Thermal Modeling of Phase Change Material (PCM) with Nanoparticles and Porous Matrix for Melting and Freezing

By

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ABSTRACT

THERMAL MODELING OF PHASE CHANGE MATERIAL (PCM) WITH NANOPARTICLES AND POROUS MATRIX FOR MELTING AND FREEZING

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Thermal enhancement of the phase change material (PCM) using nanoparticle and porous medium is studied analytically, numerically and experimentally for melting and freezing processes of the PCM.

Copper nanoparticle of 30nm is dispersed into the base PCM of Paraffin Wax to prepare the PCM with nanoparticle (NanoPCM). NanoPCM is poured into the Aluminum solid matrix of 95% porosity to have NanoPCM and porous medium matrix. Copper nanoparticle and Aluminum solid matrix are used as enhancer for thermal conductivity improvement of Paraffin Wax without affecting the effective volume of PCM and other thermophysical properties such as viscosity, latent heat of fusion and melting temperature.

Initially, a conduction model is developed for constant temperature boundary condition. The effect of the volume fraction of nanoparticle and porosity of the porous medium are studied for temperature distribution, heat transfer and melt fraction inside the cavity analytically and numerically. A scale analysis is executed to establish simplified relationships between different non-dimensional parameters such as Fourier number, Stefan number, porosity and volume fraction. The model is compared with the exact solution of existing literature for equivalent thermophysical properties of NanoPCM with porous medium and found good agreement between the exact solution and numerical result of this research.

The conduction model is modified by incorporating both convection and conduction heat transfer with constant temperature boundary condition from side. Because of the boundary condition from side, convection and conduction both heat transfer are responsible for phase change initially. After the top melts completely, the melting of remaining part occurs mostly due to conduction heat transfer. The model executes scale analysis to estimate the extent of the
complete phase change process. The scale analysis results in simplified relationships among different non-dimensional parameters such as Fourier number, Stefan number, Raleigh number, Nusselt number, porosity of the porous medium and volume fraction of nanoparticles. The natural convection melting process of NanoPCM inside the porous medium is solved numerically. The numerical simulation verifies the correctness of the relationships proposed by scale analysis and identifies the effects of nanoparticle volume fraction, time, Rayleigh number, flow field, thermal field and heat transfer process during the melting of NanoPCM inside the thermal energy storage system.

A nearly closed form analytical model with conduction heat transfer is developed to satisfy the application of phase change material under constant heat flux input conditions. From the exact solutions of the models, the temperature distribution and movement of the melting interface inside the phase change region are predicted. The model data is compared with experimental data for interface movement rate and temperature profile at one location of the melting interface.

An extensive experimental research is carried out to observe the thermal performance of PCM, NanoPCM, PCM with porous medium and NanoPCM with porous medium for conduction and convection heat transfer with constant heat boundary condition from bottom, side and top. The better thermal performance is observed for heating from bottom because of higher influence of convection heat transfer. The heating from side performs better than the heating from top. The heating from top is mostly conduction heat transfer because of insignificant presence of convection heat transfer. The results are compared with the thermal performance of base PCM, NanoPCM and PCM with foam for similar experimental conditions. From the result, the desired thermal enhancement of NanoPCM with porous medium is observed for conduction heat transfer by improving the charging/discharge time along with low temperature rise. This pioneering research with NanoPCM with porous medium may lead to many future researches for replacing the sensible energy storage system with latent heat energy storage system for various transient thermal applications.
Dedication

To my parents
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**Nomenclature**

*PCM*  
Phase change material

*NanoPCM*  
Phase change material with nanoparticles

*PCM-Foam*  
Phase change material with porous medium

*NanoPCM-Foam*  
Phase change material with nanoparticles and porous medium

**A**  
aspect ratio of the cavity, $H/L$

**C**  
specific heat, $J/kg\,^\circ C$

**g**  
gravitational acceleration, $m/s^2$

**Fo**  
Fourier number, $a_m t/H^2$

**$h_n$**  
enthalpy of fusion of NanoPCM, $J/kg$

**h**  
convective heat transfer coefficient, $W/m^2\,^\circ C$

**H**  
height of the cavity, $m$

**K**  
permeability of the porous medium, $m^2$

**k**  
thermal conductivity, $W/m\,^\circ C$

**L**  
width of the enclosure, $m$

**Nu**  
Nusselt number

**p**  
pressure, $Pa$

**q**  
heat transfer through the left wall of the enclosure, $W$

**q''**  
heat flux, $W/m^2$

**Ra**  
Rayleigh number, $K\rho_0 g \beta H \Delta T/\alpha_m \mu_n$

**Ra_{trz}**  
Rayleigh number in the transition region, $g \beta \Delta T K z_{tr}/\nu_n \alpha_m$

**s**  
horizontal distance from the heated wall to the melting front, $m$

**S**  
dimensionless horizontal distance from the heated wall to the melting front, $s/H$

**Ste**  
Stefan number, $C_n (T_w - T_f)/\varepsilon h_p$

**T**  
temperature, $^\circ C$

**$T_0$**  
a reference temperature, $^\circ C$
Greek symbols

$\varepsilon$  porosity of the porous medium (=void volume/total volume of porous medium)

$\beta$ or $\beta_f$ volumetric thermal expansion coefficient of the base-PCM, $1/K$

$\beta_p$ volumetric thermal expansion coefficient of the nano-particle, $1/K$

$\psi$ stream function, $m^2/s$

$\Psi$ dimensionless stream function, $\psi / \alpha_m$

$\rho$ density, $kg/m^3$

$\rho_0$ reference density of the base-PCM and a reference temperature $T_0$

$\mu$ viscosity, $N s/m^2$

$\phi$ volume fraction (=volume of the nano-particle/total volume of NanoPCM)

$\alpha$ thermal diffusivity ($k / \rho C$), $m^2/s$

$\Delta T$ temperature difference, $(T_w - T_f), ^\circ C$

$\sigma$ capacity ratio, $\rho_mC_m / \rho_nC_n$

$\Theta$ dimensionless temperature difference, $(T - T_f)/(T_w - T_f)$
\[ \eta \] dimensionless parameter, \[ \frac{x}{2\sqrt{\alpha t}} \]

\[ \lambda \] Dimensionless parameter at melting distance, \[ x = s, \frac{s}{2\sqrt{\alpha t}} \]

**Subscript**

1. liquid
2. solid
3. Base PCM
4. NanoPCM
5. Solid foam matrix
6. Base PCM with foam
7. NanoPCM with foam
8. mean
Chapter 1: Introduction

Increasing demand of power is now huge challenge for various transient thermal applications such as solar cell, microelectronics, space applications etc. This hunger of power density requires proper thermal management to lower the temperature for safe operation of those applications [1]. Other than the sensible energy storage system, latent heat energy storage system is now used for various transient heat transfer applications, which involve thermal cycling [2]. Latent heat energy storage systems that are used to store energy through change of state are known as phase change materials (PCMs).

1.1 Research Motivation

Phase change materials (PCMs) is extremely advantageous as latent heat storage system, since they can effectively absorb peak energy loads during one pass of the power cycle and eject the heat at another time, thereby preventing failure of circuit components due to overheating [3]. Phase change thermal management system is proposed as an alternate cooling solution in order to reduce the thermal resistance of the system and meet the requirements of safe operation of an electronic device. Because of PCM’s high latent heats of fusion, small volumes of material can absorb/store large amounts of energy when it undergoes a phase change without any temperature rise. Latent heat storage system stores energy in the form of latent heat of fusion during melting and recovers during subsequent freezing of the phase change materials. Prediction of such alternating melting-freezing heat transfer processes (Fig. 1-1) is the key for optimal design of the latent heat energy storage system [4].

![Figure 1-1: Melting and Solidification Process of PCM](image-url)
Many transient applications of photovoltaic devices [5], building applications [6], solar water heating [7], green house heating [8], microelectronics [9], satellite power testing in space [10] etc. is recently trying to take advantage of phase change material (PCM) for cooling solution as a latent heat energy storage device by changing phase during melting/freezing process without raising temperature. The high heat removal capabilities of PCM can be attractive for transient application which last only short period with a chance to recharge (solidify) between pulses.

However, despite the significance of cyclic melting-freezing processes, poor thermal conductivity of phase change material (PCM) makes it challenging to use as an alternative cooling management for transient applications [11]. The higher thermal resistance due to poor thermal conductivity of the PCM acts as a barrier for successful use of PCM in transient cooling solution. Therefore, efforts have been made to enhance the rate of melting/freezing by utilizing different thermal enhancement methods of PCM. An effective method of improving the melting/freezing rate is to incorporate a porous insert (e.g., foams, fins, random structure, and heat sinks) inside the PCM to take advantage of higher thermal conductivity of porous inserts. However, the addition of solid matrix of porous inserts reduces the effective volume of the PCM for latent heat storage and acts as a barrier of fluid current movement for natural convection. Therefore, there is a limit of using the amount of porous insert for a particular application in order to avoid the volume reduction of PCM and lower the natural convection heat transfer performance. Use of high-porosity open-foam type porous material can ensure the minimal volume reduction of PCM maintaining the desired thermal conductivity of PCM-Foam matrix for conduction and convection heat transfer [12, 13, 14, 15]. Local thermal equilibrium between PCM and metal structure of porous material inside the pore is still a challenge because of higher thermal resistance between them. In order to reduce the thermal resistance for better local thermal equilibrium, high conductive nanoparticles can be dispersed into base PCM for additional melting/freezing rate enhancement of PCM with porous medium. Such nanoparticle enhanced phase change material is called NanoPCM [16, 17, 18, 19]. However, excess use of nanoparticles in base PCM can have adverse effect (e.g., heavier fluid, sedimentation, etc.) on the thermal performance of NanoPCM based porous media. Therefore, a right combination of porous matrix porosity and NanoPCM volume fraction could be an attractive choice to enhance the melting/freezing rate for better thermal performance.
A few researches on phase problem is found in the published literature [11-19] limited to base PCM, PCM with foam or PCM with nanoparticles with simple geometry and boundary conditions. Thus, a research of PCM along with nanoparticle and porous media to address the transient heat transfer problem with various boundary conditions is yet to be investigated. This research focus on phase change material (PCM) as thermal energy storage device along with right combination of nanoparticle and porous media as heat transfer enhancer for better thermal performance in transient heat transfer application.

1.2  Research Objectives

In order to better understand and demonstrate the potential for utilization of PCM with nanoparticles and porous media, the main objectives of this research are modeling and analysis of transport process (e.g. energy, momentum etc.) of NanoPCM inside porous and non-porous medium with experimental validation. The research focuses on the following key areas for PCM, NanoPCM, PCM-Foam and NanoPCM-Foam to obtain the desired objectives.

1. Review current research status of PCM, NanoPCM, PCM-Foam and NanoPCM-Foam.
2. Review status of their thermophysical properties and modeling.
3. Modelling/analysis of heat transfer with specific attention to
   a. rectangular geometries
   b. isothermal and isoflux boundary conditions
   c. temperature distribution, rate of movement of melting front, heat transfer, thermal resistances
   d. comparison of results between PCM, NanoPCM, PCM-Foam and NanoPCM-Foam
4. Experimental verification of model for PCM, NanoPCM, PCM-Foam and NanoPCM-Foam
   a. Preparation of sample all four cases: 1) PCM 2) NanoPCM 3) PCM-Foam 4) NanoPCM-Foam
   b. Recording of temperature at various locations of thermocouples along the heat transfer path and measurement of melting distance for heating from bottom, top and side for all four cases
c. Recording of temperature at various locations of thermocouples along the heat transfer path and measurement of freezing distance for cooling from bottom, top and side for all four cases

d. Compare the results of each case for melting and freezing

e. Compare the results of four cases for heating from bottom, heating from side, heating from top and cooling from bottom

f. The methodologies of experimental objectives:
   - a unidirectional melting or freezing experimental setup
   - evenly-spaced thermocouples mounted along the melting or freezing direction
   - record continuously the transient temperature variations during the melting or freezing process
   - determination of the progress of the melting or freezing front
   - constant heat flux (isoflux) boundary condition

1.3 Organization of the Thesis

This research work contains several chapters, each around the central theme of heat transfer enhancement of phase change material with nanoparticle and porous media, but designed to stand on its own. Because a wide range of studies is considered, the nomenclature and references differ for each chapter. In order to accommodate readers, nomenclature table and references are added at the end of each chapter. The chapters are summarized as follows:


Phase change material (PCM) draws a lot of attention from researchers to be used as a latent heat energy storage device but the researcher faces many challenges for effective use of PCM as an energy storage device. The main challenge of PCM as an effective latent heat energy storage device is its poor thermal conductivity. The successful use of PCM depends on its thermal enhancement. Many thermal performance enhancement techniques of PCM are published in the literature in the form of analytical, numerical and experimental work. This chapter reviews the various forms of thermal enhancement techniques for PCM. The focus of the thermal
enhancement techniques is to address the charging/discharging (melting/freezing) rate and the amount of energy stored during the phase change.


Chapter 3 reports the conduction only model of an energy storage system filled with a porous medium and the void space inside the porous medium is occupied by a NanoPCM. The inclusion of the nanoparticles improves the effective value of thermal conductivity of the nanoparticle-enhanced phase change material (or NanoPCM). The effective heat transfer rate of NanoPCM can be improved further by incorporating a porous medium. A 2-D enclosure is considered to replicate energy storage system. Two vertical walls and the bottom wall of the enclosure are properly insulated. The NanoPCM (Paraffin + CuO nanoparticle) is considered initially at its melting temperature. The top surface of the enclosure is initially exposed to a thermal source having a temperature above the melting temperature of the NanoPCM. The effect of the volume fraction of nanoparticle and porosity of the porous medium are studied on temperature distribution, heat transfer, and melt fraction inside the cavity. A two dimensional thermal model is developed for both solid and liquid fractions of the NanoPCM. The modeled equations are solved numerically using initial, boundary, and interface conditions. A scale analysis is executed to establish simplified relationships between different non-dimensional parameters (i.e., Fourier number, Stefan number, porosity, and volume fraction).

Chapter 4: Convection Model - Isothermal: Modeling of Convection Effect on the Melting Process of NanoPCM Inside Porous Enclosure for Isothermal Condition

Chapter 4 incorporates both the conduction and convection model of porous latent heat thermal energy storage (or LHTES) system filled with nano-phase change material (or NanoPCM). In the first part of the paper, scale analysis is executed to estimate the extent of the complete phase change process, which is a key factor of designing LHTES systems. The scale analysis results in simplified relationships among different non-dimensional parameters (i.e., Fourier number, Stefan number, Rayleigh number, Nusselt number, porosity of the porous medium, and nano particle volume fraction). In the second part, the natural convection melting
process of NanoPCM inside the porous medium is solved numerically. For the porous medium, the Darcy model is employed. The numerical simulation serves two purposes: (i) it verifies the correctness of the relationships proposed by scale analysis in the first part of the paper and (ii) it identifies the effects of nanoparticle volume fraction, time, and Rayleigh number, on flow field, thermal field, and heat transfer process during the melting of NanoPCM inside the thermal energy storage system. The proposed scaling relationships can be applied to predict the progress and execution of LHTES system filled with porous medium saturated by NanoPCM.


Chapter 3 reports the conduction only model for isothermal boundary condition of an energy storage system filled with a porous medium and the void space inside the porous medium is occupied by a NanoPCM. For isothermal boundary condition, one wall is maintained higher than the melting temperature of the PCM but as the melting front moves further with time, thermal resistance grows according to the Fourier law of conduction. To maintain the constant temperature on the hot wall, heat flux adjusts to balance the higher thermal resistance. This chapter creates a model for constant heat flux boundary condition where the hot wall temperature changes with time for increasing thermal resistance as the melting front moves on. This model uses the approach of the same geometric model used for Chapter 3. The model is based on three different model 1) First model is based on conduction model without phase change for constant heat flux boundary condition to predict the time needed for the hot wall to reach the melting temperature for the second model 2) Second model includes phase change in the conduction model where constant heat flux boundary condition is used on the hot wall and melting temperature boundary condition is used on the phase change interface (melting front) and 3) third model uses conduction model beyond the melting front (solid phase of PCM) with constant temperature boundary condition at the interface and initial temperature boundary condition at the end of the solid PCM to find out the temperature distribution inside the solid PCM. From the exact solution of these three models, results are validated with the experimental results of NanoPCM-Foam for heating from top where heat transfers in phase change system only through conduction.
Chapter 6: Experimental Study: Experimental Study of Phase Change Material Thermal Storage System with Nanoparticle and Porous Medium

Chapter 6 details an extensive experimental study carried out to observe the thermal behaviour of PCM, PCM-Foam, NanoPCM and NanoPCM-Foam. Constant heat flux is applied during melting for heating from bottom, side and top to observe the conduction and convection heat transfer behaviour during melting for unidirectional heat transfer. The freezing is done by exposing one surface to constant temperature mainly ambient temperature for unidirectional heat transfer as there is no convection heat transfer during freezing. For each case of PCM, PCM-Foam, NanoPCM and NanoPCM-Foam, the results are compared for heating from bottom, side and top during melting and cooling from bottom during freezing. For each arrangement of heating from bottom, side and top during melting and cooling from bottom during freezing, the results of PCM, PCM-Foam, NanoPCM and NanoPCM-Foam are compared.

Chapter 7: Conclusion and Future Work

Chapter 7 summarizes the outcome of this research. It discusses the result of all models and experiment study to demonstrate the thermal performance of PCM with nanoparticle and porous medium. It also discusses the direction of the future study based on this current research.

1.4 Research Innovation

This research tries to address the thermal issue of latent heat energy storage system by improving the heat transfer performance of phase change materials (PCMs) with the enhancers of nanoparticle and porous medium. Analytical and numerical models are developed for conduction and convection heat transfer with isothermal and isoflux boundary conditions. An extensive experimental research is conducted to study the conduction and convection phenomenon of phase change materials (PCMs) with nanoparticle and porous medium for constant heat flux (isoflux) boundary condition.


1.5 References


Chapter 2: Literature Review

Phase change material (PCM) is a latent heat energy storage system and transfers heat by changing its phase from solid to liquid or liquid to solid while maintaining the temperature. It draws a lot of attention from researchers to be used as a latent heat energy storage device but the researcher faces many challenges for effective use of PCM as an energy storage device. The main challenge of PCM as an effective latent heat energy storage device is its poor thermal conductivity. Thermal conductivity of PCM is very low, which slows down the movement of solid-liquid interface by suppressing the energy charging/discharging rates during melting and freezing process. The energy charging/discharging rates can be improved with the thermal enhancement of PCM. The successful use of PCM depends on its thermal enhancement. Many thermal performance enhancement techniques of PCM are published in the literature in the form of analytical, numerical and experimental work. These researches include the dispersion of highly conductive nanoparticles, impregnation of PCMs in a porous media such as metal or graphite matrix, the use of fins and finned tubes, the use of agitators, using microencapsulated PCM, use of multiple PCMs, rings in PCMs, which is done to increase the thermal conductivity of PCM without much reduction in energy storage capacity. This chapter reviews the various forms of thermal enhancement techniques for PCM with conduction, convection and solid-liquid phase change heat transport mechanisms. The focus of the thermal enhancement techniques is to address the charging/discharging (melting/freezing) rate and the amount of energy stored during the phase change.

The focus of Chapter-2 is to describe the existing research on thermal conductivity enhancement of base PCM with the introduction of fixed, non-moving high-conductivity inserts. Table-1 summarizes the existing research on thermal enhancement of phase change material (PCM) based on various thermal enhancers which will be elaborated later.
Table 2-1: Thermal Enhancement Studies of PCM

<table>
<thead>
<tr>
<th>Thermal Enhancers</th>
<th>Theoretical</th>
<th>Numerical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic fillers (tube, sphere, plate, wire, fibres, heat sink etc.)</td>
<td>Knowles et al. (1987); Velraj et al. (1999)</td>
<td>Chow et al. (1996); Tong et al. (1996); Velraj et al. (1999); Mesalhy et al. (2005); Nayak et al. (2006)</td>
<td>Humphries et al. (1977); De Jong et al. (1981); Knowles et al. (1987); Bugaje (1997); Velraj et al. (1999); Fukai et al. (1999 and 2000); Cabeza et al. (2002); Ettouney et al. (2004); Koizumi et al. (2004); Ettouney et al. (2006); Nakaso et al. (2008)</td>
</tr>
<tr>
<td>Fins</td>
<td>Griggs et al. (1974); Henze et al. (1981)</td>
<td>Humphries (1974); Abhat et al. (1981); Henze et al. (1981); Eftekhari et al. (1984); Striti (2004); Agyenim et al. (2009)</td>
<td></td>
</tr>
<tr>
<td>Porous media (foam, honeycomb etc.)</td>
<td>Bejan (1989); Abhat (1976); Pal et al. (1998); Mesalhy et al. (2005);</td>
<td>Bentilla et al. (1966); Hoover et al. (1971); Abhat (1976); Ellinger et al. (1991); Leoni et al. (1997); Fossett et al. (1998); Pal et al. (1998); Py et al. (2001); Sari (2004); Khateeb et al. (2004 and 2005); Zhang et al. (2006); Mills et al. (2006); Mesalhy et al. (2006); Lafdi et al. (2007); Zhong et al. (2010); Dukhan et al. (2010); Zhao et al. (2010)</td>
<td></td>
</tr>
<tr>
<td>Meso to micro particle</td>
<td>Seeniraj et al. (2002);</td>
<td>Hoover et al. (1971); Siegel (1977); Elgafy et al. (2005); Mettawee et al. (2007)</td>
<td></td>
</tr>
<tr>
<td>Nano particle</td>
<td>Fan et al. (2012)</td>
<td>Khodadadi et al. (2007)</td>
<td>Khodadadi et al. (2007); Zeng et al. (2007); Wang et al. (2008); Liu et al. (2009); Ho et al. (2009); Wu et al. (2009); Zeng et al. (2010); Fan et al. (2012); Ho et al. (2013);</td>
</tr>
<tr>
<td>Nano fluid and porous medium</td>
<td>Nield et al. (2009); Kuznetsov et al. (2010); Kuznetsov et al. (2010a,b); Kuznetsov et al. (2011a,b); Bhadauria et al. (2011)</td>
<td>Keblinski et al. (2002); Eastman et al. (2004); Yu et al. (2003, 2004); Xue et al. (2004); Eastman et al. (2004); Alvarado (2004); Khaled et al. (2005); Koo et al. (2005); Buongiorno (2006);</td>
<td></td>
</tr>
<tr>
<td>Porous medium and nano particle matrix</td>
<td>Hossain et al. (2015); Tasnim et al. (2015)</td>
<td>Hossain et al. (2015); Tasnim et al. (2015)</td>
<td>None</td>
</tr>
</tbody>
</table>
Nanofluid is similar to the liquid phase of NanoPCM where phase transformation physics is not captured. Therefore, research of nanofluid should not be compared with that of NanoPCM.

2.1 Thermal Enhancement of PCM using Metallic Filler

Nakaso et al. [16] explored experimentally the effectiveness of carbon fibre cloths to enhance the heat transfer area by laying in contact with the copper tubes of a shell-and-tube type heat exchanger for thermal conductivity enhancement of a latent heat thermal energy storage unit. They employed a transient 3-D conduction model without convective heat transfer in the liquid phase. The model considered the effective heat capacity of the PCM/carbon fibre composite along with the latent heat of the PCM. They monitored the inlet and outlet fluid temperatures of the heat exchanger to measure the heat transfer rates for a constant flow during energy discharge for various combinations of thermal conductivity enhancement. The experiment observed shorter discharge time of the order of 20% for carbon fibre cloth with a volume fraction of 0.42%.

2.2 Thermal Enhancement of PCM using Metal Fins

Humphries [17] observed visually the phase change interface by designing a transparent test specimen. They used aluminum fins to partition the test area into cells that was filled by nonadecane paraffin. They compared the computational models of the phase change with the temperature from thermocouple readings within the paraffin, on the fins and other positions of test setup.

Griggs et al. [18] investigated numerically the thermal characteristics of PCM melting process inside a rectangular container. The internal heat transfer rate was enhanced by placing parallel plate fins of uniform thickness inside the container. The results of parametric study based on various fin widths suggested better heat transfer rate and lower contribution of latent energy to the storage with increased fin width.

Abhat et al. [19] studied experimentally the latent heat storage system for solar heating applications (290~350 K). They used DSC to investigate melting temperature, energy absorption rate and energy evolution rate of some typical materials. They used a finned-annulus heat exchanger with radial arrangement of aluminum metal fins to fill the PCM of various kinds such
as eicosane, lauric acid and \( \text{CaCl}_2 \cdot 6\text{H}_2\text{O} \) as storage materials. A prototype of practical system with a length of 0.1m was built and the temperature distribution inside the prototype was measure using thirty thermocouples. The visualization of both the transient melting and freezing processes was observed through the transparent Plexiglas covers.

Henze et al. [20] developed a simple two-dimensional heat conduction model to observe the melting front location and time of finned PCM storage devices. They validated the model by visualization experiments of a double-finned rectangular Plexiglas container filled with octadecane. They maintained constant temperature at one end using a foil heater controlled by a power supply while the other end was kept thermally insulated. The experiment used eight iron-constantan thermocouples to monitor the end temperatures and the thermal status of the air bath. Parametric studies of eleven combinations were carried out for the active wall temperature and fin thickness. They performed a numerical simulation using commercial CFD code Fluent (Fluent Inc., 2006) for one of the eleven combinations and observed good agreement between the experimental results and the numerical predictions. The authors also proposed a model for the transient melt fraction, which was for applicable for the experiments. Metal fins helped to enhance conduction heat transfer considerably though the presence of natural convection was absent significantly. They argued that the proposed model could predict better with more closely spaced fins while the effect of convection becomes negligible.

Eftekhar et al. [21] used metal fins to investigate experimentally the heat transfer enhancement of a paraffin wax thermal storage system through flow visualization and movement of the solid liquid interface. They placed two plate fins to divide the experimental set up vertically into three similar compartments. Two Plexiglas layers were used to cover the front and back side with an air gap between them for flow visualization while the top and bottom surfaces were maintained at certain temperature with constant-temperature water baths. Parametric studies of the experiments were done for different combinations of bottom-top. Red die was added to the PCM to observe the convection behaviour of the melting process. The transient interface locations were determined through a sequence of pictures taken at different time instants. The locations of moving interfaces and the volume of the liquid phase were used to develop a time-dependent bulk energy balance model to evaluate the convective heat transfer and the heat transfer coefficient effectively.
Stritih [23] studied experimentally the thermal enhancement of PCM in a rectangular shape container to replicate the wall of building energy storage system. The rectangular box was filled with Paraffin and steel fins with 5% volume fraction where five sides were made adiabatic and only one side was allowed to exchange heat. Thermocouples were paced at various locations of rectangular box to measure temperature. During fusion of Paraffin, no significant thermal improvement was observed by adding fins. This may be because of insignificant contribution of natural convection due to flow resistance caused by the presence of fins, which was not balanced by the additional conductional heat transfer due to fins. They calculated fin effectiveness, the ratio of heat transfer with and without fins to confirm the presence of natural convection during melting. The presence of natural convection during solidification was found very negligible because of the dominance of the conduction heat transfer.

Agyenim et al. [24] used circular and longitudinal copper fins to enhance the thermal performance of Erythritol PCM in a tube heat exchanger. The tube heat exchanger exchanged heat through silicone oil and water during charging and discharging respectively. Thermocouples were used to record temperature during thermal cycling and it was observed that the performance of longitudinal fins were found efficient than circular fins during melting.

2.3 Thermal Enhancement of PCM using Porous Medium

Bentilla et al. [25] studied experimentally the thermal enhancement of four PCMs (tetradecane, hexadecane, octadecane and eicosane) using filler materials such as metallic wool (aluminum), foam (aluminum and copper) and honeycomb (aluminum) as thermal enhancer. Among those thermal enhancers, the best thermal performance was obtained by the honeycomb and the honeycomb can be chosen from different thickness because of its expanded and unexpanded flexibility.

Hoover et al. [26] performed experiment for spacecraft thermal control application to compare the thermal performance of pure and composite PCM with promotes metals and other materials. The experiments investigated the various areas of PCM such as PCM system performance characteristics, determination of PCM and PCM/filler thermal diffusivities, the effects of long-term thermal cycling, PCM-container compatibility, catalyst effectiveness and stability. Among the enhancers, aluminum honeycomb was found better for thermal diffusivity.
as it increased thermal diffusivity by about 80%. They proposed a procedure using repetitive differential scanning calorimetry (DSC) measurements to assess the effects of thermal cycling (melting/freezing cycles) for evaluating the thermophysical properties of the PCM.

Abhat [27] designed and investigated aluminum honeycomb fillers as thermal enhancer for PCM (n-octadecane) based latent heat storage system. Honeycombs of uniform size were placed in parallel inside the container. Thermocouples were used to monitor the temperature of top and bottom surfaces. An isoflux heat was applied on the bottom surface through a foil heater while other five surfaces were made adiabatic. Assuming no natural convection, they developed a finite-difference-based lumped capacity thermal non-equilibrium numerical model thermal behaviour of the container. They compared the transient wall temperatures, movement of melting front and melt fraction for both experimental and numerical studies. Their observations predicted that because of heat conduction through the honeycomb, melt began on the bottom and top simultaneously. They further carried out their experiments by increasing the heat.

Bejan [28] proposed a theoretical model of porous medium filled with PCM heated from side. He assumed solid phase isothermal and considered Darcy flow model for liquid PCM. The solid phase was isothermal at the melting point. The dominance of natural convection was observed in the quasi-steady regime during melting from the matched boundary layer solution. Later he proposed a solution for pure conduction followed by mixed conduction and convection. His research observed a significant influence of Stefan number on thermal behaviour and movement of melting front.

Ellinger et al. [29] used a rectangular domain partially filled with a porous layer of aluminum beads to investigate experimentally the enhancement of heat transfer. The introduction of porous layer with PCM helped to move the solid-liquid interface faster initially during the conduction-dominated regime, but slowed down the overall melting and heat transfer rates because of the lower porosity and permeability. They suggested of using metal foams with high-porosity and high-permeability matrices to improve the natural convective heat transfer with high Rayleigh numbers.
Leoni et al. [30] used foamed aluminum to design a paraffin-based wearable electronics unit. Fossett et al. [31] applied the same technique to an avionics cooling application charged with micro-encapsulated paraffin beads.

Pal et al. [32] examined the thermal performance mainly melting process of honeycomb and PCM composite for thermal control of avionic modules both experimentally and numerically. They built a box of Plexiglas filled with hexagonal cross-sectional honeycomb and PCM (n-triacontane) with melting temperature of 65 C. Transient temperature at various locations of the box was monitored using T-type thermocouples. The device was heated from the bottom while maintaining remaining sides thermally insulated. They used single-domain enthalpy-porosity technique phase change model of Brent et al. [33] and a three-dimensional numerical model of transient heat transfer for one simplified honeycomb cell. They compared pure conduction with diffusion-convection-coupled simulations and observed very weak natural convection without any significant effect on the performance of the melt front.

Py et al. [34] and Zhang et al. [39] both used graphite matrix for the thermal conductivity enhancement of paraffin. Mills et al. [40] also filled graphite bloke with paraffin. Their research observed the thermal conductivity enhancement of the composite matrix by 20–130 times than base PCM and this composite PCM improved the performance of Li-ion battery packs. Mesalhy et al. [41] improved the thermal conductivity of PCM from 0.3 W/m.K to 14 W/m.K by impregnating paraffin wax into carbon foam matrix.

Mesalhy et al. [38] carried out research on modelling volume averaged conservation equations for PCM in a porous metal matrix and observed that optimal thermal performance of PCM matrix was obtained with high porosity and high thermal conductivity.

Lafdi et al. [42] experimentally studied the heat transfer process of regular PCM inside the high thermal conductivity metal foam. They reported that steady-state temperature was reached faster in higher porosity aluminum foam when compared to the foams with lower porosity when natural convection was considered only but for conduction only problem, low porosity foam was found better than high porosity foam. With low porosity foam, the convection effect would have been negligible because of higher flow resistance. Therefore, they recommended optimum value
for the foam porosity and pore size so that both convection and conduction effects can be captured for best possible thermal performance.

Dukhan et al. [44] investigated experimentally the thermal enhancement of Paraffin wax with aluminum foam in cubical container. They observed the reduction of freezing and melting time for PCM with aluminum foam by 42.42% and 15.37% respectively. The foam also helped uniform temperature distribution inside the wax during melting and freezing.

