al. [11] have empirically proved that axial thermal gradients are negligible during the experiments. Two approaches have been followed: first, an analytical model allows a prediction of the deviation in heat capacity measurements and, secondly, a numerical model has been used in order to evaluate these effects when the phase change process takes place. Dimensionless analysis has been used with the objective of obtaining general relations between the conditions of the T-history experiments and the deviations in h-T curve calculations.

2.1 General assumptions

In this work, only conduction heat transfer is considered and therefore the influence of natural convection during the phase change process or the effect of movement of the solid phase during the melting or solidification process are not taken into account. Additionally, it has been assumed that the cylindrical section of the sample holder is completely filled by the PCM and reference material. For these reasons, the results can only strictly be applied to the measurements of Shape Stabilized PCM (SSPCM) where a solid material is used for the reference sample. The use of the T-history method for the evaluation of the h-T curves of these solid PCM composites is very promising. For example, Rady et al. [11] applied this method for the thermal characterization of PCM granules and Palomo and Dauvergne [12] developed an experimental methodology similar to T-history –in terms of sample geometry and thermal excitation- that allowed the complete thermodynamic characterization of SSPCM by means of a mathematical inverse method analysis.

Considering the particular phenomena that take place during the phase change process, researchers have used different designs for the sample holders in order to control them with the aim of approaching the ideal case of uniform radial melting or solidification. For instance, horizontal tubes have been used in [2, 13] thus minimizing the axial displacement of the solid phase. Additionally, Hong et al. [8] located a stainless wire in the centre of the sample in order to prevent the ice from floating. With the objective of ensuring that the tubes remain filled during the experiment, a vertical volume expansion buffer was used by Peck et al. [13]. When extrapolating the results of this study to a particular T-history experimental set up, the importance of these effects has to be considered.

On the other hand, the influence of natural convection during the melting process can be evaluated using the correlation of Raithby and Hollands [14]. For the thermal gradients calculated in this work or experimentally measured by Hong et al. [9], a relation between the effective and liquid thermal conductivity of near 1.5 can be obtained. Therefore, for a general case, the results from this study can be taken as a conservative estimation of the maximum errors due to the radial thermal gradients inside the T-history tubes.

Additionally, with the aim of simplifying the dimensionless analysis of the problem, thermal conductivity and heat capacity of the liquid and solid phases are considered equal and a constant equivalent convective and radiant coefficient is assumed ($h_{r\text{-}c}$). In this work sub-cooling and hysteresis are not taken into account.

2.2 Dimensionless numbers

Assuming these simplifications, the heat transfer problem of the PCM sample can be represented by the following equations (1)-(6). An analogous formulation can be applied to the reference sample.

$$\rho_{PCM} \cdot \left(c_{p,PCM} \cdot \frac{\partial T_{PCM}}{\partial t} + h_m \cdot \frac{\partial f}{\partial t}\right) = \frac{\lambda_{PCM}}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial T_{PCM}}{\partial r}\right) \qquad 0 \le r \le R - e \tag{1}$$

$$\lambda_{PCM} \cdot \frac{\partial T_{PCM}}{\partial r}\Big|_{r=R-e} = \lambda_t \cdot \frac{\partial T_t}{\partial r}\Big|_{r=R-e} \tag{2}$$

$$\rho_t \cdot c_{p,t} \cdot \frac{\partial T_t}{\partial t} = \frac{\lambda_t}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial T_t}{\partial r}\right) \qquad R - e < r \leq R \tag{3}$$

$$\lambda_t \cdot \frac{\partial T_t(R,t)}{\partial r} = h_{r-c} \cdot \left(T_\infty - T_t(R,t)\right) \tag{4}$$

$$T_{PCM}(r, t = 0) = T_0 \qquad 0 \leq r \leq R - e \tag{5}$$

$$T_t(r, t = 0) = T_0 \qquad R - e < r \leq R \tag{6}$$

According to these conduction heat transfer problems, a set of dimensionless numbers has been defined for the analysis, shown in the following table (table 1). The range of variation for each dimensionless number is also presented. These values have been determined according to the typical thermal properties and experimental conditions used in the T-history method.

Table 1. Dimensionless numbers used in this study. In brackets values for the base case.

