

Behaviour of Thermodynamic Models with Phase Change Materials under Periodic Conditions

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Abstract

We study the thermal behaviour of some models in a steady periodic regime. The aim is to simulate the behaviour of small environments at the outermost part of our planet, subjected to the periodic solar radiation. Our approach is based on a method using lumped elements or volumes that simplifies the description of spatially distributed physical systems, through a topology consisting of discrete entities. Our models include some parts acting as energy storage systems, made with Phase Change Materials (PCMs). The storage is based on latent heats: the energy is stored during the melting and recovered during the solidification of the PCM substance. The simulation with lumped elements shows some interesting behaviours of temperatures.

Keywords: Thermodynamics, Heat Exchange, Lumped Volume Models

1. Introduction

The study of the thermal behaviour of macroscopic systems in a steady periodic regime is quite important because of its usefulness in investigating the effects produced by solar radiation on the structures located on the outermost part of our planet. The aim of these studies is the simulation of temperature behaviours and heat exchanges in local environments. Due to the current conditions created by an increasing average temperature coming from the global warming, these simulations could help in offering new solutions to reduce the energy consumption or prevent some side effects. Let us consider for instance the role of permafrost soil in the behaviour of climate of arctic regions. Permafrost is that soil always below the freezing point of water, which is located at high latitudes close to the poles. The extent of permafrost can vary as the climate changes: at the same time, it is thought that permafrost thawing could exacerbate the global warming by releasing methane and other hydrocarbons that are powerful greenhouse gases [1]. A model of the thermodynamic behaviour of permafrost could then be interesting for a forecast of future environmental conditions in arctic regions. Here we will propose and discuss the thermal behaviour of some preliminarily simple models, useful to simulate those structures including solid parts, for instance ice or permafrost or other materials, which can melt at specific temperatures.

These models are also interesting for simulating the thermal behaviour of a building with systems for energy storage. Let us note that a storage system is a fundamental counterpart of all those systems based on renewable energies working under periodic conditions.

Among the various methods to store energy, the latent thermal energy storage using Phase Change Materials (PCMs) is widely considered as a highly effective one. It has the advantage of a high density of energy, stored in an isothermal operation, during the solid/liquid phase change. In the latent heat storage, the energy is stored during the melting and released during the solidification of a PCM substance [2-10]. For what concerns the use of PCMs, it is necessary to note that some practical difficulties can arise because these materials usually have a low thermal conductivity and a poor stability of properties under extended cycling. Sometimes phase segregation and subcooling can happen. Over the past years, several studies have been performed to examine the performances of various latent heat storage systems [11-18] and on micro-encapsulations, which is the best packaging of PCM, to have good performances [19,20]. Micro-encapsulated PCMs constitutes a portable heat storage system, easy to insert in the construction materials for buildings [21-28].

As a possible approach to simulate the thermal behaviour of volumes including an energy storage system with PCMs, we propose the use of models composed of sev-

eral parts, each obeying the laws of thermodynamics. These components are interacting with heat exchanges, some of them being in connection with the external environment. The behaviour of the models will be discussed by means of an approach based on lumped elements, where we simplify the description of spatially distributed physical systems through a topology consisting of discrete entities, which approximate the behaviour of the distributed system under certain assumptions. This method, initially developed for electrical systems, is well known and useful to solve the problem of heat transport [29]. The partial differential equations of a continuous time and space model of the physical system are changed in ordinary differential equations with a finite number of parameters. Before discussing the lumped volume method, let us shortly revise the problem of heat exchange.

2. Heat Exchange with the Environment

We will consider in our models some structures with PCM material surrounded by an environment idealized as a collection of thermal baths, such as heat sources and reservoirs. We assume a time-dependent state of the surrounding in the terrestrial conditions, that is, with temperatures of the order of a few hundred Kelvin, oscillating with a defined period. Let us note that in thermodynamics, the system can have free inputs, when fuels or electric powers are used. In the case of the natural environment, we have a deterministic input, because it is the Nature to dictate the conditions. Therefore, we can consider for our models a steady periodic regime for solar radiation, pressure and temperature, as an ideal case of the conditions of the outermost part of the planet. Let us remember that the input black-body solar temperature is approximately of 400 K, the amplitude of oscillation of 30 K [30,31].

