Off-eutectic binary salt finite volume method

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Abstract

Non-linear phase diagrams for binary compositions are coupled with Thétis, a finite-volume solver, to calculate charge/discharge solutions for an off-eutectic salt thermal energy storage candidate. Previous methodologies often include linearized versions of these phase diagrams that cease to give accurate solutions when applied to materials with highly non-linear diagrams, such as the off-eutectic salt mixture NaCl-NaNO₃. Consequently, large discrepancies in the solid fraction calculation and subsequently in the heat storage capacity calculation of the storage candidate may be found. While the choice of using a linear or a non-linear phase diagram will mainly affect the solid fraction calculation and thus the latent heat calculation, the thermal properties will typically have a larger effect on the sensible heat calculation. Usually, thermal properties are taken as global averages over space and time, but this may not be an adequate approximation, especially when dealing with large temperature ranges, macrosegregation, and partial melting/solidification. Instead, local thermal properties should be calculated and applied for such cases.

A methodology is presented to include non-linear phase diagrams and locally calculated thermal properties in Thétis, starting with validation of the original methodology with published results for the widely studied alloy Pb-18%Sn. The original methodology is then modified to account for non-linear phase diagrams and variable local properties. Finally, the methodology is applied to a fully non-linear off-eutectic salt NaCl-55%NaNO₃ (a potential candidate for thermal energy storage) in order to evaluate the importance of using the more elaborate current methodology for charge/discharge solutions. The heat storage for a particular case using the current methodology is found to be 24% lower than for the original methodology, confirming the benefit of using the current methodology.

Keywords: Thermal/ thermochemical energy storage
1. Introduction

Thermal energy storage (TES) represents the main competitive advantage of concentrated solar power (CSP) in comparison to other types of renewable energy, allowing dispatchable electricity generation and management of the solar resource intermittency. If CSP is to be capable of producing 11.3% of the global electricity production by 2050 to meet greenhouse emission targets [1], substantial technological and cost reduction efforts are required. As a result, recent research is focusing on developing new, more cost-effective and energy efficient TES. Latent heat TES based on phase change materials (PCM) is a very attractive solution because it can provide high energy density storage per unit mass/volume at nearly a constant temperature, which corresponds to the phase transition of the storage material.

One of the principal challenges in the development of PCM-based TES systems is an adequate analysis of the phase change and correct evaluation of the thermophysical properties during the process. This is especially complex with multicomponent materials. A wide range of compositions of salt mixtures and metal alloys are being investigated as potential PCM [2]. Eutectic materials change phase at a constant temperature, whereas off-eutectics change phase throughout a temperature range and could perhaps prove to store energy in a more efficient manner through the same given range of temperatures. Using an off-eutectic composition could also be seen as the equivalent of using a PCM cascade [3]. The advantage is that the system will be composed of a mixture of components, instead of multiple combinations of materials and containers. Consequently, off-eutectic systems must be studied and compared to their eutectic and sensible heat TES counterparts.

Predicting the behavior of phase change systems is difficult because of their inherent non-linear nature at moving interfaces, for which the displacement rate is controlled by the latent heat lost or absorbed at the boundary [4, 5] requiring numerical analysis to resolve the thermal behavior of the system. During the PCM solid-liquid phase change certain undesirable phenomena appear such as supercooling, phase segregation, corrosion, and lack of thermal stability [4]. Microsegregation appears as the various components coalesce and melt into the distinct phases that form during phase change. Macrosegregation typically appears due to a redistribution of the segregated elements in the mushy zone (or region where the phase change takes place) that is induced by variations of density that develop with temperature and concentration gradients [6]. This fluid flow induced by thermal and solutal natural convection are in a strongly non-linear coupling, especially if there are large disparities of diffusion scales of heat, momentum and mass (very low Prandtl numbers and high Lewis numbers). These phenomena are have been extensively investigated in metallurgy [6, 7] since macrosegregation is one of the major casting defects that appear. However, macrosegregation applied to TES systems has not yet been thoroughly investigated and will be particularly important in evaluating the phase change of off-eutectic materials.