Dimensionless number	Range of variation	Dimensionless number	Range of variation
$Bi_{ref} = \frac{h_{r-c} \cdot R}{\lambda_{ref}}$	[0-0.2] (0.05)	$Ste = \frac{c_{p,PCM} \cdot (T_\infty - T_m)}{h_m}$	[0.1-1] (0.3)
$C_{r,ref} = \frac{m_{ref} \cdot c_{p,ref}}{m_{ref} \cdot c_{p,ref} + m_t \cdot c_{p,t}}$	[0.5-0.9] (0.85)	$R_t/R_{r-c} = \frac{\lambda_t}{h_{r-c} \cdot e}$	[0-0.005] (0.003)
$Bi_{PCM} = \frac{h_{r-c} \cdot R}{\lambda_{PCM}}$	[0-0.2] (0.15)	$\theta_m = \frac{\Delta T_m}{T_\infty - T_m}$	[0.02-0.16] (0.08)
$C_{r,PCM} = \frac{m_{PCM} \cdot c_{p,PCM}}{m_{PCM} \cdot c_{p,PCM} + m_t \cdot c_{p,t}}$	[0.5-0.9] (0.7)	$\theta_e = \frac{T_\infty - T_m}{T_\infty - T_0}$	[0.3-0.7] (0.06)

2.3 Analytic model: estimation of deviation in specific heat

A simplified model is proposed for the analytic estimation of the deviation in the specific heat capacity calculation. In this model the following additional assumptions are made:

-no latent heat is considered;

-the container is considered as a lumped heat capacity system: this simplification can be acceptable if $\frac{\lambda_s}{\rho_s \cdot c_{p,s} \cdot (R-e)^2} \ll \frac{\lambda_t}{\rho_c \cdot c_{p,t} \cdot e^2}$ and $h_{r-c} \ll \frac{\lambda_t}{e}$

120 According to these assumptions, the transient conduction heat transfer problem corresponding
121 to each sample can be represented by a single domain formulation (equations (7)-(8)). If this
122 is compared to the classical problem of transient conduction heat transfer in cylinders [4],
123 only one additional term –the heat capacity of the tube- is introduced into the boundary
124 condition equation (equation (8)).

125 $$\rho_s \cdot c_{p,s} \cdot \frac{\partial T_s}{\partial t} = \frac{\lambda_s}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial T_s}{\partial r}\right) \quad 0 \le r \le R - e \tag{7}$$

126 $$-\lambda_t \cdot \frac{\partial T_s(R-e,t)}{\partial r} + h_{r-c} \cdot \frac{R}{R-e}\left(T_\infty - T_s(R-e,t)\right) = \frac{m_t \cdot c_{p,t}}{2\pi \cdot (R-e)} \cdot \frac{\partial T_s(R-e,t)}{\partial t} \tag{8}$$

127 Similarly to the classical transient heat transfer problems, the solutions can be expressed using
128 a function series (equation (9)). In the following calculations, the first term approximation
129 will be used.

130 $$T(r,t) \approx T_\infty - (T_\infty - T_0) \cdot \sum_{i=1}^{\infty} C_i \cdot J_0\left(\frac{\xi_i \cdot r}{R-e}\right) \cdot e^{-\frac{\xi_i^2 \cdot \lambda_s}{\rho \cdot c_{p,s} \cdot (R-e)^2} \cdot t} \tag{9}$$

131 where ξ_i are the infinite solutions of the transcendental equation (equation (10)).

132 $$2 \cdot \frac{J_1(\xi_i) \cdot \xi_i}{J_0(\xi_i)} + \xi_i^2 \cdot \frac{m_t \cdot c_{p,t}}{m_s \cdot c_{p,s}} = 2 \cdot Bi \tag{10}$$

133 For low numbers of the Biot number, Bessel functions can be truncated in order to simplify
134 the solution. Therefore, the transcendental equation (equation (10)) can be approximated by
135 equation (11), expressed in terms of the Biot number and relative heat capacity of the sample
136 (C_r, defined in table 1), for the calculation of the first eigenvalue of the problem (ξ_1).

137 $$\xi_1^2 \approx \frac{2 \cdot Bi}{\left(1 + \frac{m_c \cdot c_{p,c}}{m_s \cdot c_{p,s}}\right)} = 2 \cdot Bi \cdot C_r \tag{11}$$

138 The exact thermal energy balance equation on which the T-history method is based is
139 equation (12). This equation can be modified in order to consider the measured temperature
140 (T_{ms}) (equation (13)) using the relative errors (e_q, $e_{\bar{T}}$) associated to the surface temperature
141 and the average sample temperature which are defined in equations (14) and (15). These heat
142 balance equations (equations (12) and (13)) are formulated in a differential form. Similar

expressions were used by Moreno-Alvarez et al. [15] in their proposed differential analysis method for the temperature evolutions measured by the T-history method.