Let us shortly discuss the boundary conditions. Let us imagine a finite body with a temperature, which is a function of time and position, and heat inputs and outputs. The temperature distribution in the bulk is subjected to the Fourier field equation:

$$c\rho \frac{\partial T}{\partial t} = \kappa \nabla^2 T, \quad (1)$$

where ρ is density, c specific heat and κ thermal conductivity of the body. T is the temperature field. This equation can have several boundary conditions. Consider a finite volume V and its surface divided in two continuous surfaces S_1 and S_2 . The model is shown in **Figure 1**. The temperature field is defined in the volume of the body and the two surfaces are in contact with two thermal baths having temperatures $T_1(t)$ and $T_2(t)$. We

can fix the temperature at the surface of the body coincident to the temperatures the local two thermal baths as:

$$\begin{aligned} (T(\mathbf{r}, t))_{S_1} &= T_1(t) \\ (T(\mathbf{r}, t))_{S_2} &= T_2(t) \end{aligned} \quad (2)$$

We can consider different boundary conditions in the following way:

$$\begin{aligned} -\kappa(\nabla T(\mathbf{r}, t) \cdot \mathbf{n})_{S_1} &= -\alpha_1 [T_1(t) - (T(\mathbf{r}, t))_{S_1}] \\ -\kappa(\nabla T(\mathbf{r}, t) \cdot \mathbf{n})_{S_2} &= -\alpha_2 [T_2(t) - (T(\mathbf{r}, t))_{S_2}] \end{aligned} \quad (3)$$

Note that the boundary conditions (2) are of the Dirichlet type, while the boundary conditions (3) are known as the Neumann conditions [31].

To have an idea of the magnitude of parameters involved in the problem, we can imagine the oscillating temperatures of the baths as the following functions: $T_1(t) = T_{01} + A \cos(\omega t)$, $T_2(t) = T_{02} + B \cos(\omega t)$, with $T_{01} = 285 \text{ K}$, $A = 15 \text{ K}$, $T_{02} = 275 \text{ K}$, $B = 5 \text{ K}$, $\omega = 2\pi/86400 \text{ s}^{-1}$, for a daily oscillation, for instance. The physical constants are: $\kappa = 1.512 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, $c\rho = 2.0 \times 10^6 \text{ J} \cdot \text{m}^{-3} \cdot \text{K}^{-1}$, corresponding to concrete and $\alpha = 10 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$ which corresponds to zero-wind concrete-air interface coupling [31,32].

Let us consider a one-dimensional case: it could be a wall with a certain thickness h (see **Figure 1**, lower part, for the frame of reference). In this case, we have an equation the boundary conditions of which are:

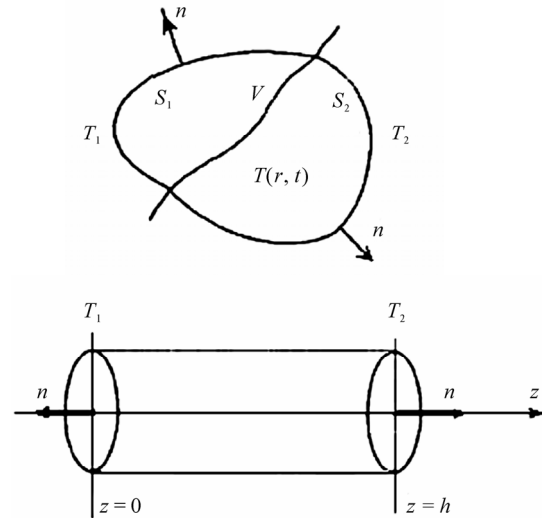


Figure 1. Upper part, a finite volume V with its surface divided in two continuous surfaces S_1 and S_2 . The temperature field is defined in the volume of the body and the two surfaces are in contact with two thermal baths having temperatures $T_1(t)$ and $T_2(t)$. Lower part, the frame of reference for a one-dimensional case, where the body is interacting with the environment through two surfaces again.

$$\begin{aligned} T(0, t) &= T_1(t) \\ T(h, t) &= T_2(t) \end{aligned} \quad (4)$$

or

$$\begin{aligned} \kappa \left(\frac{\partial T}{\partial z} \right)_{z=0} &= -\alpha_l [T_1(t) - T(0, t)] \\ \kappa \left(\frac{\partial T}{\partial z} \right)_{z=h} &= \alpha_r [T_2(t) - T(h, t)] \end{aligned} \quad (5)$$

The Fourier one-dimensional equation is simply:

$$c\rho \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial z^2}, \quad (6)$$

which is giving the temperature profile in the wall according to the chosen boundary conditions.

