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# Phase change materials characterisation and applications to the thermal simulation of buildings

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## Abstract:

This study aims at presenting the main results of the Stock-E MICMCP project, fund by the French National Research Agency (ANR). The principal goal of this project is the correct characterisation of the thermophysical properties of phase change materials (PCMs) in order to have reliable inputs when considering their use in numerical simulations of thermal behaviour of buildings.

Firstly, the method developed to determine the dependency of the enthalpy function with respect to the temperature of the material is presented. It is based on the use of experimental measurements together with an inverse method combined with a numerical modelling. By assuming an *a priori* formulation of the enthalpy, based on some basic thermodynamic constraints, a simulated heat flux may be computed. It is then compared to the measured one, which permits to define an objective function. Its minimization thus allow to determine the value of the parameters involved in the equation of state. This step is first tested with microscopic samples thanks to differential scanning calorimetry (DSC). Secondly, it will be shown that this method can be extended to macroscopic and heterogeneous materials, which are more representative of real samples. Eventually, some examples of thermal simulations of buildings are done so as to highlight the necessity to correctly represent the PCM behaviour. This is particularly important since they appeared to be a promising way to save energy and achieve a better comfort in buildings, therefore an incorrect determination of their properties may lead to wrong conclusions on their real benefits.

## Keywords:

PCM characterisation, thermal buildings simulation, energy savings.

## 1. Introduction

In the present context of the global warming, one of the main idea to limit the associated drawbacks is to reduce the total energy consumption, especially in the buildings field which represents a high part of the overall consumption (e.g., in France, it raises around 40% of the final energy consumed) and is known to have some leeways so as to increase energy efficiency. This explained why it has focused the attention of so many studies in the past and still today. Their primary goal is often to promote new devices, or new uses of older devices, in order to lower their energetic needs. Among the various solutions, the use of PCMs has been promoted [1,8]. Nonetheless, there seems to have contradictory conclusions concerning their real benefits and performances... At a first hand, it is worth mentioning that the operating conditions are often ill-known and, at a second hand, one must say that the thermodynamical modelling of PCMs in the numerical simulations (especially the thermal simulations of buildings) is often doubtful. This being said, it appears helpful to define a proper method to correctly characterise the thermophysical properties of PCMs and, secondly, to have a clear view of the potential impact of such an error on the conclusions that may be drawn from the use of PCMs inside buildings. Thus, the starting point of this study is to show the intrinsic defaults of the current available methods usually involved in the characterisation of PCMs. Indeed,

the enthalpy function is often assimilated to the thermogram obtained when the sample is passed through DSC. The aim is thus to clearly highlight the boons of the present method. In a second part is presented the approach put forward in order to circumvent these issues. The main idea relies on the use of the experimental measurements together with an inverse method coupled with a numerical model so as to obtain a correct characterisation of the PCM. This step is done for both microscopic and macroscopic samples. The first ones are representative of the kind of samples involved in DSC whereas the other ones are equivalent to the real kind of samples that may be used. Eventually, the last part will deal with the impact and consequences a misinterpreted enthalpy may lead to when one is considering the thermal behaviour of a wall and then of a complete housing.

## 2. PCM characterisation

### 2.1. Microscopic samples

Usually, one agrees to use calorimetry experiments in order to characterise the thermophysical properties of PCMs. The apparatus will set a temperature ramp (heating or cooling) and the total heat flux is measured during time. Generally, the thermogram (i.e. the curve  $\Phi = f(t)$ ) is supposed to be equivalent to the derivative of the enthalpy with respect to the temperature ( $h = f(T)$ ): this is the so-called equivalent-cp approach. Nonetheless, in the present context of phase transition, such an approach raises two difficulties, which then explain the error made in the determination of the enthalpy. Firstly, the phase change induces a temperature gradient in the sample, even if this one is very small, and consequently one cannot represent the sample with an unique temperature. Meanwhile, it implies that there will be a temperature lag between the sample and the plate. Consequently, this means that the plate temperature is no more representative of the behaviour of the sample during this moment, because of the thermal transfers occurring inside this latter one. Secondly, it appears that the results obtained with the equivalent-cp approach are dependent on the mass sample and the heating rate, which clearly violates the basic laws of thermodynamics. As a consequence, it leads to wrong conclusions such as those presented in Fig. 1. When integrating the thermogram, one gets a smoothed function which does not correspond to the kind of transition (first-order) undergone by pure substances. Moreover, the corresponding enthalpy would mean that solid state may exist above 0°C in the case of water (Fig 1.a). In the case of a solution, see Fig 1.b, the error is more difficult to see since the transition phase is no more associated to an Heavyside function. So, one could think that the integrated curves are a good estimation of the enthalpy however there is still a too great temperature range for the phase change, inducing a solid state existing above the transition domain (symbolized by the vertical grey curve in the figure).