$$C_c \cdot \frac{d\bar{T}_s}{dt} + C_s \cdot \frac{d\bar{T}_t}{dt} = \bar{h} \cdot A \cdot (T_\infty - T_{sur}) \quad (12)$$

$$C_c \cdot \frac{dT_{ms}}{dt} \cdot (1 + e_{\bar{T}}) + C_s \cdot \frac{dT_{ms}}{dt} \cdot \left(1 + e_q\right) = \bar{h} \cdot A \cdot (T_\infty - T_{ms}) \cdot \left(1 + e_q\right) \quad (13)$$

$$e_{\bar{T}} = \frac{T_{ms} - \bar{T}_s}{T_\infty - T_{ms}} \quad (14)$$

$$e_q = \frac{T_{ms} - T_{sur}}{T_\infty - T_{ms}} \quad (15)$$

For low values of the Biot number, the errors in surface and average temperatures can be approximated (equations (16) and (17)). Here, it has been considered that the temperature is measured in the centreline of the cylinder. Similarly, analogous expressions can be obtained if the temperature is measured at the surface.

$$1 + e_{\bar{T}} = \frac{T_\infty - \bar{T}_s}{T_\infty - T_{ms}} = 2 \cdot \frac{J_1(\xi_1)}{\xi_1} \approx 1 - \frac{{\xi_1}^2}{8} = 1 - \frac{Bi}{4} \cdot C_r \quad (16)$$

$$1 + e_q = J_0(\xi_1) \approx 1 - \frac{{\xi_1}^2}{4} = 1 - \frac{Bi}{2} \cdot C_r \quad (17)$$

The following equations represent the approximated method for obtaining the heat capacity of the measured material (equation (18)) and the exact formulation –taking into account 1D heat conduction effects- using the previously defined errors ($e_{\bar{T}}$, e_q) (equation (19)).

$$\hat{C}_s + C_c = \left(C_{ref} + C_t\right) \cdot \frac{\int (T_\infty - T_{ms,s}) \cdot dt}{\int (T_\infty - T_{ms,ref}) \cdot dt} = \left(C_{ref} + C_t\right) \cdot \frac{\hat{A}_s}{\hat{A}_{ref}} \quad (18)$$

$$C_s \cdot \left(1 + e_{\bar{T},s}\right) + C_t \cdot \left(1 + e_{q,s}\right) = \left[C_{ref} \cdot \left(1 + e_{\bar{T},ref}\right) + C_t \cdot \left(1 + e_{q,ref}\right)\right] \cdot \frac{\hat{A}_s}{\hat{A}_{ref}} \cdot \frac{1 + e_{q,s}}{1 + e_{q,ref}} \quad (19)$$

where $\hat{C}_s$ is the measured heat capacity of the sample and $\hat{A}_s$ and $\hat{A}_{ref}$ the time integrated difference between ambient and measured temperature of each material (sample and reference). The following relation (equation (20)) between temperature measurement deviations can be defined in order to obtain a more compact expression. It is important to note that this relation is the same whether the temperature is measured at the surface or in the centreline of the T-history samples.

$$r_e = \frac{1+e_{\bar{T}}}{1+e_q} \approx \frac{1-\frac{Bi}{4}\cdot C_r}{1-\frac{Bi}{2}\cdot C_r} \quad (20)$$

Dividing equations (18) and (19), an expression for the deviation of specific heat capacity (e_{cp}), defined in equation (21), can be obtained. This relation between equation (18) and (19) (equation (22)), can be thus expressed (equation (23)) in terms of the ratio of temperature measurement errors (r_e), the relative heat capacities of the samples ($C_{r,i}$) and the relative error in heat capacity (e_{cp}).

$$e_{c_p} = \frac{\hat{C}_s - C_s}{C_s} \quad (21)$$

$$\frac{\hat{C}_s + C_t}{C_s \cdot r_{e,s} + C_t} = \frac{C_{ref} + C_t}{C_{ref} \cdot r_{e,ref} + C_t} \quad (22)$$

$$\frac{e_{c_p} \cdot C_{r,s} + 1}{C_{r,s} \cdot (r_{e,s} - 1) + 1} = \frac{1}{C_{r,ref} \cdot (r_{e,ref} - 1) + 1} \quad (23)$$

From equation (23), an explicit formulation for the relative deviation in heat capacity can be obtained (equation (24)).

