5.1 Introduction

Nanofluids have been a topic of intense research during the last one decade due to their interesting thermophysical properties and anticipated applications in heat transfer.\textsuperscript{2, 5, 12, 18-20, 23, 38, 147, 345-349} Several factors affect the heat transfer properties of nanofluids that include thermal conductivity, viscosity, heat capacity, density and diffusion coefficient. For effective utilization of nanofluids for practical heat transfer applications, a synergetic balance of these thermophysical properties is a prerequisite. Though the thermal properties of nanofluids are investigated intensely, the studies on heat capacity of nanofluids are scarce.\textsuperscript{221, 223, 224, 227, 350} A knowledge of specific heat capacity and thermal conductivity is important in order to understand the heat transfer properties of nanofluids. Nanofluids with higher heat capacities are necessary to enhance heat transfer efficiency at lower operating costs. Thermal diffusivity, thermal conductivity and specific heat capacity are inter-related as 

$$C_p = \frac{k}{D \rho} .$$

Unlike solids and gases, the accurate determination of heat transfer parameters in nanofluids is complex. So far, thermal conductivity studies have been the main focus of nanofluid research.\textsuperscript{220} An increase of thermal conductivity is necessary but not a sufficient condition for achieving high performance in heat exchange equipments. The specific heat capacity determines the rate at which the substance will heat up or cool down.\textsuperscript{351} As the heat capacity of a material is directly related to the atomic structure, measurements of heat capacity as a function of temperature could provide structural properties of nanostructured materials.\textsuperscript{352} In ultrafine particles, both bulk and surface phonon modes contribute to the vibrational specific
heat. As the surface area to volume ratio increases, the surface mode contribution plays a prominent role over the bulk modes. Studies show that the specific heat in nanocrystals increases up to 20% under an increase of atomic-level strain due to changes in the vibrational and configurational entropy due to large anharmonic atomic vibrations at grain boundaries and disordered lattice sites.\textsuperscript{353}

There are several studies which report the strong and weak dependence of $C_p$ on the volume fraction of nanoparticles. Yang et al.\textsuperscript{354} reported that at low volume fraction and moderate temperature change, the heat capacity of nanofluid doesn’t change much when compared to the base fluid. Several studies report a decrease in the heat capacity with increase in volume fraction.\textsuperscript{220-222} Yang et al.\textsuperscript{355} reported an increase in specific heat capacity with the increase in temperature. Shin et al.\textsuperscript{224} observed a 32% increase in specific heat capacity in a eutectic salt mixture on dispersing alumina nanoparticles at 1% mass concentration. The objective of the present work is to systematically study the effect of volume fraction, properties of dispersed particle (density, thermal conductivity, morphology etc.) on the specific heat capacity of nanofluids for a better understanding of their utility in heat transfer applications such as concentrating solar power and waste heat recovery.

5.2 Materials and Methods

For the present study, kerosene based Fe$_3$O$_4$ and PAO based Al$_2$O$_3$ nanofluids (nanospheres and nanorods) are used. The Fe$_3$O$_4$ nanofluids are prepared in our laboratory using coprecipitation approach. The synthesis procedure is briefly discussed in Chapter 2. Fe$_3$O$_4$ nanoparticles and Al$_2$O$_3$ nanospheres were used to study the effect of particle volume fraction on the specific heat capacity. The effect of particle morphology on the specific heat
capacity of nanofluids was studied using Al$_2$O$_3$ nanospheres and nanorods. The effect of particle size on the specific heat capacity of nanofluids was studied using Fe$_3$O$_4$ nanoparticles of size varying from 2.3 to 8.5 nm. The Al$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles were characterized for their phase identity by XRD. The size distribution of the nanoparticles was determined by DLS. The thermogravimetric analysis of the nanofluids was carried out under inert atmosphere from 40 – 100 ºC at a heating rate of 2 ºC/min. Measurements of Specific Heat Capacity is carried out as described in Chapter 2.

5.3 Results and Discussion

5.3.1 Nanoparticles Characterization by XRD, DLS and TGA

Fig. 5.1 (a) and 5.1 (b) show the XRD patterns of Al$_2$O$_3$ (sphere) and Fe$_3$O$_4$ nanoparticles, respectively. The diffraction peaks of (120), (031), (051), (151), and (002) were indexed to an orthorhombic structure of Al$_2$O$_3$ (JCP DS card no: 21-1307).