Additionally, in order to accurately predict the thermophysical properties of the mixtures during the solidification process, local variations in the solutal and flow fields in the channels regions should be considered. This requires grid refinement up to scales on the order of microscopic dendrite arm spacing [6], imposing large computational time limitations. Thus, the applicability of available macroscopic models based on classical volume-averaging techniques is explored.

The present study uses a modified version of a CFD research code called Thétis [8] to model the phase change of multicomponent materials. Thétis currently calculates phase change using linearized phase diagrams. One of the main objectives of this work is to improve the results of linearized phase diagrams by implementing more accurate, non-linear phase diagrams. The importance of such a modification is explored through the analysis of the solidification of an off-eutectic salt. The differences between a constant thermal property model and a model where the properties are calculated with respect to the phases present and their respective compositions are also compared. Most notably, the thermal properties of the material are adjusted to take into account the local composition and temperature of the liquid and solid fraction. This modification gives an added degree of precision that in the past had not been thoroughly investigated. It is shown that the non-linearity of off-eutectic systems can be better modeled by implementing non-linear models into the CFD code.
2. Modelling approach

2.1. Equations and numerical solver

The PCM solidification problem of interest is represented by a fluid flow submitted to heat transfer and species transport. The Thétis [8] finite volume solver, developed at the University of Bordeaux, is used to solve the classical Navier-Stokes equations (Eqs. 1-2), formulated in an incompressible form, the energy equation (Eq. 3), and the solute advection equation (Eq. 4) in order to estimate velocity, temperature, and solute distribution fields, as proposed by Rappaz et al. [9] and used by Rady et al. [6].

\[ \nabla \cdot \mathbf{u} = 0 \]  
(1)

\[ \rho_0 \left( \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot (\nabla \mathbf{u}) \right) = \nabla \left( \mu_l (\nabla \mathbf{u} + \nabla^T \mathbf{u}) \right) - g_l \nabla p - \frac{\mu_l g_l \mathbf{u}}{K} + g_l \rho g \]  
(2)

\[ \rho_0 c_p \left( \frac{\partial T}{\partial t} + \nabla T \cdot \mathbf{u} \right) = \nabla \cdot (\lambda \nabla T) + S_T \]  
(3)

\[ \frac{\partial \langle C \rangle}{\partial t} + \mathbf{u} \cdot \nabla C_i = \nabla \cdot (D_i \nabla C_i) \]  
(4)

\( \mathbf{u} \) is the velocity vector, \( D_i \) is the liquid diffusion, and \( C_i \) is the composition of the liquid phase.

The source term \( S_T \) of the energy equation corresponds to the latent heat released or captured during phase change. The distinction between the solid and liquid states is obtained only via the value of the solid fraction, \( f_s \), since Thétis uses a one-fluid model to solve the Navier-Stokes equations on the whole domain. Thus the melting interface is not tracked explicitly, instead the liquid fraction (or fraction of the cell volume that is in the liquid phase) is determined through an enthalpy balance for each cell in the domain.

The solid fraction \( f_s \) is linked to the source term (Eq. 5) and to the volume-averaged concentration \( \langle C \rangle \) (Eq. 6):

\[ S_T = \rho L_f \frac{\partial f_s}{\partial t} \]  
(5)

\[ \langle C \rangle = f_s C_s + (1 - f_s) C_i \]  
(6)

where \( L_f \) is the latent heat of fusion and \( C_s \) is the solid composition.

Equations (2) and (3) mention two different densities \( \rho \) and \( \rho_0 \); the numerical cases used in this study use the Boussinesq approximation, where the density is assumed to be constant (\( \rho_0 \)) except for the buoyancy term, where the density depends on temperature and concentration, to simulate thermo-solutal convection.

\[ \rho = \rho_0 \left( 1 - \beta_T \left( T - T_{ref} \right) - \beta_C (C - C_0) \right) \]  
(7)

where \( T_{ref} \) is the melting temperature at nominal concentration \( C_0 \). Once non-linear phase diagrams have been implemented (see Section 2.4), the density is calculated as
with \( \rho_0 \) calculated from weighted averages on the individual components given by the phase diagram for the particular composition and temperature.