$$e_{c_p} = \frac{C_{r,s} \cdot (r_{e,s} - 1) - C_{r,ref} \cdot (r_{e,ref} - 1)}{C_{r,s} \cdot [C_{r,ref} \cdot (r_{e,ref} - 1) + 1]} \quad (24)$$

Finally, if the above-mentioned approximation of r_e for low Biot numbers is assumed (equation (20)) and the first terms of the Taylor series (developed from variables $Bi_i \cdot C_{r,i}$) of equation (24) are taken, a simplified expression for the deviation of the heat capacity measurement can be obtained.

$$e_{cp,s} \approx \frac{1}{4} \cdot \left(C_{r,s} \cdot Bi_s - \frac{{c_{r,ref}}^2}{C_{r,s}} Bi_{ref} \right) \quad (25)$$

It should be noted that this analytical model predicts the same deviation in the heat capacity estimation whether the temperature of the samples is measured in their centreline or on their surface, since the relation r_e is identical for both cases. Using equation (25), a maximum deviation of 6% in the specific heat estimation can be obtained if the Biot number limit ($Bi = h \cdot R/(2 \cdot \lambda) = 0.1$) is considered.

2.4 Numerical model

A finite difference scheme has been developed for calculating conduction heat transfer inside the samples during the phase change process, where the phase change is formulated using the enthalpy method. The spatial mesh is uniformly distributed and a fully implicit method is used for time discretization. A spatial resolution of 0.2 mm and a time step of 10s have been used. The h-T curve is described in the simulations by an analytical function (equation (26)). Palomo et al. [12] have already used this analytical equation in the numerical study of their experimental methodology.

$$h(T) = c_p \cdot (T - T_o) + \frac{1}{2} \cdot h_m \cdot \left[1 + tanh\left(\frac{4 \cdot (T - T_m)}{\Delta T_m}\right)\right] \quad (26)$$

2.4.1 Analysis of the errors

The results of the numerical model have been integrated following the methodology proposed by Marín et al. [6]. Other researchers have proposed alternative algorithms in order to obtain the enthalpy-temperature curve from experimental data. Kravvaritis et al. [16] proposed what they called the "thermal delay method" which was based on a comparison of the heat balance equations corresponding to both samples during the same time interval. On the other hand, Moreno-Alvarez et al. [15] proposed a differential method considering the instantaneous temperature change rate of each material. It should be noted that under the assumptions of the proposed model for the analysis –the constant heat transfer coefficient ($h_{r\text{-}c}$)-, the obtained enthalpy temperature curve is the same whichever of these methods is applied.

A constant temperature increment has been taken for the integration. This temperature increment (0.1°C) is lower than the melting temperature range and much higher than the numerical precision of the calculated temperatures. The accuracy of the integration method has been verified for all cases by comparing the original analytical enthalpy-temperature curve with the numerical table obtained from the exact formulation (considering real temperatures of each material, equation (12)). The errors attributable to this numerical

integration of the results are lower than 0.001% in the enthalpy estimation and smaller than 0.001°C in the phase change temperature measurement.

The resulting h-T curve is compared with the original analytical function. Three main parameters have been identified in this study: c_p, h_m and T_m. In figure 1 a representation of these parameters is shown. Equations (21) and (27) define the relative errors in specific heat and enthalpy that are analysed in the following sections. Since the shape of the calculated h-T can vary from the original one, an average error in melting temperature is calculated with equation (28) and made dimensionless by using equation (29).

$$e_{h_m} = \frac{\hat{h}_m - h_m}{h_m} \tag{27}$$

$$\delta T_m = \frac{\int_{f=0.1}^{f=0.9} (\hat{T}_{PCM}(f) - T_{PCM}(f)) \cdot df}{0.8} \tag{28}$$