As mentioned earlier, the idea developed in this project to correctly determine  $h(T)$  is to combine the experimental measurements with an inverse method using a numerical modelling of the sample. This one is based on the resolution of the energy equation in the conductive regime:

$$\rho \frac{\partial h}{\partial t} = \vec{\nabla} \cdot (\lambda \vec{\nabla} T) \quad (1)$$

With the associated boundary conditions:

$$-\lambda \left( \frac{\partial T}{\partial r} \right)_{r=0} = 0 \quad (2.a)$$

$$-\lambda \left( \frac{\partial T}{\partial r} \right)_{r=R} = a_1 S_1 (T - T_p) \quad (2.b)$$

$$-\lambda \left( \frac{\partial T}{\partial z} \right)_{z=H} = a_2 S_2 (T - T_p) \quad (2.c)$$

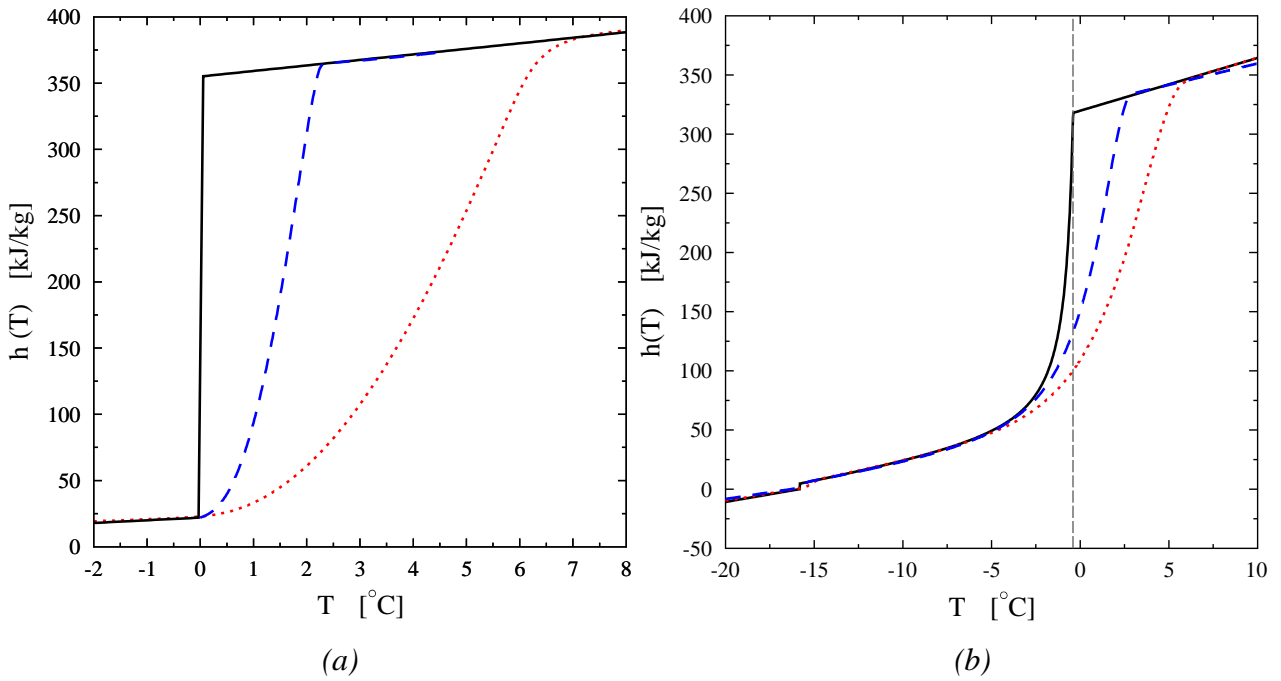


Fig. 1. Comparison of the enthalpy curves obtained with the equivalent-cp approach at two heating rates (dashed curves) with the exact solution (line). a) pure substance, b) solution.

The cornerstone of this approach lies in the closure of the system, which requires to define the relation between the enthalpy and the temperature. It has been chosen here to impose a strict respect of the thermodynamic principles, meaning that only acceptable formulations of the enthalpy may be considered, which in fact still lets a huge amount of possibilities [2,3]: pure substances, binary solutions, NRTL solid-liquid equilibrium closure...