Zhao et al. [45] did experimental investigation on the solid/liquid phase change in which paraffin wax was embedded in high porosity (> 85%) open cell copper metal foams. They found that the addition of metal foam increases the overall heat transfer by 3-10 times during the melting process. They also found that the temperature gradient in metal foam sample is significantly reduced compared to base PCM.

2.4 Thermal Enhancement of PCM using Meso to Micro Particles

Siegel [46] proposed dispersion of high conductivity particles in molten salts for thermal enhancement of PCM. Through a simplified analysis of solidification for three representative geometries (flat plate, inside and outside tube), optimum particle concentrations led to maximum enhanced heat extraction over a period were sought.

Seeniraj et al. [47] developed a theoretical quasi-steady model by assuming thermal equilibrium of the particle with the PCM. In their study, they observed the movement of the melting front by dispersing highly conductive fine particles with PCM in a latent heat thermal storage of shell-and-tube heat exchanger unit. They tried to find the optimal volume fraction of the dispersed particles for maximum energy storage extraction as the increasing volume fraction after certain volume fraction lowered the cumulative energy storage capacity as well as the instantaneous surface heat flux over a time interval. However, the model did not address the size of the fine particles.

Elgafy et al. [48] studied theoretically the thermal enhancement of pure paraffin by dispersing carbon nanofibers with average diameter and length of 100 nm and 20 μm respectively. They measured at room temperature the thermal diffusivity and heat capacity of
solid composites using the laser flash technique and DSC respectively. The measured values of the thermal diffusivity, density and heat capacity were then used to calculate the thermal conductivity of the composite. They observed that the thermal conductivity and diffusivity behaved linearly with the amount of carbon nanofibers loading whereas the rate of increase for heat capacity decreased with the increase of loading. The samples were simultaneously exposed to a uniform heat flux inside a furnace core and the temperatures of each sample were monitored at various times using K-type thermocouples during four hours of melting. From the time and temperature data, the rate of melting was found faster for nanofiber loaded composites than the pure paraffin. Electrochemically-treated nanofibers performed better thermally than the untreated fillers.

Mettawee et al. [49] prepared composites of paraffin wax through adding micron-sized aluminum powders (80 μm). The composite PCM was then tested in one sector of a compact solar collector. It was observed that the charging (melting) time due to utilization of the 0.5 wt% composite is decreased by 60%. The average daily efficiency of the collector utilizing pure paraffin wax ranged from 32~55%, whereas for the 0.5 wt% composite the efficiency was significantly increased to 82~94%.

2.5 Thermal Enhancement of PCM using Nanoparticles

Khodadadi et al. [50] studied numerically the solidification of nanofluid by preparing water-based nanofluid with 10 and 20% volume fraction of copper nanoparticles in a vertical square container. They observed the better thermal performance of nanoparticle-embedded PCM than the base fluid (water) during solidification process because of lower latent heat and higher thermal conductivity. However, they identified that apart from thermal conductivity, other thermophysical properties such as dynamic viscosity etc. can play a significant role for natural convection during the heat transfer enhancement of freezing/melting process which also supported by the study of Alvarado [64] about the influence of dynamic viscosity on the thermal enhancement of nanofluid in a square enclosure during natural convection. In the same study, Khodadadi et al. [50] prepared the nanoparticle-embedded PCM by emulsion technique using non-ionic surfactant to disperse alumina (Al₂O₃) nanoparticles in paraffin (n-octadecane) and
measured experimentally the effective thermophysical properties such as latent heat of fusion, density, dynamic viscosity, and thermal conductivity.

Wang et al. [51] studied the thermal enhancement of PCM by dispersing 0, 0.5, 1, 2 and 5 wt% mass fraction of 95% pure multi-walled carbon nanotubes (MWCNT) in PCM of 98% palmitic acid (PA). They used the transient short-hot-wire technique to measure the thermal conductivity and presented the temperature-dependent variations of the measured thermal conductivity of the PCM with nanoparticles. The thermal conductivity raised consistently by the additions of the MWCNT at constant temperatures but for 10°C temperature range around the melting points of the composites, they observed a sudden rise of thermal conductivity followed by a sharp decline whereas under and above 10°C range, the slow response of thermal conductivity was observed with temperature. Their observation found higher thermal conductivity of the solid phase than the liquid phase for the same sample.

Zeng et al [52] studied the effect of Ag nanoparticles for thermal enhancement of PCM. A nanofluid of nano-Ag and 1-tetradecanol (TD) PCM were prepared by thermal conductivity evaluation technique of TG-DSC, IR, XRD and TEM. Thermal enhancement was observed with the increase of Ag nanoparticles with relatively large phase change enthalpy of mixture. They found a linear correlation between the phase change enthalpy and the loading of TD but the phase temperature was found lower than pure TD. The composite materials and pure TD bore almost same thermal stability. They did not notice any interaction between Ag nanoparticles and pure TD and uniform dispersion of nanoparticles was observed.

Liu et al. [53] prepared PCM based nanofluid composites by dispersing titanium oxide (TiO₂) nanoparticles of volume fraction 0.167, 0.283, 0.565 and 1.13% in a saturated BaCl₂ (freezing point of –8 °C) aqueous solution. They measured the thermal conductivity of composites using THW technique and plotted the normalized thermal conductivity ratio at various temperatures against the volume fraction of nanoparticles along with the theoretical prediction of the Maxwell’s equation. They observed the linear variation of the measured thermal conductivity with the volume fraction for a given temperature and increasing tendency of the thermal conductivity with temperature for a particular volume fraction, which was found different from
the data of Wang et al. [51]. Moreover, the measured thermal conductivity values were found higher than the predicted thermal conductivity values from the Maxwell’s equation.

Ho et al. [54] prepared colloidal dispersions of alumina (Al$_2$O$_3$) nanoparticles in $n$-octadecane (C$_{18}$H$_{38}$). Thermal conductivity of the PCM with nanoparticles samples (0, 5 and 10 wt %) was measured using the THW technique. They measured thermal conductivity for various temperatures & mass fractions and observed the consistent enhancement of thermal conductivity with the increase of mass fraction at a particular temperature. The greater enhancement was also observed at higher temperatures.

Wu et al. [55] carried out experiment by employing an infrared imaging instrument and they observed a 20.5% reduction of freezing time with the freezing process of aqueous PCM and Al$_2$O$_3$ nanoparticles of 0.2 wt% composite.

Zeng et al. [56] experimentally studied the thermal performance of form-stable PCM composites from 1-tetradecanol and various volume fractions of silver (Ag) nanowires. They prepared two samples of composite & form-stable PCM applying high pressure of 20MPa and measured the thermal conductivity at room temperature using the *transient planar source (TPS) technique*. Two identical cylinder specimens (diameter of 13 mm) were prepared under higher pressure (20MPa). They plotted thermal conductivity of two samples at room temperature for various loading of Ag nanowires and observed linear dependency of thermal conductive at two ranges of mass fraction such as 0~40 wt% and 40~70 wt%. They found higher thermal enhancement with form-stable composites than the metal powder-filled solid composites.

Fan et al. [57] presented a theoretical and experimental investigation of the unidirectional freezing of PCM with nanoparticles. They solved a 1D Stefan model using a combined analytical/ integral method by assuming homogeneous distribution of static nanoparticles in the base PCM upon freezing. Their transient numerical analysis tried to find the solidification time of certain solid layer and predicted the effective thermophysical/transport properties of PCM with nanoparticles using the mixture and Maxwell models. They designed a unidirectional freezing experiment to assure a thermally stable quasi 1D freezing process in such a way that the container was cooled from below with the side walls being insulated. Thermocouple readings at
different heights along the freezing direction were recorded, thus allowing determination of the progress of the freezing front.

Ho et al. [58] conducted experiment to observe the phase change behaviour of a NanoPCM (n-octadecane+Al₂O₃) in a vertical enclosure and reported lower heat transfer performance inside the liquid region with increasing nanoparticle mass fraction because of lesser contribution of natural convection with increasing mass fraction of nanoparticle.

2.6 Research on Nanofluid with and without Porous Medium

Keblinski et al. [59] and Eastman et al. [60] studied the influence of Brownian motion of the nanoparticles, molecular-level layering of the liquid at the liquid/particle interface, the nature of heat transport in the nanoparticles, and the effects of nanoparticle clustering on the performance of nanofluid. They observed less influence of Brownian motion because of higher thermal diffusions than Brownian diffusion.

Yu et al. [61, 62] proposed a theoretical model for liquid molecular layer around the nanoparticles.

Xue et al. [63] conducted molecular dynamics simulation and observed no effect of simple monatomic liquids on the heat transfer characteristics for both normal and parallel to the surface, which suggested that that thermal transport in layered liquid was not sufficient for explanation of thermal conductivity enhancement of nanofluid with nanoparticles.

Alvarado [64] studied the heat transfer enhancement of nanofluid in a square enclosure and observed that in addition to the enhancement of thermal conductivity, the influence of natural convection because of the dynamic viscosity enhancement played a significant role for this heat transfer enhancement of nanofluid. In this study, they prepared composite PCM by dispersing alumina (Al₂O₃) nanoparticles in paraffin (n-octadecane) and observed experimentally the thermophysical properties of nanofluid such as latent heat of fusion, density, dynamic viscosity, and thermal conductivity.

Khaled et al. [65] studied the thermal enhancement of nanofluid by dispersing nanoparticle but they did not notice any thermal improvement in the core region under the influence of
nanoparticles. However, because of the nanoparticles, they observed 21% Nusselt number improvement for an isoflux boundary condition to a uniform rather than uniform distribution of nanoparticles, which was possible explanation of thermal conductivity enhancement due to nanoparticles.

Koo et al. [66] studied the thermal enhancement of nanofluid under the influence of Brownian motion, thermo-photoretic, and osmo-photoretic motions. They observed that the contribution of Brownian motion on heat transfer enhancement was larger than other two but these influences could be insignificant for nanofluid with concentration less than 0.5%. Their research is yet to be validated experimentally.

Buongiorno [67] studied convective transport in nanofluids in detail and failed to find a reasonable answer to justify the enhancement of thermal conductivity and viscosity with the addition of nanoparticles in nanofluids. He suggested that a small contribution of nanoparticles should not have significant influence on the thermal enhancement of nanofluid. Buongiorno further added that there should not be any reason to accept the enhancement as nanoparticles do not affect the turbulence of the system. He also dismissed the idea of particle rotation as this effect is very negligible. Buongiorno [67] considered absolute velocity of the nanoparticle as the sum of the base-fluid velocity and a relative velocity (the slip velocity). He introduced several slip mechanisms such as inertia, Brownian diffusion, thermophoresis, diffusiophoresis, Magnus effect, fluid drainage and gravity settling. His study suggested that the Brownian diffusion and the thermophoresis could be responsible for any enhancement if there is no turbulence effect.

Nield et al. [68] used Darcy Model for the Horton–Rogers–Lapwood Problem.

Kuznetsov et al. [69] included the effects of Brownian motion and thermophoresis for the development of a model for nanofluid. Darcy model is used for flow modeling in porous medium. A three temperature model is developed to observe the effect of local thermal non-equilibrium (LTNE) among the particle, fluid, and solid-matrix phases. Their research finds small effect of LTNE for a typical dilute nanofluid (with large Lewis number and with small particle-to-fluid heat capacity ratio). They realized that that surfactant or surface charge technology prevents nanoparticles from agglomeration and deposition on the porous matrix.
Kuznetsov et al. [70] further included the effects of Brownian motion and thermophoresis of nanoparticles in Brinkman model to investigate the thermal instability in a porous medium saturated by a nanofluid. They observed the gain or reduction of thermal Rayleigh number based on the nanoparticle distribution of top-heavy or bottom-heavy by the presence of the nanoparticles.

Bhadauria et al. [71] studied a horizontal porous medium saturated by a nanofluid to observe the effect of local thermal non-equilibrium on linear and non-linear thermal instability. They also used the Brinkman Model for porous medium with the incorporation of Brownian motion and thermophoresis for nanofluid. They also used three temperature model same as Kuznetsov et al. [69] to observe the effect of local thermal non-equilibrium among the particle, fluid, and solid-matrix phases. Normal mode technique was used for linear stability, while a minimal representation of the truncated Fourier series analysis involving only two terms was used for nonlinear analysis. They used numerical technique to observe the critical conditions of convection along with heat and mass transfer across the porous layer.

2.7 Equivalent Thermal Conductivity of Binary/Tertiary Mixture of PCM

Currently, there is no unique theoretical model for reliable prediction of effective thermal conductivity for composite PCM or nanofluid but there exist several semi-empirical models based on experimental research for apparent prediction of effective thermal conductivity. These models include various parameters such as thermal conductivities of base fluid and enhancers, the volume fraction, the particle size, the surface area, the shape of the nanoparticles, the Brownian motion and the temperature.

Maxwell [72] proposed a model to predict the effective thermal conductivity of solid-liquid mixtures composite with relatively large particles (micro-/mini- size) and low solid concentrations (low volume fraction). The effective thermal conductivity, \( k_{\text{eff}} \) of the model is shown as

\[
k_{\text{eff}} = \frac{k_p + 2k_b + 2(k_p - k_b)\Phi}{k_p + 2k_p - 2(k_p - k_b)\Phi} k_b.
\]
where \( k_p, k_b \), are the thermal conductivity of the particle and base fluid respectively and \( \phi \) is the volume fraction of particle in mixture.

Bruggeman [73] proposed a relationship for prediction of effective thermal conductivity of solid-liquid composite of any solid concentration. The effective thermal conductivity of the Bruggeman relationship is shown as

\[
\phi \left( \frac{k_p - k_{eff}}{k_p + 2k_{eff}} \right) + (1 - \phi) \left( \frac{k_f - k_{eff}}{k_f + 2k_{eff}} \right) = 0
\]

The Bruggeman relationship behaves same as the Maxwell model for low volume fraction but for high volume fraction, the Maxwell model fails to meet the experimental data whereas the Bruggeman relationship provides good agreement with the experimental result [74].

Hamilton et al. [75] introduced a shape factor, \( n \), to account for the effect of the shape of the particles for their effective thermal conductivity model of liquid-solid mixtures for nonspherical particles. This model deals with the higher thermal conductivity particles where the ratio of conductivities between the solid particles and base fluid are more than 100 and the effective thermal conductivity is shown as

\[
k_{eff} = \frac{k_p + (n - 1)k_b - (n - 1)(k_b - k_p)\phi}{k_p + (n - 1)k_b + (k_b - k_p)\phi} k_b
\]

This model includes the same parameters as Maxwell or Bruggeman model except the inclusion of an additional parameter, which is a shape factor, \( n \). The classical models of above are based on continuum formulations and vary with shape and/or volume fraction of particles assuming diffusive heat transport in both liquid and solid phases. The latest development of nanofluid contradicts with the effective thermal conductivity model of Maxwell [72] and its modified models by Hamilton et al. [75]. Other than the parameters of Maxwell and Hamilton model, latest development of nanofluid tries to address some other important parameters to address the effective thermal conductivity prediction of nanofluid. Keblinski et al. [59] dealt with the size, the clustering of particles, and the nanolayer between the nanoparticles and base fluids for their effective thermal conductivity prediction. They proposed model based on the traditional models by including additional parameters especially the parameters related to interfacial characteristics.
Yu et al. [61] developed a model based on Maxwell model and included the effect of the nanolayer. A modified thermal conductivity of particles $k_{pe}$ based on the so-called effective medium theory [76] was used instead of the thermal conductivity of solid particles $k_p$ in the Maxwell equation:

$$k_{pe} = \frac{[2(1 - \gamma) + (1 + \beta)^3(1 + 2\gamma)\gamma]}{-(1 - \gamma) + (1 + \beta)^3(1 + 2\gamma)} k_p .$$

where $\gamma = k_{layer}/k_p$ is the ratio of nanolayer thermal conductivity to particle thermal conductivity and $\beta = h/r$ is the ratio of the nanolayer thickness to the original particle radius. Hence, the Maxwell equation is transformed as:

$$k_{eff} = \frac{k_{pe} + 2k_b + 2(k_{pe} - k_b)(1 - \beta)^3\phi}{k_{pe} + 2k_b - (k_{pe} - k_b)(1 + \beta)^3\phi} k_b .$$

This model of Yu et al. [61] includes the presence of nanolayer, which can predict the effective thermal conductivity for nanolayer of thickness less 10 nm. This model observes better thermal conductivity with smaller (<10nm) nanoparticles than higher volume fraction.

Yu et al. [61] also proposed another model for non-spherical particles by modifying Hamilton-Crosser model, which also includes the presence of particle-liquid interfacial. The effective thermal conductivity of non-spherical particles is shown as

$$k_{eff} = \left(1 + \frac{n\phi_{eff}A}{1 - \phi_{eff}A}\right) k_b .$$

where $A$ is defined by $A = \frac{1}{3} \sum_{j=a,b,c} (k_{pj} - k_b)/[k_{pj} + (n - 1)k_b]$ and $\phi_{eff} = \phi \sqrt{(a^2 + t)(b^2 + t)(c^2 + t)/\sqrt{abc}}$ is the equivalent volume concentration of elliptical particles ($a \geq b \geq c$) surrounded by nanolayers. With a general empirical shape factor ($n = 3\psi^{-\alpha}$, where $\alpha$ is an empirical parameter and $\psi$ is the particle sphericity), they claimed the thermal conductivity of carbon nanotube-in-oil nanofluids can be predicted accurately with this modified model. However, Wang et al. [94] demands that this model fails to predict the nonlinear Behaviour of the effective thermal conductivity of general oxide and metal based nanofluids.
Xue [77] proposed a model for effective thermal conductivity of nanofluids based on the average polarization theory, which includes the effect of the interface between the solid particles and the base fluid. His model is expressed by

$$9 \left(1 - \frac{\Phi}{\lambda}\right) \frac{k_{\text{eff}} - k_b}{2k_{\text{eff}} + k_b} + \frac{\Phi}{\lambda} \left[\frac{k_{\text{eff}} - k_{c,x}}{k_{\text{eff}} + B_{2x}(k_{c,x} - k_{\text{eff}})} + 4\frac{k_{\text{eff}} - k_{c,y}}{2k_{\text{eff}} + (1 - B_{2x})(k_{c,y} - k_{\text{eff}})}\right] = 0 .$$

where $\lambda = abc/[(a + t)(b + t)(c + t)]$ with $a$, $b$, $c$ as half-radii of the elliptical complex nanoparticles comprising of nanoparticles and interfacial shells between particles and the base fluids. $k_{c,j}$ is the effective dielectric constant and $B_{2x}$ is the depolarization factor along x–symmetrical axis, which is derived from the average polarization theory. A test of this formula [79] confirms the inaccuracy of this model because of the wrong values of the depolarization factor.

Xue et al. [78] also developed a model for the effective thermal conductivity based on Bruggeman model [73]. They replaced the thermal conductivity of nanoparticles with the thermal conductivity of the so-called “complex nanoparticles” where the effect of the interfacial shells between the nanoparticles and the base fluids was considered. The model is shown as

$$ \left(1 - \frac{\Phi}{\alpha}\right) \frac{k_{\text{eff}} - k_b}{2k_{\text{eff}} + k_b} + \frac{\Phi}{\alpha} \frac{(k_{\text{eff}} - k_2)(2k_2 + k_1) - \alpha(k_1 - k_2)(2k_2 + k_{\text{eff}})}{(2k_{\text{eff}} + k_2)(2k_2 + k_1) + 2\alpha(k_1 - k_2)(k_2 - k_{\text{eff}})} = 0 .$$

where $\alpha$ is the volume ratio of spherical nanoparticle and complex nanoparticle. $k_1$ and $k_2$ are the thermal conductivity of the nanoparticle and interfacial shell, respectively. The modified model validates the experimental data on the effective thermal conductivity of CuO/water and CuO/EG nanofluids [80].

Xie et al. [81] included the effects of nanolayer thickness, nanoparticles size, volume fraction, and thermal conductivities of fluid, nanoparticles, and nanolayer and considered the interfacial nanolayer with linear thermal conductivity distribution in their proposed effective thermal conductivity model.

$$k_{\text{eff}} = \left(1 + 3\Theta\Theta T + \frac{3\Theta^2\Theta^2 T}{1 - \Theta\Theta T}\right)k_b .$$

with $\Theta = \beta_{tb}[(1 + \gamma)^3 - \beta_{pl}/\beta_{bl}]/[(1 + \gamma)^3 + 2\beta_{tb}\beta_{pl}]$, where

$$\beta_{tb} = (k_1 - k_b)/(k_1 + 2k_b), \ \beta_{pl} = (k_p - k_1)/(k_p + 2k_1), \ \beta_{fl} = (k_f - k_{l1})/(k_f + 2k_{l1})$$

and
\( \gamma = \delta/r_p \) is the thickness layer of nanolayer and nanoparticle. \( \vartheta_T \) is the modified total volume fraction of the original nanoparticle and nanolayer, \( \vartheta_T = \vartheta(1 + \gamma)^3 \). They claimed that their model validated some available experimental data.

Patel et al. [82] observed 9% thermal conductivity enhancement at extremely low concentrations (volume fraction) such as 0.00026% for metallic particles. This strange phenomenon may be because of the Brownian motion of nanoparticles at the molecular and nanoscale levels, which dictate the thermal behaviour of nanofluids. Das et al. [83] also observed that the thermal conductivity of nanofluids strongly depends on temperature, which is also considered from theoretical models.

Xuan et al. [84] proposed a model based on Maxwell model, which included the random motion of suspended nanoparticles (Brownian motion) and their model for effective thermal conductivity is shown as

\[
k_{eff} = k_p + \frac{2k_b - 2(k_b - k_p)\vartheta}{k_p + 2k_b + (k_b - k_p)\vartheta}k_b + \frac{\rho_p \vartheta c_p}{2} \frac{k_B T}{3\pi r_c \mu}.
\]

where Boltzmann constant \( k_B = 1.381 \times 10^{-23} \text{J/K} \), \( r_c \) is the apparent radius of clusters and depends on the fractal dimension of the cluster structure. The model includes the effect of temperature on the conductivity enhancement but the dependence is found too weak \( (\alpha T^{1/2}) \) and not validated with the experimental data of Das et al. [83].

Based on the fractal theory [85], Wang et al. [93] proposed a fractal model for thermal conductivity prediction of nanofluid, which can well describe the disorder, and stochastic process of clustering and polarization of nanoparticles within the mesoscale limit. The fractal model introduced the effective thermal conductivity of the particle clusters, \( k_{cl}(r) \), and the radius distribution function, \( n(r) \) in the Maxwell model and shown as

\[
k_{eff} = \frac{(1 - \vartheta) + 3\vartheta \int_0^{\infty} \{ k_{cl}(r)n(r)/(k_{cl}(r) + 2k_b) \} dr}{(1 - \vartheta) + 3\vartheta \int_0^{\infty} \{ k_b(r)n(r)/(k_{cl}(r) + 2k_b) \} dr}k_b.
\]

This model validates the experimental data for 50 nm CuO particle suspension in deionized water with \( \varphi < 0.5\% \).
Kumar et al. [86] suggested a model based on Stokes-Einstein formula for the large enhancement of thermal conductivity and its strong temperature dependence in nanofluids. The inclusion of Brownian motion of particles in thermal conductivity enhancement can be expressed as

\[ k_{\text{eff}} = k_b + c \frac{2k_B T}{(\pi \nu d_p^2)} \frac{\varepsilon r_b}{k_b (1 - \varepsilon) r_p} k_p . \]

where \( c \) is a constant, \( \nu \) is the dynamic viscosity of the base fluid, and \( d_p \) is the diameter of the particles. However, the model needs to be validated for high concentration of particles.

Bhattacharya et al. [87] used Brownian motion simulation to develop an effective thermal conductivity model of a nanofluid. The combination of the liquid conductivity and particle conductivity is expressed as

\[ k_{\text{eff}} = \varnothing k_p + (1 - \varnothing) k_b . \]

where \( k_p \) is replaced by the effective contribution of the particles towards the overall thermal conductivity of the system, \( k_p = \frac{1}{k_{BT}^2 \nu} \sum_{j=0}^{n} (Q(0)Q(j\Delta t)) \Delta t \). The model showed a good agreement of the thermal conductivity of nanofluids.

Jang et al. [88] proposed a theoretical model, which includes four modes such as collision between base fluid molecules \( k_b (1 - \varnothing) \), thermal diffusion in nanoparticles in fluids \( k_p \varnothing \), collision between nanoparticles due to Brownian motion (neglected), and thermal interaction of dynamic or “dancing” nanoparticles with the base fluid molecules \( f h \delta_T \). The proposed model for the effective thermal conductivity of nanofluids is shown as

\[ k_{\text{eff}} = k_b (1 - \varnothing) + k_p \varnothing + 3C \frac{d_b}{d_p} k_b Re_{d_p}^2 Pr \varnothing . \]

where \( h \sim \frac{k_b}{d_p} Re_{d_p}^2 Pr^2 \) and \( \delta \sim 3d_p \) are the heat transfer coefficient for the flow past nanoparticles and the thickness of the thermal boundary layer, respectively. This model does not include the Brownian effect because of high temperature-dependent properties affected by the Brownian motion but it does include the effects of concentration, temperature, and particle size.
Prasher et al. [89] suggested that the effective thermal conductivity enhancement of nanofluid is caused by the convection due to Brownian motion of the nanoparticles. By introducing the general correlation for heat transfer coefficient \( h \), he brought the convection of the liquid near the particles due to Brownian movement into the Maxwell model:

\[
k_{\text{eff}} = (1 + ARe^m Pr^{0.333} \phi) \left[ \frac{k_p + 2k_b + 2(k_p - k_b)\phi}{k_p + 2k_b - (k_p - k_b)\phi} \right] k_b.
\]

where \( h = k_b/\alpha \left( 1 + ARe^m Pr^{0.333} \phi \right) \) and \( A \) and \( m \) are constants. The Reynolds number can be written as:

\[
Re = \frac{1}{\nu} \sqrt{\frac{18k_b T}{\pi \rho_p d_p}}.
\]

Koo et al. [66] includes the effects of particle size, particle volume fraction and temperature dependence as well as properties of the base fluid and the particle subject to Brownian motion in their recently developed model for nanofluids, which. The resulting formula is expressed as

\[
k_{\text{eff}} = \frac{k_p + 2k_b + 2(k_p - k_b)\phi}{k_p + 2k_b - (k_p - k_b)\phi} k_b + 5 \times 10^4 \beta \phi \rho_p c_p \frac{k T f(T, \phi)}{\rho_p D k_b}.
\]

Maxwell model is used to obtain the first part of the equation. The second part of the equation is based on Brownian motion where the temperature dependence of the effective thermal conductivity is included. \( f(T, \phi) \) varies with particle volume fraction as well. \( f(T, \phi) = (-6.04\phi + 0.4705) + (1722.3\phi - 134.63) \) while \( \beta \) is related to particle motion. Koo et al. [66] also revealed significant thermal performance enhancement of microheat-sinks by mixing of 1-4\% CuO nanoparticles with high-Prandtl number base fluid such as ethylene glycol and oils based on the study of pressure gradients, temperature profiles and Nusselt numbers.

It is difficult to predict the thermal conductivity of carbon nanotubes because of their large aspect ratio. Nan et al. [90] proposed a simple formula to predict the effective thermal conductivity of carbon-nanotube-based composites based on generalized Maxwell-Garnett approximation. The Nan’s model [90] validates the experimental data of Choi et al. [91].
However, the model fails to predict the nonlinear characteristics of the effective thermal conductivity of nanotube suspensions with nanotube volume fractions.

Recently, Gao et al. [92] proposed a differential effective medium theory based on Bruggeman’s model [73] by accounting the geometric and physical anisotropy simultaneously for predicting the effective thermal conductivity of nanofluids. Their model considers the effect of aspect ratio of the nanotube but it does not include the size effect and temperature dependence. The results are not found good for the prediction of the thermal conductivity of normal nanofluids rather than nanotube-based suspensions.

Xue [78] included the effect of large axial ratio and the space distribution of the CNTs for the effective thermal conductivity model of CNTs-nanofluids based on Maxwell theory. The model validated the experimental data of Choi et al. [91] with the adjusted thermal conductivity of CNTs. With the assumed distribution function $P(B_j) = 2$, the corresponding expression of the effective thermal conductivity of CNTs-based nanofluids is shown below

$$k_{\text{eff}} = k_b \frac{1 - \varnothing + 20 \frac{k_p}{k_p - k_b} \ln \frac{k_p + k_b}{2k_b}}{1 - \varnothing + 20 \frac{k_b}{k_p - k_b} \ln \frac{k_p + k_b}{2k_b}}.$$  

2.8 Research Statement / Conclusion

Phase change material (PCM) draws a lot of attention among the researchers as a latent heat storage device for its advantage of transferring heat by changing phase without raising temperature. The main challenge of PCM as an effective latent heat energy storage device is its poor thermal conductivity. The successful use of PCM depends on its thermal enhancement. Various efforts are made to improve the heat transfer performance of PCM by improving its thermal conductivity. The focus of the thermal enhancement techniques is to address the charging/discharging (melting/freezing) rate and the amount of energy stored during the phase change. The thermal conductivity enhancement technique first focused on the use of highly-conductive fixed structures, e.g., metallic extended surfaces. The fixed structure occupies lot of space and reduces the effective volume of the PCM for phase change. Therefore, there is a limit of using the amount of metallic insert for a particular application in order to avoid the volume
reduction of PCM. Researchers are looking for alternative techniques without affecting the amount of phase change material or latent heat energy storage device.

In order to avoid the volume reduction of PCM, the use of nano-materials in the form of nanofluids has also created lot of interest among the researchers for thermal performance enhancement of PCM. Researchers are trying to disperse the high conductive nanoparticles into PCM for additional melting/freezing rate enhancement of PCM. The research includes various kind of metal and metal oxide nanoparticles, carbon nanotubes, and nanofibers. The overall thermal enhancement is limited by the loading of nanoparticles. The heavy loading of nanoparticle ends up with heavier nanofluid and sedimentation, which affects the convection heat transfer significantly. The focus of the research was the enhancement of thermal conductivity, not the heat transfer characteristics. There is also disagreement among the results in heat transfer of nanoparticles with phase change material (PCM). It is very difficult to find a literature, which can characterise accurately the heat transfer behaviour of nanoparticles with PCM. Many researchers considered the nanoparticles with PCM as single-phase fluid rather than two-phase mixture. However, the particle-liquid interaction and the movement between the particle and liquids should play important roles in affecting the heat transfer performance. A very few researchers tried to study the influence of Brownian and thermophoresis motion for thermal conductivity enhancement due to convection heat transfer but without sufficient agreement among them and experimental validation. The use of nanoparticles with PCM initially appeared promising, but the development of the field faces several challenges: (i) insufficient thermal conductivity enhancement (ii) the lack of agreement between experimental results among various groups; (ii) the poor performance of suspensions; and lack of theoretical understanding of the mechanisms.

Use of high-porosity open-foam type porous material is considered as another alternative to ensure the minimal volume reduction of PCM and enhance the thermal performance of PCM. Local thermal equilibrium between PCM and metal structure of porous material inside the pore is still a challenge for desired thermal performance of PCM because of higher thermal resistance between them. Because of the complex mechanical structure of the open-foam type porous material, experimental agreement is yet to be established among the researchers about local thermal equilibrium between the PCM and metallic structure of porous material.
Further theoretical and experimental research investigations are needed to understand the heat transfer characteristics of PCM in porous medium and nanoparticles with PCM. In order to ensure the minimal volume reduction of the PCM and reduce the pore level thermal resistance between PCM and porous medium for better local thermal equilibrium, high conductive nanoparticles can be dispersed into base PCM for additional melting/freezing rate enhancement of PCM with porous medium. However, excess use of nanoparticles in base PCM can have adverse effect (e.g., heavier fluid, sedimentation, etc.) on natural convection heat transfer for the thermal performance enhancement of NanoPCM based porous medium. Therefore, a right combination of porous matrix porosity and NanoPCM volume fraction could be an attractive choice to enhance the melting/freezing rate for better thermal performance of PCM. The review fails to find any published literature, which includes PCM along with thermal enhancer of both nanoparticles and metal foam together. Analytical, numerical and experimental study of PCM with nanoparticle and porous medium together can provide useful information for desired thermal performance enhancement of latent heat energy storage system.

