Experimental Characterization of Inward Freezing and Melting of Additive-Enhanced Phase-Change Materials Within Millimeter-Scale Cylindrical Enclosures

The inward melting and solidification of phase-change materials (PCM) within millimeter-scale cylindrical enclosures have been experimentally characterized in this work. The effects of cylinder size, thermal loading, and concentration of high-conductivity additives were investigated under constant temperature boundary conditions. Using a custom-built apparatus with fast response, freezing and melting have been measured for time periods as short as 15 s and 33 s, respectively. The enhancement of PCM thermal conductivity using exfoliated graphene nanoplatelets (xGnP) has also been measured, showing a greater than 3× increase for a concentration of 6 wt%. Reductions in the total melting and freezing times of up to 66% and 55%, respectively, have been achieved using xGnP concentrations of only 4.5 wt%. It is shown that the phase-change dynamics of pure and enhanced PCM are well predicted using a simple conduction-only model, demonstrating the validity of approximating enhanced PCM with low additive loadings as homogenous materials with isotropic properties. While general consistency between the measurements and model is seen, the effect of additives on heat transfer rate during the initial stages of freezing and melting is lower than expected, particularly for the smaller cylinder sizes of 6 mm. These results suggest that the thermal resistance of the PCM is not the limiting factor dictating the speed of the solid–liquid interface during these initial stages. [DOI: 10.1115/1.4033007]

Introduction

Solid–liquid phase-change processes are well suited to a variety of thermal systems due to their ability to store and release large amounts of energy with relatively small changes in temperature and density [1]. PCM are used in thermal management and building applications [2], solar thermal systems [3], and thermal storage devices for improving the overall performance of energy systems. Various enclosures have been studied to maximize heat transfer rates between the PCM and carrier fluid in these systems including spheres, horizontal and vertical cylinders, rectangular cavities, and flat panel systems [4]. Among these, melting and freezing in cylindrical systems have been studied both analytically and experimentally where phase change has been measured using techniques including photographic visualization [5,6], intermittent weighing of PCM [7–9], and direct measurement of changes in PCM density [1,10,11].

Sparrow and Broadbent conducted inward freezing experiments in a long vertically oriented copper cylinder with a length of 39.4 cm and diameter of 5.08 cm under moderate Stefan numbers of Ste = 0.072–0.225 [7]. They demonstrated that latent energy is
the largest contributor to the total heat transfer and showed that natural convection played only a small role over an initial short duration. Additionally, Larson and Sparrow performed experimental and numerical analysis on the effect of cylinder inclination during freezing of n-eicosane in a 3.81 cm diameter enclosure [8]. They demonstrated that the frozen mass and the energy transferred during freezing are insensitive to cylinder inclination. At work, a model neglecting the effects of natural convection was shown to underpredict the energy transfer rate by 25%, which was attributed to uncertainty in thermophysical properties of PCM and the presence of dendritic structures at the liquid–solid interface.

Additionally, Sparrow and Broadbent showed that the inward melting of n-eicosane in a vertically oriented 5.08 cm diameter cylinder is dominated by natural convection effects, following an initial conduction controlled stage [9]. Their experimental results demonstrated a 50% higher energy transfer rate than that predicted from a conduction-only model. Sparrow et al. also showed that while the latent energy was substantially larger than sensible energy, the initial subcooling of solid PCM significantly decreases the melting rate. Menon et al. conducted melting experiments in a vertical cylinder with a diameter of 5.72 cm using a commercial paraffin and visually observed a conical shape of solid PCM at later stages of melting due to natural convection [12]. They demonstrated good agreement between experimental results and a conduction-only melting model for small cylinders. Jones et al. reported a numerical model for predicting melting in a vertical cylinder for Stefan numbers up to 0.1807 [5]. Their experimental results showed that after an initial conduction controlled melting regime, the Stefan number has little effect on the average wall Nusselt number for melting within 6.38 cm diameter cylinders.

Han et al. conducted melting experiments using paraffin within vertical glass tubes with diameters from 1.26 cm to 5.78 cm and height of 25 cm, demonstrating conduction-dominated melting for diameters below 2.1 cm [13]. They showed good agreement between experimental results and a conduction-only melting model for small cylinders. Jones et al. reported a numerical model for predicting melting in a vertical cylinder for Stefan numbers up to 0.1807 [5]. Their experimental results showed that after an initial conduction controlled melting regime, the Stefan number has little effect on the average wall Nusselt number for melting within 6.38 cm diameter cylinders.

Sparrow et al. used a cylindrical coolant tube embedded inside a stainless steel cylindrical PCM container to analyze outward freezing from a 2.79 cm diameter cylinder [14]. They reported that liquid superheating produces natural convection within the liquid PCM and slows down the freezing process, eventually terminating solidification at high superheats. They also showed that for no superheating, a conduction-only model underpredicts the interface growth rate, which they attributed to the presence of whiskerlike dendrite structures. Additionally, it was reported that natural convection plays a role only at the very initial stages of short duration freezing [15]. Similar conclusions were reiterated by Wang et al. to explain an increase in the interface growth rate during outward freezing [16]. They attributed this to the formation of dendritic structures and a decrease in convective depression due to extended cooling surfaces.

While PCM can store relatively large amounts of energy with only small changes in temperature and density, their use has been limited by low intrinsic thermal conductivities and issues related to long-term stability [2]. Among the various low temperature PCM available such as water, paraffin, fatty acids, sugar, alcohols, and salt hydrates [17], paraffin-based PCM has demonstrated excellent long-term cyclic thermal stability [18,19]. However, the ability to transfer thermal energy during the melting and freezing of these PCM is greatly inhibited by their low thermal conductivities [20]. As such, a wide range of approaches have been developed to increase the heat transfer performance of systems using PCM. These include most notably the addition of conductive solid structures into the PCM, such as metal matrices [18,21], graphite matrices [22], fins [23], foils and heat pipes [1], and nanoenhanced PCM [24–27]. In particular, a variety of carbon-based nanoparticles with high intrinsic thermal conductivity, including graphite nanofibers [28,29], few-layer graphene nanoplatelets [30–32], and ultrathin graphite foams [33,34], have been used to enhance thermal conductivity of PCM, leading to up to 28 times improvement in thermal conductivity of PCM [31].