As an example the pure substance case reads:

$$h(T) = \begin{cases} h_{ref} + c_s(T - T_{ref}) & \text{if } T < T_F \\ h_{ref} + c_s(T_F - T_{ref}) + yL_F & \text{if } T = T_F \\ h_{ref} + c_s(T_F - T_{ref}) + L_F + c_l(T - T_F) & \text{if } T > T_F \end{cases} \quad (3)$$

Whereas the binary solution case (with a pure solid phase and a linear liquidus [3]) is:

$$h(T) = \begin{cases} h_{ref} + c_s(T - T_E) & \text{if } T \leq T_E \\ h_{ref} + l_1 + c_s\left(T + (T_{F,w} - T_F) \ln(T_{F,w} - T)\right) \\ + (T_{F,w} - T_F) \frac{L_{F,w}}{T_{F,w} - T} - c_l(T_{F,w} - T_F) \ln(T_{F,w} - T) & \text{if } T_E \leq T \leq T_F \\ h_{ref} + l_2 + c_l(T - T_F) & \text{if } T > T_F \end{cases} \quad (4.a)$$

with

$$l_1 = L_E - c_s(T_{F,w} - T_F) \frac{L_{F,w}}{T_{F,w} - T_E} + c_s\left(T_E + (T_{F,w} - T_F) \ln(T_{F,w} - T_E)\right) - c_l(T_{F,w} - T_F) \ln(T_{F,w} - T_E) \quad (4.b)$$

$$l_2 = l_1 + c_s\left(T_F + (T_{F,w} - T_F) \ln(T_{F,w} - T_F)\right) - c_l(T_{F,w} - T_F) \ln(T_{F,w} - T_F)$$

Concerning the current method, the underlying idea is now described: the experimental temperature plate  $T_p(t)$  is used to set the boundary condition in the numerical model, which is then solved (using a classical finite volume method). Then the heat flux between the sample and the exterior may be computed. This being done, this numerical heat flux and the experimental one may be compared and thus define a target function which is going to be minimized by changing the values of the input parameters, thermophysical ones and heat transfer coefficients. Practically, either a simplexe or genetic algorithms have been implemented to achieve this step [3]. The main advantage of this approach is once to be thermodynamically consistent since the enthalpy function expression is known from the beginning and only the correct values of the associated parameters are searched. Thus, the results are much better than what can be expected with conventional methods, as may be seen in Fig. 2. First, one may note that the identified enthalpy curves are clearly independent of the heating rates. Then, solid state is no more predicted to exist above its natural limit. Finally, the method represents with the same degree of quality either pure substances, and the associated discontinuity in enthalpy, or solutions, where the temperature range is correctly predicted.