The research gap between the current research and existing researches for thermal enhancement of latent heat energy storage system can be summarized as follows:

- **Fixed metallic structure:** Less effective volume of PCM for phase change
- **Nanoparticle:** Less enhancement of thermal conductivity because of lower loading of nanoparticle for maintaining other thermophysical properties such as viscosity, latent heat of fusion etc. to ensure desired conduction, convection and phase change heat transfer
- **Porous medium:** Challenge of lower thermal equilibrium at pore level because of higher thermal resistance between PCM and metal structure of high porosity porous medium
- **Nanoparticle and porous medium (current research):** Ensure effective volume of PCM by high porosity porous medium, desired thermal conductivity enhancement because of metallic porous medium and better local thermal equilibrium between nanoparticle doped PCM & metal structure of high porosity porous medium
2.9 References


Chapter 3: Conduction Model - Isothermal

This Chapter is published as:


Summary

A Nanoparticle-enhanced phase change material contains high thermal conductivity nanoparticles, which are assumed to be dispersed uniformly into the phase change material. The inclusion of the nanoparticles improves the effective value of thermal conductivity of the nanoparticle-enhanced phase change material (or NanoPCM). The effective heat transfer rate of NanoPCM can be improved further by incorporating a porous medium. This is the first paper in this series, which reports thermal performance of an energy storage system filled with a porous medium and the void space inside the porous medium is occupied by a NanoPCM. A 2-D enclosure is considered to replicate energy storage system. Two vertical walls and the bottom wall of the enclosure are properly insulated. The NanoPCM (Paraffin + CuO nanoparticle) is considered initially at its melting temperature. The top surface of the enclosure is suddenly exposed to a thermal source having a temperature above the melting temperature of the NanoPCM. The effect of the volume fraction of nano-particle and porosity of the porous medium are studied on temperature distribution, heat transfer, and melt fraction inside the cavity. A two dimensional thermal model is developed for both solid and liquid fractions of the NanoPCM. The modeled equations are solved numerically using initial, boundary, and interface conditions. A scale analysis is executed to establish simplified relationships between different non-dimensional parameters (i.e., Fourier number, Stefan number, porosity, and volume fraction).

Keywords: Energy storage; Fourier number; NanoPCM; Melt fraction; Porosity; Stefan number; Volume fraction
3.1 Introduction

Phase change material (PCM) already exhibits excellent potentials for various applications; for example, energy storage, electronic cooling, and building energy management [1]. PCMs are known for their low thermal conductivities. However, a faster rate of melting/freezing is a requirement for many applications [2]. Therefore, efforts have been made to enhance the rate of melting/freezing by utilizing different methods. An effective method of improving the melting/freezing rate is to incorporate a porous insert (e.g., foams, fins, random structure, and heat sinks) inside the system. Porous insert helps enhancement of thermal energy transport all over the PCM [3]. However, the addition of solid matrix of porous inserts reduces the effective volume of the PCM. Therefore, there is a limit of using the amount of porous insert for a particular application in order to avoid the volume reduction of PCM. A use of high-porosity open-foam type porous material can ensure the minimal volume reduction of PCM. In addition to the porous insert, incorporation of highly conductive nano-particles in PCM (or base PCM) can further enhance the melting/freezing rate of PCM. Such nano-particle enhanced phase change material is called NanoPCM. Nano-particles improve the thermal conductivity of the base PCM and such improvement enhances the heat transport rate [4]. However, excess use of nano-particles in base-PCM can have adverse effect (e.g., heavier fluid, sedimentation, etc.) on the thermal performance of NanoPCM based porous media. Therefore, a right combination of porous matrix porosity and NanoPCM volume fraction could be an attractive choice for the optimization of melting/freezing rate.

Phase change materials (PCM) are typically used in the latent heat energy storage system where energy is stored in the form of latent heat of fusion during the melting and recovered during the subsequent freezing of the phase change materials for various heat transfer applications. Prediction of such alternating melting-freezing heat transfer processes is an important factor to design optimally any latent heat energy storage system. Many studies are found in the literatures about this unique feature of phase change material.
3.2 PCM General Application

Phase change materials have been widely utilized for many solar-thermal applications. Typical examples are PCM-based solar water heaters [5 - 7]. Such systems are typically inexpensive, easy to fabricate, and simple in operation. PCMs are used as single or multiple layers in these systems. Reported performance results on the PCM based air heater systems are also available in the literature [8, 9]. Other noticeable solar thermal applications where use of PCMs are getting popularity are solar cooker [10] and green house [11]. PCM and PCM based systems have been utilized for thermal management of buildings and structures. Some applications include energy storing walls [12 - 15], window shutters [16], passive heating system for floors and ceiling [17 - 19], and off-peak electric storage [20 - 21]. PCM is also used to design novel heat exchanger in waste heat recovery applications [22]. As a passive temperature regulator, PCM is also used in solar-PV applications [23 - 25]. Several authors have reported limited applications of PCM for electronic systems [26 - 28]. Some other noticeable applications of PCM include air-conditioning and ventilation systems [29], cooling of electric motor [30], and thermal management of batteries and electronic devices [31-32].

3.3 NanoPCM with non-porous medium

One major issue in the engineering use of PCMs is that most PCMs have poor thermal conductivity as mentioned earlier. Many techniques applied for heat transfer enhancement are found in the literatures to overcome PCMs’ lower thermal conductivities. Such techniques required to enhance the heat transfer rate include the dispersion of highly conductive nanoparticles, impregnation of PCMs in a porous media such as metal or graphite matrix, the use of fins and finned tubes, the use of agitators, using microencapsulated PCM, use of multiple PCMs, rings in PCMs, which is done by increasing the thermal conductivity in the PCMs without much reduction in energy storage. Among all of these methods, the dispersion of highly conductive nanoparticles along with impregnation of PCM in porous media is the main interest of this research.
Khodadadi and Hosseinizadeh [4] studied the natural convection solidification process numerically inside a differentially-heated square cavity that contains a NanoPCM. They observed that NanoPCM exhibits higher heat release rate when compared to the conventional PCM partly due to simultaneous increase of the thermal conductivity and reduction of the latent heat. Fan and Khodadadi [33] conducted theoretical (modified 1-D Stefan model) and experimental investigations on freezing of NanoPCM in a vertical container. A cooled-from-bottom unidirectional freezing experimental setup was constructed to validate the theoretical result. Ho and Gao [34] experimentally examined the melting process of a NanoPCM (n-octadecane+Al₂O₃) in a vertical enclosure. Ho and Gao [34] reported that the natural convection heat transfer inside the liquid region degrades with increasing nano-particle mass fraction when compared with the natural convection result of the base PCM. Other studies include the transient characterization and identification of the efficiency of thermal energy storage packed with ‘microencapsulated phase change material’ [35].

### 3.4 Impregnation of PCM in porous media

Several authors also reported the thermal enhancement of PCM only inside the porous medium. For example, Zhao et al. [3] performed experimental investigation to characterize the phase change processes (both melting and solidification) of paraffin wax inside the copper metal foam. Their results show that the use of porous medium enhances the solidification and melting process faster than base PCM without porous medium. Lafdi et al. [36] experimentally observed the influence of convection on the melting process of paraffin wax inside the high thermal conductivity metal aluminum foam with various porosities. Lafdi et al. [36] observed that the metal foam with higher porosity assists convection mechanism while foam with lower porosity assists conduction mechanism. Therefore, the authors recommended that one should select optimum porosity and pore size to utilize both conduction and convection mechanisms effectively for better heat transfer performance.
3.5 Nano-fluid in porous and non-porous media

Buongiorno [37] presented an excellent review on the influence of several effects (e.g., inertia, Brownian diffusion, Magnus effect, fluid drainage, gravity, and thermophoresis) on nanofluid convection. The transport processes of nanofluids in porous medium have been a focus of study in recent years. In a series of pioneering articles, Kuznetsov and Nield [38-40] have developed modeling equations to study transport of nanofluid problems inside porous media. The authors have considered that nanoparticles are suspended particles in the base fluid utilizing one of the following technologies: surfactant and surface charge technologies. This could avoid nanoparticles from agglomeration and deposition inside the pore of the porous matrix.

Based on the literature reviewed no published article is identified that considers phase change process of NanoPCM inside porous medium. However, there are considerable numbers of articles, which deal with ‘nano-fluid transport in porous medium’ or ‘phase change process of NanoPCM in non-porous medium’. Therefore, we believe that this is the first article, which deals with phase change process (mainly melting), and heat transfer characteristics of a NanoPCM inside porous medium. As this is a pioneering work, we prefer to make the model and analysis less complicated using simpler models available in the literature. Therefore, non-Darcy momentum modeling, boundary and inertia effect, thermal non-equilibrium modeling, and Brownian motion and thermophoresis effect are not incorporated into the current model. These are left for future work.

3.6 Problem Formulation

A rectangular enclosure is considered, which represents a simplified thermal energy storage system, of width \( L \) and height \( H \) as shown schematically in Figure 3-1(a). The enclosure, bounded by impermeable walls, is filled with a porous medium. Initially, a solid phase of NanoPCM completely fills the void space of the porous medium inside the enclosure. For simplicity of analysis, the initial temperature of the NanoPCM is considered equal to the fusion temperature \( T_m \) of the NanoPCM. It is assumed that the local thermal equilibrium exists between the NanoPCM and the porous medium. Therefore, at any time, temperatures of the NanoPCM and the porous matrix are equal at any representative control volume. All the walls of
the enclosure are properly insulated except the top horizontal wall which is exposed to a heat source having constant temperature but higher than the fusion temperature of the NanoPCM. Because of the temperature gradient, thermal energy will start penetrating through the top wall. Such penetration of the thermal energy will initiate the phase change process (melting) of the NanoPCM inside the porous medium.

3.6.1 Governing Momentum Equations

As indicated in Figure 3-1(a) the direction of the gravity is same as the moving direction of the melting front. Therefore, as melting process advances, a layer of lighter liquid NanoPCM grows over the heavier solid NanoPCM. Any type of liquid motion or circulation will remain negligible if the interface moves relatively slowly. It is reasonable to assume that the liquid layer of NanoPCM is stable with negligible convective motion in the layer. A conduction-like heat transport process can be approximated. Nevertheless, a momentum equation is included for the sake of completeness of the modeling. As for the pioneering work, we propose the Darcy flow model for the porous medium. Darcy model establishes a relationship between the flow velocities and the pressure gradient in a particular direction inside porous medium.

![Figure 3-1:](a) schematic diagram of the problem under consideration, (b) a magnified view of a representative control volume
The momentum equations along the $x$ and $y$ directions are

\[ u = -\frac{K}{\mu_n} \frac{\partial p}{\partial x} \tag{1} \]

and

\[ v = -\frac{K}{\mu_n} \left( \frac{\partial p}{\partial y} + \rho_n g \right) \tag{2} \]

respectively. In Eq. (1) and Eq. (2), $u$, $v$, $K$, $p$, $g$, $\rho_n$, and $\mu_n$ are the velocity component in the $x$ direction, velocity component in the $y$ direction, permeability of the porous medium, pressure, gravitational acceleration, density of the NanoPCM, and viscosity of the NanoPCM, respectively. For the simplicity of analysis, it is assumed that the behaviour of liquid phase NanoPCM is similar to the typical nanofluid. In such a case, the effective density of the NanoPCM is directly related to properties of the nano-particle and base-PCM and their relative fractions as well. The viscosity of the NanoPCM can be approximated as the viscosity of a base fluid if it contains dilute suspension of fine spherical particles [41]. The density and the viscosity of the NanoPCM can be expressed as

\[ \rho_n = (1 - \phi)f\rho_f + \phi\rho_p \tag{3} \]

\[ \mu_n = \frac{\mu_f}{(1 - \phi)^{3.5}} \tag{4} \]

where, $\rho_f$, $\rho_p$, $\mu_f$, are $\phi$ the density of the base-PCM, density of the nano-particle, viscosity of the base-PCM, and volume fraction (volume of the nano-particle/total volume of NanoPCM), respectively. In the limit of small volume fraction (i.e., $\phi \to 0$), both density and viscosity of the NanoPCM approach to the density and viscosity of the base-PCM. Assuming that the Boussinesq approximation is applicable for the current problem; therefore, the buoyancy term in the $y$-momentum equation can be approximated by

\[ \rho_n g \approx \phi \rho_p g + (1 - \phi)\rho_0 \left[ 1 - \beta(T - T_0) \right] g. \tag{5} \]
where \( \rho_0 \) is the reference density of the base-PCM at a reference temperature \( (T_0) \) and \( \beta \) is the volumetric thermal expansion coefficient of the base-PCM. The volumetric thermal expansion coefficient of the base-PCM is considered sufficiently large compared to the volumetric thermal expansion coefficient of the nano-particle. Note that when the volumetric thermal expansion coefficient of the nano-particles is not negligible a different approximation of the buoyancy term is required. Using Eq. (5), the \( y \)-momentum equation can be written as

\[
v = -\frac{K}{\mu_n} \left[ \frac{\partial p}{\partial y} + \phi \rho g + (1 - \phi) \rho_0 [1 - \beta(T - T_0)] g \right].
\] (6)

A subtraction of the \( x \) derivative of Eq. (6) from the \( y \) derivative of Eq. (1) results in

\[
\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x} = -\frac{K}{\mu_n} \left[ -\frac{\partial}{\partial x} \left( \phi \rho g + (1 - \phi) \rho_0 [1 - \beta(T - T_0)] g \right) \right].
\] (7)

Introducing the stream function \( (u = \partial \psi / \partial y, v = -\partial \psi / \partial x) \) to Eq. (7) and performing mathematical simplification results in

\[
\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -(1 - \phi) \left( \frac{K \rho_0 g \beta}{\mu_n} \right) \frac{\partial T}{\partial x} = -(1 - \phi)^{3.5} \left( \frac{K \rho_0 g \beta}{\mu_f} \right) \frac{\partial T}{\partial x}.
\] (8)

Equation (8) is the dimensional form of the momentum equation for the liquid NanoPCM inside the porous medium in terms of stream function.

3.6.2 Governing Energy Equation

In this section, the energy transport by NanoPCM through the porous medium is considered. The porous medium is assumed isotropic and local thermal equilibrium condition is valid. The local thermal equilibrium assumption ensures that temperatures of the solid matrix and pore fluid are same in a given control volume; therefore, the net heat transfer rate between NanoPCM and solid matrix is negligible \([42]\). Then the governing energy equation can be obtained by integrating the energy equation for the solid matrix over the area occupied by the solid matrix and integrating the NanoPCM’s energy equation over the area occupied by the NanoPCM inside the pores, followed by a subsequent addition of two area averaged equations and simplifications.
Applying the methodology described above the following energy equation is obtained, after a lengthy calculation, for the melt region:

\[
\rho_m C_m \frac{\partial T}{\partial t} + \rho_n C_n \left[ \mu \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right] = k_m \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right].
\] (9)

In Eq. (9), the product \( \rho_n C_n \) is the heat capacity of the NanoPCM and \( \rho_m C_m \) is the mean heat capacity of the NanoPCM-porous-matrix which can be expressed as

\[
\rho_m C_m = (1 - \varepsilon) \rho_s C_s + \varphi_n C_n .
\] (10)

where \( \rho_s C_s \) and \( \varepsilon \) are the heat capacity of the solid matrix and porosity of the porous medium, respectively. The mean thermal conductivity of the porous medium (\( k_m \)) can be expressed as

\[
k_m = \varepsilon k_n + (1 - \varepsilon) k_s.
\] (11)

where \( k_s \) is the thermal conductivity of the solid matrix. The effective thermal conductivity of the NanoPCM (\( k_n \)) can be adopted from the Maxwell’s model [43] as shown below

\[
k_n = k_f \left[ \frac{(k_p + 2k_f) - 2\phi(k_f - k_p)}{(k_p + 2k_f) + \phi(k_f - k_p)} \right].
\] (12)

where \( k_f \) and \( k_p \) are the thermal conductivities of base-PCM and nano-particle, respectively. Note that the Maxwell’s model [43] is good for predicting the effective thermal conductivity of composites with spherical particles and verified by abundant experimental data.

Similar process can be applied to obtain the energy equation for the region having solid NanoPCM as shown below

\[
\rho_m C_{ms} \frac{\partial T}{\partial t} = k_{ms} \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right].
\] (13)

where the subscript ‘\( ms \)’ represent the thermophysical properties in the region having solid NanoPCM.
The required boundary conditions for the current problem, after using the velocity vector, \( \mathbf{v} = u \hat{i} + v \hat{j} \), are

- **bottom wall** (\( y = 0 \)): \(-\mathbf{n} \cdot \mathbf{v} = 0\) and \(\mathbf{n} \cdot \nabla T = 0\)
- **top wall** (\( y = H \)): \(-\mathbf{n} \cdot \mathbf{v} = 0\) and \(T = T_w\)
- **left wall** (\( x = 0 \)): \(-\mathbf{n} \cdot \mathbf{v} = 0\) and \(\mathbf{n} \cdot \nabla T = 0\)
- **right wall** (\( x = L \)): \(-\mathbf{n} \cdot \mathbf{v} = 0\) and \(\mathbf{n} \cdot \nabla T = 0\)
- **melting front** (\( y = s \)): \(-\mathbf{n} \cdot \mathbf{v} = 0\) and \(T = T_m\)

Now, the energy balance at the interface between the liquid NanoPCM and solid NanoPCM requires

\[
k_m \left[ \frac{\partial T}{\partial y} \right]_{y=s} = \left[ (1-\varepsilon) \rho_s h_s + \varepsilon \rho_n h_n \right] \frac{\partial s}{\partial t} \approx \varepsilon \rho_n h_n \frac{\partial s}{\partial t}.
\]

where \( h \) represents the enthalpy of fusion and \( s \) is the distance of the melting from the top surface. In Eq. (15), the difference between the densities of liquid and solid at the melting point is neglected. Buongiorno [37] presented an excellent review on the influence of several effects (e.g., Brownian diffusion and thermophoresis) on nanofluid convection. As an example, Buongiorno [37] showed that Brownian diffusion coefficient may vary from \(4 \times 10^{-10}\) to \(4 \times 10^{-12} \text{ m}^2/\text{s}\) for nanoparticles of diameter 1–100 nm in water. Buongiorno [37] also calculated the thermophoretic velocity (\( \approx 2 \times 10^{-6} \text{ m/s} \)) for alumina nanoparticles in water with \(10^5 \text{ K/m} \) temperature gradient. Therefore, both Brownian motion and thermophoresis effect can be neglected for present study. However, inclusion of such effects is left for future works.

### 3.7 Results and Discussion

The governing differential equations are solved with the initial/boundary conditions presented in the previous section. The numerical technique to solve the governing equations is available in Mahmud and Pop [44] and is not repeated here. Paraffin is selected as the base PCM, CuO-nanoparticles is used as nanoparticles, and Aluminum is considered as the material for the
porous matrix, respectively. The thermophysical properties of Paraffin (both solid and liquid forms) and Aluminum are presented in Table 3-1. The thermophysical properties of bulk CuO are used due to the lack of data for nanometer-sized materials.

**Table 3-1:** Thermophysical properties of Paraffin, Copper Oxide nano-particle, and Aluminum solid matrix [33, 45]

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg/m³)</th>
<th>Specific heat (J/kg K)</th>
<th>Thermal conductivity (W/m.K)</th>
<th>Latent heat of fusion (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Paraffin [33]</td>
<td>779</td>
<td>1763</td>
<td>0.127</td>
<td>32557</td>
</tr>
<tr>
<td>Solid Paraffin [33]</td>
<td>856</td>
<td>1600</td>
<td>0.136</td>
<td></td>
</tr>
<tr>
<td>Copper oxide (CuO) nano-particle [33]</td>
<td>6310</td>
<td>540</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>Aluminum (Al) solid matrix [45]</td>
<td>2702</td>
<td>903</td>
<td>237</td>
<td>-</td>
</tr>
</tbody>
</table>

It is assumed that the entire NanoPCM is initially at its solid phase with a uniform temperature. The magnitude of the initial temperature is considered equal to the melting temperature of the NanoPCM. At time \( t = 0 \), the top wall of the enclosure is suddenly exposed to a heat source having temperature higher than the melting point of the NanoPCM. Therefore, the imposed temperature gradient will drive the thermal energy penetrating through the top surface of the enclosure. Such penetration of thermal energy will initiate the phase change process (melting) of the NanoPCM inside the porous medium. Initially, the heat transfer process is dominated by pure conduction. A thin melting layer will appear at the top of the enclosure. This melting layer contains the liquid form of NanoPCM. A distinct boundary (i.e., melting front) separates the solid form of NanoPCM from the liquid NanoPCM. This melting front moves downward as time increases.

In order to visualize the melting process qualitatively, Figure 3-2 presents the thermal field inside the enclosure (both in solid and liquid layers of NanoPCM), heat flux vector, and the
Figure 3-2: Thermal field (temperature contours and surfaces), heat flux vector, and the location of melting front at three different times (500 s, 2000 s, and 3000 s) and porosity (0.95 and 0.85) when nanoparticle volume fraction, $\phi = 10\%$. 

(a) $\phi = 10\%$, $\varepsilon = 0.95$, $t = 500$ s 
(b) $\phi = 10\%$, $\varepsilon = 0.95$, $t = 2000$ s 
(c) $\phi = 10\%$, $\varepsilon = 0.95$, $t = 3000$ s 
(d) $\phi = 10\%$, $\varepsilon = 0.85$, $t = 500$ s 
(e) $\phi = 10\%$, $\varepsilon = 0.85$, $t = 2000$ s 
(f) $\phi = 10\%$, $\varepsilon = 0.85$, $t = 3000$ s
location of the melting front at three different times \( t = 500 \text{ s}, 2000 \text{ s}, \text{ and } 3000 \text{ s} \). Two different values of porosity \( \epsilon = 0.95 \text{ and } 0.85 \) are selected in Figure 3-2. The magnitude of the nanoparticle volume fraction is kept constant (i.e., \( \phi = 10\% \)). A conduction like temperature distribution is observed inside the liquid layer with maximum temperature at the top surface and minimum at the melting front. However, temperature all over the solid layer of NanoPCM remains constant \( (=T_m) \) because of the imposed initial and boundary conditions. The effective thermal conductivity of the NanoPCM is larger than the base-PCM enabling a heat transfer enhancement inside the enclosure. The lighter liquid layer of NanoPCM remains stable over the heavier solid layer of NanoPCM. A nearly insignificant effect of convection ensures a conduction like temperature distribution even at larger time. The extent of the conduction like temperature distribution influences the temperature gradient as well as the heat transfer rate inside the enclosure. This, in turns, influences the rate of melting. Therefore, the melting process slows down as time progresses. For a given nano-particles’ volume fraction, melting process is faster in a porous medium having lower porosity as can be observed from Figure 3-2(d), Figure 3-2(e), and Figure 3-2(f). In order to further understand the process described above the following scale analysis is introduced.

A two dimensional confined space is considered as shown in Figure 3-1(a), where solid NanoPCM is at its melting point. The heat flux across the incipient horizontal liquid layer is balanced entirely by the enthalpy absorbed at the two-phase interface (Eq. (15)),

\[
k_m \frac{T_w - T_m}{s} \sim \epsilon (\rho_n h_n) \frac{s}{t}.
\]  

(16)

In dimensionless terms, above equation yields

\[
\frac{s^2}{H^2} \sim \frac{k_m (T_w - T_m)}{\epsilon (\rho_n h_n) H^2 t}.
\]  

(17)

The thickness, \( s \), can be approximated as

\[
s^2 \sim \frac{H^2}{\frac{C_n (T_w - T_m)}{\epsilon h_n}} \left[ \frac{k_m}{\rho_n C_n H^2 t} \right].
\]  

(18)
Two dimensionless numbers: (i) modified Stefan number (Ste) and (ii) Fourier number (Fo) are introduced as shown below:

\[ Ste = \frac{C_n(T_w - T_m)}{\varepsilon h_n} \quad \text{and} \quad Fo = \frac{k_m}{\rho_n C_n H^2 t}. \]  

(19)

Eq. (18) can be written as

\[ s \sim H \times \sqrt{Ste \times Fo}. \]  

(20)

Finally, the scale for the dimensionless heat transfer rate can be expressed as

\[ \dot{Q}^* = \frac{\dot{Q}}{k_m (T_w - T_m)} \sim \frac{1}{\sqrt{Ste \times Fo}}. \]  

(21)

where \( \dot{Q} \) represents the heat transfer through the top surface of the enclosure per unit depth of the enclosure.

It is observed from Eq. (18) (or Eq. (20)) that the interface moves further down inside the enclosure for cases where modified Stefan number is larger if the dimensionless time (i.e., Fourier number) is constant. The porosity term appears at the denominator of the modified Stefan number (Eq. (19)). Therefore, for a given NanoPCM, a lower porosity of porous medium results in a higher modified Stefan number. A comparison between Figure 3-2(b) and Figure 3-2(e) confirms that the depth of melt layer is higher for \( \varepsilon = 0.85 \) (Figure 3-2(e)) than \( \varepsilon = 0.95 \) (Figure 3-2(b)) at time \( t = 2000 \) s and this is confirmed by the scale analysis as presented above.

Figure 3-3 presents the percentage melt fraction as a function of time at different values of porosities of the porous medium. The volume fraction of the nanofluid is varied from 5% to 20% (Figure 3-3(a) to Figure 3-3(d)). Melt fraction is the ratio of the volume of liquid NanoPCM to the total NanoPCM (liquid NanoPCM + solid NanoPCM) inside the enclosure. The volume change due to the volumetric thermal expansion during the melting process is assumed negligible. Melting process begins immediately after the top surface is exposed to a high temperature source. Within a short period of time melt fraction reaches almost 20% as can be observed from Figure 3-3. Melt fraction gradually increases with advancing time and reaches its maximum value (i.e., 100%) when the melting front touches the bottom of the enclosure. This
limit can be approximated by considering $s/H \sim 1$ in Eq. (20) which results in $Fo \sim Ste^{-1}$ (i.e., the end of melting process). Melting process of NanoPCM is slower in a porous medium with higher porosity and faster with higher volume fraction of nanoparticles.

**Figure 3-3:** Melt fraction as a function of time at different values of porosities when the volume fraction of nanofluid is (a) 5%, (b) 10%, (c) 15%, and (d) 20%.
The effect of volume fraction of nano-particle on the melt fraction is shown in Figure 3-4, where the melt fraction is plotted as a function of time at different values of volume fractions of nanofluid. Two different values of porosities (85% and 50%) are considered in Figure 3-4. For a given porosity of the porous medium, the effect of the change in the volume fraction of the nano-particle exhibits small influence on the melt fraction. A NanoPCM with higher concentration of nanoparticles reaches its limiting value of the melt fraction (i.e., 100%) earlier than a NanoPCM with lower concentration of nanoparticles as observed in Figure 3-4.

**Figure 3-4:** Melt fraction as a function of time at different values of volume fractions of nanofluid when porosity is (a) 85% and (b) 50%.

In Figure 3-5, the dimensionless heat transfer rate ($Q^*$) is plotted as a function of time for different values porosities of the porous medium. Two different values of the volume fractions are selected in Figure 3-5. Heat transfer rate is higher in magnitude at the beginning of the melting process. As time advances, heat transfer rate decreases rapidly and reaches within a few percentage of its minimum value (=1). The decreasing tendency of heat transfer slows down when the melting front reaches close to its lower extreme. The relationship obtained in Eq. (21) also supports such variation in heat transfer with time. The dimensionless heat transfer approaches to its minimum value of 1 when the melting front touches the bottom part of the enclosure. Heat transfer rate is higher in magnitude in an enclosure with higher porosity than
lower porosity of porous medium inside it. The total energy transferred to the enclosure to complete the melting process can be calculated by integrating the $\dot{Q} - t$ curve within the time limit (i.e., starting time to end time of the melting process). Energy requires to melt the NanoPCM inside an enclosure with higher porosity requires relatively larger amount of energy when compared with the enclosure having the porous medium with lower porosity. Incorporating more nanoparticles (i.e., higher volume fraction) reduces the energy requirement to complete the melting process as can be observed from Figure 3-5(b).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-5}
\caption{Time variation of dimensionless heat transfer rate at different values porosities when (a) $\phi = 10\%$ and (b) $\phi = 20\%$.}
\end{figure}

Based on the results obtained from current modeling and simulation, Table 2 presents a comparison of melt fraction between NanoPCM in porous medium and PCM in non-porous medium at different times. Melting of NanoPCM in porous medium shows significant improvement over the melting of PCM in non-porous medium. For example, 2770 sec. is required to completely melt (100%) the NanoPCM (with $\phi = 20\%$) considered in this paper inside the porous storage system having porosity, $\varepsilon = 85\%$. However, only 5.93% of the PCM ($\phi = 0.0\%$) will melt in 2770 sec. inside a non-porous medium ($\varepsilon = 100\%$) having same dimension. A reduction in the volume fraction of nano-particle increases the melting time.


Table 3-2: Comparison of percentage melt fraction between NanoPCM in porous medium and PCM in non-porous medium at different times

<table>
<thead>
<tr>
<th>Time (sec.)</th>
<th>NanoPCM in Porous Medium</th>
<th>PCM in Non-Porous Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon$</td>
<td>$\phi$</td>
</tr>
<tr>
<td>2770</td>
<td>85%</td>
<td>20%</td>
</tr>
<tr>
<td>3100</td>
<td>85%</td>
<td>10%</td>
</tr>
<tr>
<td>3440</td>
<td>85%</td>
<td>0%</td>
</tr>
<tr>
<td>840</td>
<td>50%</td>
<td>20%</td>
</tr>
<tr>
<td>940</td>
<td>50%</td>
<td>10%</td>
</tr>
<tr>
<td>1040</td>
<td>50%</td>
<td>0%</td>
</tr>
</tbody>
</table>

For comparison and validation purposes, authors used a simplified liquid-solid interface tracking equation. Hahn and Özişik [46] developed similar equation for a “Single-Phase Problem: Melting at the Freezing Point”. Note that the interface tracking equation in Hahn and Özişik [46] is developed for melting of a regular PCM inside semi-infinite non-porous medium. Using the definitions already used in this paper for different thermophysical properties, the liquid-solid interface tracking equation can be given by

$$ s(t) = 2 \lambda (\alpha_n t)^{\frac{1}{2}}. $$

(22)

where the term $\lambda$ in Eq. (22) can be obtained after solving the following equation:

$$ \lambda e^{\frac{i}{2}} \text{erf} (\lambda) = \frac{C_n (T_w - T_m)}{h_n \sqrt{\pi}}. $$

(23)

In the above equation, $C_n$ and $h_n$ can be calculated from $\rho_n C_n = (1 - \phi) \rho_f C_f + \phi \rho_p C_p$ and $\rho_n h_n = (1 - \phi) \rho_f h_f$, respectively. For comparison purpose, a NanoPCM (Paraffin + Copper Oxide nano-particle) with three different volume fractions of nano-particles ($\phi = 0.0, 0.1, \text{and } 0.2$) is considered inside a non-porous medium ($\varepsilon = 1$). By using the properties in Table 1, the values of $\lambda$ for these three cases of $\phi$ are calculated numerically as
\( \lambda_{r=1, \phi=0.0} = 0.16308 \), \( \lambda_{z=1, \phi=0.1} = 0.18377 \), and \( \lambda_{r=1, \phi=0.2} = 0.2065 \). Finally, the distance of the interface as a function of time (\( s(t) \)) is calculated from Eq. (22) and plotted in Figure 6 for a time range of 0 to 14000 sec. Numerically obtained \( s(t) \) is also plotted in Figure 6 for three cases of \( \phi \). A fair agreement is observed between the numerical and analytical results as can be seen from Figure 3-6.

![Figure 3-6: Variation in the analytically and numerically calculated liquid-solid interface with time for different values of nano-particle volume fraction](image)

### 3.8 Conclusions

Numerical and analytical investigations are performed to study the melting process and heat transfer phenomena of NanoPCM inside an enclosure filled with porous medium. Two dimensional differential equations were derived and solved to analyze the NanoPCM-porous-medium composite phase change process. Aluminum foam was selected as the porous medium.
and “Paraffin + CuO nanoparticle” was used as the NanoPCM. From the result, it is observed that the movement of PCM melting front is more significant under the influence of porous medium than that of nanoparticles. NanoPCM melts at a faster rate inside the porous medium with lower porosity. For a given porosity of the porous medium, a faster melting rate is observed for NanoPCM with higher volume fraction of nano-particles. From heat transfer rate, it is observed the NanoPCM inside an enclosure with higher porosity requires relatively larger amount of energy to melt when compared with the enclosure having the porous medium with lower porosity. Incorporating more nanoparticles (i.e., higher volume fraction) reduces the energy requirement to complete the melting process. The current work will be extended into a detailed experimental study for various nanoparticles and porous medium materials based on the requirements of a specific thermal management application.