$$e_{\delta T_m} = \frac{\delta T_m}{(T_\infty - T_m)} \tag{29}$$

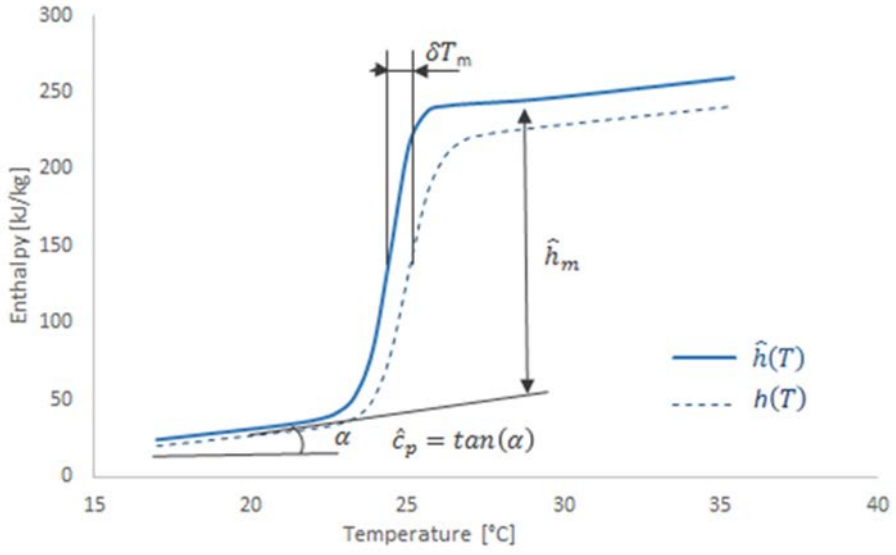

Figure 1. Graphical representation of the analysed parameters

3. Results

3.1 Parametric analysis

A first parametric analysis has been made in order to identify the dimensionless variables that influence the errors defined in the previous section. In this analysis each dimensionless variable has been independently modified within the range shown in Table 1 –while the rest of the variables remain at the fixed values shown in the same table. The influence of each independent dimensionless variable on the deviations is plotted in figures 2 and 3. The influences that are considered relevant in this study are highlighted with a continuous line. This analysis shows Bi and C_r as the most relevant numbers for the calculation of e_{cp} and e_{hm}. Considering the error in the phase change temperature estimation ($e_{\delta Tm}$), the most influential variables are Bi_{PCM} and the dimensionless temperature θ_m. As predicted by the previously defined analytical model, the estimation of the heat capacity is the same whether the temperature is measured at the surface of the tube or in the centreline.

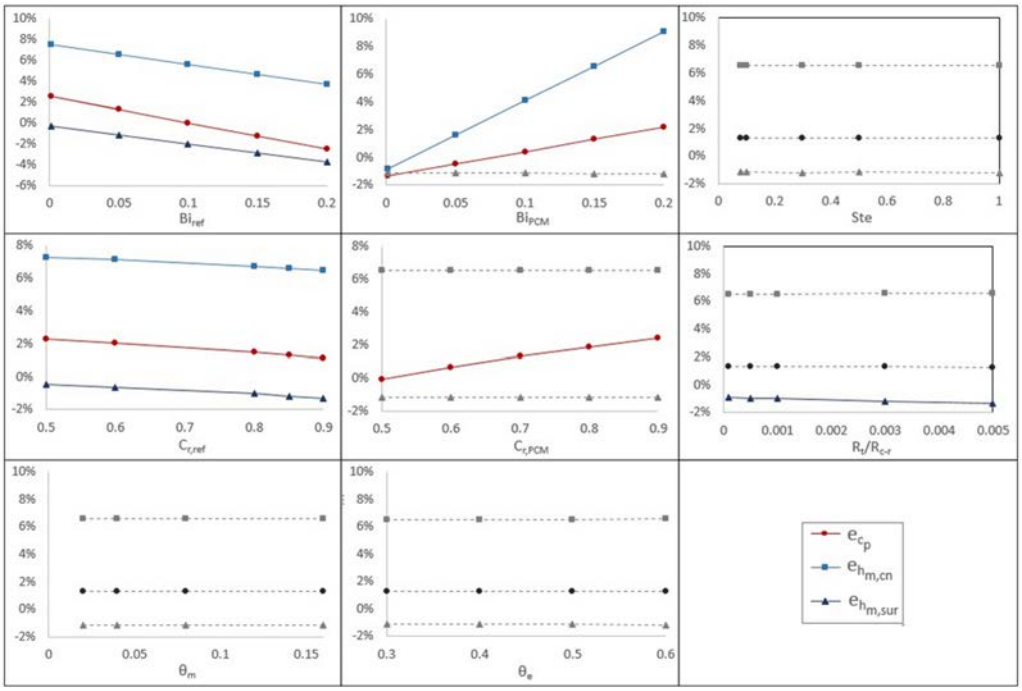

Figure 2. Parametric analysis of the errors.