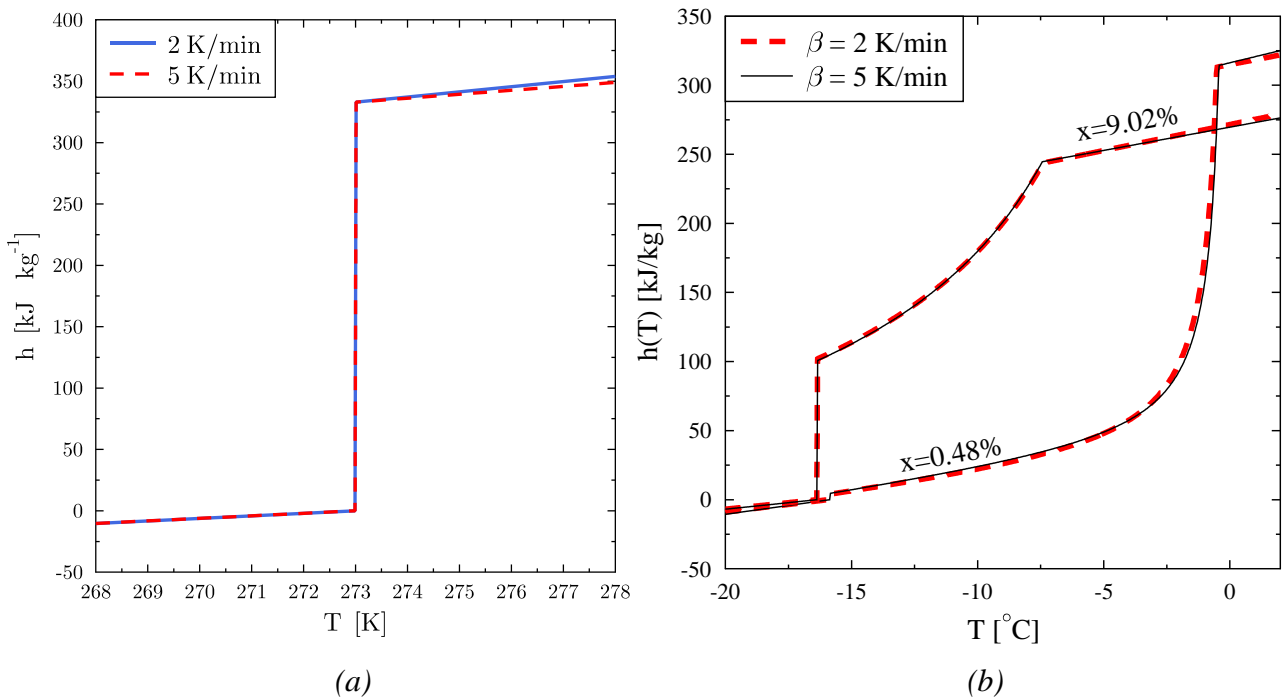


Fig. 2. Enthalpy curves obtained after identification with the present method at two heating rates. a) pure substance, b) solution.

## 2.2. Macroscopic samples

Since a protocol is now available to precisely determine the thermophysical properties of a PCM, the goal is now to apply this method to real materials such as those potentially used in buildings. The reason for such a study is first to show the capabilities of the current approach. But an other goal is also to show that materials may be directly characterised in their final shape, thus avoiding the question of how to combine the microscopic characterisation of the PCM alone with the properties of the real material, which is an heterogeneous mixture of the PCM with some other materials. Present study focuses on a cement mortar containing 12%<sub>w</sub> of micro-encapsulated PCM.

Furthermore, an additional in-house experimental device, presented in Fig. 3, has been developed so as to characterise the average properties of the real materials [6]. This one will be used so as to compare the associated results with the corresponding identified ones.

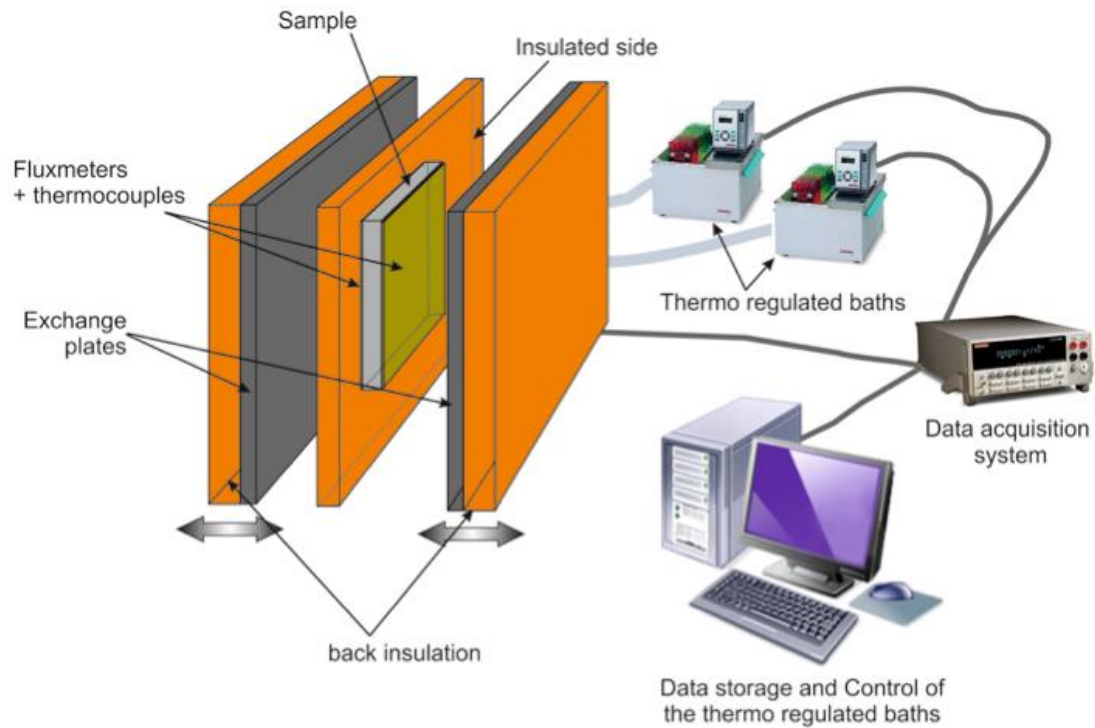


Fig. 3. Experimental in-house device developed to characterise macroscopic samples.

The sample to be tested is placed between the two isothermal plates, which are linked to thermoregulated baths. Tangential fluxmeters and thermocouples permit to measure the heat flux and the temperature on both faces. Finally, a thermal insulator is put around the sample in order to ensure the heat flux will be one-dimensional. Thus, different thermal conditions (constant temperature, low or fast heating/cooling ramp...) may be imposed at the two sides of the sample ( $T_L$  and  $T_R$ ), between two limit temperatures ( $T_b$  and  $T_t$ ).