This work systematically examines the effects of nanoadditives on freezing and melting within different cylinder enclosure sizes and at different thermal loadings. This has allowed the impacts of these individual effects on short-term energy storage systems to be isolated and characterized. While existing studies have investigated the melting and freezing of PCM with and without additives, these prior works have generally examined geometries with characteristic lengths of several centimeters or larger and phase-change times on the order of several minutes or even hours. This work, however, focuses on the inward melting and freezing of n-eicosane within millimeter-scale cylindrical enclosures, with characteristic freezing and melting times of down to tens of seconds. This investigation has been carried out to evaluate the effectiveness of small diameter PCM geometries, with high surface-to-volume ratios, for short-term thermal storage. It has been conducted using direct measurements of the phase-change phenomena and PCM temperatures with fast time responses. By quickly charging and discharging the PCM volumes, novel systems using recirculating PCM can be designed to transfer heat from one working fluid to another. These systems have potential use in dry cooling of thermoelectric power plants, as well as other applications such as heating, ventilation, and air condition applications and industrial heat exchangers. This work has experimentally characterized the effects of thermal loading, PCM diameter, and nanoaditive concentration on the freezing and melting processes in small diameter cylinders, as well as their associated transient heat transfer rates.

Experimental Methods

Freezing and Melting of PCM. A custom-built experimental apparatus has been used to study the inward freezing and melting of PCM within cylindrical enclosures of different diameters. Figure 1 shows a schematic of the test setup as well as a photograph of the apparatus for PCM cylinder diameter of D = 14 mm. The assembly consists of a 1 mm thick-walled copper (Alloy 122) tube surrounded by a polycarbonate cylinder to create an annular space. Using plastic manifolds at the top and bottom, water is passed through the annulus at high flow rates to maintain an isothermal cylinder wall conditions. Measurements verify negligible temperature change (<1 °C) of the water through the annular space, verifying spatially uniform boundary condition. This allows the temperature of the thin copper tubing to be dynamically controlled by varying the temperature of the flowing water. Figure 1(a) shows a schematic of the test setup where two constant temperature baths (one hot and one cold) are used to control the PCM wall temperature during melting and solidification. By simultaneously switching the three-way valves, the temperature of the water flowing through the system is abruptly changed leading to freezing or melting of the PCM. The assembly is instrumented with two type-T thermocouples (labeled TC in Fig. 1(a)), measuring temperature at the geometric center of the PCM (Tc), as well as the temperature notably the copper wall (Twall). The Biot number for the copper tube was calculated assuming fully developed annular flow and is found to be Bi = 0.009 ≪ 0.1. As such, the copper wall can be considered isothermal and the thermocouple embedded in the wall provides an accurate measurement of the PCM–copper interface temperature. The thermal resistance of the thin copper tube is negligible, and its time response to the dynamic changes in
water temperature has been shown to be only a few seconds for both cylinders. Therefore, all the data collected during this short initial time period is discarded, ensuring that the thermocouple at the wall is accurately measuring the temperature at the PCM–copper interface. Additionally, an electronic pressure transducer (labeled PT in Fig. 1(a)) is used to measure the pressure of the air within the enclosure above the PCM. By monitoring the change in air pressure ($\Delta P_{\text{air}}$), the expansion or contraction of PCM due to phase change is measured and the amount of PCM having undergone phase change can be calculated using Eq. (1), based on the technique previously reported by Sharifi et al. [1]. See Appendix A for the derivation of the following equation:

$$\frac{V}{V_0} = \left( \frac{\rho_{\text{PCM}, i}}{\rho_{\text{PCM, f}} - \rho_{\text{PCM, i}}} \right) \left[ 1 + \frac{V_{\text{initial}}}{V_{\text{air}, i}} \left( \frac{P_{\text{air}, i} + \Delta P_{\text{air}}}{P_{\text{air}, i}} \right) \right]^{-1}$$  \hspace{1cm} (1)

In Eq. (1), $V$ is the volume of PCM having undergone phase change (freezing or melting) at any instant and $V_0$ is the total volume of PCM mixture. $V_{\text{initial}}$ is the initial volume of the PCM before phase change, and the density of the initial and final phases of PCM is given by $\rho_{\text{PCM, i}}$ and $\rho_{\text{PCM, f}}$, respectively. $P_{\text{air}, i}$ and $\Delta P_{\text{air}}$ are the initial pressure and the change of pressure of the air within the system above the PCM. A 4 mm air gap was maintained at the top of the PCM (when in the liquid phase) to make sure that the PCM do not contact the top of the cylindrical enclosure. The majority of the air volume, however, is actually contained within a long thin tube connecting the apparatus to the pressure transducer. The air volume of this tube is approximately 94% of the total air volume. This tube length was chosen to create pressure changes on the order of 4–5 kPa during freezing and melting, resulting in an uncertainty of < 1% in the pressure measurement. As such, the air temperature was assumed constant throughout the tests and at the ambient room temperature, simplifying the approach used by Sharifi et al. [1]. The initial volume of PCM within the enclosure and the resulting volume of the air within the system are calculated prior to each individual test and used in Eq. (1).