![XRD patterns of (a) Al$_2$O$_3$ and (b) Fe$_3$O$_4$ Nanoparticles.](image)

Figure 5.1: XRD patterns of (a) Al$_2$O$_3$ and (b) Fe$_3$O$_4$ Nanoparticles.
The diffraction peaks of (220), (311), (400), (422), (511), and (440) were indexed to a cubic spinel structure of Fe$_3$O$_4$ (JCP DS card no: 89-3854). An inverse spinel structure consists of oxide ions that form a cubic close-packed arrangement in which 1/3 of tetrahedral interstices and 2/3 of octahedral interstices coordinate with oxygen. The parallel alignment of Fe$^{2+}$ and Fe$^{3+}$ ions spin in the adjacent octahedral sites leads to a net magnetization and thus a ferromagnetic behavior\textsuperscript{156}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(a) Volume averaged hydrodynamic size distribution of Fe$_3$O$_4$ and Al$_2$O$_3$ nanoparticles. (b) Volume averaged hydrodynamic size distribution of Fe$_3$O$_4$ nanoparticles of different size.}
\end{figure}

\textbf{Figure 5.2} (a) shows the hydrodynamic diameter of the PAO based Al$_2$O$_3$ and kerosene based Fe$_3$O$_4$ nanofluids. The average hydrodynamic sizes are found to be 10 and \textasciitilde{} 8 nm for Al$_2$O$_3$ and Fe$_3$O$_4$ nanoparticles, respectively. The size distribution is found to be narrow for both Al$_2$O$_3$ and Fe$_3$O$_4$ nanofluids. The time dependent hydrodynamic measurements carried out in these systems showed a time independent hydrodynamic size, which indicate the good stability of the dispersions.\textsuperscript{148} \textbf{Fig. 5.2} (b) shows the hydrodynamic size distribution of
Fe$_3$O$_4$ nanoparticles of different sizes synthesized with different solvent dielectric constants. The hydrodynamic diameters of particles prepared with ethanol water ratio of 20:80, 40:60, 50:50 and 60:40 are found to be 3.6, 4.8, 6.5 and 8.6 ± 0.8 nm, respectively.

**Figure 5.3**: Thermogravimetric curves for (a) PAO based Al$_2$O$_3$ nanofluid and (b) oleic acid coated Fe$_3$O$_4$ nanoparticle.

The thermogravimetric curve for PAO based Al$_2$O$_3$ nanofluid in **Fig. 5.3 (a)** shows a single step weight loss at ≈ 468 °C (~88 wt%) due to the decomposition of PAO. The TGA curve for the Fe$_3$O$_4$ nanoparticles shows a two-step weight loss between 199-310 °C (~ 4 wt%) and 310-400 °C (~12 wt%) **Fig. 5.3 (b)**. The first step (solid arrow) is due to the removal of loosely bound or free surfactant and the second step (dotted arrow) should be due to the removal of strongly bound surfactant molecules.
5.3.2 Effect of Volume Fraction of Nanoparticles on the Specific Heat Capacity of Nanofluids

The variation of absolute specific heat capacity with temperature for different concentrations and the ratio of the specific heat capacity of nanofluid \( \left( C_{p,nf}/C_{p,bf} \right) \) with respect to the \( C_p \) of base fluid for kerosene based nanofluids are shown in Fig. 5.4 (a) and Fig. 5.4 (b), respectively.

**Figure 5.4:** (a) The variation of specific heat capacity with temperature for different concentration of kerosene based Fe\(_3\)O\(_4\) nanofluids. (b) Specific heat capacity ratio as a function of temperature for different concentration of Fe\(_3\)O\(_4\) nanoparticles.

**Fig. 5.4** shows a marginal increase in the specific heat capacity with increase in temperature. As the nanoparticle concentration increases, the specific heat capacity of the kerosene based
Fe$_3$O$_4$ nanofluid is found to decrease. In general, the specific heat capacity of nanofluids can be explained using two models. The model I, which is similar to the mixing theory for ideal gas mixtures,\textsuperscript{228} calculates the specific heat of nanofluids ($C_{p,nf}$) by averaging the $C_p$ of the base fluid ($C_{p,bf}$), the $C_p$ of nanoparticle ($C_{p,np}$) and its volume fraction. According to model I,

$$C_{p,nf} = \varphi C_{p,np} + (1-\varphi)C_{p,bf}$$

(5.1)

This equation has been used for the evaluation of heat transfer behavior of nanofluids in many experiments\textsuperscript{37, 357} and also in theoretical simulations.\textsuperscript{358-360}

In Model II, $C_{p,nf}$ is derived by assuming thermal equilibrium between particles and the surrounding fluid, using classical and statistical mechanics.\textsuperscript{220} According to Model II,

$$C_{p,nf} = \frac{\varphi(\rho C_p)_n + (1-\varphi)(\rho C_p)_f}{\varphi \rho_n + (1-\varphi)\rho_f}$$