The direct determination of the thermophysical properties ( $\lambda_1$ ,  $\lambda_s$ ,  $c_s$ ,  $c_l$  and  $L_F$ ) are done by setting several heatings and coolings at different rates, and then by imposing complete melting and freezing of the PCM involved in the sample. Relations and procedures to obtain the average properties are described in [6,4]. The experimental values are presented in Table 1.

Table 1. Comparison of the thermophysicals properties identified experimentally and numerically

Properties	$c_s$	$c_l$	$T_F$	$L_F$	$\lambda$
Exp.	$1120 \pm 60$	$1080 \pm 60$	$25,5 \pm 0,2$	$11590 \pm 1160$	$0,55 \pm 0,02$
Num.	$1130 \pm 60$	$1110 \pm 60$	$25,5 \pm 0,1$	$12000 \pm 600$	$0,51 \pm 0,02$

Then, as previously, these parameters are going to be identified with the current method combining the experimental measures and a numerical model through an inverse procedure. Here, the boundary conditions will correspond to the experimental temperatures associated to each face of the composite material. Then the calculated heat flux, obtained after the resolution of (1) with closure (4), is compared to the experimental one in order to estimate the objective function permitting to characterise the various thermophysical parameters. In Fig. 4, a comparison of the experimental and numerical heat fluxes is presented, together with the faces temperatures, at the end of the inversion process. The identified parameters are also presented in Table 1. Be it on this table or in Fig 4., one may remark the excellent comparison between the results [4,7].