Degas n-eicosane, with a melting temperature of 36.4°C [15], was used as the PCM for all the experiments. While the interface shape and speed will dictate the exact temperature at the liquid–solid interface, throughout this work it has been assumed that interface temperature is equal to the melting temperature, $T_m = 36.4°C$. During testing, the temperature and pressure profiles were recorded using a data acquisition system (Natural Instruments, Austin, TX) at a frequency of 1 Hz. Figure 2 shows a representative set of raw data collected during a melting and freezing cycle. The PCM was initially maintained at a set subcooled temperature ($\Delta T_{\text{sub}}$) by passing cold water through the assembly for 1 hr to reach thermal equilibrium. The water flow was then abruptly switched from cold to hot, initiating melting of the PCM with an imposed superheating of $\Delta T_{\text{sup}}$. Figure 2(a) shows the transient wall and PCM center temperatures, and Fig. 2(b) shows the liquid volume within the enclosure as a function of time, as calculated using Eq. (1). A plateau in the PCM center temperature is seen around the melting temperature, followed by complete thermal equilibrium of the entire system at the set superheat temperature. Simultaneously, the liquid volume reaches a constant value as all of the PCM are melted. After melting was complete, the water flow was abruptly changed again to subcool the cylinder and the freezing process began. Similar behavior is seen during freezing as the whole system eventually reaches equilibrium at the set subcooling temperature. The reproducibility of the applied boundary conditions as well as experimental measurement technique has been validated through repeatability testing. Continuous freezing and melting at a fixed superheating and subcooling were conducted for pure PCM (no additives) for over 50
cycles. This corresponded to over 24 hrs of active melting and freezing and was carried out over a period of 3 days with the system stored in the solidified state when not in operation. The standard deviation of the measured freezing and melting times over this extended period was ~3.29% for freezing and ~2.29% for melting. While extended testing could not be conducted for enhanced PCM due to sedimentation, all the tests showed repeatable results during successive trials.

In addition to measuring the dynamic temperatures and volumes of the PCM undergoing phase change, the transient heat transfer rates can also be calculated using the data shown in Fig. 2. The total heat transfer rate is given by the sum of its latent and sensible components

\[ q_{\text{tot}} = q_{\text{lat}} + q_{\text{sen}} \]  

(2)

where the heat transfer rate due to phase change is given by

\[ q_{\text{lat}} = \rho h_{\text{SL}} \frac{dV}{dt} \]  

(3)

and the heat transfer rate due to sensible heating or cooling is given by

\[ q_{\text{sen}} = \frac{dE_{\text{sen}}}{dt} \]  

(4)

In Eq. (3), \( \rho \) and \( V \) represent the density and volume of the PCM having undergone phase change (liquid for the melting process and solid for the freezing process), and \( h_{\text{SL}} \) is the latent heat of fusion. In Eq. (4), \( E_{\text{sen}} \) is the thermal energy stored in the PCM in the form of sensible heat and is given by

\[ E_{\text{sen}} = \rho L c_p \cdot V_1 T_i + \rho_S c_p S V_S T_S \]  

(5)

where \( c_p \) is the heat capacity of the PCM, and the subscripts \( L \) and \( S \) refer to liquid and solid, respectively. \( T_i \) and \( T_S \) are the average temperatures of the liquid phase and solid phase at any instant during the process. The average temperature of the outermost PCM phase (liquid during melting and solid during freezing) is estimated as

\[ T_{\text{L,melt or S,freeze}} = \frac{1}{2} (T_i + T_w) \]  

(6)

Similarly, the temperature of the innermost PCM phase (solid during melting and liquid during freezing) is estimated as

\[ T_{\text{S,melt or L,freeze}} = \frac{1}{2} (T_i + T_c) \]  

(7)

In Eqs. (6) and (7), \( T_w \) and \( T_c \) are the measured transient wall and PCM center temperatures, and \( T_i \) is the solid–liquid interface temperature assumed to be equal to the melting temperature 36.4°C. Combining Eqs. (2)–(7), the total heat transfer rate as a function of time has been calculated during the melting and freezing processes for all the experiments.

### Thermophysical Properties of PCM

While paraffin-based materials have reasonably large latent heats of fusion (153–266 kJ/kg), their thermal conductivities are low (0.1–0.5 W/m K) [2]. This limits their use and performance in thermal systems. Experimental studies have shown the enhancement of PCM thermal conductivity with the addition of a variety of nanoscale high-conductivity additives [30,31,35,36]. In this work, 99% pure n-eicosane (Sigma Aldrich) is used as the PCM and various concentrations of exfoliated graphene nanoplatelets (xGnPs) (XG Sciences Grade H-25) are added to enhance thermal conductivity. The thermal conductivity of the composite PCM was measured using a custom-built experimental apparatus based on the Wheatstone bridge hot wire measurement technique [37,38].

This transient thermal conductivity measurement apparatus uses a cylindrical test chamber consisting of two concentric cylinders of diameter 4.5 cm and 8.9 cm, with a vertically oriented 20 µm diameter and 16 cm long Pt wire in its center. The material to be tested was placed in the inner cylinder with the hot wire embedded within its center. The temperature of the test material was controlled by flowing water from a constant temperature bath through the annulus between the two cylinders. The dynamic temperature of the wire was determined by measuring its electrical resistance using a Wheatstone bridge circuit, with high precision resistors (100 Ω) on three legs and the hot wire with a potentiometer on the other leg. The potentiometer was used to zero the circuit at the beginning of each test, and a wave generator was used to synchronize all the measurements, which were recorded using an oscilloscope. A preset power input was abruptly delivered to the hot wire while the dynamic change in electrical resistance of the wire was measured as the heat conducted into the surrounding test material. Given the wire’s electrical resistance as a function of its temperature, the thermal conductivity of the test material can be obtained using a 1D cylindrical transient conduction model as given by the following equation [38,39]:

\[ k = \frac{q}{4\pi L \frac{d\ln(T)}{dT}} \]  

(8)

The hot wire setup was first calibrated using two well-established materials of low thermal conductivities in the range relevant to this work. The measured conductivities of air and soybean oil at 23 °C were found to be 0.027 ± 0.003 W/m K and 0.147 ± 0.012 W/m K, respectively, closely matching the tabulated values of 0.0257 W/m K and 0.158 W/m K to within the experimental uncertainty [40]. This technique was then used to measure the thermal conductivity of pure n-eicosane as well as n-eicosane with four different concentrations of xGnPs up to 6 wt.%. Different concentrations of xGnPs were added to pure n-eicosane following the methods reported by Warzoha and Fleischer [31]. Initially, the required amounts of pure solid eicosane and xGnPs were weighed using a high precision balance. The solid eicosane was then melted and stirred magnetically on a hot plate at 50 °C for approximately 2 hrs. Following that the xGnPs were added to the liquid PCM in increments of 0.75% of the solid PCM weight until the desired concentration was achieved. Each increment was followed by magnetic stirring on a hotplate for 20 min and then 20 min of sonication at 50 °C. The stability of the additive-enhanced PCM was estimated by measuring their thermal conductivities every 30 min after a sample was prepared. The thermal conductivity of the xGnP composite PCM was found to be constant (within the measurement uncertainty) for greater than 1 hr with no apparent effects of sedimentation.