3. Lumped Volumes and PCM

It is interesting to consider a volume balance of Equation (6), as proposed in [31]:

$$\begin{aligned} c\rho \int_0^h \frac{\partial T}{\partial t} dz &= \kappa \int_0^h \frac{\partial^2 T}{\partial z^2} dz = \kappa \left(\frac{\partial T}{\partial z} \right)_{z=h} - \kappa \left(\frac{\partial T}{\partial z} \right)_{z=0} \\ &= \alpha_r [T_2(t) - T(h, t)] - \alpha_l [T(0, t) - T_1(t)] \end{aligned} \quad (7)$$

In performing the volume balance, let us assume that the thermal conductivity is so high to be considered as practically infinite. The temperature is no more depending of the z -coordinate, $T(z, t) = T(t)$, and then Equation (7) turns out to be:

$$c\rho h \dot{T} = \alpha_r [T_2(t) - T(h, t)] - \alpha_l [T(0, t) - T_1(t)] \quad (8)$$

Equation (8) is a function of time only, and it is depending on the specific heat and mass of the body and its ability to exchange heat with the environment. The dot is representing the derivative with respect to time. Equation (8) describes the behaviour of a lumped volume.

Let us consider a body with a certain volume and surfaces as in **Figure 1**. The volume balance equation governing this lumped system is:

$$\begin{aligned} c\rho V \dot{T} = C\dot{T} &= \alpha_2 S_2 [T_2(t) - T(h, t)] \\ &\quad - \alpha_1 S_1 [T(0, t) - T_1(t)], \end{aligned} \quad (9)$$

where V is the volume and S_1 , S_2 are the two surfaces, through which the body exchanges the heat with the surrounding [31]. Equation (9) is the basic equation we use in our models.

Let us consider the simple case shown in **Figure 2**. We have a body 1 containing inside a smaller body 2. Only the body 1 is exchanging heat with the environment. It is quite simple to write the equations of the volume balance for the two bodies:

$$\begin{aligned} C_1 \dot{T}_1 &= \alpha_{1E} S_1 [T_E(t) - T_1(t)] + \alpha_{12} S_2 [T_2(t) - T_1(t)] \\ C_2 \dot{T}_2 &= \alpha_{12} S_2 [T_1(t) - T_2(t)] \end{aligned} \quad (10)$$

where $c_1 \rho_1 V_1 = C_1$; $c_2 \rho_2 V_2 = C_2$.

The system of equations (10) can be solved by numerical methods. The numerical solutions have been found using a two-step Runge-Kutta method. The time interval Δt , that is the step of time in the numerical solution, was chosen small enough, that its further reduction was not able to change the final result in an appreciable manner. We considered a temperature difference to be appreciable, only in the case it is greater than 0.05 K, which is the sensitivity of common instruments.

If the external temperature is oscillating with a certain period, after a transitory time, the temperatures of the two bodies are oscillating with the same period, as shown in **Figure 3**.

The body 2 could contain a PCM. In this case, when 2 reaches its transition temperature, the heat gained or lost by body 2 with body 1, that is $Q = \alpha_{12} S_2 [T_1(t) - T_2(t)]$, could be used for melting or solidification of PCM. During the phase change, the temperature of body 2 remains constant.

A control on the mass percentage of solid/liquid phases of PCM (body 2) is inserted in the numerical procedure to solve Equation (10). With an upgrade of their values according to the heat exchange with body 1, the quantities of liquid and solid PCM can be evaluated, according to the specific latent heat H . Let us remember that the latent heat is the amount of energy in form of heat required to have a complete phase change of a unit of mass. The phase change is described by the following equation:

$$Q = \alpha_{12} S_2 [T_1(t) - T_{2,melt}] = mH \quad (11)$$

Q is the amount of energy released or absorbed during the change of phase of the substance, m is the mass of the substance, and H is the specific latent heat (J/kg^{-1}). $T_{2,melt}$ is the phase transition temperature. In the numerical procedure, we considered, instead of a precise value of the melting temperature, an interval one degree wide about it, as in Ref.33. The upper panel of **Figure 3** shows the behaviours of the temperatures that we obtained when body 2 is a PCM.