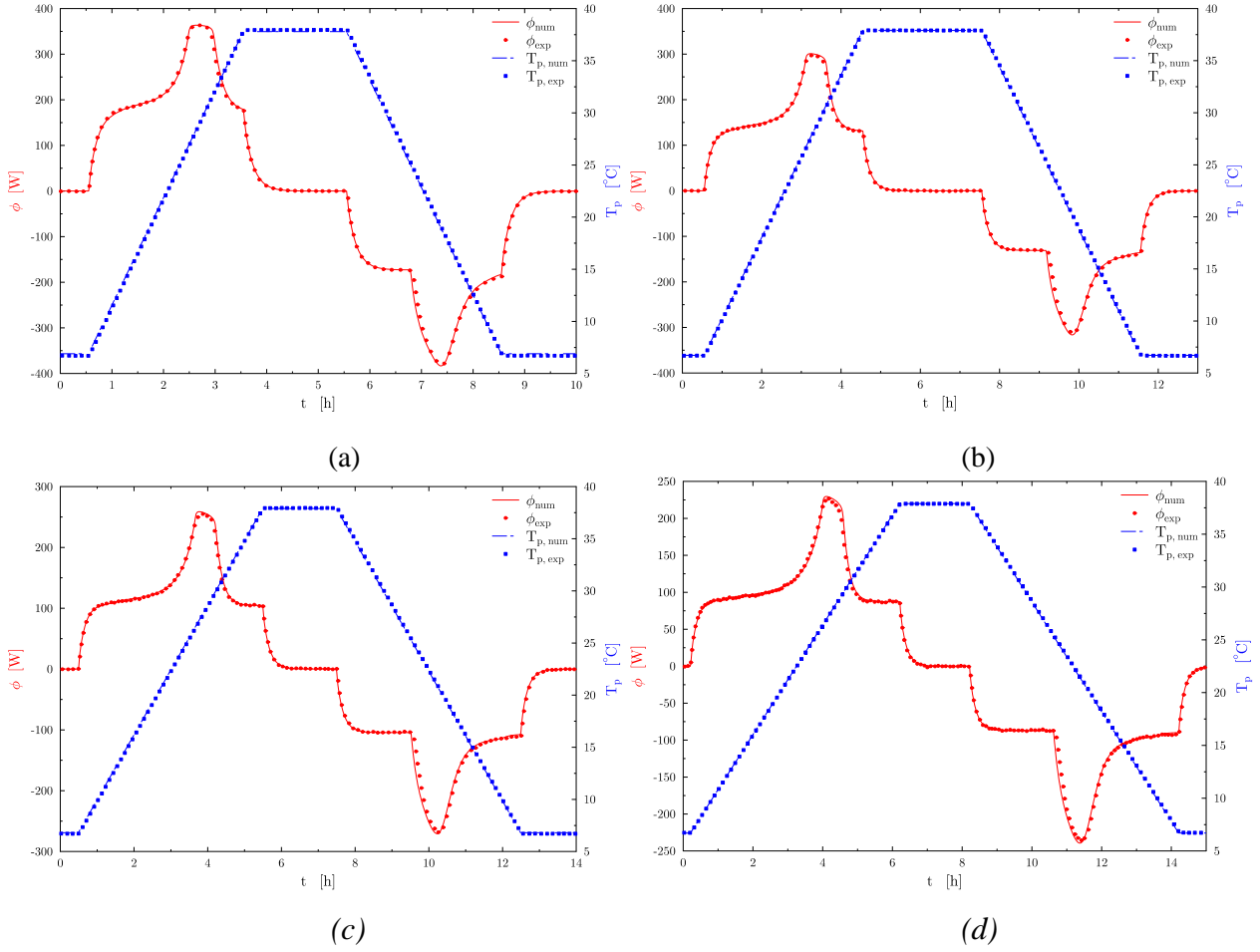


Fig. 4. Comparison of the numerical heat fluxes obtained after identification with the experimental ones. a) 3h ramp, b) 4h ramp, c) 5h ramp, d) 6h ramp.

### 3. Influence of the characterisation of the PCM on building thermal simulations

In this section, the main goal is to clearly show the consequences of an incorrect determination of the enthalpy function when one wants to simulate the thermal behaviour of a composite material containing PCM, be it a single wall or a complete housing [2, 5].

#### 3.1. Single wall

First, a single wall containing 15% of PCM is considered, its width is 200 mm. The main purpose here is mainly pedagogic: this case allowing to consider only one-dimensional computations, which are obviously faster to obtain, several kinds of examples may be tested in order to further highlight the errors done when an incorrect characterisation has been done.

Thus, the results obtained using the correct enthalpy function (noted DTF=0) and those obtained when one uses incorrect enthalpy curves presenting a thermal lag (noted respectively DTF = 2, 5 and 10 K) will be compared altogether. Concerning the external conditions, they are represented either by a first order progressive heating or by a sinusoidal solicitation, which is more representative of the real conditions associated to day/night rhythms:

$$T_{ext}(t) = T_i + (T_h - T_i) \left( 1 - \exp\left(-\frac{t}{\tau}\right) \right) \quad (5.a)$$

$$T_{ext}(t) = T_i + (T_h - T_i) \cos\left(\frac{2\pi t}{\tau}\right) \quad (5.b)$$

On Fig. 5 is shown the temperature at a depth of 40 mm inside the wall for the two external conditions defined above and for each of the four enthalpy curves, the correct one and the three others which all present a bias. On this figure, the classical case is also represented, that is to say without any PCM, to have a kind of reference case (it corresponds to the curve noted  $L_f=0$ ). Clearly, there are major differences between the various models. Dynamics of the heat transfer is rather different, with several hours variation, and the maximum temperature varies a lot, up to several degrees. One may note that this kind of error is increased when the erroneous thermal lag DTF increases [2].