Until now, the relation between the liquid composition \((C_l)\) and the rest of the variables in Eq. 6 was introduced in Thétis through a linearized phase diagram (Fig. 1). Further details of the solver may be found in the bibliography [6, 8, 9]. The phase diagram allows the concentration of the liquid phase (among others) to be tracked as solidification takes place. The microsegregation of the different components during melting and solidification results in liquid and solid phases that have distinct compositions that evolve with temperature and composition change. The effects of this microsegregation can be represented by a linearized phase diagram in some cases where the variation of the composition in the various phases follows a nearly linear relationship with the temperature and volume-averaged composition of the finite volume. On the other hand, when the local composition of the phases does not follow such a linear relationship, a fully non-linear phase diagram will be necessary. As mentioned above, the main contribution of the present work is to evaluate the effect of introducing a more accurate, non-linear phase diagram.

\[
\rho = \rho_0 \left(1 - \beta \left(T - T_{\text{ref}}\right)\right)
\]  

(8)

2.2. Previous calculations with Thétis (linear phase diagrams and constant properties)

M. Rady et al. [6] used the Thétis solver to calculate solutions for a Pb-18%Sn alloy, whose phase diagram may be seen in Fig. 2a. This system was initially all liquid, and cooled from one of the boundary walls. The objective was to solidify the material, taking into account the free thermo-solutal convection effects. In the mushy region, solute partitioning among the solid/liquid phases causes buoyancy, which in turn gives rise to macrosegregation of the global composition. The concentration of tin and the temperature were initially homogeneous. Also, solid diffusion was considered negligible compared to liquid diffusion. All of the thermophysical properties except density were considered constant throughout the domain at all times.

The domain was a 50mm x 60mm rectangle. All of the walls were assumed adiabatic except the right wall, where a heat transfer coefficient of 400W/m²·K and a temperature of 298.15K were applied. All walls were considered to have a Neumann condition applied for the transport equation. All walls except for the left wall were considered to have a no-slip boundary condition for the velocity, and the left wall was symmetric.
Fig. 2. Binary phase diagram for (a) lead-tin alloy (b) NaCl-NaNO₃ mixture

2.3. Preliminary validation

A preliminary validation has been undertaken for the previously mentioned Pb-18%Sn alloy system from [6] as a base case to be able to compare to the modifications included in this study. The computations have been carried out with a 192 x 231 mesh, and the equations are solved with a time step of 0.01 seconds. The properties of the lead-tin alloy are given in [6]. The results are compared to the literature at 60 seconds, at which point macrosegregation has already begun to appear. This segregation and the solidification of the material leads to the microchannels as seen in [6] and as is reproduced in the current simulation. The microchannels from this simulation may be seen in the upper-right corner of Fig. 3a and Fig. 3b.
The number, shape, and angle of the microchannels are congruent with the results given by Rady et al. [6]. At the same time, there are some slight differences in the flow patterns; these differences are attributed to differences in the numerical code.

2.4. Current approach: introducing non-linear phase diagrams

In some cases, the linearized phase diagram in Fig. 1 does not suffice for calculations. This occurs when the phase diagram is not very linear (see Fig. 2b) or when there is a phase change through a zone that does not resemble the “liquid + α solid” zone in Fig. 1. In cases such as these, it is necessary to use the full phase diagram and to calculate the liquid composition as a function of the volume-averaged composition and the liquid fraction using the liquidus and solidus lines of the phase diagram. For this study, the phase diagrams are taken from FactSage’s phase diagram database [10]. These diagrams are based on the Calphad method, described in more detail in [11]. Unfortunately, introducing non-linear phase diagrams adds further numerical complexity to the code and increases the computational time. This is because the non-linear phase diagrams require a separate interpolation within the phase diagram for each solution point. The solid fraction results for Pb-18%Sn at 60 s after the cold boundary condition on the right wall is applied are presented for both linear and non-linear phase diagrams (Fig. 4).