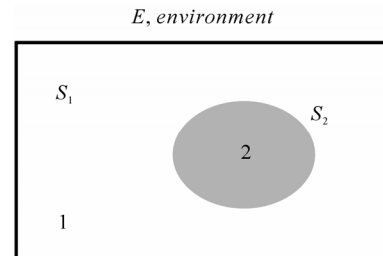


Figure 2. A certain finite body 1 is surrounded by surface S_1 . It contains a body 2 having surface S_2 . Only body 1 is in contact with the environment.

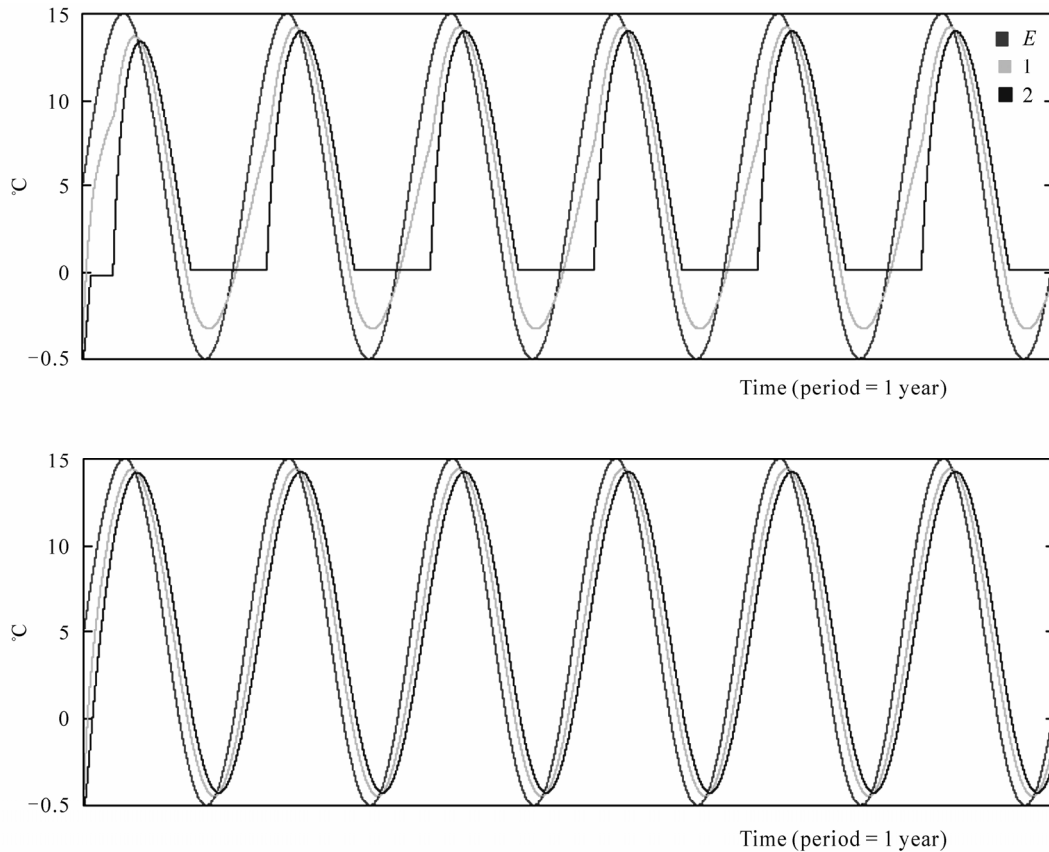


Figure 3. Behaviour of the temperatures T_1 , T_2 and T_e , for the model in Figure 2 as a function of time. In the upper part of the figure, it is supposed that body 2 is a PCM. The period of oscillation is one year. In the specific simulation, the PCM is imagined as a certain quantity of water. Note that, when the water reaches its liquid-solid transition, the temperature remains constant. If body 2 is made of a material having no phase change, the behaviour is different, as shown in the lower part of the image. The presence of PCM changes the minimum temperature of body 1.