Nomenclature:

\[ C_m \] mean specific heat, \( J/\text{kg}^\circ\text{C} \)
\[ C_{ms} \] mean specific heat in the region having solid NanoPCM, \( J/\text{kg}^\circ\text{C} \)
\[ C_n \] specific heat of NanoPCM, \( J/\text{kg}^\circ\text{C} \)
\[ C_s \] specific heat of the solid matrix, \( J/\text{kg}^\circ\text{C} \)
\[ g \] gravitational acceleration, \( m/s^2 \)
\[ Fo \] Fourier number, (Eq. (19))
\[ h \] enthalpy of fusion, \( J/\text{kg} \)
\[ H \] height of the cavity, \( m \)
\[ K \] permeability of the porous medium, \( m^2 \)
\[ k_f \] thermal conductivity of base-PCM, \( W/m^\circ\text{C} \)
\[ k_m \] mean thermal conductivity, \( W/m^\circ\text{C} \)
\[ k_p \] thermal conductivity nano-particle, \( W/m^\circ\text{C} \)
\[ L \] width of the enclosure, \( m \)
\[ p \] pressure, \( Pa \)
\( \dot{Q} \)  heat transfer through the top surface of the enclosure per unit depth, W/m

\( \dot{Q}^* \)  dimensionless heat transfer rate, (eq. (21))

\( T \)  temperature, °C

\( T_0 \)  a reference temperature, °C

\( T_m \)  melting temperature, °C

\( T_w \)  wall temperature, °C

\( s \)  distance of the melting from the top surface, m

\( \text{Ste} \)  modified Stefan number, (Eq. (19))

\( t \)  time, s

\( u \)  velocity component in x-direction, m/s

\( v \)  velocity component in y-direction, m/s

**Greek symbols**

\( \varepsilon \)  porosity of the porous medium

\( \beta \)  volumetric thermal expansion coefficient of the base-PCM, 1/K

\( \psi \)  stream function, m²/s

\( \rho_p \)  density of the nano-particle, kg/m³

\( \rho_f \)  density of the base-PCM, kg/m³

\( \rho_m \)  mean density, kg/m³

\( \rho_{ms} \)  mean density in the region having solid NanoPCM, kg/m³

\( \rho_n \)  density of the NanoPCM, kg/m³

\( \rho_s \)  density of the solid matrix, kg/m³

\( \mu_n \)  viscosity of the NanoPCM, Ns/m²

\( \mu_f \)  viscosity of the base-PCM, Ns/m²

\( \phi \)  volume fraction (=volume of the nano-particle/total volume of NanoPCM)
3.9 References


Chapter 4: Convection Model – Isothermal

This Chapter is published as:


Summary

This paper reports thermal performance of porous latent heat thermal energy storage (or LHTES) system filled with nano-phase change material (or NanoPCM). In the first part of the paper, scale analysis is executed to estimate the extent of the complete phase change process which is a key factor of designing LHTES systems. The scale analysis results in simplified relationships among different non-dimensional parameters (i.e., Fourier number, Stefan number, Rayleigh number, Nusselt number, porosity of the porous medium, and nano particle volume fraction). In the second part, the natural convection melting process of NanoPCM inside the porous medium is solved numerically. For the porous medium the Darcy model is employed. The numerical simulation serves two purposes: (i) it verifies the correctness of the relationships proposed by scale analysis in the first part of the paper and (ii) it identifies the effects of nano-particle volume fraction, time, and Rayleigh number, on flow field, thermal field, and heat transfer process during the melting of NanoPCM inside the thermal energy storage system. The proposed scaling relationships can be applied to predict the progress and execution of LHTES system filled with porous medium saturated by NanoPCM.

Keywords: Numerical simulation; NanoPCM; Porous medium; Scale analysis; Thermal conductivity enhancers; Thermal energy storage
4.1 Introduction

Storage of energy is essential in order to ensure energy security, efficiency, and environmental quality. There are two different ways one can store thermal energy in a storage material by heating and cooling: sensible and latent. In sensible-heat thermal energy storage (SHTES) system, the temperature of the storage material (e.g., water and rock) changes with the amount of energy added or removed from the system. Alternatively, in a latent-heat thermal energy storage (LHTES) system, thermal energy can be added or removed as latent heat when a material (e.g., wax) changes its phase from liquid-state to solid-state (freezing process) or solid-state to liquid-state (melting process). The melting and freezing processes usually occur at constant temperatures for pure substances. Of the two types of storage systems, LHTES technique has certain advantages over SHTES; for example, high energy density (energy per given volume) and compact design. Researchers have investigated various configurations of LHTES units and found several potential engineering applications; for example, heating of water using solar-thermal energy [1-5], solar-thermal air heating systems [6,7], cooking system using solar energy [8,9], solar green house [10-12], buildings energy management [13-21], waste heat recovery [22, 23], low temperature storage unit [24], refrigeration system for refrigerated trucks [25] management of vehicle heat [26], cooling of photovoltaic (PV) devices [27], electronics cooling [28, 29], conventional satellite solar power systems [30], and heat protection [31].

Similar to any other system, LHTES system exhibits certain self-defeating traits. One of its less desired features is the PCM’s lower magnitude of thermal conductivity, which slows down the melting/freezing rate of PCM. A faster melting/freezing rate is a requirement for many engineering applications [32]. Many heat transfer enhancement techniques are found in the literature that investigated the method of increasing the low thermal conductivity of PCMs. These techniques include the dispersion of highly conductive nanoparticles [33], use of stationary highly conductive structures [34], microencapsulated PCM [35], multiple PCMs [36], porous metals [37], and rings in PCMs [38]. Among all these approaches, dispersion of highly conductive nanoparticles along with impregnation of porous medium in PCM is the main interest of this research. Incorporation of porous medium and nano-particles in PCM modify phase change process, as well as, the heat transfer rate which will be discussed in the present study.
Khodadadi and Hosseinizadeh [39] were the first to numerically study the natural convection solidification process of nanofluid by preparing water-based nanofluid with 10 and 20% volume fraction of copper nanoparticles in a vertical square cavity. The authors predicted the effective thermophysical/transport properties of PCM with nanoparticles using the mixture, Brinkman, and Maxwell models. They reported that NanoPCM exhibits higher heat release rate when compared to the base fluid due to two effects: (i) increase in the thermal conductivity and (ii) reduction of the latent heat. Fan and Khodadadi [40] conducted theoretical analysis using modified 1-D Stefan problem and experimental investigation on freezing of NanoPCM (paraffin based nanofluid containing 0.5 – 2 vol. % of copper oxide nanoparticles) inside a vertical container. In their numerical study, the authors predicted the effective thermophysical/transport properties of PCM with nanoparticles using the mixture and Maxwell models. A cooled-from-bottom unidirectional freezing experimental setup was constructed to validate the theoretical results. The authors observed an expedited freezing due to the presence of the copper oxide nanoparticles in comparison to pure paraffin. But the catch is that this is a cooled-from-bottom one-dimensional solidification process involving only conduction heat transfer. Since, addition of nanoparticles enhances the thermal conductivity of the nanofluid; therefore addition of nanoparticles may enhance conduction heat transfer. Ho and Gao [41] experimentally examined the melting process of NanoPCM samples of paraffin (n-octadecane) based nanofluid containing 0, 5, and 10 wt.% of aluminum oxide nanoparticles inside a square-shaped enclosure. They reported that free convection heat transfer inside the liquid region degrades with increasing nano-particle mass fraction when compared with the natural convection result of the base PCM. The authors reasoned that the enhancement of dynamic viscosity is far greater than that of thermal conductivity while nanoparticles are added. Thus melting in the convection heat transfer region is degraded while nanoparticles are added. Other studies include the identification of the thermophysical properties of NanoPCM to be used in the low temperature cool storage system by Ho and Gao [42]. Arasu and Mujumdar [43] numerically investigated melting of a nono-PCM (base PCM: paraffin wax; nanoparticles: 2% and 5% by volume of alumina) in a square cavity. Authors concluded that, due to the natural convection enhancement, the melting rate is higher when the cavity is heated from a side than the melting rate inside the cavity heated from below. A comprehensive two dimensional numerical study was conducted by Sebti et al. [44] to investigate the modification of heat transfer during the melting process using NanoPCM.
(paraffin-based nanofluid containing 2.5 and 5% by volume of copper nanoparticles). Authors identified that the incorporation of nanoparticles leads to a decrease in melting time. They further reported that melting time decreases significantly when the difference between the fusion temperature and the hot wall temperature increases. Recently, Zeng et al. [45] performed an experimental study by dispersing multi-walled carbon nanotubes (CNTs) with various loadings (0 wt.%, 1 wt.%, and 2 wt.%) in 1-dodecanol PCM. It was shown in [45] that melting in a bottom heated vertical cylindrical cavity is decreased in the presence of the CNTs as a result of the powerful increased viscosity, directing to major degradation of natural convection during melting. From the literature survey mentioned above, it is apparent that there are inconsistencies among various studies concerning natural convection heat transfer effectiveness of using NanoPCM in cavities. The potential contributing factors for experimental studies may include (a) not providing enough information regarding the nanoparticle, for example, variations of the particle size and shape, clustering of nanoparticles, and uncertainties in the nanofluid thermophysical properties, especially dynamic viscosity and the effective thermal conductivity, (b) type and amount of additives used in the samples, pH value of the sample, base fluid, ultrasonic vibration, and (c) not providing enough information regarding the tests, for example, Rayleigh number, experimental uncertainty, the relative strength of melting heat transfer by conduction or convection, etc. On the other hand, the possible contributing factors for numerical studies may include (a) different modeling approximations for momentum equation, (b) different modeling approximations for defining nanofluid thermophysical/transport properties, (c) different approximations for defining Nusselt number, etc.

The phase change processes of PCM inside porous media were studied extensively by Jany and Bejan [46] and Bejan et al. [48]. Jany and Bejan [46] identified four distinct regions of melting process assisted by natural convection inside enclosure (filled with porous material) heated from one vertical side with remaining adiabatic walls. The melting phenomenon described by the scale analysis is similar to the natural convection melting process in enclosures developed by Jany and Bejan [47] for non-porous medium. Jany and Bejan [46] also used numerical method to validate the scale analysis. For significantly large buoyancy forces, Bejan et al. [48] predicted advancement of the horizontal melting layer next to the top of the cavity inside a porous medium.
Recently, Zhao et al. [49] experimentally investigated the phase change processes of paraffin wax inside high porosity (95%) copper metal foam. The authors also developed a mathematical model to compare their experimental work. They found that the use of porous medium increases the overall heat transfer by 3-10 times during the melting process. They also found that the temperature gradient in metal foam sample was significantly reduced compared to pure PCM. Han et al. [50] proposed a one-dimensional mathematical model to characterise phase change heat transfer process inside metal foam. One of the key features of their model is that it considers PCM’s volumetric thermal expansion during melting process. The only limitation of this model is that it is based on one dimensional conduction heat transfer only without considering natural convection. As a result, it under predicts the experimental data because of natural convection heat transfer in the liquid regime. Zhou and Zhao [51] experimentally compared the heat transfer performance of two pairs of composites; Paraffin/Expanded Graphite and Paraffin/Metal foam on the melting of PCM. The authors found that both composites resulted in augmentation of heat transfer with metal foams showing better performance. They reasoned that the advantage of metal foam’s continuous inter-connected structure over expanded graphite’s discontinuous structure was responsible for the better performance of metal foam. The numerical and experimental investigations of Tian and Zhao [52] also reported heat transfer enhancement of PCM inside metal foams. Their “two-equation thermal non-equilibrium heat transfer model” considered the effect of heat conduction and natural convection. They observed that larger flow resistance of metal foam suppressed the effect of natural convection at the two-phase and liquid zone. However, because of the dominance of conduction heat transfer thorough the metal foam’s solid structure, the overall thermal performance was observed better with PCM-metal foam than pure PCM. Lafdi et al. [53] experimentally studied the phase change (mainly melting) heat transfer process of regular PCM inside aluminum foams of porosities range from 88.4% to 96.6%. The authors concluded that an optimum value of foam porosity and pore size should be selected such that both conduction and convection heat transfer effects can be utilized in such a way that will improve thermal performance of PCM foam composite. Mesalhy et al. [54] performed numerical analysis to investigate the performance of a cylindrical PCM storage having high thermal conductivity porous material. The authors reported an enhanced melting and heat transfer rates in the presence of porous matrix. They also concluded that a lower porosity matrix increases the melting rate and suppresses the convection motion. Chen et al. [55]
experimentally and numerically (using lattice Boltzmann model) studied melting of PCMs (paraffin wax) in aluminum foam (porosity 91.3%) at pore scale. A constant heat flux boundary condition is maintained at one end of the cavity containing the test sample. The experimental results indicated that the metal foam is capable of increasing the heat transfer during melting because of the increased thermal conductivity of the metal matrix. The authors compared their numerical results to that of Jany and Bejan [46] and found good agreement.

The transport processes of nanofluids in porous medium have been a focus of several studies in recent years. In a series of groundbreaking studies, Kuznetsov and Nield [56, 57] and Nield and Kuznetsov [58, 59] proposed mathematical models to study nanofluid transport inside porous medium with thermal instability results for different cases of natural convection. Authors considered Brownian motion and thermophoresis effects in their modeling.

The literature review shows that nanofluid in phase change processes is a relatively new field of study. Very few studies ([39] – [45]) are available in the existing literature. More importantly, these studies produced contradictory results. Furthermore, there is no work in the existing literature that considers NanoPCM embedded in porous medium except Hossain et al. [60]. Hossain et al. [60], in a pioneering work, investigated the thermal performance of an energy storage system filled with a porous medium saturated by a NanoPCM. Nanoparticles of CuO were used to form paraffin-based nanofluids with particle volumetric fractions between 5% and 20%. The enclosure, representing the thermal energy storage system in Hossain et al. [60], considered heated from the top situation with remaining adiabatic walls. As a porous material, aluminum metal foam was used with porosity ranges from 50 to 95%. The 2-D numerical results showed that the movement of PCM melting front is faster with porous medium and NanoPCM combination when compared with an enclosure filled with either NanoPCM or porous medium.

Hossain et al. [60] additionally used scale analysis method in the conduction regime to verify the correctness of the results produced by numerical simulations. Note that in Hossain et al. [60]’s work, the melting process is dominated by conduction heat transfer.

This paper analytically and numerically investigated the melting process and heat transfer characteristics of a porous medium in an enclosure heated from the side and the void space inside the porous medium is occupied by NanoPCM. The objective of the current study is to investigate
the convection effect on the phase change phenomenon of NanoPCM embedded in porous medium.

4.2 Problem Formulation

A rectangular enclosure of size $L \times H$ is considered as shown in Figure 4-1(a). The enclosure is filled with a porous medium and the walls of the enclosure are impermeable. Initially, the void space of the porous medium is filled with a solid phase of NanoPCM. In the current analysis, it is assumed that the initial temperature of the NanoPCM is equal to the fusion temperature ($T_f$) of the NanoPCM. It is further assumed that the local thermal equilibrium exists between the NanoPCM and the porous medium. Two horizontal and right vertical walls of the enclosure are adiabatic. However, the left vertical wall is exposed to a constant temperature heat source with temperature higher than the fusion temperature of the NanoPCM. Thermal energy will start penetrating through the left wall due to the temperature difference and will initiate the phase change process (melting).

**Figure 4-1:** (a) schematic diagram of the problem under consideration, (b) a magnified view of a representative control volume
Initially, heat transfer process is dominated by pure conduction. The melting front, separating the liquid and solid phases of the NanoPCM, remains nearly parallel to the left wall during the initial conduction dominated melting process. As time progresses, the melting front moves to the right gradually. As time progresses further, motion of the liquid NanoPCM will be observed at the top of the melt region followed by a nearly motionless liquid NanoPCM below it. Both conduction and convection heat transfer processes dominate such transition regime of the melting process. The transition regime is characterized by the distinct curvature of the melting front at the upper part of the liquid region (convection dominated) followed by a melting front parallel to the left wall at the lower part of the liquid region (conduction dominated). The height of the convection dominated zone in the transition regime increases as time advances further. At a particular time, the convection dominated zone of the transition regime will fill the entire height of the cavity, which will be the starting point of the convection regime. The natural circulation of the liquid NanoPCM confined between the left vertical wall and right curved melting front is the characteristic feature of this regime. As time progresses further, the upper part of the curved melting front touches the right vertical wall at a particular time. This is the initiation of the variable height regime. The liquid NanoPCM gradually occupies the right vertical wall while shrinking the melting front in size. In summary, two distinct phases (solid phase and liquid phase) of variable amount of NanoPCM exist inside the porous medium for a significant time during the melting process. These phases are separated by a distinct boundary (melting front). Heat transfer occurs in the liquid phase mainly by convection and in the solid phase by conduction. Therefore, the governing equations and material properties are different in liquid and solid phases.

4.2.1 Momentum Equation

Momentum transfer modeling of fluids inside a porous medium is a complex issue. Therefore, the many models proposed in the current literature are mainly empirical in nature and developed based on specific applications and several assumptions. The momentum modeling complexity increases further in the presence of the nano-fluid. However, as for the pioneering work, we propose the Darcy flow model for the porous medium, which establishes a relationship between the flow velocities to the pressure gradient in certain direction inside the porous medium. The momentum equations according to Bejan [61] along the \( x \) and \( y \) directions are
\[ u = -\frac{K}{\mu_n} \frac{\partial p}{\partial x}, \]  

(1)

and

\[ v = -\frac{K}{\mu_n} \left( \frac{\partial p}{\partial y} + \rho_n g \right). \]  

(2)

respectively. In Eq. 1 and 2, \( u, \ v, \ K, \ p, \ g, \ \rho_n, \) and \( \mu_n \) are the velocity component in the \( x \) direction, velocity component in the \( y \) direction, permeability of the porous medium, pressure, gravitational acceleration, density of the NanoPCM, and viscosity of the NanoPCM, respectively. The porous medium is also assumed to be homogeneous; therefore, \( K \) in Eq. 1 and 2 represents the permeability for homogeneous porous medium. For the simplicity of analysis it is assumed in this paper that the liquid phase NanoPCM behaves like a typical nanofluid. In this case, the effective density of the NanoPCM is directly related to properties of the nano-particle and base-PCM and their relative fractions as well. The viscosity of the liquid form of NanoPCM can be approximated using the model proposed by Brinkman [62] applicable to nanofluid. The density and the viscosity of the NanoPCM can be expressed as

\[ \rho_n = (1 - \phi) \rho_f + \phi \rho_p, \]

(3)

\[ \mu_n = \frac{\mu_f}{(1 - \phi)^{2.5}}, \]  

(4)

where, \( \rho_f, \rho_p, \mu_f, \) are \( \phi \) the density of the base-PCM, density of the nano-particle, viscosity of the base-PCM, and volume fraction (volume of the nano-particle/total volume of NanoPCM), respectively. In the limit of small volume fraction (i.e., \( \phi \rightarrow 0 \)), both density and viscosity of the NanoPCM approach to the density and viscosity of the base-PCM. After using the Boussinesq approximation the buoyancy term in the \( y \) -momentum equation can be approximated by

\[ \rho_n g \approx \phi \rho_p g + (1 - \phi) \rho_0 \left( 1 - \beta (T - T_0) \right) g. \]  

(5)

where \( \rho_0 \) is the reference density of the base-PCM and a reference temperature \( (T_0) \) and \( \beta \) is the volumetric thermal expansion coefficient of the base-PCM. The volumetric thermal expansion coefficient of the base-PCM is considered sufficiently large compared to the volumetric thermal expansion coefficient of the nano-particle. Note that when the volumetric thermal expansion
coefficient of the nano-particle is not negligible a different approximation of the buoyancy term is required. Using Eq. 5, the $y$-momentum equation becomes

$$v = -\frac{K}{\mu_n} \left[ \frac{\partial p}{\partial y} + \phi \rho_p g + (1 - \phi) \rho_0 [1 - \beta (T - T_0)] g \right].$$

(6)

A subtraction of the $x$ derivative of Eq. 6 from the $y$ derivative of Eq. 1 results in

$$\frac{\partial u}{\partial y} - \frac{\partial v}{\partial x} = -\frac{K}{\mu_n} \left[ -\frac{\partial}{\partial x} \{ \phi \rho_p g + (1 - \phi) \rho_0 [1 - \beta (T - T_0)] g \} \right].$$

(7)

Introducing the stream function ($u = \frac{\partial \psi}{\partial y}, v = -\frac{\partial \psi}{\partial x}$) to Eq. 7 and performing mathematical simplification results in

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -(1 - \phi) \left( \frac{K \rho_p \beta}{\mu_n} \right) \frac{\partial T}{\partial x}.$$ 

(8)

Equation 8 is the dimensional form of the momentum equation for the liquid NanoPCM inside the porous medium.

4.2.2 Energy Equation

Energy transport by NanoPCM through the porous medium is considered in this section. The porous medium is assumed isotropic and local thermal equilibrium condition is valid. The local thermal equilibrium assumption considers that there is no net heat transfer between NanoPCM and solid matrix (Bejan [61]). Then the governing energy equation inside the porous medium can be derived after integrating energy equations for the solid matrix and NanoPCM inside the pores over the respective areas and with a subsequent addition of two area-averaged equations (Bejan [61]). Applying the methodology described above the following energy equation is obtained for the melt region:

$$\rho_n C_n \frac{\partial T}{\partial t} + \rho_m C_m \left[ \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right] = k_m \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right].$$

(9)

In Eq. 9, the product $\rho_n C_n$ and $\rho_m C_m$ are the heat capacity of the NanoPCM and mean heat capacity of the porous medium, respectively. The products $\rho_m C_m$ and $\rho_n C_n$ can be expressed as
\[ \rho_mC_m = (1-\varepsilon)\rho_sC_s + \varepsilon \rho_nC_n, \quad \rho_nC_n = (1-\phi)\rho_fC_f + \phi \rho_pC_p. \tag{10} \]

where \( \rho_sC_s, \varepsilon, \rho_pC_p, \) and \( \rho_fC_f \) are the heat capacity of the solid matrix, porosity of the porous medium, heat capacity of the nano-particle, and heat capacity of the base-PCM, respectively. The mean thermal conductivity of the porous medium \( (k_m) \) can be expressed as

\[ k_m = \varepsilon k_n + (1-\varepsilon)k_s. \tag{11} \]

where \( k_s \) is the thermal conductivity of the solid matrix and \( \varepsilon \) is the porosity of the porous medium (void volume/total volume). Using the Maxwell’s model [63], the effective thermal conductivity of the NanoPCM \( (k_n) \) can be expressed as

\[ k_n = k_f \left[ \frac{(k_p + 2k_f) - 2\phi(k_f - k_p)}{(k_p + 2k_f) + \phi(k_f - k_p)} \right]. \tag{12} \]

where \( k_f \) and \( k_p \) are the thermal conductivities of base-PCM and nano-particle, respectively.

Note that the Maxwell’s model [63] is good for calculating the effective thermal conductivity of composites with spherical particles and low volume fraction and verified by abundant experimental data [64]. The literature review [64] shows that there exists major inconsistency in the experimental data associated with thermal conductivity of nanofluids. And there is still controversy about the underlying mechanisms of the thermal conductivity enhancement of nanofluids. Therefore, effect of particle size on the thermal conductivity of nanofluids has not been absolutely understood yet and has not been considered in the present study. Murshed et al. [65] discussed about the effect of particle size on the dynamic viscosity of nanofluids. From earlier research, we observe that size of nanoparticles is not included in the theoretical models of nanofluid for calculation of physical properties such as equivalent density and equivalent viscosity [65]. Those properties largely depend on volume fraction of nanoparticles but size of nanoparticle can influence the heat transfer performance by influencing natural convection, Brownian motion, inertia motion as well as gravity motion with the variation of temperature and available surface area of nanoparticles. Size of nanoparticles can affect the preparation of nanofluid, which depends on viscosity of base fluid and density of nanoparticles. Based on the base fluid, the heavier particle can settle at the bottom without mixing with the base fluid during preparation of nanofluid. The literature review finds no studies that consider phase change process of NanoPCM inside porous medium heated from the side. As this is a pioneering work,
we prefer to make the model and analysis less complicated using theoretical models available in the literature. Measuring nanofluid properties and incorporating into the numerical model are left for future work. Note that in the current work it is assumed that the mean dimension of the nanoparticles is order of magnitude lower that the average pores dimension of the porous medium. Therefore, the transport of nanoparticles within the pores will remain uninterrupted. However, this assumption will be relaxed in future work when the size of the nanoparticle is such that a collection of nanoparticle movement is obstructed by the pore. Such case creates a variable and dynamic pore size scenario which may require additional equation/ modeling [66].

Now applying the similar methodology as discussed earlier in Section 4.2.2 one can obtain the energy equation for the region having solid NanoPCM as shown below

$$\rho_{ms} C_{ms} \frac{\partial T}{\partial t} = k_{ms} \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right].$$

(13)

where the subscript ‘$ms$’ represent the thermophysical properties in the region having solid NanoPCM.

The required boundary conditions for the current problem are

- bottom wall ($y = 0$): $v = 0$ and $\frac{\partial T}{\partial y} = 0$  
  (14a)
- top wall ($y = H$): $v = 0$ and $\frac{\partial T}{\partial y} = 0$  
  (14b)
- left wall ($x = 0$): $u = 0$ and $T = T_w$  
  (14c)
- right wall ($x = L$): $u = 0$ and $\frac{\partial T}{\partial x} = 0$  
  (14d)
- melting front ($x = s$): $u = 0$ and $T = T_m$.  
  (14e)

In Eq. 14e, $s$ represents the horizontal distance between the left isothermal wall and melting front. Additionally, an energy balance at the common boundary (i.e., the melting front) between the liquid NanoPCM and solid NanoPCM requires

$$-k_m \left( \frac{\partial T}{\partial x} - \frac{\partial s}{\partial y} \frac{\partial T}{\partial y} \right) = \left[ (1 - \varepsilon) \rho_s h_i + \varepsilon \rho_n h_n \right] \frac{\partial s}{\partial t} \approx \varepsilon \rho_n h_n \frac{\partial s}{\partial t}. $$

(15)
where $h_n$ represents the enthalpy of fusion. Note that in Eq. 15, the density difference of liquid and solid at the melting point is assumed negligible.

The governing equations derived so far are converted into their dimensionless forms to capture important heat transfer parameters and to characterize the phase change process of NanoPCM inside the porous medium. The momentum and energy equations can be converted into their dimensionless forms using the following dimensionless variables:

$$
X = \frac{x}{H}, \quad Y = \frac{y}{H}, \quad S = \frac{s}{H}, \quad \Theta = \frac{T - T_f}{T_w - T_f}, \quad \Psi = \frac{v}{\alpha_m}, \quad U = \frac{u}{\alpha_m}, \quad V = \frac{v}{\alpha_m}.
$$

(16)

After substituting the variables, defined in Eq. 16, into Eq. 8, the dimensionless form of the momentum equation becomes

$$
\frac{\partial^2 \Psi}{\partial X^2} + \frac{\partial^2 \Psi}{\partial Y^2} = -(1 - \phi) \left( \frac{K \rho_o \beta \Delta H T}{\alpha_m \mu_n} \right) \frac{\partial \Theta}{\partial X} = -(1 - \phi) Ra \frac{\partial \Theta}{\partial X}.
$$

(17)

where $Ra$ is the Rayleigh number. Similarly, the dimensionless form of the energy equation in the liquid NanoPCM is

$$
\frac{\partial \Theta}{\partial Fo} + \left[ U \frac{\partial \Theta}{\partial X} + V \frac{\partial \Theta}{\partial Y} \right] = \left[ \frac{\partial^2 \Theta}{\partial X^2} + \frac{\partial^2 \Theta}{\partial Y^2} \right].
$$

(18)

Dimensionless form of the energy equation in the solid NanoPCM is

$$
\frac{\partial \Theta}{\partial Fo} = \Phi \left[ \frac{\partial^2 \Theta}{\partial X^2} + \frac{\partial^2 \Theta}{\partial Y^2} \right].
$$

(19)

In Eq. 19, the dimensionless parameter $\Phi$ can be obtained from following equations:

$$
\Phi = \frac{\Phi_1}{\Phi_2}.
$$

(20a)

$$
\Phi_2 = \frac{\rho_m C_{ms}}{\rho_m C_m} = \frac{[(1 - \epsilon) \rho_s C_s + \varphi_n \rho_n C_n]}{[(1 - \epsilon) \rho_s C_s + \varphi_n \rho_n C_n]} \text{SolidphasePCM} \quad \text{and}
$$

(20b)

$$
\Phi_1 = \frac{k_{ms}}{k_m} = \frac{[\varphi_n k_n + (1 - \epsilon) k_s]}{[\varphi_n k_n + (1 - \epsilon) k_s]} \text{LiquidphasePCM}.
$$

(20c)
It should be noted that a total of three parameters appear in the governing equations, namely, Rayleigh number \( (Ra) \), Fourier number \( (Fo) \), and modified Fourier number \( (\bar{Fo}) \). The definitions of these parameters are given below:

\[
Ra = \frac{K \rho_n \alpha \beta H \Delta T}{\alpha_m \mu_n}, \quad Fo = \frac{\alpha_m t}{H^2}.
\]

\[
\bar{Fo} = \frac{Fo}{\sigma} = \left( \frac{\rho_n C_n}{\rho_m C_m} \right) \left( \frac{\alpha_m t}{H^2} \right), \quad \sigma = \frac{\rho_m C_m}{\rho_n C_n}, \quad \alpha_m = \frac{k_m}{\rho_n C_n}.
\] (21)

Further discussion is required to understand the relative magnitude of the dimensionless parameter \( \Phi \) defined in Eq. (20). To calculate \( \Phi \) thermophysical properties of paraffin is selected as the base PCM, CuO-nanoparticles is used as nanoparticles, and aluminum is considered to be the material for the porous matrix. Using the thermophysical properties (Table 4-1) and considering 10% of nano-particle volume fraction (i.e., \( \phi = 0.1 \)) and 10% porosity of the porous medium (i.e., \( \varepsilon = 0.1 \)), the magnitudes of \( \Phi_1 \) and \( \Phi_2 \) are 0.99 and 1.01, respectively. This gives \( \Phi \approx 0.98 \) in Eq. (20a).

**Table 4-1:** Thermophysical properties of paraffin [40], copper oxide nano-particles [40], and aluminum solid matrix [33, 45]

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg/m³)</th>
<th>Specific heat (J/kg K)</th>
<th>Thermal conductivity (W/m.K)</th>
<th>Latent heat of fusion (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Paraffin</td>
<td>779</td>
<td>1763</td>
<td>0.127</td>
<td>32557</td>
</tr>
<tr>
<td>Solid Paraffin</td>
<td>856</td>
<td>1600</td>
<td>0.136</td>
<td></td>
</tr>
<tr>
<td>Copper oxide (CuO) nano-particles</td>
<td>6310</td>
<td>540</td>
<td>18</td>
<td>-</td>
</tr>
<tr>
<td>Aluminum (Al) solid matrix</td>
<td>2702</td>
<td>903</td>
<td>237</td>
<td>-</td>
</tr>
</tbody>
</table>

Therefore, for any particular combination of \( \phi \) and \( \varepsilon \) which produces \( \Phi \approx 1 \) the dimensionless energy equation in the solid region can be replaced by the dimensionless equation
in the liquid region without the advection term. Therefore, computational efforts can be reduced in case of $\Phi \approx 1$.