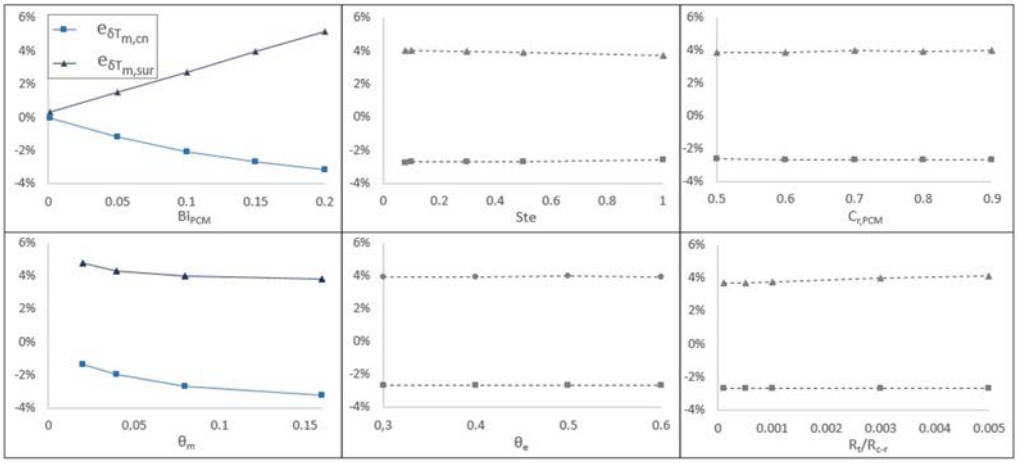

Figure 3. Parametric analysis of the errors in phase change temperature measurement.

3.2 Interaction between dimensionless variables

Secondly, the interaction of the influential dimensionless variables identified in the previous parametric analysis has been investigated. First of all, the influence of different combinations of Bi_{PCM}, Bi_{ref}, $C_{r,PCM}$ and $C_{r,ref}$ on the estimation of c_p and h_m has been analysed. In the case of the estimation of the phase change enthalpy when the temperature is measured at the surface, the influence of $R_t/R_{r\text{-}c}$ has also been analysed. The correlations obtained from this analysis are plotted in figure 4. They show a good fit to the calculated deviations. Furthermore, the correlation for the error in the specific heat capacity estimation is the same as the expression predicted by the analytical approach.

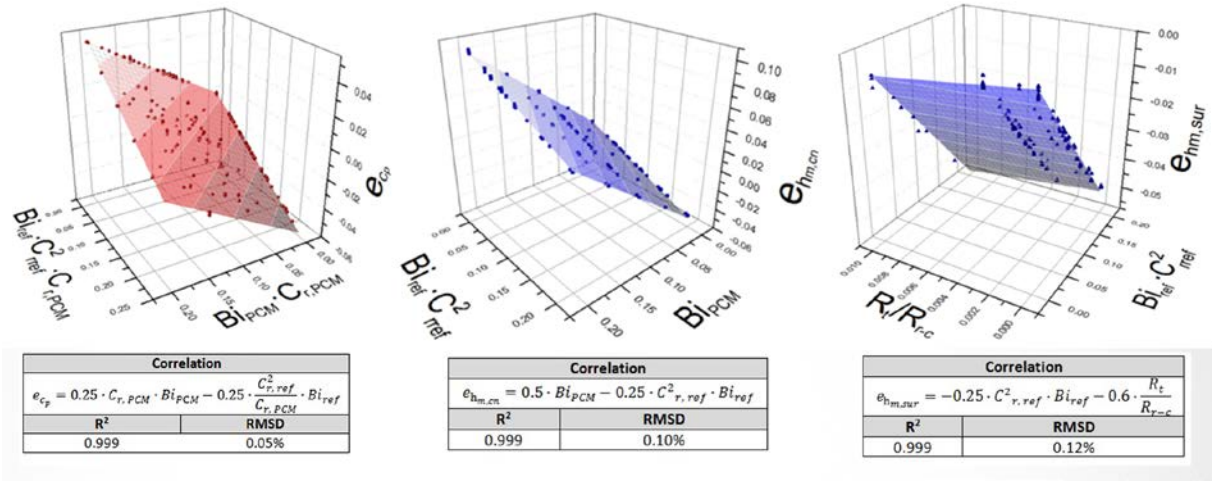

Figure 4. Correlations obtained from the study.