Figure 3 shows the behaviour of the temperatures T_1 , T_2 and T_e , for the model in **Figure 2**, with suitable parameters of thermal exchanges among bodies. The upper part of the image corresponds to the case where body 2 is a PCM. When PCM reaches its phase transition, its temperature remains constant. The quantity of heat gained or lost in the exchange with body 1 does not change the temperature of 2, but changes the relative amount of liquid and solid PCM. In the lower part of the figure, it is shown the case with a body 2 made of a material having no phase transitions. Note that the presence of a PCM influences the minimum temperature of body 1, which is different of a few degrees, as it is possible to see comparing the two panels of the figure. The parameters used in the model of **Figure 2** are: $C_1 = 2.0 \times 10^6 \text{ J}\cdot\text{K}^{-1}$, $C_2 = 1.0 \times 10^5 \text{ J}\cdot\text{K}^{-1}$, $\alpha_{1e}S_1 = 1.0 \text{ W}\cdot\text{K}^{-1}$, $\alpha_{12}S_2 = 0.5 \text{ W}\cdot\text{K}^{-1}$, $T_{\text{melt}} = 0^\circ\text{C}$; $m_{\text{PCM}} = 100 \text{ kg}$ and $H = 333.0 \text{ kJ/kg}$. Varying the amount of PCM and the exchange parameters αS with the environment and between the bodies, we can control, for instance, the amplitude of oscillation of the temperature in body 1.

4. A Container with a Heat Storage System

The model we want to propose in this section is more complex. It is supposed to be a container 1, in which we have inside two bodies: 2 is made of PCM and 3 is a cavity. The container is supposed to be in thermal contact with a substrate S having a constant temperature and the environment E, having an oscillating temperature.

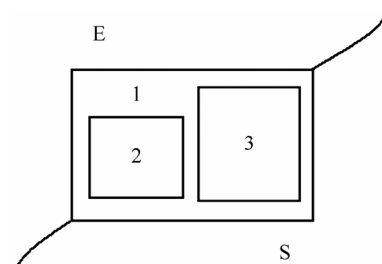


Figure 4. Container 1 has inside two bodies: 2 is made of PCM and 3 is a cavity. The container is supposed to be in thermal contact with a substrate S at constant temperature and the environment E, having an oscillating temperature.

The equations of the volume balance for the three bodies are:

$$\begin{aligned} C_1 \dot{T}_1 &= \alpha_{1E} S_{1E} [T_E(t) - T_1(t)] + \alpha_{1S} S_{1S} [T_S - T_1(t)] \\ &\quad + \alpha_{12} S_{12} [T_2(t) - T_1(t)] + \alpha_{13} S_{13} [T_3(t) - T_1(t)] \\ C_2 \dot{T}_2 &= \alpha_{12} S_{12} [T_1(t) - T_2(t)] \\ C_3 \dot{T}_3 &= \alpha_{13} S_{13} [T_1(t) - T_3(t)] \end{aligned} \quad (12)$$

The parameters we use for calculations are $C_1 = 2.0 \times 10^6 \text{ J}\cdot\text{K}^{-1}$, $C_2 = 4.18 \times 10^6 \text{ J}\cdot\text{K}^{-1}$, $C_3 = 1.0 \times 10^5 \text{ J}\cdot\text{K}^{-1}$, $\alpha_{1E} S_{1E} = 2.0 \times 10^6 \text{ W}\cdot\text{K}^{-1}$, $\alpha_{1S} S_{1S} = 20 \text{ W}\cdot\text{K}^{-1}$, $\alpha_{12} S_{12} = 100 \text{ W}\cdot\text{K}^{-1}$, $\alpha_{13} S_{13} = 20 \text{ W}\cdot\text{K}^{-1}$, $m_{PCM} = 10^4 \text{ kg}$ and $H = 333.0 \text{ kJ/kg}$. Note that we suppose a high value of the exchange parameter $\alpha_{12} S_{12}$ between container and PCM, imaging a high value of the surface between

the bodies. The substrate S is at a fixed temperature, $T_S = 270.0 \text{ K}$, that is the temperature of a permafrost soil for instance.