Figure 3(a) shows the measured conductivities as a function of the isothermal PCM temperature at various xGnP concentrations, including results for both solid and liquid phases. Figure 3(b) shows the conductivity enhancement factor as a function of xGnP concentration, where good agreement is seen with the previous experimental work of Warzoha and Fleischer using commercially available solid paraffin (IGI 1230 A) [31]. Additionally, these results agree well with the model predictions of Nan et al. [41], with an effective xGnP thermal conductivity of 98 W/m K, the value experimentally measured for loosely packed carbon paper comprised of xGnPs [42]. While the intrinsic in-plane conductivity of high-quality graphene can be as high as 2000 W/m K [43], the loosely packed xGnP is believed to be the configuration of xGnPs dispersion in n-eicosane in the present study.

The conductivity of n-eicosane is nearly doubled with 3 wt.% of xGnP, and more than tripled using 6 wt.%, where the linear trend of the enhancement factor versus xGnP concentration shown in Fig. 3(b) suggests that the xGnP concentrations tested in this work are below the percolation limit [29,32]. For all the tests, particular care was taken to collect data prior to the onset settling of nanoplatelets so as to ensure that the properties of the composite PCM were spatially uniform. Table 1 lists the properties of pure PCM and with 3.0 and 4.5 wt.% of xGnP loading, where the
thermal conductivities of the n-eicosane and eicosane-xGnP composites are experimentally measured. All the other properties are assumed to be the weighted averages of the reported pure PCM and xGnP properties \[27,32,44\].

**Analysis**

**Nondimensional Parameters.** The quantities measured experimentally in this work have been nondimensionalized using Eqs. (9)-(13) to compare against the analytical predictions of the melting and freezing processes. The volume of PCM having undergone phase change is nondimensionalized using the total volume of PCM mixture

\[
\phi = \frac{V}{V_0} = 1 - \left(\frac{r_i}{r_w}\right)^2
\]

(9)

where \(r_i\) is the radius of the inwardly propagating solid–liquid interface, and \(r_w = D/2\) is the radius of the cylinder, as shown in Fig. 4. The time and temperature differences driving phase change are nondimensionalized using the Fourier and Stefan numbers, with the radius of the cylinder used as the characteristic length scale

\[
Fo = \frac{\alpha t}{r_w^2}
\]

(10)

\[
Ste = \frac{cp[T_w - T_i]}{h_{SL}}
\]

(11)

where \(\alpha\) is the thermal diffusivity of the PCM having undergone phase change. In Eq. (11), the absolute value of the temperature difference between the wall and the solid–liquid interface is used to account for both freezing and melting conditions. Finally, the heat transfer rates can be given in the form of a Nusselt number, using the radius of the cylinder as the characteristic length scale

\[
Nu = \left(\frac{q_{tot}}{A \Delta T}\right)\frac{r_w}{k} = \frac{q_{tot}}{2\pi H k[T_w - T_i]}
\]

(12)

In Eq. (12), the term in parentheses is an effective heat transfer coefficient, defined using the surface area of the cylinder \(A\) and the wall-to-interface temperature difference \(\Delta T\). The effect of

**Fig. 3** Thermal conductivity enhancement of n-eicosane with xGnP, showing (a) thermal conductivity as a function of xGnP concentration and isothermal PCM temperature and (b) enhancement factor relative to n-eicosane as a function of xGnP concentration, compared against the theoretical predictions from Nan et al. [41] using the thermal interface resistance between graphite nanoplatelet and paraffin as \(R_i \approx 0.9 \times 10^{-7} \text{m}^2 \text{K/W} [32]\) and measurements from Warzoha and Fleischer [31]. In (b), the solid n-eicosane conductivity is measured at 23°C and the liquid n-eicosane conductivity is taken as the average of the values at 40°C and 55°C, as shown in (a). The representative experimental uncertainties are estimated from the standard deviation of six conductivity tests.

**Table 1** Thermophysical properties of additive-enhanced n-eicosane \[32,42,44\]

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<th>xGnP (wt.%)</th>
<th>(\rho_S (\text{kg/m}^3))</th>
<th>(c_{p,S} (\text{J/kg K}))</th>
<th>(k_S (\text{W/m K}))</th>
<th>(\rho_L (\text{kg/m}^3))</th>
<th>(c_{p,L} (\text{J/kg K}))</th>
<th>(k_L (\text{W/m K}))</th>
<th>(h_{SL} (\text{kJ/kg}))</th>
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</table>

**Fig. 4** Inward freezing and melting within a cylindrical geometry
natural convection on heat transfer can be characterized using Rayleigh number defined as

$$Ra = \frac{g\beta(T_\text{w} - T_i)D^3}{\nu^2}$$  \hspace{1cm} (13)$$

where $\beta$ and $\nu$ are the volumetric expansion coefficient and the kinematic viscosity of the liquid PCM, respectively.

**Modeling of Inward Freezing and Melting.** The problem of solid–liquid phase change in a one-dimensional cylindrical configuration (in the absence of liquid motion and assuming constant thermophysical properties) can be described by the energy equation in the bounded domain between the wall and an inwardly moving solid–liquid interface

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) = \frac{1}{\tau} \frac{\partial T}{\partial \tau}, \hspace{0.5cm} r_i < r < r_w$$  \hspace{1cm} (14)$$

For a constant wall temperature and a constant solid–liquid interface temperature, the imposed boundary conditions are

$$T(r_w, \tau) = T_\text{w}$$  \hspace{1cm} (15)$$

$$T(r_i, \tau) = T_i$$  \hspace{1cm} (16)$$

It is assumed that the inner phase of the PCM is isothermal at the melting temperature for all the times including the initial condition. Additionally, the rate at which the solid–liquid interface propagates inward is dictated by

$$k \frac{\partial T}{\partial r} \bigg|_{r=r_i} = \rho \beta \text{SL} \frac{dr_i}{d\tau}$$  \hspace{1cm} (17)$$

where $k$ is the thermal conductivity of the outer PCM having undergone phase change. It has been previously shown that an integral method using a second-order logarithmic temperature profile can be used to satisfy Eqs. (14)–(17) and solve for the solid–liquid interface location as a function of time [45]. This yields a nondimensional solution of the form

$$\phi + (1 - \phi) \ln(1 - \phi) = 4Fo \sqrt{1 + 2Ste} - 1$$  \hspace{1cm} (18)$$

where the interface location is related to the volume fraction using Eq. (9), and the Fourier and Stefan numbers are given by Eqs. (10) and (11).