As Fig. 4 shows, the solid fraction results are substantially different between (a) linear and (b) non-linear diagrams. This difference in results will be much more noticeable in materials where the phase diagram is visibly non-linear, such as the one presented in Fig 2b. As Fig. 2a shows, the liquidus and solidus lines are quite linear in the Pb-Sn phase diagram. The discrepancy in solid fraction between the two models will translate to a latent heat storage calculation that will depend heavily on the phase diagram used.
2.5. **Variable local properties**

Although the solid fraction results will mostly depend on the non-linearity of the phase diagram for the particular material, the thermal properties will become even more important for larger temperature ranges and uneven partial charging and discharging of a potential thermal energy storage material. This is especially true when there are one or more phase changes and is of great interest in off-eutectic mixtures where macrosegregation is probable. In this respect, it is important to calculate locally the thermal properties of the material. For example, previously the specific heat capacity has been defined as having one value for the whole domain. This does not, however, take into account the varying amounts of the components in the liquid and solid phases as the system undergoes phase change. To illustrate the importance of using local thermal properties, another simulation with non-linear phase diagrams and local thermal properties is compared to the previous simulation with non-linear phase diagrams and global thermal properties. The thermal properties of the two pure components may be seen below in Table 1. The properties are calculated with weighted averages based on the local composition of the phases.

This method does not take into account the crystal structure nor the microstructure of the material. The thermal conductivity, for example, will change depending on the orientation of the phases in the microstructure. For the moment, however, this approximation will be considered sufficient for this study.

<table>
<thead>
<tr>
<th>Property</th>
<th>Pb</th>
<th>Sn</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid specific heat capacity</td>
<td>251.2</td>
<td>132</td>
<td>J/kg-K</td>
</tr>
<tr>
<td>Solid specific heat capacity</td>
<td>130</td>
<td>210</td>
<td>J/kg-K</td>
</tr>
<tr>
<td>Latent heat of fusion</td>
<td>23</td>
<td>59</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>Liquid thermal conductivity</td>
<td>15.4</td>
<td>30.1</td>
<td>W/m-K</td>
</tr>
<tr>
<td>Solid thermal conductivity</td>
<td>31.4</td>
<td>66.8</td>
<td>W/m-K</td>
</tr>
</tbody>
</table>

The results for specific heat capacity after 60 seconds for constant and variable thermal properties (with non-linear phase diagrams) are presented in Figure 5. The specific heat capacities can locally vary by up to 30% and will cause a large discrepancy in calculated sensible heat for a TES system as the energy stored will scale with the local specific heat capacity.

![Fig. 5. Specific heat for Pb-18%Sn with (a) constant properties, non-linear phase diagram; (b) variable properties, non-linear phase diagram](image)

### 3. Results

The current methodology that has been developed with the alloy Pb-18%Sn is now applied to a candidate material for off-eutectic salt thermal energy storage system. The system has the same geometry as for the previous
case, but now the system is composed of 45% NaCl and 55% NaNO₃. The salt mixture phase diagram may be seen in Fig. 2b and the thermophysical properties in Table 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>NaCl</th>
<th>NaNO₃</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid specific heat capacity</td>
<td>1170</td>
<td>1655</td>
<td>J/kg-K</td>
</tr>
<tr>
<td>Solid specific heat capacity</td>
<td>629</td>
<td>3470</td>
<td>J/kg-K</td>
</tr>
<tr>
<td>Latent heat of fusion</td>
<td>492</td>
<td>177</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>Liquid thermal conductivity</td>
<td>0.63</td>
<td>0.55</td>
<td>W/m-K</td>
</tr>
<tr>
<td>Solid thermal conductivity</td>
<td>6.4</td>
<td>0.7</td>
<td>W/m-K</td>
</tr>
</tbody>
</table>