The volumetric thermal expansion coefficient of the base-PCM is considered sufficiently large compared to the volumetric thermal expansion coefficient of the nano-particle in the earlier derivations in this paper. When the volumetric thermal expansion coefficient of the nano-particle is not negligible a different approximation for the buoyancy term is required to be used. Considering the volumetric thermal expansion coefficient of the nano-particle, the $y$-momentum equation becomes

$$v = -\frac{K}{\mu_n} \frac{\partial p}{\partial y} - \frac{K}{\mu_n} \rho_n g + \frac{K}{\mu_n} \left[(1 - \phi) \rho_f \beta_f + \phi \rho_p \beta_p \right] \left(T - T_0\right) g .$$  \hspace{1cm} (22)

With some simplifications, Eq. 22 can be rewritten as

$$v = -\frac{K}{\mu_n} \frac{\partial p}{\partial y} - \frac{K}{\mu_n} \rho_n g + \frac{K}{\mu_n} \left[(1 - \phi) + \phi \left(\frac{\rho_p}{\rho_f}\right) \left(\frac{\beta_p}{\beta_f}\right)\right] \rho_f \beta_f \left(T - T_0\right) g .$$  \hspace{1cm} (23)

Using Eq. 23, one can write the stream function form of the momentum equation as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{K}{\mu_n} \left[(1 - \phi) + \phi \left(\frac{\rho_p}{\rho_f}\right) \left(\frac{\beta_p}{\beta_f}\right)\right] \rho_f \beta_f \frac{\partial T}{\partial x} .$$  \hspace{1cm} (24)

or, using the definition of nanofluid’s viscosity, as

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{K}{\mu_n} \left[(1 - \phi) + \phi \left(\frac{\rho_p}{\rho_f}\right) \left(\frac{\beta_p}{\beta_f}\right)\right] \rho_f \beta_f \frac{\partial T}{\partial x} .$$  \hspace{1cm} (25)

Equation 26 below shows the dimensionless form of the modified momentum equation which can be obtained by considering the dimensionless variables already defined in Eq. 16:

$$\frac{\partial^2 \psi}{\partial X^2} + \frac{\partial^2 \psi}{\partial Y^2} = -\left(\frac{K \rho_f g \beta_f H \Delta T}{\alpha_m \mu_n}\right) \left[(1 - \phi) + \phi \left(\frac{\rho_p}{\rho_f}\right) \left(\frac{\beta_p}{\beta_f}\right)\right] \frac{\partial \Theta}{\partial X} .$$  \hspace{1cm} (26)

By substituting $Ra_m = \frac{KH \rho_f \beta_f g \Delta T}{\alpha_m \mu_n}$, Eq. 26 becomes,

$$\frac{\partial^2 \psi}{\partial X^2} + \frac{\partial^2 \psi}{\partial Y^2} = -Ra_m \left[(1 - \phi) + \phi \left(\frac{\rho_p}{\rho_f}\right) \left(\frac{\beta_p}{\beta_f}\right)\right] \frac{\partial \Theta}{\partial X} .$$  \hspace{1cm} (27)
Now the average Nusselt number, which is the dimensionless representative of the measure of the heat transfer, can be calculated from

\[ Nu = \frac{1}{L} \int_0^L \left( \frac{\partial \Theta}{\partial X} \right)_{X=0} dY. \]  

(28)

4.3 Results and Discussions

4.3.1 Scale Analysis

Scale analysis is performed to create order of magnitude estimates for the quantities of interest; for example, the sizes of the relevant time and length scales of four different zones and the heat transfer scales of the natural convection-melting phenomenon of NanoPCM in a porous layer heated from the side. Figure 4-2 shows four distinct regimes of melting obtained through scale analysis for the proposed system.

![Four regime model for scale analysis of melting of NanoPCM in an enclosure filled with porous medium](image)

Figure 4-2: Four regime model for scale analysis of melting of NanoPCM in an enclosure filled with porous medium
4.3.1.1 Conduction Region

It is assumed that the NanoPCM inside the enclosure is initially at its solid phase with uniform temperature which is equal to the melting temperature of the NanoPCM. The left vertical wall is suddenly exposed to a thermal reservoir having a temperature higher than the melting temperature of the NanoPCM. Temperature difference between the wall and the solid NanoPCM drives the thermal energy inside the enclosure which will initiate the melting process. Initially, the melting process is governed by pure conduction [61] which is characterized by a thin liquid layer of NanoPCM near the heated wall. In the conduction dominated region, the conduction heat flux in the thin layer of liquid NanoPCM is completely balanced by the energy absorbed at the interface of the liquid and solid NanoPCM and which can be expressed by

\[ -k_m \frac{dT}{dx} \approx \varepsilon \rho_n h_n \frac{ds}{dt}. \]  \hspace{1cm} (29)

Using the proper scale, Eq. 29 can be expressed as

\[ -k_m \frac{\Delta T}{s} \approx \varepsilon \rho_n h_n \frac{s}{\tau}; \quad \Delta T = T_w - T_f. \]  \hspace{1cm} (30)

Figure 4-3: The shape of the solid region during the fourth regime
Equation 30 can be non-dimensionalized as follows
\[
\left( \frac{s}{H} \right)^2 \sim \frac{k_m (T_w - T_f)}{\varepsilon (\rho_n h_n) H^2} t. \tag{31}
\]
The thickness, \( s \), of the conduction domain can be approximated as
\[
s \sim H \left[ \frac{C_n (T_w - T_f)}{\varepsilon h_n} \right]^\frac{1}{2} \left[ \frac{k_m}{\rho_n C_n H^2} \right]^\frac{1}{2}. \tag{32}
\]
Introducing a dimensionless number Stefan number (\( Ste \))
\[
Ste = \frac{C_n (T_w - T_f)}{\varepsilon h_n}. \tag{33}
\]
and with the definition of \( Fo \) which is the time through which thermal energy diffuses across the distance \( H \) as defined in Eq. 21, Eq. 32 can be written as
\[
s \sim H \times (Ste \times Fo)^\frac{1}{2}. \tag{34}
\]
It is observed from Eq. 32 that the liquid layer thickness in the conduction region depends on time, properties of NanoPCM, and porosity of the porous matrix.

Using Eq. 32, one can obtain a scale of Nusselt number after substituting \( h \sim k_m / s \)
\[
Nu = \frac{hH}{k_m} \sim \frac{H}{k_m} \times \frac{k_m}{\Delta T} \times \frac{\Delta T}{s} \sim \frac{H}{s} \sim (Ste \times Fo)^\frac{1}{2}. \tag{35}
\]
In Eq. 35, the effect of nano-particle volume fraction, \( \phi \) on \( Nu \) is embedded within the definition of \( Ste \) and \( Fo \).

4.3.1.2 Transition/Mixed Region

As time progresses, the initial conduction dominated heat transfer process inside the liquid NanoPCM is gradually replaced by convection. The combined conduction and convection processes in the liquid NanoPCM region are characterized by a slowly circulating liquid having distinct lateral boundary layer of thickness \( \delta_f \) at the top followed by an almost motionless slender liquid at the bottom. In order to obtain time and length scales of the mixed region, we
will follow the approach proposed by Bejan [61]. Mass conservation equation is required to perform the scale analysis in addition to the momentum and energy equations presented earlier.

At the earlier stage of the melting process, the energy equation (Eq. 9) states a balance between inertia and heat conduction into a layer of thickness \( \delta_r(t) \),

\[
\sigma \frac{\Delta T}{t} \sim \alpha_m \frac{\Delta T}{\delta_r^2},
\]

which gives

\[
\delta_r \sim \left( \frac{\alpha_m t}{\sigma} \right)^{1/2}.
\]

From the mass conservation equation [59]

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0.
\]

we get the following relationship

\[
\frac{u}{\delta} \sim \frac{v}{H}.
\]

Now, the scales of three terms appearing in Eq. (7) are

\[
\frac{u}{H} \frac{v}{\delta_r} \left(1 - \phi\right) \frac{Kg \beta \Delta T}{v_n} \frac{1}{\delta_r}.
\]

After dividing all the three terms of Eq. 40 by the second term and using the mass conservation scale (Eq. 39), one obtains

\[
\left( \frac{\delta_r}{H} \right)^2 \sim \left(1 - \phi\right) \frac{Kg \beta \Delta T}{v_n} \frac{1}{\delta_r}.
\]

In case of \( \delta_r < H \), the momentum equation shows a balance between the second and third terms in Eq. 41. This balance results in a vertical velocity scale near the left vertical wall,

\[
v \sim \left(1 - \phi\right) \frac{Kg \beta \Delta T}{v_n} \frac{1}{\delta_r}.
\]
Once this vertical fluid motion is initiated, the energy equation is ruled by three different scales; inertia, convection, and conduction

\[ \sigma \frac{\Delta T}{t} \; v \frac{\Delta T}{H} \; \alpha_m \frac{\Delta T}{\delta^2}. \]  \hspace{1cm} (43)

The time \( t_f \) when the vertical layer becomes convective is given by the balance between inertia and convection, hence

\[ t_f \sim \frac{\sigma H}{v}. \]  \hspace{1cm} (44)

After this time, the boundary layer, \( \delta_T \) will not change with time, hence

\[ \delta_T \sim H \left[(1 - \phi)Ra\right]^{1/2}. \]  \hspace{1cm} (45)

From Eq. 45, the boundary layer thickness scale in the upper zone of the transition region is

\[ \frac{\delta_T}{z_{tr}} \sim [(1 - \phi)Ra_{z_{tr}}]^{1/2} \; \text{or} \; \delta_T \sim z_{tr} \left[(1 - \phi)Ra \frac{z_{tr}}{H}\right]^{1/2}. \]  \hspace{1cm} (46)

where \( Ra_{z_{tr}} = \frac{g \beta \Delta T K z_{tr}}{v_n \alpha_m} \) and \( z_{tr} \) is the vertical height of the upper liquid region which is dominated by convection. Now, in the lower zone of the transition region, the boundary layer thickness scale is the width (~\( s \)) of the conduction dominated zone of height \((H - z_{tr})\). Therefore, using Eq. 35 the boundary layer thickness scale for the lower transition region becomes

\[ z_{tr} \left[(1 - \phi)Ra \frac{z_{tr}}{H}\right]^{-1/2} \sim s \sim H \left(Ste \times Fo\right)^{1/2}. \]  \hspace{1cm} (47)

Using Eq. 47, the scale of the height of the convection dominated upper zone, after some manipulation, becomes

\[ z_{tr} \sim (1 - \phi) \times H \times Ra \times Ste \times Fo. \]  \hspace{1cm} (48)

The mixed regime ends when \( z_{tr} \sim H \). Therefore, Eq. 48 implies that the termination of mixed regime occurs at a time of order

\[ (Ste \; Fo)_1 \sim (1 - \phi)^{-1}(Ra)^{-1} \; \text{or} \; \theta^1 \sim (1 - \phi)^{-1}(Ra)^{-1}. \]  \hspace{1cm} (49)
where $\theta = Ste\ Fo$ is the non-dimensional time and $\theta_1$ is the special case of time scale when the mixed regime ends.

From Eq. 48, it can be observed that $Ra$ comes into play when convection is considered. It is also noticed that $z_{tr}$ (elevation of the upper zone dominated by convection) depends on the height of the cavity, $Ra$, $Ste$, and $Fo$. Unlike the conduction region, the scale of the overall $Nu$ for the transition region is the summation of the conduction and convection heat transfer integrated over the respective height $(H - z_{tr})$ and $z_{tr}$. Using Eq. (48) and $\delta_r/y \sim [(1 - \phi)Ra]^{1/2} \sim (Ste \times Fo)^{1/2}$, the result is

$$Nu \sim \frac{H - z_{tr}}{s} + \int_0^{z_{tr}} \frac{dz}{\delta_r} \sim (Ste \times Fo)^{1/2} + \frac{(1 - \phi) \times H \times Ra \times Ste \times Fo}{H (Ste \times Fo)^{1/2}}. \quad (50)$$

Therefore,

$$Nu \sim (Ste \times Fo)^{1/2} + (1 - \phi)Ra (Ste \times Fo)^{1/2}. \quad (51)$$

In the transition region, $Nu$ is dependent on $Ra$, $Ste$, $Fo$, and $\phi$. From Eq. 51, we see that addition of nano-particle reduces the overall heat transfer.

Equation 48 is valid in the time interval $(0, \theta_1)$. From Eq. 51, we can predict a minimum $Nu$ of order

$$Nu_{\min} \sim (1 - \phi) Ra^{1/2}. \quad (52)$$

and this $Nu_{\min}$ occurs at the end of the mixed conduction and convection regime at a time of order

$$\theta_{\min} \sim \theta_1 \sim [(1 - \phi)Ra]^{-1}. \quad (53)$$
4.3.1.3 Convection Region

It is observed in Eq. 48 that the convection region extends further downwards as time progresses. A faster extension can be obtained at higher $Ra$. At certain point of time for a given $Ra$ and $Ste$, the convection region will touch the bottom of the enclosure which is the starting point of the convection dominated zone. In this region, the progress of melting front and the heat transfer are governed by the two distinct thermal resistances having thickness $\delta_r$. The overall $Nu$ scale using Eq. 45 is

$$Nu \sim \int_0^H \frac{dz}{\delta_r} \sim [(1-\phi)Ra]^{1/2}.$$  \hspace{1cm} (54)

In the convection region, $Nu$ depends only on $Ra$ and $\phi$ is independent of time. The average melting front location for the convection region corresponds to Eq. 54 is

$$S_{av} \sim H[(1-\phi)Ra]^{1/2} Ste Fo.$$ \hspace{1cm} (55)

where

$$S_{av} = \frac{1}{S} \int_0^S d\left(\frac{y}{H}\right).$$ \hspace{1cm} (56)

and

$$dS_{av}/d(Ste Fo) \sim Nu.$$ \hspace{1cm} (57)

The convection region terminates as soon as the interface touches the right wall of the enclosure, i.e., when $S_{av} \sim L$. From Eq. 55, one can obtain a time scale when the convection region ends

$$(Ste Fo)^2 \sim \frac{L}{H} [(1-\phi)Ra]^{1/2} \text{ or } \theta_2 \sim \frac{L}{H} [(1-\phi)Ra]^{1/2}.$$ \hspace{1cm} (58)

If $\theta_2 > \theta_1$, then the convection regime exists, that is when

$$Ra^{1/2} > \frac{H}{L} (1-\phi)^{1/2}.$$ \hspace{1cm} (59)

The mixed conduction and convection regime of Fig. 4-2 terminates at a time of order $\theta_2$ when Eq. 59 is not fulfilled. If Eq. 59 is not satisfied, the $Nu$ vs. $\theta$ or $Ste Fo$ curve has no time to reveal its minimum.
4.3.1.4 Variable Height Region

In this region the height of the liquid-solid interface \((z_H)\) decreases steadily until the solid region disappears entirely. In order to predict the melting process in the variable height region some approximations are necessary. Jany and Bejan [46, 47] described several possible scenarios for the movement of the interface in this region. Using similar approximation [46, 47] one can establish the following relationship for the present problem

\[
Nu_{z_H} \sim (1 - \phi) Ra_{z_H}^{\frac{1}{2}}. \tag{60}
\]

After using following relationships, \(Nu_{z_H} = (z_H / H) Nu\) and \(Ra_{z_H} = (z_H / H) Ra\), Eq. 60 can be approximated as

\[
Nu \sim \left[(1 - \phi) \frac{z_H}{H} Ra \right]^{\frac{1}{2}}. \tag{61}
\]

Now, the time scale will be found when the fourth region expires. The solid is assumed approximately a triangle in which the hypotenuse hinges around the bottom end of the liquid-solid interface as shown in Fig. 4-3. The cross-sectional area of the solid region scales as the product \(lz_H\), where \(l\) is unchanged. In this arrangement, heat transfer from the hot wall through the porous liquid layer is obstructed by two thermal resistances, between the hot wall and the liquid, and between the liquid and the solid-liquid interface. The resistance due to the thermal boundary layer down the hot wall is of order \(Ra^{-\frac{1}{2}}\) and the equivalent resistance down the solid-liquid interface is of order \(Ra_{z_H}^{-\frac{1}{2}}\). The melting front resistance controls the heat transfer rate requires to melt the solid, since \(Ra_{z_H}^{-\frac{1}{2}} > Ra^{-\frac{1}{2}}\). Therefore, the energy balance at the solid-liquid interface becomes

\[
k_m (T_w - T_m) [(1 - \phi) Ra]^{\frac{1}{2}} \sim \varepsilon \rho_n \chi_n \left[\frac{d(z_H)}{dt}\right]. \tag{62}
\]
Since \( z_h \) decreases with time, the minus sign in Eq. 62 is used. Equation 62 can be non-dimensionalized as follows

\[
\frac{H}{l} \left[ (1 - \phi) Ra \right]^\frac{1}{2} \sim -\left( \frac{z_h}{H} \right)^{\frac{1}{2}} \left[ \frac{d}{d\theta} \left( \frac{z_h}{H} \right) \right].
\] (63)

Integrating Eq. 63 from \( \theta \sim \theta_2 \) when \( \frac{z_h}{H} \sim 1 \) yields,

\[
1 - \frac{H}{l} \left[ (1 - \phi) Ra \right]^\frac{1}{2} \left( \theta - \theta_2 \right) \sim \left( \frac{z_h}{H} \right)^{\frac{1}{2}}.
\] (64)

When \( \frac{z_h}{H} \ll 1 \), the solid region disappears entirely at a time \( \theta_3 \) and Eq. 64 becomes

\[
(\theta_3 - \theta_2) \sim \frac{l}{H} \left[ (1 - \phi) Ra \right]^\frac{1}{2}.
\] (65)

In Eq. 65, \( \theta_3 \) is the theoretical estimate of the extent of the complete melting process. A detailed study of calculating the extent of complete melting process in a cylindrical enclosure with vertical pipe in the center can be obtained in a crucial paper by Lorente et al. [67]. Identical expression as Eq. 65 can be derived if we assume that the solid-liquid interface advances as such both \( h \) and \( l \) decrease proportionately instead of \( l \) being fixed. Using Eqs. 64 and 65, Eq. 61 can be further approximated as

\[
Nu \sim \left( \frac{l}{H} \right)^{-1} \left( 1 - \phi \right)^{\frac{1}{2}} Ra Ste Fo.
\] (66)

4.3.2 Numerical Simulation

The governing differential equations presented in Section 4.2 are solved with the initial/boundary conditions and discussed in detail in Section 4.2. The numerical technique to solve the governing equations is available in Mahmud and Pop [68] and is not repeated here. The numerical simulations are performed to identify the followings:
1. To examine the position and shape of the melting front with time.

2. To analyse the conduction, convection, and phase change processes in the proposed thermal storage system.

3. To determine the effect of nanoparticles in the conduction, convection and phase change processes in the proposed thermal storage system.

4. To identify the effect of $Ra$ on the heat transfer and melting of PCM in the thermal storage system.

Furthermore, numerical modeling results will be used to validate the scaling rules developed in the earlier section. The numerical results are presented in two parts: In the first part, melting of NanoPCM in a square thermal storage system has been investigated. In the second part, melting results in a rectangular enclosure have been presented.

4.3.2.1 Melting in a Square Enclosure

The heat transfer process inside the Paraffin PCM with and without the CuO nanoparticles is qualitatively presented at different $Ra$ in Figs. 4-4 and 4-5. The numerical modeling considers the melting process inside the porous aluminum foam where the void space is occupied by the NanoPCM (Paraffin + CuO nanoparticles). Note that the porosity and permeability are two important parameters to describe a porous medium. Permeability and porosity appear in the momentum and energy equations, respectively. However, because of the non-dimensional approach applied to the governing equations, both parameters are embedded inside dimensionless numbers. The dimensionless parameters considered in this study are $Ra$, $Fo$, $Fo$, $Ste$, and $\phi$. Effects of these parameters on the heat transfer will be presented in this section.
Figure 4-4: Patterns of isotherms, heat flux vectors, and melting front in the melting process of PCM with and without nanoparticles for $Ste \times Fo = 0.1$
Figure 4-5: Patterns of isotherms, heat flux vectors, and melting front in the melting process of PCM with and without nanoparticles for $Ste \times Fo = 0.07$.
For $Ste \times Fo = 0.1$, Fig. 4-4 shows the isothermal lines, heat flux vectors, and the location of the melting front at three different $Ra$ (0, 5, and 12.5) with and without nano particles. The effect of conduction heat transfer is observed by the equidistant isothermal lines that are almost parallel to the left vertical wall at $Ra=5$. The horizontal heat flux vectors show the direction of conduction heat transfer from the high temperature region to the low. This heat flux is responsible for the phase change process in the conduction regime.

As $Ra$ increases (for example, from 5 to 12.5) convection mechanism starts dominating over conduction and distinct motion of the fluid occurs. Therefore, isothermal lines are not parallel anymore to the left vertical wall being observed in the case of conduction dominated heat transfer process. The heat flux vectors are not horizontal near the left vertical wall as well. At $Ra = 50$ (Fig. 4-5), dominance of convection intensifies. The isothermal lines are observed crowded near the bottom of the left vertical wall compared to the top, meaning high heat transfer at the bottom. This is the evidence of the appearance of a distinct thermal boundary layer. Melted PCM at the bottom of the left vertical wall becomes heated as it comes into contact with that part of the wall, moves upward and turns to the right. As the warm liquid PCM comes into contact with the relatively cold solid PCM to the right, the solid starts to melt at relatively faster rate. Because of the heat transfer between the liquid and solid, the warm liquid becomes cooler, descends and completes the circulation. That is how the circulation of the liquid PCM continues until all the solid PCM melts. Because of the thermal stratification warmer layers of liquid PCM remains at the upper part of the enclosure. Therefore, a relatively wider melting region is observed at the top of the cavity and the width of the liquid PCM region gradually decreases towards the downward direction. As time advances further, the melting process continues and the liquid PCM at the upper part of the cavity will touch the right vertical wall. The melting front will descend along the right vertical wall to finish the melting process (partially shown in Fig. 4-6). The motion of the liquid PCM can be better understood by observing the streamlines as shown in Figs. 7 and 8 and will be discussed later.
Figure 4-5 further depicts how the melting front shape changes as $Ra$ increases. As $Ra$ increases (50 and higher in Fig. 4-5), convection intensifies and dominates the heat transfer or melting of solid PCM. A lower melting rate is observed toward the bottom of the enclosure, since the liquid cools down as it descends along the interface. Now the right column of Figs. 4-4 and 4-5 show the effects of the presence of nanoparticles on the melting of NanoPCM qualitatively. The isothermal lines, heat flux vectors, and the location of the melting front are presented at $\phi=0.1$ and $Ste \times Fo = 0.44$. Similar results have been obtained for other values of $\phi$ and not shown here. Figure 4-4 shows that the melting of PCM is unchanged when nanoparticles are added at low $Ra$ ($Ra = 5$ and 12.5) i.e., in the conduction region. It is observed from the scale analysis in the conduction region (Eq. (35)) that the solid liquid interface moves further to the right inside the enclosure for the cases when $Ste$ is larger provided that $Fo$, $H$, and $Ra$ are constant. In the current study the porous medium property is unchanged. Therefore, in this case in Eq. (35), $Ste$ can be increased or decreased depending on the properties of NanoPCM. Depositing nanoparticles in the PCM increases thermal conductivity but decreases the heat capacity of the NanoPCM which ultimately keeps $Ste$ almost constant. And hence, the width of the melt layer remains unchanged in the conduction regime. Therefore, scale analysis validates the numerical results. The width of the melt layer is lower when nanoparticles are added to the PCM at higher $Ra$ ($Ra = 50$ and higher in Fig. 4-5). At higher $Ra$, convection starts to dominate the heat transfer and so does the melting. When nanoparticles are added to the PCM, the enhancement of
viscosity and density of the NanoPCM increases the resistance to convection heat transfer and hence the reduction in PCM melting process.

Figures 4-7 and 4-8 illustrate the effect of nanoparticles on fluid motion by streamline contours and the location of the melt fraction with and without nanoparticles at five different $Ra$ (5, 12.5, 50, 100, and 200). Corresponding isothermal lines are added to demonstrate how fluid motion changes the thermal field. There is no change in the streamline pattern when nanoparticles are added to the PCM at a constant $Ste$ and $Fo$. Figures 4-7 and 4-8 show that the maximum stream function values decrease when nanoparticles are added to the base PCM. The decrease in stream function values is an indication of the reduction of liquid PCM motion when nanoparticles are added. The reason is described earlier and also can be explained by the definition of $Ra$ in Eq. (21). Equation (21) shows that when nanoparticles are added to the PCM, the effective $Ra$ decreases because of the increase of the thermal diffusivity, $\alpha_m$, compared to the base PCM case. Figure 4-8 shows that the streamline patterns and the propagation of the melting front change with $Ra$. A noticeable feature of Fig. 4-7 is that the streamline patterns at the core of the enclosure are oval shape at lower $Ste Fo$. At higher $Ste Fo$, this oval shape changes to circular in Fig. 4-6 (b).
Figure 4-7: Effect of $\phi$ on the patterns of streamlines in the melting process of PCM $Ste \times Fo = 0.1$
Figure 4-8: Effect of $\phi$ on the patterns of streamlines in the melting process of PCM at $Ste \times Fo = 0.07$

The effect of using modified momentum equation, Eq. (27) to stream function contours is shown in Fig. 4-9. When thermal expansion coefficient of nanoparticle is not negligible compared to the base fluid, a higher maximum stream function values are observed in Fig. 4-9, meaning increase in fluid motion.
Figure 4-9: Effect of considering Eq. (27) on streamlines at $\phi = 0.1$
Figure 4-10 shows $Nu$ as functions of $Ste \times Fo$ and $Ra$. In Fig. 4-10, the present simulation results without nanoparticles are compared to that of Janny and Bejan [46] at $Ra=12.5$ and $50$. A very good agreement is obtained between the present results to that of Janny and Bejan [46]. The filled square symbol on each curve represents the time when the interface touches the right vertical wall.

![Graph showing Nu as functions of Ste Fo and Ra](image)

**Figure 4-10:** The $Nu$ is plotted as functions of $Ra$ and $Ste \times Fo$ at $H/L=1$ and compared with numerical results of Jany and Bejan [46]

Figure 4-11 illustrates the effects of $Ra$ and $\phi$ on $Nu$. $Nu$ inversely depends on $Ste \times Fo$ in the conduction regime (Eq. 35). Therefore, as $Ste \times Fo$ increases, $Nu$ decreases. Figure 4-11 shows that $Nu$ departs from the absolute conduction case when $Ra$ becomes 50. In the conduction regime, addition of nanoparticles to the PCM does not change the $Nu$, which is also supported by
the unchanged melting front location in Figs. 4-4 (a), (b), and (c). The scale analysis (Eq.35) further supports and validates this result. In the transition and convection regimes, as nanoparticles are added, $Nu$ decreases which is supported by the stream function values in Figs. 4-7 and 4-8 and the scale analysis by Eqs. (51) and (54). Therefore, scale analysis supports and validates the numerical results. Figures 4-10 and 4-11 are for a $Ra$ range of 12.5 to 200. At these low $Ra$ values the mixed conduction and convection regime of melting ends at a time of order $\theta_2$ (Eq. (58)) which is lower than $\theta_1$ (Eq. (53)). At higher $Ra$, the $Nu$ vs. $Ste Fo$ curve will show all the four regions of melting. In conclusion, convection regime of melting does not exist in Figs. 4-10 and 4-11. Figure 4-10 shows three regimes of melting: conduction followed by mixed conduction and convection, and variable height regimes. In the fourth regime, the $Nu$ vs. $Ste Fo$ curve in Fig.4-10 shows a downward trend. And Fig. 4-11 shows two regimes of melting: conduction and mixed conduction and convection. The variable height regime starts right after mixed conduction and convection regime ends which is not shown in this figure. From Fig. 4-10, we can estimate times for each regime of melting corresponding to each $Ra$. For $Ra = 12.5$, conduction will end at approximately 0.02, mixed conduction and convection at 0.385, and variable height regime or melting will end at 0.49. As $Ra$ increases from 12.5 to 50, the approximate dimensionless time reduces from 0.49 to 0.3.
Figure 4-11: The $Nu$ is plotted as functions of $Ra$, $\phi$, and $Ste \times Fo$ at $H/L=1$.

Figure 4-12 shows $Nu/Ra^{1/2}$ for a range of $Ra$ 12.5-200 at different $Ste \times Fo$. This figure validates Eq. (54) which is developed by the scale analysis for the convection regime. In Fig. 4-12, the $Nu/Ra^{1/2}$ ratio is close to 0.5 for the range of $Ra$ considered. The value of $Nu/Ra^{1/2}$ is 0.577 for convection regime in a rectangular porous medium [46]. Therefore, Fig. 12 further demonstrates that heat transfer by natural convection in porous media is qualitatively similar to what is examined during melting in enclosures with NanoPCM embedded in porous media. There is no significant change in $Nu$ values when modified momentum equation, Eq. (27) is used.
Figure 4-12: The $Nu$ scaling law: $Nu \sim Ra^{0.5}$ in the convection regime at $H/L=1$

4.3.2.2 Melting in a Rectangular Enclosure

Figure 4-13 shows the isothermal lines, heat flux vectors, melt fraction location, and streamlines for a rectangular cavity of aspect ratio $H/L = 2$. From Fig. 4-13, it is apparent that the $Ra=12.5$ case corresponds to a situation controlled by conduction heat transfer. And the isothermal lines appear to depart from conduction solution at a $Ra = 50$, which is also observed for a square cavity. Comparisons between Fig. 4-5 and Fig. 4-13 show that isothermal lines and the shape of the melting front vary as the shape of the enclosure changes. The patterns of streamlines in Fig. 4-13 further reveal the effect of shape of the cavity when compared with Fig. 4-8. Addition of nanoparticles decreases the maximum stream function values and reduces the width of the melt front as observed earlier for a square enclosure at a fixed $Ra$. 

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(a) $Ra=12.5, \phi = 0$

(b) $Ra=50, \phi = 0$

$Ra=12.5, \phi = 0.1$

$Ra=50, \phi = 0.1$
Figure 4-13: Patterns of isotherms, heat flux vectors, melting front, and streamlines in the melting process of PCM without nanoparticles at $Ste \times Fo = 0.1$ and $AR=2$
4.4 Conclusions

The scale analysis and its numerical counterpart presented in the current study explain the melting phenomenon in a rectangular enclosure occupied by a porous medium and saturated with NanoPCM. The effect of heat transfer by natural convection in porous media is qualitatively similar to what is examined during melting in enclosures with NanoPCM embedded in porous media. The main features of the melting phenomenon are explained on the basis of both scale analysis and numerical simulations. The scale analysis shows that the melting of the entire NanoPCM passes through a sequence of four regimes (Fig. 4-2), and that each regime has its own $Nu$ and melting front location scaling rules. The scaling laws are validated by the numerical modeling results. The numerical results are presented in terms of isothermal lines, heat flux vectors, location of melting front, streamlines, and the $Nu$ as functions of $Ra$ and $Ste Fo$. The numerical results and scaling analysis show that both conduction and convection heat transfer in a rectangular cavity are degraded by the presence of nano-particles. The location of melting front shows that melting of PCM is prolonged when nano-particles are added. The scale analysis calculates the extent of the entire phase change process, which is essential in the design of LHTES systems.

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Nomenclature

$A$ aspect ratio of the cavity, $H/L$

$C_m$ mean specific heat, $J/kg\,^\circ C$

$C_{ms}$ mean specific heat in the region having solid NanoPCM, $J/kg\,^\circ C$

$C_n$ specific heat of NanoPCM, $J/kg\,^\circ C$

$C_s$ specific heat of the solid matrix, $J/kg\,^\circ C$
gravitational acceleration, \( \text{m/s}^2 \)

Fourier number, \( \alpha_m \frac{t}{H^2} \)

enthalpy of fusion of NanoPCM, \( \text{J/kg} \)

convective heat transfer coefficient, \( \text{W/m}^2 \text{°C} \)

height of the cavity, \( \text{m} \)

permeability of the porous medium, \( \text{m}^2 \)

thermal conductivity of base-PCM, \( \text{W/m°C} \)

mean thermal conductivity, \( \text{W/m°C} \)

thermal conductivity of nano-particle, \( \text{W/m°C} \)

width of the enclosure, \( \text{m} \)

Nusselt number

pressure, \( \text{Pa} \)

heat transfer through the left wall of the enclosure, \( \text{W} \)

Rayleigh number, \( K \rho_0 g \beta \Delta T / \alpha_m \mu_n \)

Rayleigh number in the transition region, \( g \beta \Delta T K z_n / \nu_n \alpha_m \)

horizontal distance from the heated wall to the melting front, \( \text{m} \)

dimensionless horizontal distance from the heated wall to the melting front, \( s/H \)

Stefan number, \( C_n (T_w - T_f) / \varepsilon h_n \)

temperature, \( \text{°C} \)

a reference temperature, \( \text{°C} \)

melting temperature, \( \text{°C} \)

wall temperature, \( \text{°C} \)

time, \( \text{s} \)

velocity component in \( x \)-direction, \( \text{m/s} \)

velocity component in \( y \)-direction, \( \text{m/s} \)

dimensionless horizontal distance, \( x/H \)
$Y$  dimensionless vertical distance, $y/H$

$U$  dimensionless horizontal velocity, $uH/\alpha_m$

$V$  dimensionless vertical velocity, $vH/\alpha_m$

$z_{tr}$  vertical height of the upper liquid region dominated by convection in the transition region

**Greek symbols**

$\varepsilon$  porosity of the porous medium (=void volume/total volume of porous medium)

$\beta$ or $\beta_f$  volumetric thermal expansion coefficient of the base-PCM, $1/K$

$\beta_p$  volumetric thermal expansion coefficient of the nano-particle, $1/K$

$\psi$  stream function, $m^2/s$

$\Psi$  dimensionless stream function, $\psi/\alpha_m$

$\rho_f$  density of the base-PCM, $kg/m^3$

$\rho_m$  mean density, $kg/m^3$

$\rho_{ms}$  mean density in the region having solid NanoPCM, $kg/m^3$

$\rho_n$  density of the NanoPCM, $kg/m^3$

$\rho_0$  reference density of the base-PCM and a reference temperature $T_0$

$\rho_p$  density of the nano-particle, $kg/m^3$

$\rho_s$  density of the solid matrix, $kg/m^3$

$\mu_n$  viscosity of the NanoPCM, $Ns/m^2$

$\mu_f$  viscosity of the base-PCM, $Ns/m^2$

$\phi$  volume fraction (=volume of the nano-particle/total volume of NanoPCM)

$\alpha_m$  thermal diffusivity of NanoPCM porous medium, $m^2/s$,  $k_m/\rho_n C_n$

$\Delta T$  temperature difference, $(T_w - T_f)$, °C

$\sigma$  capacity ratio, $\rho_mC_m/\rho_n C_n$

$\Theta$  dimensionless temperature difference, $(T - T_f)/(T_w - T_f)$
4.5 References


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Chapter 5: Conduction Model - Isoflux

A Nanoparticle-enhanced phase change material contains high thermal conductivity nanoparticles, which are assumed to be dispersed uniformly into the phase change material. The inclusion of the nanoparticles improves the effective value of thermal conductivity of the nanoparticle-enhanced phase change material (or NanoPCM) [1]. The effective heat transfer rate of NanoPCM can be improved further by incorporating a porous medium. This chapter reports thermal performance of an energy storage system filled with a porous medium and the void space inside the porous medium is occupied by a NanoPCM. A 2-D enclosure is considered to replicate energy storage system. Two vertical walls and the bottom wall of the enclosure are properly insulated. The top surface of the enclosure is exposed to a heat source to generate enough heat for melting the PCM. The effect of the volume fraction of nanoparticle and porosity of the porous medium are studied on temperature distribution, melt rate, and melting distance inside the cavity. A two dimensional thermal model is developed for both solid and liquid fractions of the NanoPCM. The modeled equations are solved for exact solutions using initial, boundary, and interface conditions.