For small Stefan numbers, it can be readily shown that the right-hand side of Eq. (18) can be simplified to the form of

$$\phi + (1 - \phi) \ln(1 - \phi) = 4FoSte$$  \hspace{1cm} (19)$$

Considering the range of Stefan numbers characterized in this work, this simplification introduces an error of 4–8%, which is comparable to or less than the associated experimental uncertainties. This analysis can also be used to predict dynamic heat transfer rate during inward melting and freezing. By assuming that the heat transfer associated with sensible heat is sufficiently small ($q_\text{hut} \approx q_\text{hst}$), Eq. (3) can be combined with Eq. (13) and nondimensionalized using Eqs. (9)–(11), resulting in

$$Nu = \frac{d\phi}{d(\text{FoSte})}$$  \hspace{1cm} (20)$$

Evaluating the differential in Eq. (20) using Eq. (19) yields the Nusselt number as a function of volume fraction of

$$Nu = -\frac{4}{\ln(1 - \phi)}$$  \hspace{1cm} (21)$$

Equation (19) has been used here to predict the transient volume fraction ($\phi$) as a function of nondimensional time (FoSte), while Eqs. (20) and (18) are combined to predict the nondimensional heat transfer rate ($Nu$) as a FoSte. This analysis has been used to compare predicted PCM volumes having undergone phase change and heat transfer rates to those measured during the melting and freezing experiments. It should be noted that this modeling approach neglects the effects of sensible heating, as well as the effects of natural convection during phase change. It also assumes that the inner phase of PCM is isothermal at the melting temperature, the solid–liquid interface remains planar and is at the melting temperature, and that the interface is moving slowly enough so that interface kinetics are negligible.

**Results and Discussion**

The experimental apparatus shown in Fig. 1 was used to characterize the phase-change dynamics and transient heat transfer of the three PCM listed in Table 1. These include n-eicosane with 0 wt.% (pure), 3 wt.%, and 4.5 wt.% concentrations of xGnP's undergoing both freezing and melting, in 6 mm and 14 mm cylindrical enclosures. Additionally, the effects of thermal loading have been investigated by applying two different sets of boundary conditions, resulting in 24 distinct tests. During freezing, the PCM is initially superheated to a value of $\Delta T_{\text{sup}}$ and then subjected to an abrupt subcooling of $\Delta T_{\text{sub}}$. During melting, the PCM is initially subcooled to a value of $\Delta T_{\text{sub}}$ and then subjected to an abrupt superheating of $\Delta T_{\text{sup}}$. Each experiment is conducted with symmetric superheating and subcooling conditions, with $\Delta T_{\text{sup}} = \Delta T_{\text{sub}} = 10^\circ \text{C}$ or $\Delta T_{\text{sub}} = \Delta T_{\text{sup}} = 25^\circ \text{C}$. Prior to each test, the liquid PCM is degassed in an ultrasonic bath for 30 min and then placed in a vacuum chamber for an additional 10 min. It is then thoroughly mixed and poured into the enclosure in a layer-by-layer fashion to ensure no settling of the xGnPs during loading and to eliminate the formation of voids. The apparatus is fully assembled and sealed with RTV silicone overnight to ensure an airtight seal. The integrity of the sealing procedure was evaluated by pressurizing the test assembly to 15 kPa using compressed nitrogen and monitoring the pressure. No loss of pressure was seen over a 24-hr period, including thermal cycling tests to investigate the effects of thermal expansion. All the measurements of the additive-enhanced PCM performance are collected over a span of time where the PCM has been in a liquid form for less than 20 min total and limited to 2–3 cycles total. As mentioned previously, this time span has been independently shown to ensure no significant settling or redistribution of the xGnPs has taken place. Additionally, after each set of tests the solid PCM is removed from the cylinder to visually confirm that no appreciable sedimentation has occurred. While the stability of additive-enhanced PCM over extended cycles is a critical issue, it is not a focus of this work.

**Freezing and Melting of PCM.** Figure 5 shows the volume of PCM having undergone phase change as a function of time for pure n-eicosane in cylindrical enclosures of diameter 6 mm (Fig. 5(a)) and 14 mm (Fig. 5(b)). Each data set is plotted up to 95% of the final PCM volume for clarity, which is taken to represent fully solidified or melted within the experimental uncertainty. The experimental apparatus has been used to accurately measure freezing times of less than 40 s, with melting times as high as 1040 s for the pure PCM data shown in Fig. 5. As can be seen, the solidification times are notably less than the melting times for both cylinder sizes under both thermal loadings. The time to solidify is measured to be anywhere from 30% to 60% of the time required to melt the pure PCM for the four cases shown here. This discrepancy is explained by examining the differences in thermal conductivity of the liquid and solid phases. The ratio of the measured liquid and solid thermal conductivities was found to be $k_L/k_s = 33–52\%$ (accounting for experimental uncertainties), which is consistent with the observed differences in solidification
and melting times. Similarly, the larger applied temperature differences resulted in a decrease in time to melt and solidify, as would be expected.