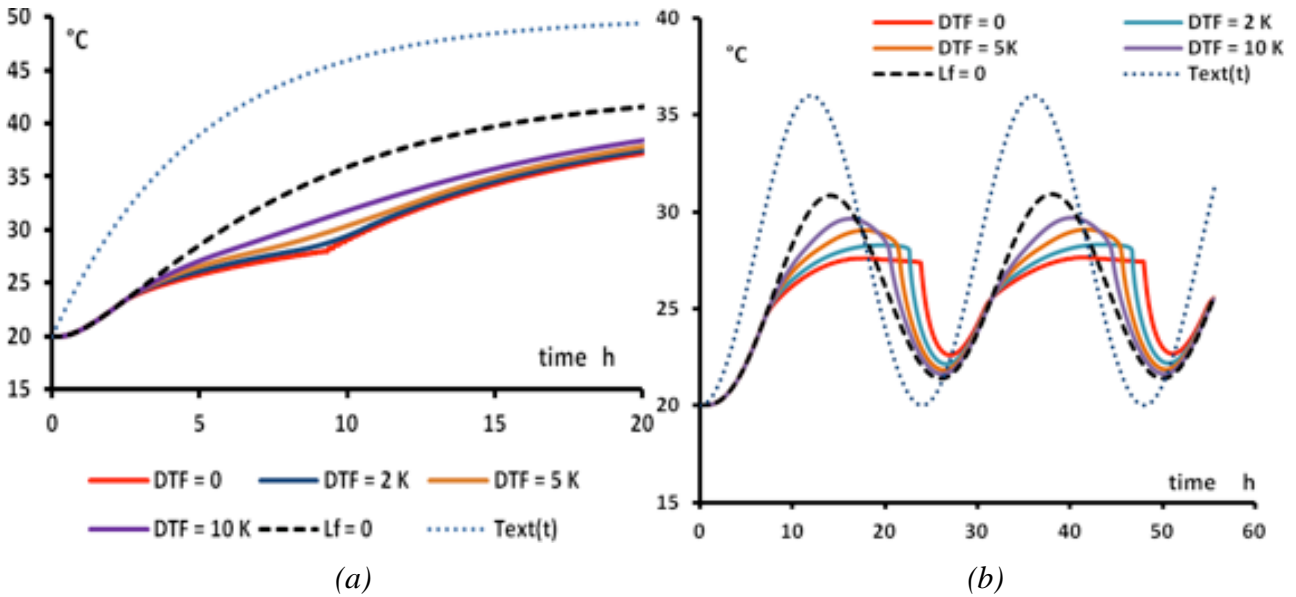


Fig. 5. Comparison of the computed temperatures inside the wall for the reference case ( $L_f=0$ ) and the wall containing PCM, depending on the thermodynamical modelling used for the PCM. a) first order progressive heating, b) sinusoidal heating.

### 3.2. Complete housing

Given the previous results, the study is now going to be extended to the thermal simulation of an individual house, the Mozart type depicted in Fig. 6, whose floor involves a composite material containing 12%<sub>w</sub> of PCM (cement mortar identical to that presented in the section 2.2).

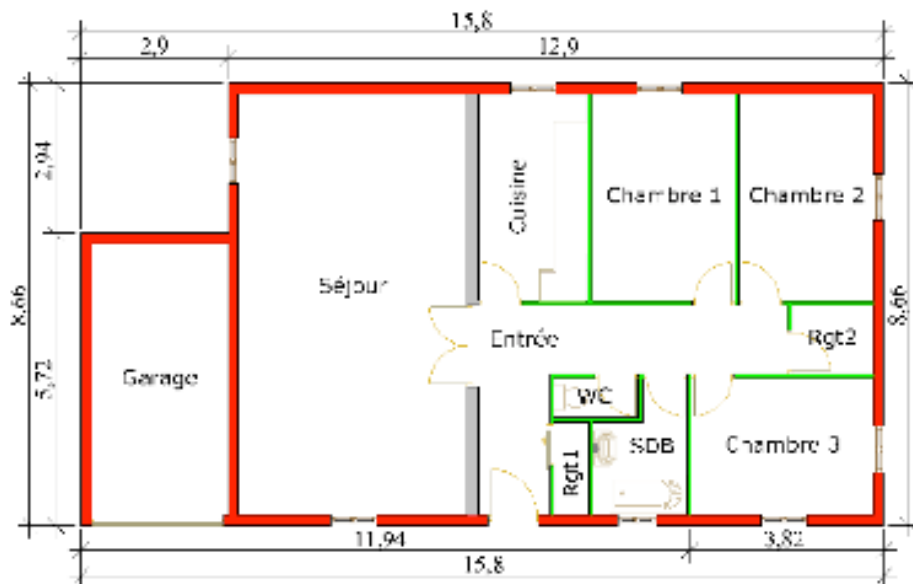


Fig. 6. Sketch of the Mozart house.



To simulate the behaviour of the PCM, only two modelling will be used here. The first one will be the one corresponding to the correct enthalpy curve, obtained with the present method (noted “binary model”). The second one will correspond to an incorrect enthalpy curve, obtained with a conventional raw analysis of a DSC thermogram (noted “DSC model”). Here, two periods will be considered: one between the 21<sup>st</sup> and the 28<sup>th</sup> of April, and an another one between the 8<sup>th</sup> and the 14<sup>th</sup> of August [5].

The surface temperatures are presented in Fig. 7, with here again a reference case corresponding to the situation without any PCM. Once more, it is clear that some error may arise from an inconsistent thermodynamic modelling of the PCM, for the two periods. Thus, in summer, the results obtained with the incorrect enthalpy curve (“DSC model”) may suggest that the PCM still limits the increase in temperature after the fifth day nonetheless the correct modelling unambiguously show that the PCM is completely melt and does not come back to its solid state, which means that it cannot play any role in the thermal regulation of the house. The 2°C decrease of the peak temperature predicted by the “DSC model” is thus fictitious, implying for example that an hypothetical upper limit of temperature in summer (which is current) may be attained. In the same way, for the spring period, one could think that the PCM is not very useful however with a good representation of its enthalpy, it appears that this conclusion is not relevant. As a rule of thumb, these results show clearly that one could draw wrong general conclusions on the role of the PCM in a building if its thermodynamic properties are not well defined.