5.1 Introduction

Chapter 3 reports the conduction only model for isothermal boundary conditions of an energy storage system filled with a porous medium and the void space inside the porous medium is occupied by a NanoPCM. For isothermal boundary condition, one wall is maintained higher than the melting temperature of the PCM. As the melting front moves further with time, thermal resistance grows according to the Fourier law of conduction. To maintain the constant temperature on the hot wall, heat flux adjusts to balance the higher thermal resistance. This chapter creates a model for constant heat flux boundary conditions where the hot wall temperature changes with time for increasing thermal resistance as the melting front moves on. This model uses the approach of the same geometric model used for Chapter 3. The model is created by combining three different models:
- **Isoflux conduction model for solid PCM**: This model is based on conduction physics without phase change for constant heat flux boundary conditions to find out the time needed for the hot wall to reach the melting temperature of the PCM.

- **Isoflux conduction model with phase change upto melting front**: This model includes both phase change and conduction physics where constant heat flux boundary condition is used on the hot wall and melting temperature boundary condition is at the interface of melting front.

- **Isothermal conduction model for solid PCM beyond melting front**: This model uses conduction physics beyond the melting front inside the solid region of PCM. Constant temperature boundary conditions of melting and ambient temperature are applied at the interface of melting front and at the end of the solid PCM respectively to find out the temperature distribution inside the solid PCM.

From the exact solution of these three models, results are compared with the experimental results of Chapter 6 discussed in the following chapter.

### 5.2 Model Development

The following four models are developed for formulating the problem of phase change material with constant heat boundary conditions:

1) **Models for equivalent thermophysical properties**: Models for thermal conductivity, specific heat, latent heat of fusion and density are discussed.

2) **Model before phase change**: This model identifies the time for melting temperature on hot wall. It uses conduction heat transfer only with constant heat flux boundary condition at the hot wall.

3) **Phase change model**: This is the main model used for temperature distribution and melting rate of phase change material. This model uses conduction heat transfer along with phase change physics for constant heat flux boundary condition.

4) **Model beyond melting front**: This model uses conduction heat transfer only with constant temperature boundary condition of melting temperature at the interface of melting front.
5.2.1 Model Development: Equivalent Thermophysical Properties

The model is used to calculate the equivalent property of density, specific heat, thermal conductivity, thermal diffusivity and latent heat of fusion for solid and liquid phase of nanoparticle with PCM (NanoPCM), PCM with porous medium (PCM-Foam) and NanoPCM with porous medium (NanoPCM-Foam).

5.2.1.1 Liquid NanoPCM

The equivalent density, specific heat and heat of diffusion are obtained from arithmetic mean of mixture theory [2].

The density of liquid NanoPCM, \( \rho_{nf1} \) can be expressed as

\[
\rho_{nf1} = (1 - \phi) \rho_{f1} + \phi \rho_{np}.
\]

where \( \rho_{f1} \) and \( \rho_{np} \) are the density of liquid base PCM and nanoparticle respectively, and \( \phi \) is the volume fraction of nanoparticles in base PCM.

The specific heat of liquid NanoPCM, \( C_{nf1} \) can be expressed as

\[
C_{nf1} = (1 - \phi) C_{f1} + \phi C_{np}.
\]

where \( C_{f1} \) and \( C_{np} \) are the specific heat of liquid base PCM and nanoparticle.

The thermal conductivity of the liquid NanoPCM \( (k_{nf1}) \) can be adopted from the Maxwell’s model [3] as shown below

\[
k_{nf1} = k_{f1} \left[ \frac{(k_{np} + 2k_{f1}) - 2\phi(k_{f1} - k_{np})}{(k_{np} + 2k_{f1}) + \phi(k_{f1} - k_{np})} \right].
\]

where \( k_{f1} \) and \( k_{np} \) are the thermal conductivities of liquid base PCM and nanoparticle respectively. Though Maxwell’s model [3] does not account for interfacial thermal resistance but it is found good for predicting the effective thermal conductivity of composites with spherical particles and verified by abundant experimental data.
The thermal diffusivity of the liquid NanoPCM ($\alpha_{nf1}$) is defined as

$$\alpha_{nf1} = \frac{k_{nf1}}{\rho_{nf1}C_{nf1}}.$$  \hspace{1cm} (4)

The latent heat of fusion of NanoPCM, $h_{nf}$ can be expressed as

$$h_{nf} = \frac{(1-\phi)\rho_{f1} \times h_f}{\rho_{nf1}}.$$  \hspace{1cm} (5)

where $h_f$ is the latent heat of fusion of base PCM.

5.2.1.2 Solid NanoPCM

The density of solid NanoPCM, $\rho_{nf2}$ can be expressed as

$$\rho_{nf2} = (1-\phi)\rho_{f2} + \phi\rho_{np}.$$  \hspace{1cm} (6)

where $\rho_{f2}$ is the density of solid base PCM.

The specific heat of solid NanoPCM, $C_{nf2}$ can be expressed as

$$\rho_{nf2}C_{nf2} = (1-\phi)\rho_{f2}C_{f2} + \phi\rho_{np}C_{np}.$$  \hspace{1cm} (7)

where $C_{f2}$ is the specific heat of solid base PCM.

The thermal conductivity of the solid NanoPCM ($k_{nf2}$) can be adopted from the Maxwell’s model [3] as shown below

$$k_{nf2} = k_f \left[ \frac{(k_{np} + 2k_{f2}) - 2\phi(k_{f2} - k_{np})}{(k_{np} + 2k_{f2}) + \phi(k_{f2} - k_{np})} \right].$$  \hspace{1cm} (8)

where $k_{f2}$ is the thermal conductivities of solid base PCM.
The diffusivity of the solid NanoPCM ($\alpha_{nf2}$) is defined as

$$\alpha_{nf2} = \frac{k_{nf2}}{\rho_{nf2}C_{nf2}}.$$  \hspace{1cm} (9)

5.2.1.3 Liquid PCM- Foam

The equivalent density, specific heat and heat of diffusion are obtained from arithmetic mean of mixture theory [2].

The density of liquid PCM-Foam, $\rho_{sf1}$ can be expressed as

$$\rho_{sf1} = \varphi \rho_f + (1 - \varepsilon) \rho_s,$$ \hspace{1cm} (10)

where $\rho_s$ is the density of solid part of foam and $\varepsilon$ is the porosity (volume of the porous portion of foam /total volume of porous medium) of foam.

The specific heat of liquid PCM-Foam, $C_{sf1}$ can be expressed as

$$\rho_{sf1}C_{sf1} = \varphi C_f + (1 - \varepsilon) \rho_s C_s.$$ \hspace{1cm} (11)

where $C_s$ is the specific heat of solid portion of foam.

Because of the complex structure of the porous medium, it is better to measure the equivalent thermal conductivity of the porous medium filled with PCM experimentally. For simplicity, equivalent thermal conductivity is calculated theoretically from parallel conduction model of porous medium and PCM through arithmetic mean [4], which is widely used in the literature.

The thermal conductivity of the liquid PCM-Foam ($k_{sf1}$) is defined as

$$k_{sf1} = \varphi k_f + (1 - \varepsilon) k_s.$$ \hspace{1cm} (12)

where $k_s$ is the thermal conductivity of solid part of foam.

The thermal diffusivity of the liquid PCM-Foam ($\alpha_{sf1}$) is defined as

$$\alpha_{sf1} = \frac{k_{sf1}}{\rho_{sf1}C_{sf1}}.$$ \hspace{1cm} (13)
The latent heat of fusion of PCM-Foam, $h_s$ can be expressed as

$$h_s = \frac{\varphi f_1 \times h_f}{\rho_{sf1}}.$$  \hspace{1cm} (14)

5.2.1.4 Solid PCM- Foam

The density of solid PCM-Foam, $\rho_{sf2}$ can be expressed as

$$\rho_{sf2} = \varphi f_2 + (1 - \varepsilon) \rho_s .$$  \hspace{1cm} (15)

The specific heat of solid PCM-Foam, $C_{sf2}$ can be expressed as

$$\rho_{sf2} C_{sf2} = \varphi f_2 C_f + (1 - \varepsilon) \rho_s C_s .$$  \hspace{1cm} (16)

The thermal conductivity of the solid PCM-Foam ($k_{sf2}$) is defined as

$$k_{sf2} = \varepsilon k_f + (1 - \varepsilon) k_s .$$  \hspace{1cm} (17)

The thermal diffusivity of the solid PCM-Foam ($\alpha_{sf2}$) is defined as

$$\alpha_{sf2} = \frac{k_{sf2}}{\rho_{sf2} C_{sf2}} .$$  \hspace{1cm} (18)

5.2.1.5 Liquid NanoPCM-Foam

The density of liquid NanoPCM-Foam, $\rho_{snl}$ can be expressed as

$$\rho_{snl} = \varphi n_1 + (1 - \varepsilon) \rho_s .$$  \hspace{1cm} (19)

The specific heat of liquid NanoPCM-Foam, $C_{snl}$ can be expressed as

$$\rho_{snl} C_{snl} = \varphi n_1 C_n + (1 - \varepsilon) \rho_s C_s .$$  \hspace{1cm} (20)

The thermal conductivity of the liquid NanoPCM-Foam ($k_{snl}$ ) is defined as

$$k_{snl} = \varepsilon k_n + (1 - \varepsilon) k_s .$$  \hspace{1cm} (21)
The thermal diffusivity of the liquid NanoPCM-Foam \((\alpha_{sn1})\) is defined as
\[
\alpha_{sn1} = \frac{k_{sn1}}{\rho_{sn1} C_{sn1}}.
\] (22)

The latent heat of fusion of NanoPCM-Foam, \(h_{sn}\) can be expressed as
\[
h_{sn} = \frac{\varphi_{n1} \times h_n}{\rho_{sn1}}.
\] (23)

5.2.1.6 Solid NanoPCM- Foam

The density of solid NanoPCM-Foam, \(\rho_{sn2}\) can be expressed as
\[
\rho_{sn2} = \varphi_{n2} + (1 - \varepsilon) \rho_s.
\] (24)

The specific heat of solid NanoPCM-Foam, \(C_{sn2}\) can be expressed as
\[
\rho_{sn2} C_{sn2} = \varphi_{n2} C_{n2} + (1 - \varepsilon) \rho_s C_s.
\] (25)

The thermal conductivity of the solid NanoPCM-Foam \((k_{sn2})\) is defined as
\[
k_{sn2} = \varphi_{n2} k_{n2} + (1 - \varepsilon) k_s.
\] (26)

The thermal diffusivity of the solid NanoPCM-Foam \((\alpha_{sn2})\) is defined as
\[
\alpha_{sn2} = \frac{k_{sn2}}{\rho_{sn2} C_{sn2}}.
\] (27)
5.2.1.7 Relationship between base PCM, NanoPCM, PCM-Foam and NanoPCM-Foam

Table 5-1 shows the relationship between base PCM, NanoPCM, PCM-Foam and NanoPCM-Foam based on the volume fraction ($\phi$) and porosity ($\varepsilon$).

Table 5-1: Relationship based on volume fraction ($\phi$) and porosity ($\varepsilon$)

<table>
<thead>
<tr>
<th>Volume Fraction ($\phi$)</th>
<th>Porosity ($\varepsilon$)</th>
<th>Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>NanoPCM-Foam($sn$)=Base PCM ($f$)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>1</td>
<td>NanoPCM-Foam($sn$)=NanoPCM ($nf$)</td>
</tr>
<tr>
<td>0</td>
<td>$\varepsilon$</td>
<td>NanoPCM-Foam($sn$)=NanoPCM ($sf$)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>$\varepsilon$</td>
<td>NanoPCM-Foam($sn$)</td>
</tr>
</tbody>
</table>

(28)

5.2.2 Model Development: Model for Melting Temperature

The model at 5.2.3 discussed later assumes constant melting temperature at the interface of melting front. Phase change begins after the hot wall reaches higher than the melting temperature. This model helps to predict the time needed for hot wall to reach more than melting temperature before phase change begins. The model is developed based on transient one-dimensional heat transfer with in a semi-infinite solid where constant heat flux applied on hot wall.

5.2.2.1 Problem Formulation

A rectangular enclosure of width $L$ and height $H$ shown schematically in Fig. 5-1(a) represents a simplified thermal energy storage system. The enclosure, bounded by impermeable walls, is filled with a porous medium. A solid phase of NanoPCM completely fills the void space of the porous medium inside the enclosure. It is assumed that the local thermal equilibrium exists between the NanoPCM and the porous medium. Therefore, at any time, temperatures of the NanoPCM and the porous matrix are equal at any representative control volume. All the walls of
the enclosure are properly insulated except the top horizontal wall, which is exposed to a heat source with constant heat flux. Because of the temperature gradient caused by the thermal resistance associated with the enclosure, thermal energy will start flowing from top to bottom. Such penetration of the thermal energy will create a temperature distribution from top to bottom for various times.

5.2.2.2 Governing Energy Equation

This section describes the energy transport by NanoPCM through the porous medium. The porous medium is assumed isotropic and local thermal equilibrium condition is valid. The local thermal equilibrium assumption ensures that temperatures of the solid matrix and solid NanoPCM are same in a given control volume and the net heat transfer rate between NanoPCM and solid matrix is negligible [5]. Then the governing energy equation is obtained by integrating the energy equation for the solid matrix over the area occupied by the solid matrix and integrating the NanoPCM’s energy equation over the area occupied by the NanoPCM inside the pores, followed by a subsequent addition of two area averaged equations and simplifications [5].
Applying the methodology described above the following energy equation is obtained:

\[
\rho_2 C_2 \frac{\partial T}{\partial t} = k_2 \frac{\partial^2 T}{\partial x^2}.
\]  

(29)

where the subscript "2" represent the thermophysical properties of solid phase of base PCM, NanoPCM, PCM-Foam NanoPCM-Foam matrix.

\[
\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha_2} \frac{\partial T}{\partial t}.
\]  

(30)

where the subscript "2" stands for solid phase of base PCM, NanoPCM, PCM-Foam NanoPCM-Foam matrix.

The required boundary conditions for the current problem are

- bottom wall \((x \to \infty; t > 0): T = T_i\) (31)

  where \(T_i\) is the initial temperature of the enclosure

- top wall \((x \to 0; t > 0): q'' = -k_2 \frac{\partial T}{\partial x}\) (32)

  where \(q''\) is the constant heat flux imposed on top wall.

A dimensionless similarity parameter, \(\eta\), which is function of \((x,t)\), is introduced to convert the dimensionless PDE equation of Eq. 30 into ODE. \(\eta\) is obtained by scale analysis but the similar expression is found in literature [6].

\(\eta\) is expressed as

\[
\eta = \frac{x}{2\sqrt{\alpha_2 t}}.
\]  

(33)

The boundary conditions can be written as

- at \(x \to \infty; \eta \to \infty: T = T_i\). (34)

- at \(x \to 0; \eta \to 0: q'' = -k_2 \frac{\partial T}{\partial x}\). (35)
After substituting \( \eta \) into Eq. 30, the PDE diffusion equation transforms into ODE equation and is shown as

\[
\frac{\partial^2 T}{\partial \eta^2} + 2\eta \frac{\partial T}{\partial \eta} = 0. \tag{36}
\]

The solution of Eq. 36 is found as

\[
T = A \left[ \frac{\sqrt{\pi}}{2} \text{erf} (\eta) \right] + B. \tag{37}
\]

Applying boundary condition of Eq. 34 and Eq. 35 into Eq. 37:

\[
A = -\frac{2q^* \sqrt{\alpha_z t}}{k_2}
\]

\[
B = T_i + \frac{q^* \sqrt{\pi \alpha_z t}}{k_2}
\]

Substituting \( A, B \) and \( \eta \) of Eq. 33, the solution of Eq. 37 becomes

\[
T_{(x,t)} = T_i + \frac{q^* \sqrt{\pi \alpha_z t}}{k_2} \text{erfc} \left( \frac{x}{2\sqrt{\alpha_z t}} \right). \tag{38}
\]

Equation 38 is the temperature distribution inside the solid.

By substituting \( x = 0 \) and \( T = \text{Melting temperature (} T_f \) of PCM, time of melting temperature on the hot wall can be calculated. This model is valid only to predict the time of melting temperature on hot wall when no phase change occurs.

The final solution for temperature distribution of this model is found different from the solution found in only one literature [7]. As the literature provides only the solution without any detailed procedure, the author of this research is convinced to proceed with the solution developed in this model.
5.2.3 Model Development: Model for Moving Interface of Phase Change

The model used in section 5.2.2 is developed to predict the time at which temperature of hot wall reaches the melting temperature. There is no exact solution found yet for this problem [8]. Most of the existing approximate solution is obtained for steady state conduction problem. The author tries to develop a model for exact solution using the same enclosure used in section 5.2.2 but includes both solid and liquid phase to observe the movement of melting interface inside the enclosure.

5.2.3.1 Problem Formulation

A rectangular enclosure of width $L$ and height $H$ shown schematically in Fig. 5-2(a) represents a simplified thermal energy storage system. The internal and external energy exchange condition is same as section 5.2.2.1. All the walls of the enclosure are properly insulated except the top horizontal wall, which is exposed to a heat source with constant heat flux. Initially, the distance of melting front is assumed as "$s$" at $x > 0$ and the melting temperature is assumed at the melting interface of PCM. The temperature distribution from the melting interface to the end of solid phase is discussed by the development of another model in the section 5.2.4. Because of the temperature gradient caused by the thermal resistance inside the enclosure, thermal energy will start flowing from top to bottom. The energy will store in the form of phase change because of latent heat during melting and in the form of sensible heat within the liquid for any temperature change during heat flow from top to bottom.
Applying the methodology described in section 5.2.2.2, the following energy equation is obtained:

$$\rho_i C_i \frac{\partial T}{\partial t} = k_i \frac{\partial^2 T}{\partial x^2}. \quad (39)$$

where the subscript "1" represents the thermophysical properties of liquid phase of base PCM, NanoPCM, PCM-Foam and NanoPCM-Foam matrix.

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha_i} \frac{\partial T}{\partial t}. \quad (40)$$

where "1" stands for liquid phase of base PCM, NanoPCM, PCM-Foam and NanoPCM-Foam matrix.
The required boundary conditions for the current problem are

At the melting interface \( x \to s ; t > 0 \): \( T = T_f \) \hspace{1cm} (41)

where \( T_f \) is the melting temperature of the PCM.

Top wall \( x \to 0 ; t > 0 \): \( q'' = -k_1 \frac{\partial T}{\partial x} \) \hspace{1cm} (42)

where \( q'' \) is the constant heat flux imposed on top wall.

A dimensionless parameter \( \eta \), which is function of \((x,t,\alpha_t)\), is introduced to convert the dimensionless PDE equation of Eq. 30 into ODE.

\( \eta \) is expressed as

\[ \eta = \frac{x}{2 \sqrt{\alpha_t t}}. \] \hspace{1cm} (43)

The boundary conditions of Eq. 41 and eq. 42 can be written as using Eq. 43

at \( x \to s ; \eta \to \frac{s}{2 \sqrt{\alpha_t t}} = \lambda \): \( T = T_f \) \hspace{1cm} (44)

where \( \lambda \) is a constant for melting distance \( s \).

at \( x \to 0 ; \eta \to 0 : q'' = -k_1 \frac{\partial T}{\partial x} \) \hspace{1cm} (45)

After substituting \( \eta \) into Eq. 40, the PDE diffusion equation transforms into ODE equation and is shown as

\[ \frac{\partial^2 T}{\partial \eta^2} + 2\eta \frac{\partial T}{\partial \eta} = 0. \] \hspace{1cm} (46)

The solution of Eq. 36 is found as

\[ T = A \left[ \frac{\sqrt{\pi}}{2} \text{erf}(\eta) \right] + B. \] \hspace{1cm} (47)
Applying boundary condition of Eq. 44 into Eq. 47

\[ T_f = A \sqrt{\frac{\pi}{2}} \text{erf}(\lambda) + B. \] (48)

Applying boundary condition of Eq. 45 into Eq. 47

\[ A = -\frac{2q'' \sqrt{\alpha_x t}}{k_1}. \] (49)

Substituting \( A \) from Eq. 49 into Eq. 48

\[ B = T_f + \frac{2q'' \sqrt{\alpha_x t}}{k_1} \text{erf}(\lambda). \] (50)

After substitution of \( A \) and \( B \) from Eq. 49 and Eq. 50, Eq. 47 becomes

\[ T - T_f = \frac{q'' \sqrt{\pi \alpha_x t}}{k_1} [\text{erf}(\lambda) - \text{erf}(\eta)]. \] (51)

Applying energy balance at the melting interface,

\[ q'' = k_1 \frac{\partial T}{\partial x} \bigg|_{x=s} = \rho_s h \frac{dx}{dt} \bigg|_{x=s}. \] (52)

where \( h \) is the latent heat of fusion of PCM, NanoPCM, PCM-Foam and NanoPCM-Foam.

After manipulation, Eq. 52 becomes

\[ s = \frac{2q'' t}{\rho_s h}. \] (52)

where \( s \) is the melting distance for any given time, \( t \).

Substitution of \( s \) from Eq. 52 into Eq. 44 gives

\[ \lambda = \frac{q''}{\rho_s h} \sqrt{\frac{t}{\alpha_1}}. \] (53)
After Substitution of $\lambda$ from Eq. 53 and $\eta$ from Eq. 43, Eq. 51 becomes

$$T_{(s,t)} = T_f + \frac{q'' \sqrt{\pi \alpha_1 t}}{k_1} \left[ \text{erf} \left( \frac{q''}{\rho_1 h \sqrt{\alpha_1 t}} \right) - \text{erf} \left( \frac{x}{2 \sqrt{\alpha_1 t}} \right) \right].$$

Equation 54 is the exact solution for temperature distribution of phase change for constant heat flux during melting and the model is valid up to melting distance "s".

5.2.4 Model Development: Model beyond Melting Front (Solid Phase of PCM)

The model developed in section 5.2.3 is valid up to melting distance "s" as the model assumes constant melting temperature at the melting interface and beyond inside the solid region. The temperature distribution inside the solid region beyond the melting front can be predicted by assuming constant wall temperature of "$T_f$" at "s" and initial temperature of "$T_i$" at "H".

5.2.4.1 Problem Formulation

A rectangular enclosure of width $L$ and height $H$ shown schematically in Fig. 5-3(a) represents a simplified thermal energy storage system. The internal and external energy exchange condition is same as section 5.2.2.1. All the walls of the enclosure are properly insulated except the wall of melting front at melting distance "s" maintained at the melting temperature of "$T_f$". Initially, the distance of melting front at "s" is assumed as $x = 0$ and the temperature distribution between "s" to "H" occurs due to energy flow from hot wall to cold wall.
Applying the methodology described in section 5.2.2.2, the following energy equation is obtained:

\[ \rho_2 C_2 \frac{\partial T}{\partial t} = k_2 \frac{\partial^2 T}{\partial x^2}. \]  

(55)

where the subscript "2" represents the thermophysical properties of liquid phase of base PCM, NanoPCM, PCM-Foam and NanoPCM-Foam matrix.

\[ \frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha_2} \frac{\partial T}{\partial t}. \]  

(56)

where "2" stands for liquid phase of base PCM, NanoPCM, PCM-Foam and NanoPCM-Foam matrix.
The required boundary conditions for the current problem are

At the melting interface ( \( X \to s; x \to 0 \) and \( t > 0 \)): \( T = T_f \)  

(57)

where \( T_f \) is the melting temperature of the PCM

Bottom wall ( \( X \to H - s; x \to \infty \) and \( t > 0 \)): \( T = T_i \)  

(58)

where \( T_i \) is the ambient/initial temperature

For simplicity, a dimensionless temperature, \( \theta \) is introduced

\[
\theta = \frac{T_{(x,t)} - T_i}{T_f - T_i}.
\]

(59)

For dimensionless temperature, \( \theta \), boundary conditions of Eq. 57 and 58 become

At the melting interface ( \( X \to s; x \to 0 \) and \( t > 0 \)): \( \theta = 1 \)  

(60)

Bottom wall ( \( X \to H - s; x \to \infty \) and \( t > 0 \)): \( \theta = 0 \)  

(61)

After substitution of \( \theta \), Eq. 56 becomes

\[
\frac{\partial^2 \theta}{\partial x^2} = \frac{1}{\alpha_t} \frac{\partial \theta}{\partial t}.
\]

(62)

A dimensionless parameter \( \eta \), which is function of \( (x, t, \alpha_t) \), is introduced to convert the dimensionless PDE equation of Eq. 62 into ODE.

\( \eta \) is expressed as

\[
\eta = \frac{x}{2\sqrt{\alpha_t} t}.
\]

(63)

The boundary conditions of Eq. 60 and Eq. 61 can be written as

at \( x \to 0 \); \( \eta \to \frac{x}{2\sqrt{\alpha_t} t} = 0 \): \( \theta = 1 \)  

(64)

at \( x \to \infty \); \( \eta \to \frac{x}{2\sqrt{\alpha_t} t} = \infty \): \( \theta = 0 \)  

(65)
After substituting $\eta$ into Eq. 62, the PDE diffusion equation transforms into ODE equation and is shown as

$$\frac{\partial^2 \theta}{\partial \eta^2} + 2\eta \frac{\partial \theta}{\partial \eta} = 0. \tag{66}$$

The solution of Eq. 66 is found as

$$\theta = A \int_0^\eta e^{-\eta'} d\eta + B. \tag{67}$$

Applying boundary condition of Eq. 64 into Eq. 67

$$B = 1. \tag{68}$$

Applying boundary condition of Eq. 65 into Eq. 67

$$A = -\frac{2}{\sqrt{\pi}}. \tag{69}$$

Substitution of $B$ and $A$ from Eq. 68 and Eq. 69 into Eq. 67 gives

$$\theta = -\frac{2}{\sqrt{\pi}} \int_0^\eta e^{-\eta'} d\eta + 1. \tag{70}$$

The definition of error function is written as

$$erf(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx. \tag{71}$$

Using the definition of error function of Eq. 71, Eq. 70 can be written as

$$\theta = -erf(\eta) + 1$$

$$\theta = erfc(\eta). \tag{72}$$
Substituting $\theta$ from Eq. 59 and $\eta$ from Eq. 63, Eq. 72 is found as

$$\frac{T_{(x,t)} - T_i}{T_f - T_i} = \text{erfc}\left(\frac{x}{2\sqrt{\alpha_t}}\right).$$

$$T_{(x,t)} = T_i + \left(T_f - T_i\right)\text{erfc}\left(\frac{x}{2\sqrt{\alpha_t}}\right).$$  (73)

Equation 73 is the temperature distribution equation for any $x$ or $t$ from melting front to the end of solid region for constant temperature boundary condition. The exact solution of this model is found similar to the solution of the existing literature [7].

5.2.5 Models Comparison

Table 5-2 shows the model developed for various boundary conditions.

<table>
<thead>
<tr>
<th>Case of Model</th>
<th>Boundary Condition</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>For predicting time of melting</td>
<td>Constant Heat Flux $x \rightarrow \infty; t &gt; 0: T = T_i$</td>
<td>$T_{(x,t)} = T_i + \frac{q''}{k_2} \frac{\sqrt{\pi \alpha_t}}{2} \text{erfc}\left(\frac{x}{2\sqrt{\alpha_t}}\right)$</td>
</tr>
<tr>
<td>temperature on hot wall</td>
<td>$x \rightarrow 0; t &gt; 0:$</td>
<td>$q'' = -k_2 \frac{\partial T}{\partial x}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For temperature distribution</td>
<td>Constant Heat Flux $x \rightarrow s; t &gt; 0: T = T_f$</td>
<td>$T_{(x,t)} = T_f + \frac{q''}{k_1} \sqrt{\frac{\pi \alpha_t}}$</td>
</tr>
<tr>
<td>and melting distance of PCM</td>
<td>$(x \rightarrow 0; t &gt; 0):$</td>
<td>$\left[\text{erf}\left(\frac{q''}{2\sqrt{\alpha_t}}\right) - \text{erf}\left(\frac{x}{2\sqrt{\alpha_t}}\right)\right]$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$s = \frac{2q''t}{\rho_i h}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>For Temperature distribution</td>
<td>Constant Temperature $X \rightarrow s; x \rightarrow 0; t &gt; 0$</td>
<td>$T_{(x,t)} = T_i + \left(T_f - T_i\right)\text{erfc}\left(\frac{x}{2\sqrt{\alpha_t}}\right)$</td>
</tr>
<tr>
<td>from melting front to end of solid</td>
<td>$T = T_f$</td>
<td></td>
</tr>
<tr>
<td>region</td>
<td>$X \rightarrow H - s; x \rightarrow \infty$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$t &gt; 0 T = T_i$</td>
<td></td>
</tr>
</tbody>
</table>
5.3 Results and Discussion

This section discusses the results of all three models developed in this chapter and compares the combined results of all three models with the experimental results discussed in Chapter 6.

5.3.1 Model-1: Melting Time on Hot Wall

Using the data of Table 3-1, 0.5% volume fraction of nanoparticles and 95% porosity of porous medium, Fig. 5-4 shows the temperature distribution inside the solid NanoPCM-Foam when the hot wall temperature becomes melting temperature of 52°C (325K).

Figure 5-4: Temperature distribution inside the solid PCM to obtain melting temperature on Hot Wall
From the Fig. 5-4, it is found that linear distribution is observed up to 0.2m. After that, temperature decreases rapidly and reaches a plateau after 0.6m.

Figure 5-5 shows the time needed for hot wall to reach the melting temperature of 52°C (325 K) with NanoPCM-Foam. It takes hot wall 3568 seconds to reach melting temperature of 52°C (325 K) with constant heating.

**Figure 5-5**: Time to reach melting Temperature on hot wall

After 3568 seconds, the hot wall temperature will be over melting temperature and the phase change will begin. During phase change, the temperature distribution will follow the model developed in section 5.2.3.
5.3.2 Model-2: Modeling of Phase Change Region

The model of section 5.3.1 is developed with the thermophysical properties for liquid phase. Therefore, the model is valid up to the melting interface for melting distance of $s$. Beyond the melting interface, the temperature distribution inside the solid region may not be found accurate from that model as the model does not capture the thermophysical properties of solid PCM. Beyond the melting interface, the model developed in the section 5.2.4 can be applied for temperature distribution inside the solid region with the assumption of constant hot wall temperature as melting temperature of PCM at the melting interface.