The temperature of the environment E is oscillating assuming that the solar radiation changes during the day and over the year, as shown by the red curve (E) in **Figure 5**. We see a red band then, composed by the daily oscillation and the seasonal oscillation during the year. The green band (1) represents the temperature of the container walls, which is oscillating too with smaller amplitude during the day. The blue curve (2) is the temperature of the PCM, assumed water. Note that the temperature (2) is constant for a quite long period during which the material freezes or melts. Then we can see the temperature of the cavity 3 (purple line).

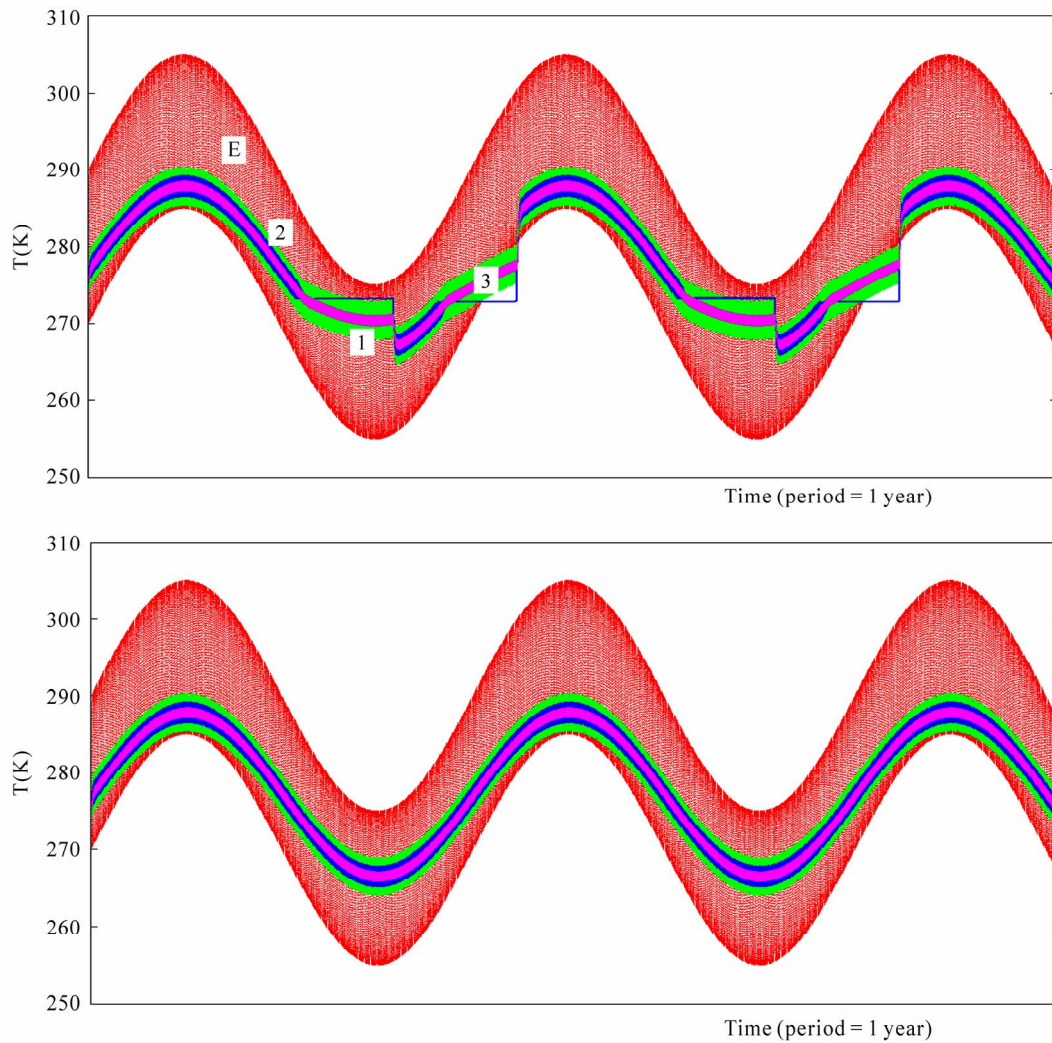


Figure 5. The temperature of the environment is oscillating with a daily oscillation and with a seasonal oscillation during the year, as shown by the red curve (E). The green band (1) represents the temperature of the container walls. The blue curve (2) is the temperature of the PCM, assumed to be water. Note that the temperature (2) is constant when the material is freezing and melting. The temperature of the cavity 3 is the purple line. In the lower panel, 2 contains a material without the phase transition, for instance water always in the liquid phase.