\( x\text{GnP}\)s have been added to the pure n-eicosane at 3.0 wt.% and 4.5 wt.% and characterized during both solidification and melting at the two thermal loadings. The effects of these high-conductivity additives on phase change are shown in Fig. 6 for both cylinder sizes under a superheating and subcooling of 10 °C. Figures 6(a) and 6(b) show the solid volume during freezing for each cylinder, while Figs. 6(c) and 6(d) show the liquid volume during the melting process. As expected, the inclusion of high-conductivity \( x\text{GnP}\)s has reduced the time required to complete each of the phase-change processes. Freezing times and melting times as low as 34 s and 74 s, respectively, have been measured with 4.5 wt.% \( x\text{GnP}\) in the 6 mm cylinder at the low temperature difference of 10 °C. Additionally, freezing and melting times as low as 15 s and 33 s have been achieved at the higher temperature difference of 25 °C (not shown in Fig. 6). Figure 3(b) shows that the addition of \( x\text{GnP}\)s at a concentration of 4.5 wt.% results in an enhancement in liquid thermal conductivity of \( k_L, 4.5\% / k_L, \text{pure} = 2.9 \pm 0.32 \) and solid thermal conductivity of \( k_S, 4.5\% / k_S, \text{pure} = 2.6 \pm 0.29 \). Figure 6 shows that these enhancements in conductivity lead to a consistent reduction in melting time, where \( t_{\text{melt, 4.5 wt.\%}} / t_{\text{melt, pure}} \) is 34% and 41% for the 6 mm and 14 mm cylinders, respectively. Similarly, a reduced freezing time is observed where \( t_{\text{freeze, 4.5 wt.\%}} / t_{\text{freeze, pure}} \) is 60% and 45% for the 6 mm and 14 mm cylinders, respectively.

It can be seen that the enhancement of PCM thermal conductivity has a seemingly minimal effect on solidification and melting rates during the very initial stages of phase change. Figure 6 shows indistinguishable differences in dynamic volume change for the pure and additive-enhanced n-eicosane at low volume fractions, this is particularly true for the smaller diameter cylinder. The freezing and melting dynamics within 6 mm cylinders are shown in Figs. 6(a) and 6(b), respectively, where the behaviors of the pure and enhanced PCM are indistinguishable until almost 50% of the PCM undergoes phase change. For the 14 mm diameter cylinders, the additives enhanced and pure PCM behave nearly identical up until ~25% of the total final volume for both melting and freezing tests. This shows that while the use of additives provides a substantial decrease in the time required to complete the entire solidification or melting processes, their impact on the highly dynamic early stages is minimal. Additionally, these results suggest that the effect of high-conductivity additives diminishes with smaller cylinder sizes.

To compare the measured freezing and melting dynamics to the closed-form predictions, the data from each of the 24 distinct testing cases has been nondimensionalized using Eqs. (9)–(11). Figure 7 shows the volume fraction of PCM having undergone phase change, \( \phi \), plotted against the nondimensional time given by the product of the Fourier number and Stefan number, \( FoSte \). For clarity, the eight data sets for pure n-eicosane are plotted in Fig. 7(a), while Fig. 7(b) shows the 16 data sets for the additive-enhanced n-eicosane. Both graphs show comparisons against the modeling predictions from Eq. (19), and Fig. 7(a) includes results from the seminal work of Larson and Sparrow [8]. Good agreement is seen between the results from all of the tested cases and the closed-form modeling approach, with the discrepancies being mainly attributed to the experimental uncertainties.

The results in Fig. 7(a) strongly suggest that the effects of natural convection are insignificant for melting and freezing in both cylinder sizes considered, as was predicted by Han et al. [13]. The Rayleigh number for the eight data sets shown in Fig. 7(a) spans nearly 2 orders of magnitude, ranging from \( 4 \times 10^3 \) to \( 1.3 \times 10^5 \), and yet no discernable impact of Rayleigh number can be seen. Additionally, the effects of initially superheating the PCM prior to freezing and initially subcooling the PCM prior to melting are not evident. These initial superheatings and subcoolings are not accounted for in the model, and no clear discrepancies due to these effects can be seen. This would be expected by simple examination of the relevant Stefan numbers and the magnitude of sensible heat relative to latent heat. The pure n-eicosane data sets also closely match the freezing work of Larson and Sparrow, where a simple experimental method based on pouring liquefied PCM out of a container and weighing the remaining frozen mass at various intervals was used [8]. In that work, inward freezing within a 38 mm cylindrical enclosure was studied, with characteristics freezing times on the order of tens of minutes. The tests conducted here show excellent agreement with this earlier work and has allowed for the measurement of phase-change dynamics within enclosures that are 3–6 times smaller in diameter, with freezing and melting occurring up to 2 orders of magnitude faster using additives. While the data generally match the modeling predictions within the experimental uncertainty, the model consistently underpredicts the experimental results at low to moderate volume fractions. Larson and Sparrow, as well as others, have...
attributed this phenomena to increased freezing rates due to the existence of a complex liquid-solid interface comprised of dendritic structures [6,14–16]. The existence of a highly dendritic interface has been visually observed previously during the inward freezing of eicosane in millimeter-scale cylindrical geometries in the absence of natural convection [45], thus providing a possible explanation for the observed trends. Similarly, the effects of natural convection during the very early stages (which have been neglected in the model) could provide an explanation of the underprediction during the initial stages of melting. Additionally, the variability in the data presented in Fig. 7, as well as its consistency with the modeling prediction, is comparable to the estimated experimental uncertainty.

Figure 7(b) shows the results of the additive-enhanced n-eicosane compared to the model prediction where the nondimensional parameters are evaluated using the properties of additive-enhanced PCM from Table 1. As expected, the effects of natural convection and initial superheating or subcooling are not apparent. The viscosities of the additive-enhanced PCM were measured to be 10.0 cP and 15.9 cP for the xGnP concentrations of 3 wt.% and 4.5 wt.%, respectively, over a shear rate range of 150–350 s⁻¹. This corresponds to a range of Rayleigh numbers for the cases shown in Fig. 7(b) (enhanced PCM) of Ra = 4 × 10² to Ra = 3.5 × 10³, roughly an order of magnitude lower than those for pure eicosane. General agreement between the measured and predicted performance can be seen, as well as consistency with the pure PCM data in Fig. 7(a). This indicates that the composite PCM with xGnP's behave like (and can therefore be modeled as) homogeneous materials with isotropic properties as given in Table 1, and that no sedimentation has occurred during testing.