Using the data of Table 3-1, 0.5% volume fraction of nanoparticles and 95% porosity of porous medium, Fig. 5-6 shows the temperature distribution inside the phase change region. The temperature distribution up to the melting temperature of 325K for PCM shows the melting distance of the phase change material. The melting distance is observed as 0.05m.
From the Fig. 5-6, it is found that linear distribution is observed up to 0.25m. After that, temperature decreases rapidly and reaches a plateau after 0.85m.

Figure 5-7 shows the melting time for various positions of melting front. It takes melting front 205 minute to reach melting distance of 90mm with an average speed of 7.3μm/sec. 90 mm is the enclosure distance used for the experiment in Chapter 6.
5.3.3 Model-3: Modeling of Solid Region Beyond Melting Front

Model-2 is valid for melting distance of "s" where the interface temperature is maintained at the melting temperature of PCM. Beyond the melting interface, the temperature distribution inside the solid region is predicted based on the model developed at section 5.2.4 for constant melting temperature at the melting interface with the thermophysical properties of solid PCM.
Figure 5-8 shows the temperature distribution inside the solid region for constant wall temperature maintained at the melting temperature of PCM. From the Fig. 5-8, it is found that linear distribution is observed up to 0.35m. After that, temperature decreases rapidly and reaches a plateau after 0.85m.

![Temperature distribution](image)

**Figure 5-8:** Temperature distribution inside the solid region

Figure 5-9 demonstrates the temperature distribution of Model-2, 3 and their combination. From combination of two models, the temperature distribution inside phase change region follows the distribution of Model-2 up to the melting front at 0.05m; beyond the melting front in solid region, the temperature distribution follows the distribution of Model-3.
5.3.4 Comparison of Model with Experimental Data

The model is compared with the experimental data of Chapter 6 for melting rate and the temperature profile at a particular distance of melting interface. The temperature profile at melting interface of 0.02m is used for verification.

Figure 5-10 compares the melting rate of model and experimental data. The time to reach hot wall temperature more than the melting temperature of phase change material is obtained from Model-1 and this time is added to the melting time of Model-2 during melting.
Figure 5-10: Validation of model with experimental data for melting rate

Linear relationship of melting rate is obtained for both model and experimental data. The model overpredicts the experimental data up to the melting distance of almost 20mm. The average overprediction is observed as 3.6% and this may be because of heat loss during the initial stage of experimental heating as perfect thermal insulation is difficult to obtain. Beyond the melting interface of 20mm, the model underpredicts the experimental data. The average rate of underprediction is 10.9% and this underprediction may be caused by the leakage of liquid through the weep holes of experimental setup. These weep holes accommodate volumetric expansion of liquid PCM during the phase change from solid to liquid. As a result, a fine air gap is formed between the heating plate and phase change material (PCM). This air gap creates a thermal resistance higher than that of phase change material and results in higher melting time beyond the melting front of 20 mm during melting.
Figure 5-11 shows the temperature profile of melting interface at 20mm for the model and experiment during the entire duration of experiment (240 minute).

Initial stage of melting, the temperature of model overpredicts the experiment may be because of heat loss during the experimental heating as perfect thermal insulation is difficult to obtain. Later stage of the melting, the model underpredicts the experiment. This may be caused by the leakage of liquid through the weep holes of experimental setup. These weep holes accommodate volumetric expansion of liquid PCM during the phase change from solid to liquid. As a result, a fine air gap is formed between the heating plate and phase change material (PCM).

Figure 5-11: Temperature profile at 20mm of melting interface for model and experiment
This air gap creates a thermal resistance higher than that of phase change material and results in higher temperature of the experiment. The difference between model and experiment may grow further for increasing distance of melting interface because of higher thermal resistance.

5.4 Conclusion

Three models are created to predict the temperature distribution inside the phase change region with the assumption of constant heat flux boundary condition. First model is based on conduction heat transfer through the solid PCM without any phase change and it assumes constant heat flux on the hot wall to find out the time needed for the hot wall to reach more than the melting temperature of phase change region. Second model includes the physics of both phase change and conduction heat transfer with the boundary conditions of constant heat flux on the hot wall and melting temperature at the melting interface to predict the temperature distribution inside the phase change region. Third model uses conduction physics only beyond the melting front inside the solid phase of PCM with constant melting temperature of phase change material at the interface and initial temperature maintained at the end of the solid PCM. This model is used to find out the temperature distribution inside the solid PCM. From the exact solution of these three models, temperature distribution and interface movement rate are predicted for NanoPCM with porous medium. Results are compared with the experimental results discussed in Chapter 6 for heating from top of NanoPCM with porous medium where heat transfers only through conduction. The model over predicts the experimental data during the initial stage of the melting by 3.6% and under predicts the experimental data during the later stage of the melting by 10.9% due to heat loss and leakage of liquid PCM respectively.
5.5 References


Chapter 6: Experimental Research

6.1 Introduction

Development of analytical or numerical model deals with the fundamental physics and is based on assumptions. The physics should be relevant and the assumptions should capture the real life situations. The validation of model with experimental study is very important to have better confidence of the model which can later be used for parametric analysis or optimization purpose as the cost of experiment is very expensive [1]. The model can be validated with the already published experimental work [2-12] but it is very difficult to find the exact match of experimental data for any pioneering work which is discussed in Chapter 2 in details. In the literature, the experimental data of base PCM [13-14], PCM with porous medium [2-5] or nanofluid/NanoPCM (nanoparticle with PCM) [6-12] or found but there is no experimental data available for NanoPCM with porous medium. Moreover, it is very difficult to have confidence of the published data because of the inconsistency/uncertainty associated with the experimental data [2-14]. For this reason, a detailed experimental work is carried out to validate the model developed in Chapter 5 and acquire sufficient data for evaluating the ability of the models to accurately predict the thermal and fluid characteristics of NanoPCM in porous media.

6.2 Experimental Design

An experimental program is designed to observe the temperature response and melting/freezing front movement of PCM, NanoPCM, PCM in porous medium and NanoPCM in porous medium. Experiment deals with various parameters:

- One sample of PCM
- NanoPCM with various volume fractions (0.25%, 0.5%, 1%, 2% and 4%)
- One sample of porous medium.
- For observing the conduction, convection and mixed convection characteristic, each experiment is carried out for bottom, top and side heating.
6.3 Materials and Methods

This section covers the following items:

- Materials: PCM, nanoparticle and porous medium
- Preparation: NanoPCM, PCM in porous medium and NanoPCM in porous medium
- Experimental setup
- Instrumentation
- Data acquisition, Visualization and Recording

6.3.1 Materials: PCM, nanoparticle and porous medium

6.3.1.1 PCM

The selection of PCM from various phase change materials for energy storage application depends on their melting and freezing temperatures correspond to the particular application and operating temperature [14]. It is important to have desired thermophysical, kinetic, chemical and economic properties of PCM for a particular application. The melting temperature of PCM should be according to the need of application [13]. PCM should melt consistently with minimum sub-cooling and it should be chemically stable, low in cost, non-toxic, and non-corrosive. The materials exhibiting most of these properties can be used as PCM for the experiment. For this research work, a paraffin wax of melting temperature 52-55°C is selected as the phase change material. The melting temperature of 52-55°C is above the common ambient temperature and it is compatible with wide variety of application such as transient application of solar cells, microelectronics and space applications [13]. Moreover, paraffin is a popular choice for most of the existing studies which is helpful for further comparison to the previous studies. The paraffin used for this experiment is collected from SIGMA-ALDRICH, Canada [15]. Table 6-1 shows the thermophysical properties of paraffin wax.
Table 6-1: Thermophysical properties of paraffin [1]

<table>
<thead>
<tr>
<th>Property</th>
<th>Solid</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density [kg/m$^3$]</td>
<td>856</td>
<td>779</td>
</tr>
<tr>
<td>Specific Heat [J/kg.K]</td>
<td>1600</td>
<td>1763</td>
</tr>
<tr>
<td>Thermal Conductivity [W/m.K]</td>
<td>0.136</td>
<td>0.127</td>
</tr>
<tr>
<td>Latent Heat [J/Kg]</td>
<td>32557</td>
<td></td>
</tr>
<tr>
<td>Melting Temperature [°C]</td>
<td>52-54</td>
<td>-</td>
</tr>
<tr>
<td>Viscosity at 50°C [cp]</td>
<td>-</td>
<td>3.28</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion [1/K]</td>
<td>120e-6</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6-1 indicates that a significant density change occurs during the phase change from solid phase of 856 kg/m$^3$ to liquid phase of 779 kg/m$^3$. The density of solid phase is almost 10% higher than the liquid phase. This density difference results in the volume expansion of PCM during the liquid phase which corresponds to the almost of 10% cavity inside the test container when the PCM becomes solid. Figure 6-1 shows the sample paraffin.

![Sample paraffin](image)

Figure 6-1: Sample paraffin
6.3.1.2 Nanoparticle

A nanoparticle is an ultrafine particle measured in nanometres (nm) which in metric system is same as one-billionth of a meter \((10^{-9} \text{m})\) [16]. In general, the sizes of these ultrafine particles are in the range of 1 nm to several hundred nanometres depending on materials. There is no accepted international definition of a nanoparticle and the term ‘nanoparticle’ is utilized to refer to particles of size between 10nm to 100nm [16]. Depending on size (diameter), they are also known as fine particles covering 100-2,500 nm range [16] while ultrafine particles have dimensions 1-100 nm [16]. Due to unique properties, nanoparticles of different materials are used for various applications of engineering and science [16]. In engineering field, nanoparticles are employed to improve mechanical and thermal properties of materials for different applications such as thermal performance improvement of heat transfer fluids, strength enhancement for materials used in vehicles and space-crafts, improving lubricating properties of oils, etc. [16].

The selection of nanoparticles is based on several parameters such as thermal conductivity, particle size, cost, volume fraction and type of base fluid etc. [17]. Particle size is an important parameter because particles settle down to nano scale increases the surface area relative to volume and provide better dispersion into the base PCM [17]. Experimental evidence indicates that effective thermal conductivity increases with decrease in particle size. Moreover, time required for melting is higher for nanoparticles with higher concentration (or volume fraction) than base PCM or nanoparticles with lower concentration (or volume fraction) [17]. This is because dynamic viscosity increases significantly with nanoparticle of higher volume fraction and enhancement in dynamic viscosity plays an important role in lowering the performance of natural convection dominated melting of nanoparticle mixed with PCM. In case of natural convection dominated heat transfer rate in melting process, the higher viscosity reduces the buoyancy effect significantly and slows down the melting process [17]. In this research, copper nanoparticle with an average diameter of 35nm is used to improve the thermal performance of paraffin used as a base fluid. The copper nanoparticle is purchased from Nanostructured and Amorphous Materials (NANOAMOR), Inc. [18]. Table6-2 shows the thermophysical properties of copper nanoparticle.
Table 6-2: Thermophysical properties of copper nanoparticle [3]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size [nm]</td>
<td>35</td>
</tr>
<tr>
<td>Density [kg/m$^3$]</td>
<td>8933</td>
</tr>
<tr>
<td>Specific Heat [J/kg.K]</td>
<td>385</td>
</tr>
<tr>
<td>Thermal Conductivity [W/m.K]</td>
<td>401</td>
</tr>
</tbody>
</table>

Figure 6-2 shows the picture of sample copper nanoparticles.

![Image of copper nanoparticles](image)

**Figure 6-2: Sample copper nanoparticle (35nm)**

6.3.1.3 Porous Medium (Metal Foam)

Porous structure is available in various materials such as aluminum, copper, graphite etc. [19]. The selection of porous medium depends on material properties such as thermal conductivity, density etc. and structural properties such as porosity and pore size. Although the lower porosity provides higher effective thermal conductivity but it dampens the fluid motion for buoyancy driven flow and lowers the natural convection heat transfer within the liquid [19]. Open-cell light-metallic foams are popular choice for impregnation of phase change material for its density of high surface-area and strong capability of mixing. This research uses aluminum foam with pore size of 10 ppi (pores per inch) and 95% porosity from ERG Aerospace, California, USA [20]. Table 6-3 shows the thermophysical properties of aluminum foam.
Table 6-3: Thermophysical properties of aluminum Foam [21]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size [ppi]</td>
<td>10</td>
</tr>
<tr>
<td>Porosity</td>
<td>95%</td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>2702</td>
</tr>
<tr>
<td>Specific Heat [J/kg.K]</td>
<td>903</td>
</tr>
<tr>
<td>Thermal Conductivity [W/m.K]</td>
<td>237</td>
</tr>
</tbody>
</table>

Figure 6-3 shows the picture of sample aluminum foam.

![Sample aluminum foam (95% porosity)](image)

**Figure 6-3:** Sample aluminum foam (95% porosity)

6.3.2 Sample Preparation: NanoPCM, PCM and NanoPCM in porous medium

6.3.2.1 NanoPCM

The preparation of NanoPCM needs to ensure the condition of stability, no chemical change, and low agglomeration of particles. These characteristics of NanoPCM can be obtained by (1) the addition of acid or base to change the pH of the suspension or (2) addition of some surfactants to disperse particles into fluid and/or (3) the use of vibration [22]. In practical applications, it is expected to stabilize the particles with suitable third agent (surfactant) such as oleic acid or laurate salts but this experiment ignores the addition of any additive and uses the technique of vibration only. This is because of the fact that the time required for the experiments...
is much less than the time required for the first sedimentation to occur. Moreover, the addition of the third agent may influence the thermophysical properties of base fluid itself and thus hinder the real enhancement by using nanoparticles [23]. If the settlement of nanoparticles does not occur within three hours, the nanofluid is assumed as a stable fluid for the experiment [22]. Normally, the nanofluid used for the experiment does not settle in one day. If it settles before three hours, the nanofluid is not considered for the experiments [22]. In order to maintain consistency, the nanofluid immediately after vibration is used for each experiment so that there is no chance of sedimentation during 1.5 to 2 hours of experiment [23].

The NanoPCM samples are prepared by mixing desired amount of Cu nanoparticles into the liquid base PCM, which is Paraffin. The mass of nanoparticles for a particular volume fraction is used to prepare each sample. Equation 1 is used to calculate the mass of nanoparticles.

\[
\phi_{np} = \frac{V_{np}}{V_{np} + V_{paraffom}} = \frac{V_{np}}{V_{Nano-pcm}},
\]

where, \( \phi_{np} \) is volume fraction of nanoparticle, \( V_{Nano-pcm} \) is total volume of the NanoPCM sample, \( \rho_{np} \) is the density of nanoparticle and \( m_{np} \) is the mass of nanoparticle for a particular volume fraction.

\[
m_{np} = \phi_{np} \times V_{Nano-pcm} \times \rho_{np}
\]

The Smart Weigh Digital Precision Scale [24] (Fig. 6-4) is used to measure the weight of copper nanoparticle. This scale can weigh up to 2kg within accuracy of 1 milligram.
Table 6-4 shows the mass of copper nanoparticle needed to prepare the desired volume fraction of NanoPCM. It also demonstrates the corresponding weight fraction (concentration) of the nanoparticle in NanoPCM.

Table 6-4: The Mass of nanoparticle for various volume fractions

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{Nano-PCM}$ [mL]</th>
<th>$\phi_{np}$ [%]</th>
<th>$V_{np}$ [mL]</th>
<th>$\rho_{np}$ [kg/m$^3$]</th>
<th>$m_{np}$ [gm]</th>
<th>$\rho_{paraffin}$ [kg/m$^3$]</th>
<th>$m_{paraffin}$ [gm]</th>
<th>$w_{np}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0.25</td>
<td>0.25</td>
<td>8933</td>
<td>2.2</td>
<td>779</td>
<td>77.7</td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>0.5</td>
<td>0.5</td>
<td>8933</td>
<td>4.5</td>
<td>779</td>
<td>77.5</td>
<td>5.4</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>1.0</td>
<td>1.0</td>
<td>8933</td>
<td>8.9</td>
<td>779</td>
<td>77.1</td>
<td>10.4</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>2.0</td>
<td>2.0</td>
<td>8933</td>
<td>17.9</td>
<td>779</td>
<td>76.3</td>
<td>19.0</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>4.0</td>
<td>4.0</td>
<td>8933</td>
<td>35.7</td>
<td>779</td>
<td>74.8</td>
<td>32.3</td>
</tr>
</tbody>
</table>

The preparation of NanoPCM uses a Scilogex [25] 86143101 Model MS-H280-Pro LED Circular-Top Digital Magnetic Hot Plate Stirrer with 5.3" Diameter Ceramic Coated Plate and magnetic stirrer bar (Fig. 6-5). The hot plate of stirrer can be heated up to 360°C and magnetic stirrer bar can rotate up to 1500 rpm.
Figure 6-5: Magnetic hot plate stirrer and magnetic Stirrer Bar

The digital temperature display of magnetic hot plate stirrer provides the temperature of the ceramic hot plate but the stirrer is also supplied with a temperature sensor, which can display the temperature of the solution when it is connected to the magnetic stirrer. It is important to maintain the temperature of solution above the melting temperature of the paraffin to have proper mixing of base PCM (liquid paraffin) and copper nanoparticle without any phase transformation from liquid to solid. The temperature of solution is maintained at 70°C as the melting temperature of paraffin is found as 52-54°C.

Most of the nanoparticles are pyrophoric substance [18], which ignites spontaneously in the air at or below 55°C. The handling of elemental metal nanoparticles needs special care. The nanoparticles are kept inside a plastic bag with vacuum inside in order to avoid any contact with air. Nanoparticles are recommended to handle in Argon atmosphere only. In case of air, it is suggested to make several small openings on bag corner to allow for a slow contact of air. If the powder heats up, it is recommended to fold the opening corner to stop contacting with air, wait until it cools down, open it; repeat the above until there is no heating up. It is suggested to stay for 4 hours to allow for a full passivation so that it can be ready to use at ambient temperature in air. It is mandatory to wear gloves, breathing mask and safety glass during handling of nanoparticles in order to avoid skin contact, inhalation and eye contact of nanoparticle [26].
Figure 6-6 displays the five samples of NanoPCM prepared for the experiment from paraffin and nanoparticles with volume fraction of 4%, 2%, 1%, 0.5% and 0.25%. Unfortunately, the liquid NanoPCM with volume fraction of 4% and 2% was found very thick like clay so that it was very difficult to pour liquid NanoPCM inside the aluminum foam. As a result, NanoPCM with volume fraction of 4% and 2% are excluded from the plan of experiment and experiments are planned to carry out with the volume fraction of 1%, 0.5% and 0.25%.

Figure 6-6: The Samples of NanoPCM
6.3.2.2 PCM and NanoPCM in Porous Medium

The PCM or NanoPCM is completely melted and maintained at a temperature higher than the melting temperature of PCM or NanoPCM before pouring into the aluminum foam of 90mmx77mmx14mm placed inside an enclosure. Prior to filling the foam, each foam module is preheated to a temperature higher than the melting temperature of PCM or NanoPCM in order to prevent the solidification of the PCM or NanoPCM at initial foam contact. Liquid PCM or NanoPCM is then poured into the heated foam. Extreme care is taken to fill the foam slowly and completely. The larger pore size of aluminum foam results in an easier filling process. Figure 6-7 shows the foam filled with PCM and NanoPCM.

![Figure 6-7: Foam Filled with PCM and NanoPCM](image)

6.3.3 Experimental Setup

The module used for the experiment is shown in Fig. 6-8. The four sides are made of 12mm thick transparent Plexiglas to allow the visual observation of the melting front movement inside the container. The thermal properties of Plexiglas [thermal conductivity: 0.19 W/m.K or thermal resistance of 9 C/W (larger side) and 50 C/W (smaller side)] is such that it almost acts as a thermal barrier to prevent flow of heat from inside to outside. The top and bottom walls of the container are made of 5 mm thick aluminum plate. The aluminum plates are attached to the Plexiglas with six screws along with gaskets to prevent any leakage of liquid from inside. Some weep holes along with tubes are provided to the smaller sides of the Plexiglas to accommodate the volumetric expansion during the change of phase from solid to liquid.
In order to prevent the further heat loss through natural convection and radiation heat transfer from the walls, all walls except the bottom plate is covered with the thermal insulating material of Styrofoam (Fig. 6-9). The arrangement provides unidirectional heat flow from one aluminum plate to another. The Styrofoam of front wall is removed periodically to visualize the movement of melting/freezing front and measure the position of melting/freezing front with respect to time (Fig. 6-9). A graduated scale is provided on the back wall for the location of thermocouples and the scale of front wall is used to measure the movement of the melting/freezing front distance (Fig. 6-9).
Kapton® (Polyimide Film) Insulated Flexible Heater of 1800 Watt/m² from OMEGA Engineering, Inc. [27] is attached at the back of the bottom aluminum plate with pressure sensitive adhesive (Fig. 6-10) to provide continuous supply of heat during experiment.

The heat of flexible heaters is controlled by Xantrax XPL 30-2D dual output DC power supply by adjusting the voltage and current (Fig. 6-10). The applied heat can be measured by Eq.-3.

\[ P = V \times I \]  

(3)

where, \( P \) is heat in Watt, \( V \) is in voltage and \( I \) in current

![Figure 6-10: Bottom aluminum plate attached with heater](image)

Figure 6-11 shows the connection of heater to the power supply.
The bottom aluminum plate is placed on the high temperature thermal insulating slab to prevent any heat flow from bottom plate to outside and ensure only unidirectional flow of heat from hot plate to cold plate.

6.3.4 Instrumentation, Data Acquisition, Visualization and Data Recording

Instruments are used for this experiment to observe the movement of melting/freezing interface through the temperature response of the thermocouples implanted at various locations as shown below in Fig. 6-12. Thermocouples are positioned at the centre of the module with certain distance intervals by making holes at back wall of Plexiglas and the gap between holes and thermocouples are filled with thermally nonconductive epoxy (Fig.6-12).
Figure 6-12: Locations of thermocouples for the experiment

Fifteen T-type thermocouples labelled as TC-1 to TC-15 are used to measure the temperature of the experiment. TC-2 to TC-13 are used to measure the inside temperature of the module to track the movement of the melting/freezing front at various locations. TC-1 is used to measure the temperature of the heater on aluminum plate and TC-14 is used to measure the temperature of the other aluminum plate without heater. There is another thermocouple (TC-15), which is used to measure the ambient temperature during the experiment. Conduction losses through the leads were assumed to be negligible (around 0.6% for PCM and 0.01% for NanoPCM-Foam) because of the small diameter of wires and relatively large value of $Q$. The accuracy of the thermocouples is found as ±0.2°C from the manufacturer datasheet. Output terminals of all thermocouples are connected to a 16-channel cDAQ-9171 data acquisition system (Fig. 6-13).
A Windows based laptop running Labview v.13.0f2 software is programmed and controlled for data acquisition. Labview is a very popular programming language for the data acquisition software because of its good communication with the instrumentation, huge library of data acquisition driver files, and its powerful computational along with visual interface (Fig. 6-14). Labview also allows to record data in a text file from where data can be analysed later in Excel spreadsheet.

**Figure 6-13:** Connection of thermocouples to the data acquisition system

**Figure 6-14:** Labview interface for data controlling, visualization and recording
6.3.5 Uncertainty of the Experiment

The uncertainty of the experiment is associated with the measurement of temperature. The bias and precision elemental error within the instrumentation such as thermocouples and cDAQ-9171 data acquisition system contribute to the uncertainty of the experiment. The root sum square method (RSS) is used to calculate the uncertainty of individual instrument for bias and precision error. Later, same RSS method is applied to calculate the uncertainty of the experiment by combining the uncertainty associated with the each of two instruments. Table 6-5 shows the uncertainty associated with the temperature measurement of the experiment.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermocouple</td>
<td>±0.2°C</td>
</tr>
<tr>
<td>Data Acquisition System (DAQ)</td>
<td>±1.26°C</td>
</tr>
<tr>
<td>Temperature</td>
<td>±1.28°C</td>
</tr>
</tbody>
</table>

Over the range of temperature from 52-80°C, the error of the measurement varies from 3.8% to 2.5%, which can be acceptable for the accuracy of the experiment.

6.4 Result and Discussion

The objective of this experimental research is to study the melting/freezing performance of phase change material as a heat storage device and observe the influence of the thermal enhancer such as foam and nanoparticles on the melting/freezing rate of phase change material. The module is heated from bottom, side and top to observe the effect of conduction and convection heat transfer with constant heat flux boundary condition during melting. As there is no convection effect during freezing, constant temperature (mainly ambient) boundary condition is applied from bottom during freezing. Table 6-6 shows the experimental parameters used for conducting various sets of experiment.
Table 6-6: Parameters of the experiment

<table>
<thead>
<tr>
<th>Expt. No</th>
<th>Base PCM</th>
<th>Foam</th>
<th>Nanoparticle Vol. (%)</th>
<th>Melting/heating from</th>
<th>Freezing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Paraffin</td>
<td>Aluminum</td>
<td>0.5</td>
<td>Top</td>
<td>Bottom</td>
</tr>
<tr>
<td>1</td>
<td>√</td>
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<td>-</td>
<td>√</td>
<td>√</td>
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<td>√</td>
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<td>√</td>
<td>1.0</td>
<td>√</td>
<td>√</td>
</tr>
</tbody>
</table>

The experimental research plans to conduct 26 various configurations of experiment as per Table 6-6. During experiment, the movement of melting front was observed through the Plexiglas and pictures were taken through a camera for various locations of melting front periodically. The movement of the melting front is also compared with the temperature recorded through the thermocouples to confirm the melting temperature. The melting experiment is done for heating from top, bottom and side to observe the pattern of conduction and convection heat transfer. The freezing experiment is done only for cooling from bottom as there is no influence of convection during freezing. During freezing, the cold surface is exposed to ambient temperature instead of maintaining temperature just below the freezing temperature. Because of higher temperature gradient of energy release, the gradual movement of freezing front is very difficult to observe. As freezing starts immediately for the entire system, the visualization of freezing front was not possible and the behaviour of freezing is studied only through the temperature profile of thermocouples. Because of dark color of NanoPCM, the visualization of phase change is difficult so thermal behaviour associated with NanoPCM is studied through the temperature data of thermocouples. For the same reason, the melting experiment for heating
from side was not conducted for experiments associated with NanoPCM. The experiment with NanoPCM is planned to carry out for volume fraction of 0.25%, 0.5% and 1% as the thicker concentration of NanoPCM is observed with 2% and 4% of volume fraction, which was discussed before.

6.4.1 Thermal Behaviour of Base PCM (Paraffin Alone)

The experiment with base PCM is done for heating from bottom, top and side during melting and the freezing experiment is done for cooling from bottom as there is no effect of convection during freezing. The pictures of experiments are taken for the visualization of experiments.

6.4.1.1 Thermal Behaviour of Base PCM for Bottom Heating

Figure 6-15 shows the visual display of the melting front with PCM for heating from bottom.

Figure 6-15: Melting front movement visualization for heating from bottom with PCM

Figure 6-16 shows the movement of melting front with respect to time. The average melting speed is observed as 11.4 micron/second.
Figure 6-16: Melting distance with respect to time for heating from bottom with PCM

Figure 6-17 shows the thermal response of various thermocouples with respect to time at various locations of melting front for heating from bottom. Because of heating from bottom, buoyancy affect comes into play for natural convection heat transfer. Figure 6-17 reveals the natural convection affect with the stabilization of thermocouple readings at various elevations due to buoyancy driven recirculation of relatively cold and hot liquid PCM from top to bottom over a period of time during melting. After complete melting, the readings start climbing due to sensible heat, as there is no PCM left for latent heat storage.
Figure 6-17: Thermocouple readings for heating from bottom with PCM

Melting front line tells when phase change occurs for each thermocouple and it matches very well with the visual measurement of the melting front in Fig. 6-15.
6.4.1.2 Thermal Behaviour of Base PCM for Heating from Side

Figure 6-18 shows the visual display of the melting front with PCM for heating from side.

**Figure 6-18: Melting front movement visualization for heating from side with PCM**

From experiment of heating from side with base PCM, it is observed that it melts faster at the beginning because of both conduction and convection heat transfer. After the complete melt at the top, melting slows down significantly because of the absence of natural convection heat transfer. It takes 275 minute to melt completely whereas the melting time for heating from bottom is observed as 132 minute. The average melting speed of heating from side is found as 5.5 micron/second, which is lower than the melting speed of heating from bottom, 11.4 micron/second. The slowdown of melting rate during heating from side confirms the less dominance of natural convection heat transfer during melting.
Figure 6-19 shows the movement of melting front with respect to time. The average melting speed is found as 5.5 micron/second.

![Graph showing the movement of melting front with respect to time. The average melting speed is found as 5.5 micron/second.](image)

**Figure 6-19:** Melting distance with respect to time for heating from side with PCM

Figure 6-20 shows the thermal response of various thermocouples with respect to time at various locations of melting front for heating from side. Because of heating from side, buoyancy affect comes into play for natural convection heat transfer at beginning of melting. Figure 6-20 reveals the natural convection affect with the stabilization of thermocouple readings at various elevations due to buoyancy driven recirculation of relatively cold and hot liquid PCM from top to bottom over a period of time during melting. The slower melting rate is observed at the later stage of melting because of the absence of natural convection after the melt reaches the top.

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After complete melting, the readings start climbing due to sensible heat, as there is no PCM left for latent heat storage.

**Figure 6-20:** Thermocouple readings for heating from side with PCM

Melting front line tells when phase change occurs for each thermocouple and it matches very well with the visual measurement of the melting front.
6.4.1.3 Thermal Behaviour of Base PCM for Heating from Top

Figure 6-21 shows the visual display of the melting front with PCM for heating from top.

![Melting front movement visualization for heating from top with PCM](image)

**Figure 6-21**: Melting front movement visualization for heating from top with PCM

From experiment of heating from top with base PCM, it is observed that PCM melts faster for first few millimetres. After that, it slows down significantly as there is no influence of convection heat transfer for heating from top. Heat transfers from top to bottom only because of conduction. It took melting front almost 5hrs to reach 40mm distance and it was slowing down more and more. As a result, the experiment for heating from top had to stop after five hrs to save time. The average melting speed of heating from top is found as 3.8 micron/second, which is lower than the melting speed of heating from bottom, 11.4 micron/second and the melting speed of heating from side, 5.5 micron/second. The slowdown of melting rate during heating from top confirms the almost absence of natural convection heat transfer during melting.
Figure 6-22 shows the movement of melting front with respect to time. The average melting speed is found as 3.8 micron/second.

![Graph showing the movement of melting front with respect to time.](image)

**Figure 6-22**: Melting distance with respect to time for heating from top with PCM

Figure 6-23 shows the thermal response of various thermocouples with respect to time at various locations of melting front for heating from top. Because of heating from top, it is expected to have no natural convection due to absence of buoyancy effect. Figure 6-23 reveals that there is no stabilization of thermocouple readings at various locations over a period during melting and temperature keeps climbing with time. Melting front line tells when phase change occurs for each thermocouple and it matches very well with the visual measurement of the melting front.
Freezing starts instantaneously for the entire system and this makes the visualization of freezing front very difficult. As a result, no picture is taken for freezing front and the behaviour of freezing is studied only through the temperature profile of thermocouples. The freezing experiment is done only for cooling from bottom as there is no influence of convection during freezing. As the freezing temperature is around 52-53°C, the bottom surface is exposed to ambient temperature of 22°C for cooling while maintaining other surfaces insulated to ensure unidirectional heat flow through the bottom surface.

Figure 6-23: Thermocouple readings for heating from top with PCM

6.4.1.4 Thermal Behaviour of Base PCM for Freezing

Freezing starts instantaneously for the entire system and this makes the visualization of freezing front very difficult. As a result, no picture is taken for freezing front and the behaviour of freezing is studied only through the temperature profile of thermocouples. The freezing experiment is done only for cooling from bottom as there is no influence of convection during freezing. As the freezing temperature is around 52-53°C, the bottom surface is exposed to ambient temperature of 22°C for cooling while maintaining other surfaces insulated to ensure unidirectional heat flow through the bottom surface.
Figure 6-24 shows the movement of freezing front with respect to time. The average freezing speed is observed as 5.8 micron/second.