From the upper panel of **Figure 5**, we can see that when the PCM is freezing or melting, according to the thermal exchange, its temperature is constant. We can also imagine the same system that, instead of PCM in 2, has a material that does not possess a phase change, for instance water that always remains in its liquid state. In this case, the temperature 2 is oscillating as reported in the lower panel of **Figure 5**. It is interesting to compare the two cases, to evaluate the influence of the presence of PCM on the local average temperature of cavity 3. **Figure 6** shows this comparison. The minimum temperatures observed in 3 are slightly different, but in the case

of the presence of PCM, during its freezing, cavity 3 has a temperature (grey curve) which is 5 degrees greater than that observed without PCM (black curve).

We can then try to increase the amount of PCM: for an amount that is twice, we have the behaviour shown in **Figure 7**, for the same temperatures of environment and substrate. We see that the increase of PCM is strongly influencing all the system. It is interesting to note that the minimum temperature in the cavity 3 is always 5 degrees above the minimum temperature reached by the system without PCM (**Figure 8** shows the comparison for the two cases). This simulation shows that with a suitable

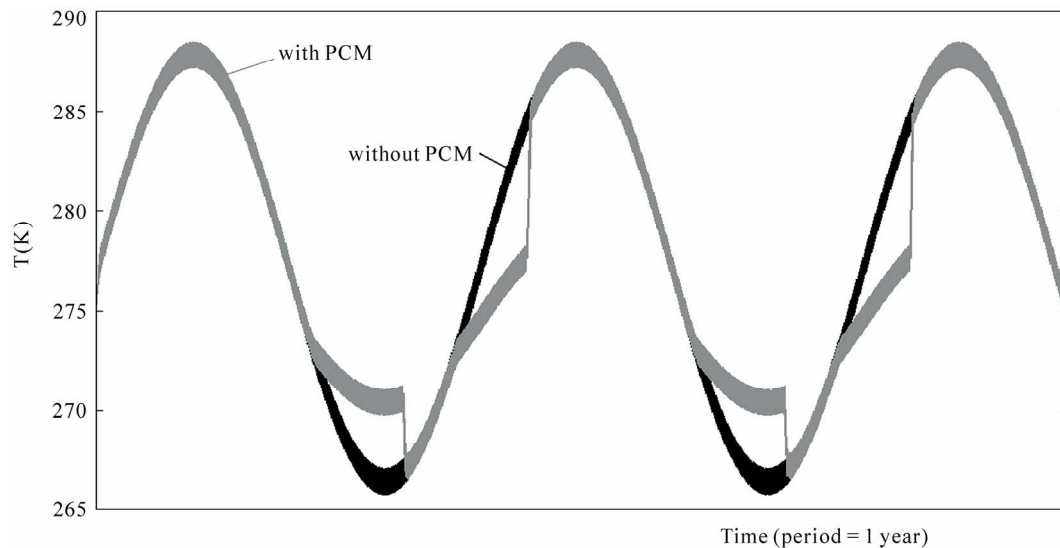


Figure 6. The temperature in the cavity 3 has a different behaviour in the case that body 2 is a PCM or not.