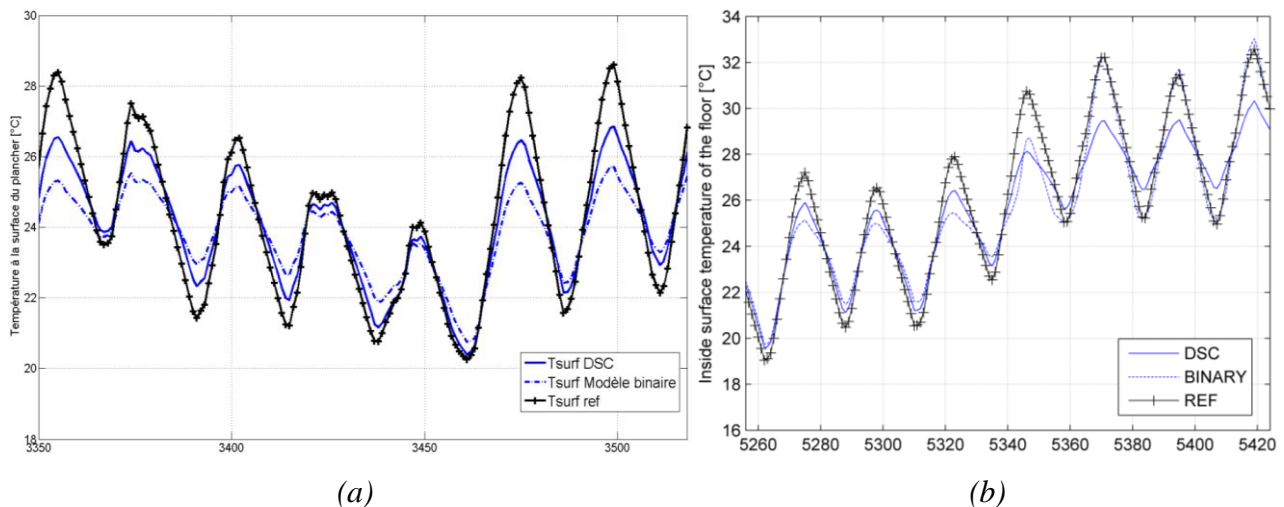


Fig. 7. Comparison of the surface temperatures for the Mozart house, depending on the thermodynamical modelling used for the PCM. a) first period in April, b) second period in August.

## 4. Conclusion

Thanks to this project, it has been possible to highlight the intrinsic defaults of the current methods used to characterise the thermophysical properties of phase change materials, and then to propose a new methodology which is more realistic (from a thermodynamical point of view) and above all more efficient. Assuming an *a priori* formulation of the enthalpy function, it is possible to simulate the behaviour of the PCM and therefore to compute a numerical heat flow rate. By comparing this latter one with the one experimentally measured, an objective function may be defined which is minimized via an inverse procedure that modify the value of the thermophysical parameters involved in the above equation of state.

Such an approach has been shown to be efficient and useable for microscopic samples, involving DSC measurements, but also for macroscopic samples, involving here an in-house experimental device. Thus, the current method has permitted to characterise both single PCMs, be it pure substances or solutions, and composite materials, involving a mixture of a classical material with a PCM. Each time, the results show an excellent agreement with the experiments.

Eventually, the need for correctly characterising the PCM thermodynamic properties has been shown when one wants to simulate the thermal behaviour of buildings containing PCMs. By considering first a single wall and secondly an individual house, the Mozart one, it has appeared that an incorrect characterisation of the PCM would lead to incorrect conclusions concerning its consequences on the thermal behaviour of the building.

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## Nomenclature

### Latin letters

- $c$  specific heat, J/(kg K)
- $e$  width of the sample, m
- $H$  height of the sample, m
- $h$  specific enthalpy, J/kg
- $L$  latent heat, J/kg
- $R$  radius of the sample, m
- $r$  spatial coordinate, m
- $S$  surface, m<sup>2</sup>
- $T$  temperature, °C
- $t$  time, s
- $Y$  mass fraction, –
- $z$  spatial coordinate, m

### Greek symbols

- $\alpha$  heat transfer coefficient, W/(m<sup>2</sup> K)
- $\phi$  heat flux, W
- $\lambda$  thermal conductivity, W/(m K)
- $\rho$  density, kg/m<sup>3</sup>
- $\tau$  time constant, s

### Subscripts and superscripts

- F fusion
- f final
- i initial
- L left
- l liquid
- p plate
- R right
- b bottom
- s solid
- t top
- w solvent

### Acronyms

- DTF: “width” of the thermogram, K

DSC: Differential Scanning Calorimetry

NRTL: Non Random Two Liquids

PCM: Phase Change Materials

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