![Graph showing freezing distance with respect to time for cooling from bottom with PCM](image)

**Figure 6-24:** Freezing distance with respect to time for cooling from bottom with PCM

Figure 6-25 shows the thermal response of various thermocouples with respect to time at various locations of freezing front for cooling from bottom. It shows the gradual lowering of temperature at various locations of the PCM and the cooling happens faster at the bottom than the top as the bottom surface is in contact with the cold surface. Gradual phase change from liquid to solid occurs from bottom to top. The average speed of freezing is observed as 5.8 micron/second, which is found slower than the average speed of melting for heating from bottom as there is no convection heat transfer during freezing.
6.4.1.5 Comparison of Melting Rate for Heating from Bottom, Side, Top and Freezing Rate for Cooling from Bottom for Base PCM

Figure 6-26 compares the phase change interface (melting/freezing front) movement time with respect to distance for base PCM for heating from bottom, side, top and cooling from bottom. From Fig. 6-26, it is observed that PCM melts much faster for bottom heating than side heating because of greater influence of natural convection but melts slowly for heating from top as there is no natural convection. The freezing time of PCM is found higher than the melting time of heating from bottom as there is no natural convection during freezing.
6.4.2 Thermal Behaviour of PCM with Porous Medium (Metal Foam)

The experiment of PCM with metal foam is done for heating from bottom, top and side during melting and the freezing experiment is done for cooling from bottom as there is no effect of convection during freezing. The pictures of melting front at different melting distance were taken for visualization as well as temperature profile from thermocouples is also studied. Freezing experiment is done only through the temperature profile of thermocouples.
6.4.2.1 Thermal Behaviour of PCM with Porous Medium for Bottom Heating

Figure 6-27 shows the visual representation of melting front for PCM with porous medium at various time intervals while heating from bottom.

(a) Melting distance: 10mm; time: 24 minute

(b) Melting distance: 30mm; time: 31 minute
(c) Melting distance: 50mm; time: 58 minute

(d) Melting distance: 70mm; time: 75 minute
Figure 6-27: Melting front visualization for heating from bottom for PCM with Foam

Figure 6-28 shows the movement of melting front with respect to time. The average melting speed is observed as 16.4 micron/second, which is found 44% (PCM: 11.4 micron/second) higher than the speed of base PCM.
Figure 6-28: Melting time with respect to distance for heating from bottom with PCM and Foam

Figure 6-29 shows the thermal response of PCM with foam for temperatures at various melting locations of thermocouples with respect to time for heating from bottom. Because of heating from bottom, buoyancy affect due to density gradient comes into play for natural convection heat transfer but because of the resistance from foam, the natural convection effect is not as dominant as base PCM. The Figure 6-28 reveals this natural convection affect with the less stabilization of thermocouple readings at various locations over a period during melting. After complete melting, the readings start climbing due to sensible heat as there is no PCM left for latent heat storage.
Figure 6-29: Thermocouple readings for heating from bottom with PCM and Foam

6.4.2.2 Thermal Behaviour of PCM with Porous Medium for Heating from Side

Figure 6-30 shows the visual representation of melting front for PCM with porous medium at various time intervals while heating from side.
(a) Melting distance: 20mm; time: 50 minute

(b) Melting distance: 30mm; time: 70 minute
(c) Melting time: 103 minute

(d) Melting time: 135 minute
(e) Melting time: 153 minute

(f) Melting time: 162 minute
Figure 6-30: Melting front visualization for heating from side with PCM and Foam

(g) Melting time: 183 minute

(h) Complete Melting time: 201 minute
From Fig. 6-30, it is observed that it melts faster at the beginning but the meting rate is slower than the base PCM as the fluid motion of convection heat transfer is dampened by the metal structure of foam. After the complete melt at the top, melting slows down significantly because of the absence of convection heat transfer but it melts faster than the base PCM as the metal structure of foam enhances the thermal conductivity of PCM with foam for better conduction heat transfer. It takes 201 minute to melt completely, which is lower than the melting time of PCM (275 minute) for heating from side. The melting time for heating from side (201 minute) is higher than that of heating from bottom (92 minute) because of less natural convection effect while heating from side. The average melting speed of heating from side is found as 7.5 micron/second, which is faster than that of the base PCM (5.5 micron/sec) for heating from side but slower than the melting speed of heating from bottom (16.4 micron/sec) for PCM with foam. The slowdown of melting rate during heating from side confirms the less dominance of natural convection heat transfer during melting.

Figure 6-31 shows the movement of melting front with respect to time. The average melting speed is observed as 7.5 micron/second, which is slower than the speed of the melting front heating from bottom (16.4 micron/second).
Figure 6-31: Melting time with respect to distance for heating from side with PCM and Foam

Figure 6-32 shows the thermal response of various thermocouples with respect to time at various locations of melting front of PCM with foam for heating from side. Because of heating from side, buoyancy affect comes into play for natural convection heat transfer at the beginning of the melting. Figure 6-32 reveals the natural convection affect with the stabilization of thermocouple readings at various locations over a period during melting but the stabilization is not observed as distinct as base PCM due to less natural convection effect because of foam resistance to fluid motion. The slower melting rate is observed at the later stage of melting because of the absence of natural convection after the melt reaches the top. After complete melting, the readings start climbing due to sensible heat as there is no PCM left for latent heat.
storage. Melting front line tells when phase change occurs for each thermocouple and it matches very well with the visual measurement of the melting front shown Fig. 6-30.

**Figure 6-32:** Thermocouple readings for heating from side with PCM and Foam

### 6.4.2.3 Thermal Behaviour of PCM with Porous Medium for Heating from Top

Figure 6-33 displays qualitatively the melting front of PCM with porous medium at various time intervals while heating from top.
(a) Melting distance: 10mm; time: 42 minute

(b) Melting distance: 20mm; time: 65 minute
(c) Melting distance: 30mm; time: 85 minute

(d) Melting distance: 40mm; time: 105 minute
(e) Melting distance: 50mm; time: 134 minute

(f) Melting distance: 60mm; time: 158 minute
(g) Melting distance: 70mm; time: 190 minute

(h) Melting distance: 90mm; time: 228 minute

Figure 6-33: Melting front movement visualization for heating from top with PCM and Foam
From Fig. 6-33, it is observed that PCM melts relatively faster up to 60 millimetres but after that, it slows down significantly because of higher thermal resistance towards the bottom due to conduction heat transfer. It took almost 4hrs to melt completely. The average melting speed of heating from top is found as 6.6 micron/second, which is lower than the melting speed of heating from bottom, 16.4 micron/second and the melting speed of heating from side, 7.5 micron/second. The slowdown of melting rate during heating from top confirms the absence of natural convection heat transfer during melting.

Figure 6-34 shows the movement of melting front with respect to time. The average melting speed is observed as 6.6 micron/second.

![Figure 6-34](image)

**Figure 6-34:** Melting time with respect to distance for heating from top with PCM and Foam
Figure 6-35 shows the thermal response of various thermocouples with respect to time at various locations of melting front for heating from top. Because of heating from top, it is expected to have no natural convection because of absence of buoyancy effect. The Figure 6-34 reveals that as there is no stabilization of thermocouple readings at various locations over a period during melting and temperature keeps climbing with time. The lack of natural convection makes the movement of melting front very slow and the experiment takes almost 4 hrs to melt completely. Melting front line tells when phase change occurs for each thermocouple and it matches very well with the visual measurement of the melting front shown in Fig. 6-33.
6.4.2.4 Thermal Behaviour of PCM with Foam for Freezing

Freezing starts instantaneously for the entire system and this makes the visualization of freezing front very difficult. As a result, no picture is taken for freezing front and the behaviour of freezing is studied only through the temperature profile of thermocouples. The freezing experiment is done only for cooling from bottom as there is no influence of convection during freezing. As the freezing temperature is around 52-53°C, the bottom surface is exposed to ambient temperature of 22°C for cooling while maintaining other surfaces insulated to ensure unidirectional heat flow through the bottom surface.

Figure 6-36 shows the thermal response of various thermocouples with respect to time at various locations of freezing front for cooling from bottom. Figure 6-36 indicates the gradual lowering of temperature at various locations of the PCM-Foam and the cooling happens faster at the bottom than the top as the bottom surface is in contact with the cold surface. Gradual phase change from liquid to solid occurs from bottom to top. The average speed of freezing is observed as 16.2 micron/second, which is found little bit slower than the average speed of melting (16.4 micron/second) for heating from bottom.
Figure 6-36: Thermocouple readings for cooling from bottom with PCM and Foam

Figure 6-37 shows the movement of freezing front with respect to time. The average freezing speed is observed as 16.2 micron/second
Figure 6-37: Freezing rate for cooling from bottom with PCM and Foam

6.4.2.5 Comparison of Interface Movement for PCM with Foam for Heating from Bottom, Side, Top and Cooling from Bottom

Figure 6-38 compares the interface movement rate of PCM with foam for heating from bottom, side, top and cooling from bottom during melting and freezing. From Figure 6-38, it is observed that PCM melts much faster for bottom heating than side and top heating because of greater influence of natural convection. Though there is no natural convection during freezing, the freezing time of PCM is found almost same as melting time of heating from bottom.
6.4.3 Thermal Behaviour of PCM with Nanoparticle (NanoPCM)

The experiment of NanoPCM is planned to conduct with the volume fraction of 0.25% (wt% 2.8), 0.5% (wt% 5.4) and 1.0% (wt% 10.4). It is decided to carry out the experiment with the volume fraction of 0.5% (wt% 5.4) first and after observing the result of this experiment, the decision is to be made for further conducting the experiment with the volume fraction of 0.25% (wt% 2.8) and 1.0% (wt% 10.4). The experiment is done for heating from bottom and top during melting, and the freezing experiment is done for cooling from bottom as there is no effect of
convection during freezing. The copper nanoparticle is used for the preparation of NanoPCM, which makes the color of NanoPCM very dark (Fig. 6-39). Because of the dark color of NanoPCM, it is very difficult to observe the movement of melting/freezing front so no picture is taken during the experiment. The temperature profile from various thermocouples is observed to study the thermal behaviour of NanoPCM.

Figure 6-39: Experimental Module with PCM and Nanoparticle

6.4.3.1 Thermal Behaviour of NanoPCM with 0.5% Volume Fraction for Heating from Bottom

Figure 6-40 shows the thermal response of various thermocouples with respect to time at various locations of melting front for heating from bottom. Because of heating from bottom, buoyancy affect should come into play for natural convection heat transfer. Figure 6-40 reveals very little (not as good as base PCM) stabilization of thermocouple readings at various locations over a period during melting which is a clear indication of insignificant natural convection effect. The lack of natural convection is because of lesser buoyancy effect by heavier NanoPCM liquid after mixing of heavier copper nanoparticle with base PCM.
Figure 6-40: Thermocouple readings for heating from bottom for NanoPCM with 0.5% volume fraction of nanoparticles. The average melting speed is observed as 5.7 micron/second whereas melting speed of base PCM is observed as 11.4 micron/second for heating from bottom. This slower melting rate is because of lack of natural convection for heavier NanoPCM.
6.4.3.2 Thermal Behaviour of NanoPCM with 0.5% volume fraction for heating from top

From the experiment, it is observed that PCM melts faster for first few millimetre; after that, it slows down significantly as there is no influence of convection heat transfer for heating from top. Heat transfers from top to bottom only because of conduction. It took melting front more than 4hrs to reach 50mm distance and it slows down further after that. As a result, the experiment for heating from top had to stop as it is not wise to run the experiment indefinitely. The average melting speed (4.1 micron/second) of heating from top is found higher than the melting speed (3.8 micron/second) of base PCM due to the thermal conductivity enhancement of
base PCM with the mixing of copper nanoparticles and heating from top is purely a conduction heat transfer.

Figure 6-42 shows the thermal response of various thermocouples with respect to time at various locations of melting front for heating from top. Because of heating from top, it is expected to have no natural convection because of absence of buoyancy effect. The Figure 6-41 reveals that as there is no stabilization of thermocouple readings at a particular temperature over a period of time during melting and temperature keeps climbing with time. The lack of natural convection makes the movement of melting front very slow and the experiment had to stop after more than 4 hrs when the melting front reached up to 50mm only.

![Figure 6-42: Thermocouple readings for heating from top for NanoPCM with 0.5% volume](image_url)
Figure 6-43 shows the melting rate of NanoPCM for heating from top. The average melting speed is observed as 4.1 micron/second which is found slower than the melting speed of NanoPCM heating from bottom because of absence of natural convection heat transfer.

![Graph showing melting rate of NanoPCM](image)

Figure 6-43: Movement of NanoPCM with 0.5% volume for heating from top

6.4.3.3 Thermal Behaviour of NanoPCM with 0.5% Volume Fraction for Freezing

Freezizing starts from bottom and the behaviour of freezing is studied through the temperature profile of thermocouples. The freezing experiment is done only for cooling from bottom as there is no influence of convection during freezing. During cooling, the bottom surface
is exposed to the ambient temperature of 22°C, which is lower than the freezing temperature of 52-53°C while maintaining other surfaces insulated to ensure unidirectional heat flow through the bottom surface.

Figure 6-44 shows the thermal response of various thermocouples with respect to time at various locations of freezing front for cooling from bottom. The Figure 6-44 indicates the gradual lowering of temperature at various locations of the PCM and the cooling happens faster at the bottom than the top as the bottom surface is in contact with the cold surface. Gradual phase change from liquid to solid occurs from bottom to top. The average speed of freezing is observed as 7.6 micron/second, which is found faster than the average speed of melting for NanoPCM with heating from bottom and top. This may be because of constant temperature cooling during freezing.

**Figure 6-44:** Thermocouple readings of NanoPCM with 0.5% volume for freezing from bottom
Figure 6-45 shows the movement of freezing front with respect to time. The average freezing speed is observed as 7.6 micron/second.

![Graph showing freezing distance vs. freezing time for NanoPCM with 0.5% volume fraction.](image)

**Figure 6-45**: Movement of NanoPCM with 0.5% volume for freezing

6.4.3.4 *Comparison of Interface Movement for NanoPCM with 0.5% Volume Fraction of Nanoparticle for Heating from Bottom, Top and Cooling from bottom*

Figure 6-46 compares the interface movement rate for NanoPCM with 0.5% volume of copper nanoparticle for heating from bottom, top and cooling from bottom. From Fig. 6-46, it is observed that NanoPCM melts faster for bottom heating than top heating because of influence of
natural convection. Though there is no natural convection during freezing, the freezing time of NanoPCM is found faster than the melting time of NanoPCM for heating from bottom and top.

![Graph showing comparison of interface movement for NanoPCM](image)

**Figure 6-46:** Comparison of Interface Movement for NanoPCM

### 6.4.4 Thermal Behaviour of NanoPCM with Foam

The experiment of NanoPCM is planned to conduct with the nanoparticle’s volume fraction of 0.25% (wt% 2.8), 0.5% (wt% 5.4) and 1.0% (wt% 10.4). It is decided to carry out the experiment with the volume fraction of 0.5% (wt% 5.4) first and after observing the result of this experiment, the decision is to be made for further conducing the experiment with the volume fraction of 0.25% (wt% 2.8) and 1.0% (wt% 10.4). The experiment is done for heating from
bottom and top during melting, and the freezing experiment is done for cooling from bottom as there is no effect of convection during freezing. The copper nanoparticle is used for preparation of NanoPCM which makes the color of NanoPCM with foam very dark (Fig. 6-47). Because of the dark color of NanoPCM, it is very difficult to observe the movement of melting/freezing front so no picture is taken during the experiment. The temperature profile from various thermocouples is observed to study the thermal behaviour of NanoPCM with foam.

Figure 6-47: Experimental Module with NanoPCM with Foam

6.4.4.1 Thermal Behaviour of NanoPCM with 0.5% Volume Fraction and Foam for Heating from Bottom

Figure 6-48 shows the thermal response of various thermocouples with respect to time at various locations of melting front for heating from bottom with NanoPCM and foam. Because of heating from bottom, buoyancy affect should come into play for natural convection heat transfer
but because of the resistance from foam and high viscosity of NanoPCM liquid for heavier copper nanoparticle, the effect of natural convection is found very little in Fig. 6-48 as no stabilization of thermocouple readings at a particular temperature is observed during melting. As a result, the melting front moves slower than that of PCM with foam.

Figure 6-48: Thermocouple readings of heating from bottom for NanoPCM with 0.5% volume and foam

Figure 6-49 shows the melting rate of NanoPCM with foam for heating from bottom. The average melting rate is observed as 7.9 micron/second, which is found faster than the melting rate of NanoPCM (6 micron/second) but slower than the melting rate of PCM with foam (16.4
micron/second). This lower melting rate is affected by the less influence of natural convection heat transfer due to heavier NanoPCM liquid after mixing of base PCM with heavier copper nanoparticles.

![Figure 6-49: Melting Rate of NanoPCM with foam for heating from bottom](image)

**Figure 6-49:** Melting Rate of NanoPCM with foam for heating from bottom
6.4.4.2 Thermal Behaviour of NanoPCM with 0.5% Volume Fraction and Foam for Heating from Top

Figure 6-50 shows the thermal response of various thermocouples with respect to time at various locations of melting front for heating from top. Because of heating from top, it is expected to have no natural convection due to absence of buoyancy effect. Figure 6-50 reveals that there is no stabilization of thermocouple readings at a particular temperature over a period of time during melting and the temperature keeps climbing with time. The absence of natural convection makes the movement of melting front very slow and the experiment took around 4 hrs to melt completely.

Figure 6-50: Thermocouples readings of NanoPCM with foam for heating from top
Figure 6-51 shows the melting rate of NanoPCM with foam for heating from top. The average melting speed of 7.0 micron/second is found faster than the melting speed of base PCM, PCM with foam and NanoPCM for heating from top, which signifies the thermal enhancement of NanoPCM with foam when heating is done from top because of better conduction heat transfer for higher thermal conductivity of NanoPCM and foam matrix.

**Figure 6-51:** Melting rate of NanoPCM with foam for heating from top
6.4.4.3 Thermal Behaviour of NanoPCM with Foam for Freezing

Freezing starts from the bottom and the freezing is studied through the temperature profile of thermocouples. As there is no influence of convection during freezing, the freezing experiment is done for cooling from bottom. As the freezing temperature is around 52-53°C, the freezing is done by exposing the bottom surface to the ambient temperature of 22°C while maintaining other surfaces insulated to ensure unidirectional heat flow bottom to top surface.

Figure 6-52 shows the thermal response of various thermocouples with respect to time at various locations of freezing front for cooling from bottom. Figure 6-52 indicates the gradual lowering of temperature at various locations of the PCM and the cooling happens faster at the bottom than the top as the bottom surface is in contact with the cold surface. Gradual phase change from liquid to solid occurs from bottom to top. The average speed of freezing is observed as 23.8 micron/second, which is found significantly faster than the average speed of any other melting or freezing. This is because copper nanoparticles enhance the thermal conductivity of NanoPCM and foam matrix for better heat transfer.
Figure 6-52: Thermocouples readings of NanoPCM with foam for freezing from bottom

Figure 6-53 shows the freezing rate of NanoPCM with foam for cooling from bottom. The average freezing speed is observed as 23.8 micron/second.
Figure 6-53: Freezing rate of NanoPCM with foam for cooling from bottom

6.4.4.4 Comparison of Interface Movement for NanoPCM with 0.5% Volume of Nanoparticle and Foam matrix for Heating from Bottom, Side, Top and Cooling from Bottom

Figure 6-54 compares the interface movement rate of NanoPCM with foam matrix for heating from bottom and top as well as cooling from bottom during melting and freezing. From Fig. 6-54, it is observed that NanoPCM melts faster for bottom heating than top heating because of influence of natural convection but the influence of natural convection is found very little for heating from bottom as the heavier nanoparticles make NanoPCM heavier and dampen the fluid...
motion for convection heat transfer. Though there is no natural convection during freezing, the freezing time is found faster than the melting time for heating from top and bottom.

Figure 6-54: Melting rate comparison for NanoPCM with Foam matrix
6.4.4.5 Thermal Behaviour of NanoPCM with 0.25% and 1% Volume Fraction and Foam

From the experimental data of 0.5% volume fraction nanoparticles, a very insignificant amount of natural convection is observed for bottom heating. There is no chance of improvement of natural convection with higher volume fraction of 1%. There may be some gain of thermal conductivity with higher volume fraction of 1% during top heating and bottom freezing but the gain is proved to be insignificant from the data available for volume fraction of 0.5%. Therefore, it should be wastage of time for conducting experiment with 1% volume fraction. There can be some gain of natural convection with the volume fraction of 0.25% but the gain can be proved to be insignificant from the data available for volume fraction of 0.5%. Moreover, there is no chance of better conduction heat transfer with the volume fraction of 0.25% so it won’t be worthy of conducting experiment with volume fraction of 0.25% as well. Therefore, though it is planned earlier to conduct experiment with the volume fraction of 0.25% and 1%, it is decided not to carry out further experiment with the volume fraction of 0.25% and 1%.

6.4.5 Thermal Performance (Melting/Freezing Rate) Comparison

The experiments for base PCM, PCM-Foam matrix, NanoPCM and NanoPCM-Foam matrix with heating from bottom, top and side during melting and cooling from bottom during freezing are done to observe the melting and freezing performance. The performance comparison of each case of heating from bottom, top and side during melting and cooling from bottom during freezing for base PCM, PCM-Foam matrix, NanoPCM and NanoPCM-Foam matrix can tell the choice of enhancer for thermal enhancement of PCM.

6.4.5.1 Melting Performance Comparison for Heating from Bottom

Figure 6-55 shows the melting performance comparison of base PCM, PCM-Foam matrix, NanoPCM and NanoPCM-Foam matrix for heating from bottom. From Fig. 6-55, it is observed that the best melting performance is witnessed for PCM with Foam because of the influence of both conduction and convection heat transfer. The desired enhancement with NanoPCM with Foam matrix is not noticed because the heavier nanoparticles make the NanoPCM liquid heavy and dampens the fluid motion for natural convection heat transfer.
Figure 6-55: Comparison of melting performance for heating from bottom

6.4.5.2 Melting Performance Comparison for Heating from Top

Figure 6-56 shows the melting performance comparison of base PCM, PCM with foam matrix, NanoPCM and NanoPCM with foam matrix for heating from top. From Fig. 6-56, it is observed that the best melting performance is noticed with NanoPCM and foam matrix. For heating from top, there is no convection heat transfer and the addition of nanoparticles and metal foam matrix enhances the thermal conductivity for better conduction heat transfer.
6.4.5.3 Melting Performance Comparison for Heating from Side

The experiment of heating from side is done for base PCM and PCM with foam matrix only as the visualization of melting front movement in NanoPCM not possible because of dark color. Figure 6-57 shows the melting performance comparison of base PCM and PCM with foam for heating from side. From Fig. 6-57, it is observed that best melting performance is performed with PCM and foam matrix where higher thermal conductivity of metal foam matrix helps to dominate conduction heat transfer over better natural convection heat transfer of PCM.
6.4.5.4 Freezing Performance Comparison for Cooling from Bottom

Figure 6-58 shows the freezing performance comparison of base PCM, PCM with foam matrix, NanoPCM and NanoPCM with foam matrix for cooling from bottom. From Fig. 6-58, it is observed that best cooling performance is performed with NanoPCM and foam matrix. For cooling from bottom, there is no convection heat transfer and the addition of nanoparticles and metal foam matrix enhances the thermal conductivity for better conduction heat transfer during freezing.
Figure 6-58: Comparison of freezing performance for cooling from bottom

6.5 Conclusion

An extensive experimental research is done to study the thermal performance of base PCM, PCM with foam, NanoPCM and NanoPCM with foam. For each case, four sets of experiment are done for heating from bottom, heating from side and heating from top during melting and cooling from bottom during freezing. The lowest melting time is observed for heating from bottom during melting because of the influence of higher natural convection heat transfer. The influence of natural convection was observed through visualization of base PCM and PCM with
foam for heating from bottom during melting. This effect of natural convection was also observed from the temperature reading of the thermocouples at various locations as the readings of thermocouples get stabilized around a certain temperature during the period of melting. The influence of natural convection for base PCM and NanoPCM was also observed through temperature stabilization during melting for heating from side until the the top melts completely. After that, there is no natural convection for heating from side and it takes more time to melt the remaining part of the unmelt PCM due to conduction heat transfer only. As there is no natural convection effect for heating from top, the heat transfer occurs only through conduction and it takes more time to melt than other two. For NanoPCM and NanoPCM with foam matrix, the visualization of natural convection was not possible because of dark color of NanoPCM and no temperature stabilization was observed from the temperature readings of thermocouples for heating from bottom and side. From the melt rates of heating from bottom and side, a very insignificant presence of natural convection is observed for NanoPCM and NanoPCM with metal foam for heating from bottom and side.

From the experimental result, for heating from top, the best thermal performance (melting rate) was observed for NanoPCM with foam because of better conduction heat transfer due to the better thermal conductivity of NanoPCM and foam matrix. For heating from bottom and side, the best thermal/melting performance is observed with PCM and foam. The melting rate of base PCM for heating from bottom and side is found better than the NanoPCM with foam and NanoPCM alone. The presence of heavier copper particle in the NanoPCM makes the liquid PCM heavier, dampens the fluid motion for buoyancy driven flow and lowers the natural convection heat transfer significantly. For freezing, the best thermal/freezing performance was observed with NanoPCM and foam. The freezing is happened through conduction heat transfer and enhanced thermal conductivity for conduction heat transfer is observed with NanoPCM and foam matrix.

The further experiment can be done to observe the natural convection effect inside the NanoPCM with foam and NanoPCM for heating from bottom and side by bolstering the buoyancy effect with lighter nanoparticles such as boron nitride, aluminum nitride, graphite, aluminum etc. and less viscous base PCM. The melting temperature of base PCM used for the
The preparation of NanoPCM does not include any surfactant for dispersion in this experiment. For any future experiment, surfactant can be added for better dispersion but the amount of surfactant should be such that it does not affect the thermophysical properties of NanoPCM.

### 6.6 References


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Chapter 7: Conclusion and Future Work

7.1 Conclusion

Phase change latent heat storage system is gradually becoming popular choice for thermal management of various transient heat transfer applications by storing energy by changing phase but without raising temperature. The challenge of phase change energy storage system is its poor thermal performance because of low thermal conductivity of PCM. Various efforts are made for thermal enhancement of PCM. Two of those are: 1) PCM with nanoparticle (NanoPCM) and 2) PCM with porous medium. For NanoPCM, the careful loading of nanoparticle is needed for enhancement of thermal conductivity without affecting the other thermophysical properties such as viscosity, density, latent heat of fusion, melting temperature etc., which can be important for other form of heat transfer such as natural convection and phase change. Moreover, with low loading of nanoparticle, the effective thermal conductivity of NanoPCM does not improve significantly. For PCM with porous medium, the porosity of porous medium needs to be high enough to ensure fluid current through the pore for natural convection. Moreover, pore level heat transfer between foam and PCM is not satisfactory because of high thermal resistance due to low thermal conductivity of PCM. To address the heat transfer issues of NanoPCM and PCM in porous medium, this research tries to combine them together as NanoPCM in porous medium for thermal enhancement of latent heat storage system.

The research starts with the development of a conductional model for constant temperature boundary condition on top. As the boundary condition is applied from top, there is no presence of buoyancy effect for natural convection heat transfer and heat flux varies with the movement of melting front due to the change of thermal resistance. The effect of the volume fraction of nanoparticle and porosity of the porous medium are studied on temperature distribution, heat transfer and melt fraction inside the cavity analytically and numerically. A scale analysis is executed to establish simplified relationships between different non-dimensional parameters such as Fourier number, Stefan number, porosity and volume fraction. The analysis finds good agreement between the exact solution of analytic model and numerical result.
Second model includes both convection and conduction heat transfer with constant temperature boundary condition from side. Because of the boundary condition from side, the presence of buoyancy effect for natural convection helps to melt the top side first. After the top side melts completely, the remaining of melting occurs mostly because of conduction heat transfer. The model executes scale analysis to estimate the extent of the complete phase change process, which is a key factor of designing latent heat thermal energy storage system (LHTES). The scale analysis results in simplified relationships among different non-dimensional parameters such as Fourier number, Stefan number, Raleigh number, Nusselt number, porosity of the porous medium and volume fraction of nanoparticles. The model uses Darcy model in the porous medium. The natural convection melting process of NanoPCM inside the porous medium is solved numerically. The numerical simulation verifies the correctness of the relationships proposed by scale analysis and identifies the effects of nanoparticle volume fraction, time, Rayleigh number, flow field, thermal field and heat transfer process during the melting of NanoPCM inside the thermal energy storage system. This research understands that the penetration flow of Darcy model may not be the right choice for flow in the high porosity porous medium as it does not satisfy the no-slip condition. The Darcy model is preferred for validation of this research with many existing research for porous medium flow based on Darcy model. Brickman form of Darcy model where effective viscosity term is included for no-slip boundary condition can be used in the future study.

A third model is developed to satisfy the need of phase change material for constant heat applications. From the exact solutions of the models, the temperature distribution and movement of the melting interface inside the phase change region are predicted. The model data is compared with experimental data for interface movement rate and temperature profile at one location of melting interface.

During the development of above three models, equivalent value of thermophysical properties is needed to calculate for NanoPCM, PCM-Foam and NanoPCM-Foam. The equivalent value of density, specific heat and latent heat of fusion is determined using simple mixture theory for NanoPCM, PCM-Foam and NanoPCM-Foam. Same proportional distribution is used for calculating the effective thermal conductivity of PCM-Foam and NanoPCM-Foam, which is widely used by the most of the researchers. The effect of natural convection, foam
mechanical structure and thermal contact resistance between porous medium and inside substance are not captured in this effective thermal conductivity of PCM-Foam and NanoPCM-Foam. A very few researchers tried to address these issues but yet to get support from other researchers as this research needs mostly experimental evidence because of the complex porous medium structure. This research uses Maxwell model to predict the effective thermal conductivity of NanoPCM. Maxwell model for dilute mixture is widely used among the researchers to calculate the effective thermal conductivity of nanofluid. The nanostructure of the particle and interfacial effect are not included in the Maxwell model. Brownian motion and thermophoresis effect of nanoparticle can have significant impact on the effective thermal conductivity of NanoPCM when natural convection is present. Researchers tried to include these effects for predicting the effective thermal conductivity of nanofluid but because of inconsistency and controversy among those researches, this research prefers to stick with the widely used model of Maxell for prediction of equivalent thermal conductivity. Further research needs to be done with experimental validation to include the effect of Brownian motion and thermophoresis for calculation of effective thermal conductivity of NanoPCM.

This research carries out an extensive experimental work to observe the thermal performance of PCM, NanoPCM, PCM-Foam and NanoPCM-Foam for both conduction and convection heat transfer with the application of constant heat. More than fifty experiments are conducted because of various challenges and each experiment takes an average of four hours to complete. Constant temperature takes more time than constant heat to complete one experiment and constant heat is more common in real life application. That is why constant heat is chosen over constant temperature for this experimental work. Thermal enhancement of NanoPCM-Foam is observed for conduction only experiment but the desired thermal enhancement of NanoPCM is found absent for convection. Heavier Copper nanoparticle of 0.5% volume fraction makes the liquid NanoPCM more viscous and fails to generate desired natural convection current for thermal improvement of NanoPCM-Foam for convection. The better thermal performance is observed with PCM-Foam for better natural convection performance. Further experimental research needs to be done with lighter nanoparticle such as aluminum, zinc, magnesium, graphite etc. and less viscous phase change material with lower melting temperature little bit higher than ambient temperature to have lighter liquid NanoPCM for natural convection. Lower melting temperature also needs less heat to have lower hot wall temperature above melting temperature and reduces
chance of any heat loss to the surrounding through the thermal insulation. This experimental research satisfies the need of model described in Chapter 5 but further experimental research needs to be done with constant temperature boundary condition to validate the model of Chapter 3 and 4.

The objective of this research is to have enhanced heat transfer performance with NanoPCM-Foam by improving the thermal performance of phase change material. The desired thermal enhancement is observed for conduction heat transfer by improving the charging/discharge time along with low temperature rise. NanoPCM-Foam fails to achieve any thermal gain for natural convection because of heavier liquid NanoPCM. Better thermal performance for natural convection may be obtained by using lighter nanoparticle and less viscous phase change material but a balance needs to be ensured to take advantage of both conduction and convection heat transfer for best possible thermal enhancement of NanoPCM-Foam. This pioneering research with NanoPCM-Foam may lead to many future researches for replacing the sensible energy storage system with latent heat energy storage system for various transient thermal applications.

7.2 Future Work

Based on above discussion, the following future works are identified.

- Experimental work with lighter nanoparticle such aluminum, graphite etc. for various volume fraction
- Experimental work with low melting temperature and less viscous PCM
- Experimental work with various porosity and material of porous medium
- Experimental work for measurement of thermophysical properties such as viscosity and thermal conductivity of PCM, NanoPCM, PCM with porous medium and NanoPCM with porous medium
- Experimental work for isothermal boundary conditions
- Inclusion of Brownian motion and Thermophoresis motion in the model of equivalent thermal conductivity for convection heat transfer based on experiment
- Replacement of Darcy model of Chapter 4 with Brickman form of Darcy model