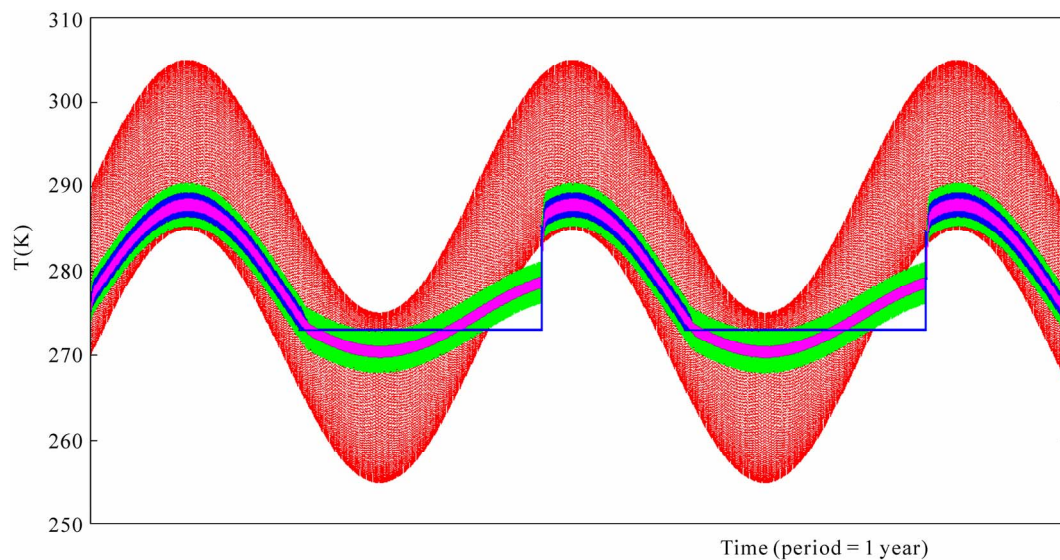


Figure 7. The temperature of the environment is oscillating, as shown by the red curve. The green band represents the temperature of the container walls. The blue curve is the temperature of the PCM material 2, assumed water. The temperature of the cavity 3 is the purple line. Note that the presence of PCM maintains the minimum temperature of the cavity five degrees above the case without PCM (see the next figure for comparison).

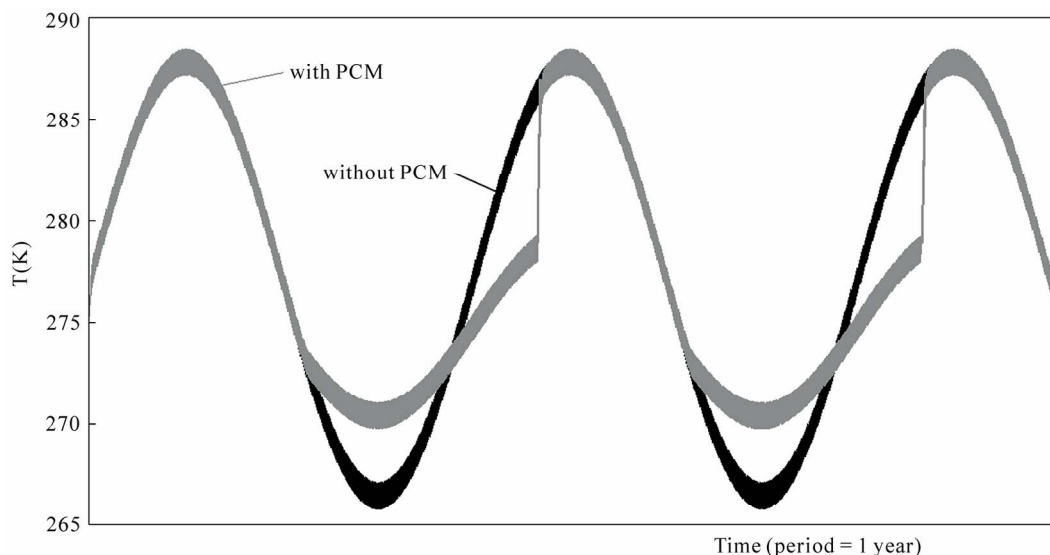


Figure 8. Temperature in the cavity 3 has a different behaviour, in the case that body 2 is a PCM or not. Increasing the amount of PCM, the minimum temperature of the cavity 3 is always at higher values (a difference of approximately 5 degrees).

choice of the PCM quantities, it is possible to manage the excursion of the temperature inside the cavity (and in the walls of container).

5. Conclusions

We proposed the study of the thermal behaviour of lumped volume models in a steady periodic regime created by the solar radiation. The method with lumped elements is based on the volume balance of the thermal conductivity equation. The description of spatially distributed physical systems is approximated with a topology consisting of discrete entities.

According to the authors' knowledge, our proposed approach to the study of lumped systems under periodic conditions is new because it is including some elements acting as energy storage systems. The storage is based on the latent thermal energy storage with Phase Change Materials (PCMs), where the energy is stored during the melting and recovered during the solidification of PCM. We did simulations with simple models, to show the method. These models are indicating that a temperature control can be obtained with a suitable choice of the PCM. Of course, realistic models simulating buildings or larger environments can be created, including more elements in the calculation, to study the possibility to have a passive control of the temperature inside the specific environments.

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