Heat Transfer Rate. The experimental approach used here has a relatively high sampling frequency of the temperature and volume change data (1 Hz). This allows for the calculation of transient heat transfer rates via numerical differentiation of the phase-change volume and temperatures with respect to time. Using Eqs. (2)–(7), the contributions of sensible and latent heat to the total heat transfer rate have been calculated for all the tests. Figure 8 shows representative plots of the dynamic heat transfer rates in the early stages of freezing in 6 mm cylinder at two different thermal loadings. These transient results are consistent with the relevant total Stefan numbers, Steₜₐₑ = cₚ (∆Tₑₑₐₑ + ∆Tₑₑₐₜ)hₑₑₜ, calculated to include the effects of the initial superheating prior to freezing. This result in Steₜ = 0.15 for the conditions in Fig. 8(a) and Steₜ = 0.39 for the conditions in Fig. 8(b), which closely match the ratio of the sensible to latent heat transfer rates during the early stages of freezing. As can be seen, the heat transfer rates

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Fig. 6 The effects of exfoliated graphene nanoplatelets additives (xGnP) on n-eicosane phase-change dynamics, showing solid volume during inward freezing within a (a) 6 mm and (b) 14 mm cylinder, as well as liquid volume during inward melting within a (c) 6 mm and (d) 14 mm cylinder.
are initially very high and decay sharply as the solid–liquid interface propagates inward due to increased resistance across the solidified volume. Similar behaviors are seen for both cylinder sizes and during the melting process.

The effect of xGnP additives on the total transient heat transfer rate is shown in Fig. 9 for 6 mm cylinders during the initial stage of both freezing and melting, at two different thermal loadings. For both freezing (Fig. 9(a)) and melting (Fig. 9(b)), the effect of high-conductivity additives on the observed heat transfer rates is less pronounced than would have been expected. Using xGnP additives at a concentration of 4.5 wt.% increases the bulk thermal conductivity of PCM by a factor of 2.6 and 2.9 for the solid and liquid phases, respectively. However, the enhancement of heat transfer rates in the early stages of phase change is modest, with a maximum increase of about 30% to 40% during melting at $\Delta T_{\text{sup}} = 25 \degree C$ (Fig. 9(b)). Conversely, during freezing at $\Delta T_{\text{sup}} = \Delta T_{\text{sub}} = 10 \degree C$ (Fig. 9(a)) the differences between pure and additive-enhanced PCM is comparable to the experimental uncertainties. This is consistent with the trends seen in Fig. 6 for low volume fractions. These results suggest that for these very initial stages of freezing and melting, the thermal resistance of the PCM is not the limiting factor dictating the inward propagation of the solid–liquid interface and the resulting heat transfer rate.

Figure 10 shows the transient total heat transfer rate, nondimensionalized using the Nusselt number given by Eq. (12), for all the testing conditions. For clarity, the results from the 6 mm and 14 mm cylinders are plotted separately in Figs. 10(a) and 10(b), respectively, and compared against the modeling predictions combining Eqs. (19) and (21). The experimental results are generally well predicted by the model, closely following the overall trend. At later stages, the model and data match to within the experimental uncertainties, but deviations between the two are seen in the
earlier stages. Figure 10(b) is intentionally plotted over small non-dimensional times to highlight both the high heat transfer rates as well as the discrepancies between the data and model. While all of the nondimensionalized data sets (in both graphs) collapse to within their experimental uncertainties and closely follow the predicted trend, the model consistently and notably underpredicts heat transfer in the very initial stages of freezing and melting. This underprediction is attributed to discrepancies between the measured and modeled heat transfer rates from both the latent and sensible heat components. The heat transfer associated with phase change is calculated using the derivative of volume with respect to time in Eq. (3). As seen in Fig. 7, the closed-form modeling approach used in Eqs. (14)–(19) underpredicts the speed of the inwardly propagating solid–liquid interface at small times ($\text{FoSte} < 0.01$). This results in an underprediction of the solidification and melting rates ($dV/dt$) in Eq. (3). Additionally, the predicted Nusselt number given by Eq. (21) does not entirely incorporate the effects of sensible heating. While the effects of wall subcooling and wall superheating are included in the prediction of the interface position for freezing and melting, respectively, the change in sensible energy of the initial and final PCM phases are not included. As seen in Fig. 8, these effects account for anywhere from 15% to 39% of the total heat transfer rates for the tested conditions. Additionally, these sensible effects are most pronounced in the early stages of solidification and melting as the initially superheated or subcooled PCM quickly reaches the melting temperature, as seen in Fig. 2.

Conclusions

An experimental characterization of solid–liquid phase change within millimeter-scale cylindrical systems has been conducted. Using a testing apparatus with fast time responses, the phase-change dynamics and heat transfer rates of inwardly freezing and inwardly melting n-eicosane have been measured as a function of time. Freezing times varying from 15 s to 7 min and melting times varying from 33 s to 15 min were recorded. The fast response times and high sampling rates used in the current work have allowed for the direct calculation of transient heat transfer during melting and solidification, including the separate effects of
sensible and latent heat. A phase-change Nusselt number was defined to nondimensionalize the measured heat transfer rates and compare to a simple 1D analytic model neglecting natural convection, with general agreement seen between the two within the experimental uncertainties. While the model captured the trend of the transient heat transfer data, a notable underprediction was seen in the very initial stages, which has been attributed to the effects of sensible heating as well as an apparent underprediction of the solid–liquid interface speed.

The thermal conductivity of pure n-eicosane was varied with the addition of xGnPs to investigate the performance of additive-enhanced PCM. The bulk thermal conductivity of pure and enhanced PCM was measured using a custom-built experimental apparatus up to a xGnP concentration of 6 wt.%, below the percolation threshold. Enhanced PCM with 3.0 wt.% and 4.5 wt.% additive concentrations, corresponding to conductivity enhancements of a factor of 2–3, were studied during dynamic melting and freezing. This use of high-conductivity additives was shown to decrease the total melting times by up to 66% and freezing times by up to 55% as compared to pure PCM under identical conditions. Conversely, it was seen that in the initial stages of freezing and melting, the effects of the high-conductivity additives were much less pronounced. Only modest enhancements in heat transfer rates were observed, suggesting that the PCM thermal resistance is not the only factor limiting the speed of the inwardly propagating interface and therefore the heat transfer rate. Finally, the behavior of the additive-enhanced PCM during melting and solidification was consistent with that of the pure PCM, closely matching the nondimensionalized experimental data as well as the model. This shows that the composite PCM with xGnPs can be treated as a homogenous material with isotropic properties, and its performance can be predicted using the closed-form model for the conditions tested in this work.