Figures 6-7 show a comparison of the calculations with (a) the previous Thétis methodology, i.e. constant properties except for density and linear phase diagram, and (b) variable properties and non-linear phase diagrams. The results are presented for an initial concentration C₀=0.55, an initial temperature T₀=913K, and a right wall temperature of 773K. Although not presented here, time step convergence of the solution has been verified for time steps of 0.005, 0.01, 0.02, 0.05, and 0.1 s. The same has been done for grid sizes of 0.0001, 0.0002, 0.001, 0.002, and 0.00333 m.
The resulting solid fractions and specific heats shown in Fig. 6-7 are considerably different. As mentioned before, the main reason for the difference in solid fraction (Fig 6a and 6b) is that the phase diagram of the salt mixture in question is very non-linear and a composition far from the eutectic (Fig 2b) is being considered. For example, at T=773K and composition 0.55 this yields a solid fraction of 0.036 for the linear diagram (Fig 6a) and 0.30 for the non-linear diagram (Fig 6b), approximately a 26% difference. Therefore, in cases like this one, it seems much more suitable to use non-linear phase diagrams.

Note that the reference case (Fig 6a and 7a) uses global constant properties (except for a linearized density that allows buoyancy induced flows), which explains the expected homogenous specific heat result in Fig. 7a. It can be thus expected to find large errors in the mixture phase change process with constant property models.

The differences explained above result in a significant disparity in the calculated heat stored. The heat stored is defined as:

\[
\Delta H = \sum_i^n \rho_i V_i \left( f_{i,L} L_{f,i} + c_{p,i} \Delta T_i \right)
\]

where \(i\) is the finite volume index, \(V\) is the volume, and \(f_i\) is the liquid fraction.

With this definition, the discrepancy between the heat storage in the cases presented in Figs. 6-7 amounts to 24%. The portion coming from sensible heat is larger for the original methodology since both specific heat capacity and density are higher in this case. On the other hand, the latent heat stored is much higher for the current methodology results. This is due to the higher solid fraction of the domain. This illustrates once again the necessity of precise, local calculations for the thermophysical properties as these will have an appreciable effect on the magnitude of the results. This is especially true for cases where there is only partial melting/solidification.

4. Conclusions

Phase diagrams represent the rejection and absorption of components in a mixture into the solid and liquid phases, and a linearization of this process is not always a good approximation. For example, when considering a 45% NaCl and 55% NaNO\(_3\) mixture, using a non-linear phase diagram and variable local properties results in variations of solid fraction by almost 30% when changing from linear to non-linear phase diagrams. This difference can be directly translated to the amount of energy stored in the system. For some materials it will thus be imperative to use the non-linear phase diagram to obtain an accurate TES system calculation. It should also be noted that non-linear diagrams also allow for much more complex systems to be taken into account. Many different types of phase transition can be systematically calculated: eutectic, off-eutectic, eutectoid, off-eutectoid, monotectic, etc. Ternary systems and higher-order systems could also be modeled quite easily with minimal modifications to the code.

It is also necessary to use local thermal properties when analyzing large temperature ranges, various phase changes, and/or large composition changes. This will be especially important when considering partial melts/solidifications of the TES system, since the global properties will not be the same as for a full melt/solidification. Additionally, off-eutectic compositions are more likely to display complex phenomena such as macrosegregation, which usually only appears as a result of density variations, but can be further affected when including local property variations.

There are many modifications that remain to make the method more precise. Among them, the thermal conductivity should be calculated taking into account the microstructure as well as the crystal structure. The other properties as well should take into account the crystal structure.
In thermal energy storage design, it is important to study the charge/discharge time for the energy storage as well as the amount of heat that may be stored. All of the previously stated concerns will help achieve more precise calculations of these systems. Accurate calculations for off-eutectic systems will aid in finding those that have a significant advantage over eutectic systems. Whenever heat transfer from a heat transfer fluid to a thermal energy storage system takes place over a range of temperatures, the best PCM will most likely not be a eutectic material. The methodology is thus applied to a salt system in an effort to pave the way for accurate calculations of next generation inexpensive and efficient thermal storage systems in concentrated solar power plants.

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