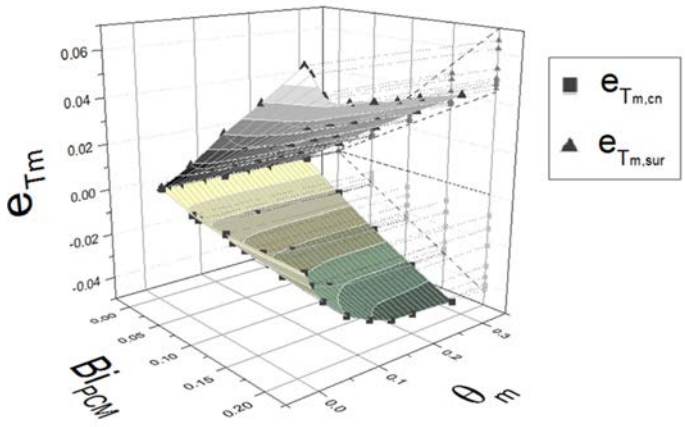

Figure 5. Influence on the phase change temperature of Biot number and θ_m

As can be seen in figure 5, a more complex relation has been found between the Biot number of the PCM sample and the dimensionless temperature θ_m with the error in the phase change temperature measurement. If a melting T-history experiment is considered, the phase change temperature is always overestimated when the temperature is measured at the surface whereas the opposite effect is observed if the temperature of the centreline is used. For low values of θ_m (corresponding to materials with a narrower phase change temperature range), the error is reduced if the centreline temperature is taken and increased if the surface temperature is considered. Some useful simplified relations can be extracted from this analysis in order to provide some bounds for these errors (equations (30)-(31)).

$$-0.22 \cdot Bi_{PCM} \leq \frac{(T_\infty - T_m)\cdot \delta T_{m,c}}{|T_\infty - T_m|^2} \leq 0 \quad (30)$$

$$0.22 \cdot Bi_{PCM} \leq \frac{(T_\infty - T_m)\cdot \delta T_{m,c}}{|T_\infty - T_m|^2} \leq 0.35 \cdot Bi_{PCM} \quad (31)$$

3.3 Analysis of the correlations obtained over a sample of the whole space of dimensionless numbers

The expressions obtained for the error estimations are based on a correlation over a sample space where only the "active" dimensionless numbers are varied. However, in this analysis the influence of some dimensionless numbers may have remained concealed. Therefore, the

correlations have been tested and verified within a more representative sample of the input variable space (defined in table 1). Since the number of input variables is high, a Montecarlo based sampling method has been used for this purpose. A sample of 100 cases has been obtained using Latin Hypercube (LH) Sampling [17], where each dimensionless number has been considered as a uniformly distributed random variable over the intervals defined in table 1. The previously obtained relations for the errors are compared to the results corresponding to the Montecarlo sample. As can be seen in figure 6, these relations fit these numerical results: the maximum root-mean-square deviation (RMSD) is 0.12% and the worst coefficient of determination is 0.992.

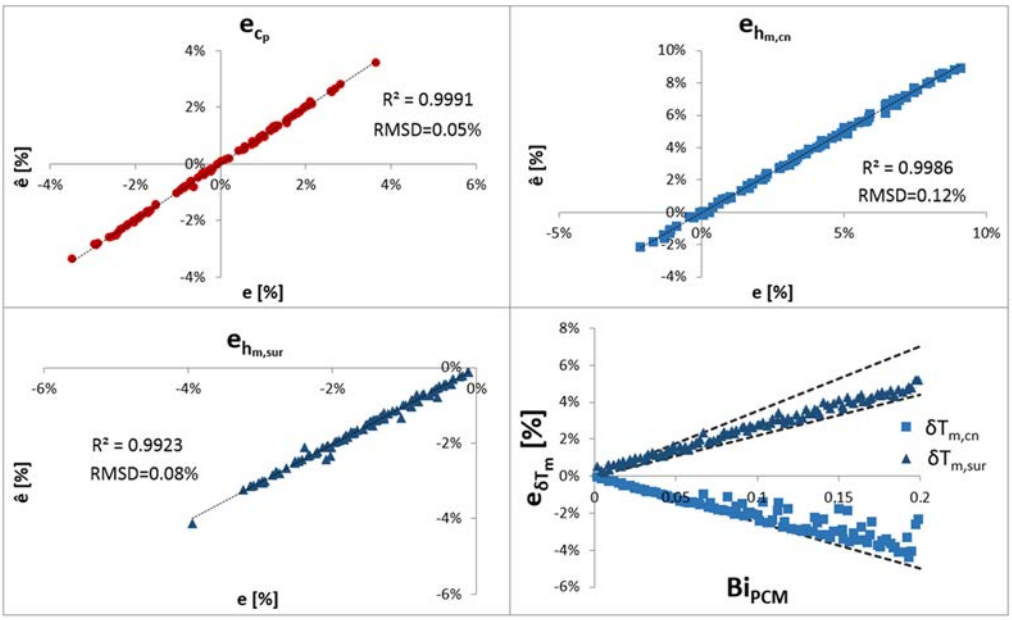

Figure 6. Comparison of the relations obtained with the results over the LH sample.