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Nomenclature
- \( c_p \) = specific heat, J/kg K
- \( D \) = PCM cylinder diameter, m
- \( E_{sen} \) = sensible thermal energy, J
- \( F_o \) = Fourier number
- \( g \) = gravitational acceleration, m/s²
- \( H \) = PCM height, m
- \( h_{SL} \) = latent heat, J/kg
- \( k \) = thermal conductivity, W/m K
- \( L \) = length of wire, m
- \( m \) = mass
- \( Nu \) = Nusselt number
- \( P \) = pressure, Pa
- \( q \) = heat transfer rate, W
- \( r \) = radius, m
- \( R \) = gas constant, J/kg K
- \( Ra \) = Rayleigh number
- \( R_k \) = thermal interface resistance, m² K/W
- \( Ste \) = Stefan number
- \( t \) = time, s
- \( T \) = temperature, °C
- \( V \) = volume, m³
- \( \Delta P \) = change in pressure, Pa
- \( \Delta T \) = temperature difference, °C

Greek Symbols
- \( \nu \) = kinematic viscosity, m²/s
- \( \rho \) = density, kg/m³
- \( \phi \) = volume fraction

Subscripts
- air = air
- air,i = initial air
- c = center
- i = interface
- initial = initial
- L = liquid
- lat = latent
- PCM,f = final PCM phase
- PCM,i = initial PCM phase
- S = solid
- sens = sensible
- sub = subcool
- sup = superheat
- tot = total
- w = wall

Appendix A: Volume Fraction
The volume fraction of PCM having undergone phase change can be directly calculated from measurements of the change in pressure of the air volume above the PCM. The conservation of the PCM mass can be written as

\[
\rho_{\text{PCM},i} \Delta V_{\text{PCM},i} + \rho_{\text{PCM},f} \Delta V_{\text{PCM},f} = 0 \tag{A1}
\]

where \( \Delta V_{\text{PCM},i} \) is the change in volume of the initial PCM phase, and \( \Delta V_{\text{PCM},f} \) is the change in volume of the final PCM phase. For a fixed total volume of the closed system (including the air)

\[
\Delta V_{\text{PCM},i} + \Delta V_{\text{PCM},f} + \Delta V_{\text{air}} = 0 \tag{A2}
\]

where \( \Delta V_{\text{air}} \) is the change in air volume. Combining Eqs. (A1) and (A2), the change in volume of the final PCM phase can be written as

\[
\Delta V_{\text{PCM},f} = -\Delta V_{\text{air}} = \left( \frac{\rho_{\text{PCM},i}}{\rho_{\text{PCM},i} - \rho_{\text{PCM},f}} \right) \Delta V_{\text{air}} \tag{A3}
\]

The volume fraction can be defined as

\[
\frac{V}{V_0} = V_{\text{PCM},f} / V_{\text{PCM},i} + V_{\text{PCM},f} \tag{A4}
\]

where \( V \) denotes the volume of the PCM having undergone phase change at any instance, and \( V_0 \) denotes the total volume of both PCM phases. At any time during freezing or melting, \( \Delta V_{\text{PCM},i} \) and \( \Delta V_{\text{PCM},f} \) can be written as

\[
V_{\text{PCM},i} = V_{\text{initial}} + \Delta V_{\text{PCM},i} \tag{A5}
\]

\[
V_{\text{PCM},f} = \Delta V_{\text{PCM},f} \tag{A6}
\]

Combining Eqs. (A2)–(A6), the volume fraction from Eq. (A4) can be written as

\[
\frac{V}{V_0} = \left( \frac{\rho_{\text{PCM},i}}{\rho_{\text{PCM},i} - \rho_{\text{PCM},f}} \right) \times \left[ \frac{\Delta V_{\text{air}}}{\Delta V_{\text{air}} - \Delta V_{\text{initial}}} \right] \tag{A7}
\]

From the ideal gas law

\[
P_{\text{air}} = P_{\text{air},i} + \Delta P_{\text{air}} \tag{A8}\]
\[
V_{air} = V_{air,i} + \Delta V_{air}
\]  
\[
m_{air} = \frac{P_{air}}{R_T} \frac{V_{air,i}}{R_T} - \frac{P_{air} V_{air}}{R_T}
\]  

Here, \(m_{air}\) is the mass of air, and \(R\) is the gas constant. Applying Eqs. (A8)–(A10) and assuming \(T_{air} \approx T_{air,i}\), Eq. (A7) can be rewritten as

\[
V = \left( \frac{P_{PCM,i}}{P_{PCM,i} - \rho PCM} \right) \left( 1 + \frac{1}{V_{air,i}} \left( \frac{P_{air} V_{air} + \Delta P_{air}}{\Delta P_{air}} \right) \right)^{-1}
\]  

\[
\theta = f(\eta_1, \eta_2, \ldots, \eta_N)
\]

\[
\Delta u = \left( \sum_{i=1}^{N} \left( \frac{\partial \eta_i}{\partial \eta} \right)^2 \right)^{1/2}
\]

This approach was used for the data shown in Figs. 5–10, where the partial derivatives in Eq. (B2) are evaluated at nominal conditions for each single test. The experimental uncertainty associated with the pressure transducer (Omega PX419-2.5DWU5V) is \(\pm 14\text{ Pa}\), the T-type thermocouples (Omega TMQSS-062G-6) is \(\pm 1\text{ °C}\), Vernier calipers for geometric measurements (Mitutoyo ABSOLUTE 500-197-20) is \(\pm 0.0254\text{ mm}\), and the precision balance (Metler Toledo PL303) is \(\pm 0.001\text{ g}\), while all the material properties are assumed accurate to \(1\%\) of the nominal properties as specified by the manufacturers or references. The uncertainty in the thermal conductivity measurements was presented as the standard deviation of six-independent measurements, which was found to be larger than the propagation of experimental error as given by Eq. (B2).

References