4. Conclusions

The effect of radial conduction heat transfer inside T-history samples on the deviations produced in the h-T curve evaluation has been analysed. In this study, the measurement of temperature in the centreline of the sample and at its surface has been taken into account. The errors have been quantified and some useful relations have been obtained between the

dimensionless numbers that define the experiments and the errors produced in heat capacity, phase change enthalpy and temperature (table 2).

According to the results of the analysed heat transfer model, the deviation of heat capacity and phase change enthalpy does not depend on the Stefan number and temperature levels of the experiment (related to θ_m and θ_e). The difference between the Biot numbers corresponding to the PCM and the reference substance is the most important contribution to the deviation of the heat capacity estimation, whereas the Biot number of the PCM sample is the most relevant dimensionless variable in the phase change enthalpy evaluation if the temperature is measured in the centreline. Considering the heat capacity estimation, the same results are obtained whether the temperature is measured in the centreline or at the surface of the sample. A lower error in phase change enthalpy is obtained if the temperature is measured at the surface. Furthermore, this error does not depend on the PCM thermo-physical properties. However, this temperature measure produces a higher deviation in the phase change temperature estimation, especially when testing pure substances or materials with a narrow phase change temperature range.

As previously mentioned, the results of this study can only be strictly applied to T-history experiments with SSPCM where a solid material is used as the reference sample. In these cases, the relations obtained can be utilized to size the samples, to determine the favourable experimental conditions and to calibrate or correct the results. Calibration of the T-history is an interesting method for improving the accuracy of the measurements. For instance, Rathgeber et al. [18] applied a calibration to the heat capacity and phase change enthalpy measured values based on the characterization of reference materials that produced an improved agreement with DSC results.

315 **Table 2.** Correlations and bounds for T-history deviations owing to radial conduction

Correlation	Bounds for T_m deviations
$e_{c_p} = 0.25 \cdot C_{r,PCM} \cdot Bi_{PCM} - 0.25 \cdot \frac{C^2_{r,ref}}{C_{r,PCM}} \cdot Bi_{ref}$	
$e_{h_{m,cn}} = 0.5 \cdot Bi_{PCM} - 0.25 \cdot C^2{}_{r,ref} \cdot Bi_{ref}$	$-0.22 \cdot Bi_{PCM} \leq \frac{(T_\infty - T_m) \cdot \delta T_{m,cn}}{\lvert T_\infty - T_m \rvert^2} \leq 0$
$e_{h_{m,sur}} = -0.25 \cdot C^2{}_{r,ref} \cdot Bi_{ref} - 0.6 \cdot \frac{R_t}{R_{r-c}}$	$0.22 \cdot Bi_{PCM} \leq \frac{(T_\infty - T_m) \cdot \delta T_{m,sur}}{\lvert T_\infty - T_m \rvert^2} \leq 0.35 \cdot Bi_{PCM}$

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317 The extrapolation of these results to a general case of T-history measurement has to be done
318 carefully: the similarity of each particular case to the main assumptions of the analysed model
319 has to be revised (free convection and solid PCM movement inside the sample being
320 neglected, having a fully filled section). However, considering free convection effects, the
321 analysed heat conduction model overestimates thermal gradients inside the samples. Since it
322 produces a conservative estimation of the deviations, the relations obtained can be used in
323 order to establish some bounds for these errors. For example, if the temperature is measured
324 inside the sample the following relations (equations (32)-(34)) can be applied. These can be
325 useful to complete the classical restriction for the Biot number since they relate some
326 parameters associated with the experimental conditions to the accuracy of the method.
327 Considering these relations, the more restrictive Biot conduction ($Bi=h \cdot R/\lambda<0.1$) is
328 recommended in order to ensure that the deviations in heat capacity and phase change
329 enthalpy measurements are lower that 5%.

330 $$e_{c_p} \leq 0.25 \cdot C_{r,PCM} \cdot Bi_{PCM} \quad (32)$$

331 $$e_{h_{m,c}} \leq 0.5 \cdot Bi_{PCM} \quad (33)$$

332 $$-0.22 \cdot |T_\infty - T_m| \cdot Bi_{PCM} \leq \delta T_{m,c} \cdot \frac{(T_\infty - T_m)}{|T_\infty - T_m|} \leq 0 \quad (34)$$

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