(5.2)

where, $\rho_n$ and $\rho_f$ are the particle and fluid densities, respectively and the nanofluid density $\rho_{nf}$ is given by,

$$\rho_{nf} = \frac{m_{nf}}{V_{nf}} = \rho_n + (1-\varphi)\rho_f$$

(5.3)

where, $m_{nf}$ and $V_{nf}$ are the mass and volume, respectively of the nanofluid. The specific heat of the bulk and nanosized Fe$_3$O$_4$ are 0.6512 and 0.79 J/g. °C, respectively.\textsuperscript{361} The specific heat capacity of pure kerosene is 2.01 J/g. °C.\textsuperscript{362} According to the theoretical model I, the effective specific heat of the nanofluid should be lower than the specific heat of pure kerosene. Here, the lower specific heat of nanoparticles in the base fluid results in a decrease in specific heat capacity of the nanofluid with increase in particle concentration. An earlier
study showed a similar decrease in the heat capacity of nanofluid with increase in volume concentration and an increase with temperature in kerosene based iron oxide nanofluids. Such a behavior was also observed in CuO nanofluids where the constrained liquid layering at the surface of nanoparticle free boundary is attributed as the cause for the variations in the Gibbs free energy and change in specific heat capacity. Studies on the effect of volume fraction on the specific heat capacity of water-based Al$_2$O$_3$ nanofluid showed that the specific heat capacity decreases with increase in particle concentration. Studies also conclude that, the solid-liquid interfacial conformation plays a critical role in the heat capacity changes because of the changes in the phonon vibration mode at the interface. Murshed et al. reported that the thermal diffusivity of nanofluids increases significantly with increasing volume fraction of nanoparticles in the case of TiO$_2$, Al$_2$O$_3$ and aluminum nanoparticles dispersed in ethylene glycol and engine oil. Their study revealed that the particle size and shape can influence the effective thermal diffusivity of nanofluids. Zhang et al. observed an increase in the thermal diffusivity with particle concentration in Au/toluene, Al$_2$O$_3$/water and CNT/water nanofluids.

**Fig. 5.5** shows the variation of $C_{p,nf}$ of kerosene based Fe$_3$O$_4$ nanofluids along with theoretical fit using Model I and Model II at different temperatures. **Fig. 5.5** shows that the experimental data fits better with the Model II than Model I. Similar agreement with model II was observed by Zhou et al. in water based Al$_2$O$_3$ nanofluid and Higano et al. in kerosene based Fe$_3$O$_4$ nanofluid.
Figure 5.5: Variation of specific heat capacity as a function of volume fraction of kerosene based Fe₃O₄ nanofluid at different temperatures along with Model I (dotted line) and Model II (solid line) fits. The corresponding wt% is shown in the top x-axis.

Fig. 5.6 (a) and (b) shows the variation of specific heat capacity with temperature for different concentration of PAO based Al₂O₃ nanofluids and the variation of specific heat capacity ratio, respectively. Surprisingly, the specific heat capacity of Al₂O₃ / PAO increases upto 4 wt% nanoparticle concentration. Further increase in Al₂O₃ concentration led to a decrease in the $C_{p,nf}$ but larger than the $C_{p,bf}$. These results suggest that PAO molecules strongly modify the interfacial thermal characteristics of Al₂O₃ nanoparticles that increases the heat capacity of PAO based Al₂O₃ nanofluids.
Figure 5.6: (a) Specific heat capacity of alumina nanofluids with different weight percentage of Al₂O₃ nanoparticles in PAO and (b) Specific heat capacity ratio of alumina nanofluid with respect to PAO.

In general, the mechanisms considered for the unusual enhancement of the specific heat capacity are: (1) enhanced specific heat capacity of nanoparticle due to higher specific surface energy (compared with bulk material); (2) additional thermal storage mechanisms due to interfacial interactions (e.g., such as interfacial thermal resistance and capacitance) between nanoparticle and the adhering liquid molecules because of the extremely high specific surface area of the nanoparticle; and (3) the existence of semi-solid liquid layer adhering to the nanoparticles, which are likely to enhance the specific heat capacity due to
the smaller intermolecular spacing similar to the nanoparticle lattice structure on the surface (compared to the higher intermolecular spacing in the bulk liquid).

Nelson et al.\textsuperscript{226} reported a specific heat capacity enhancement of 50\% in 0.6\% exfoliated graphite nanoparticle fibers suspended in PAO. The specific heat capacity of Al\textsubscript{2}O\textsubscript{3} nanoparticle was found to increase up to 25\% compared with the bulk value of Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{352} A volumetric heat capacity (\(C_v\)) enhancement with increase in temperature in Al\textsubscript{2}O\textsubscript{3} and ZnO dispersed in 60:40 by mass of ethylene glycol/water and in water based SiO\textsubscript{2} nanofluids is reported.\textsuperscript{228} The enhancement of specific heat capacity of the silica nanocomposite is attributed to the high surface energy of nanoparticles that includes a phase transformation in the solvent material (liquid ordering). Such ordering of liquids on nanoparticles are expected to have semi-solid properties that gives rise to an increase in specific heat capacity of nanofluids.\textsuperscript{350, 364} The heat capacities of ionic salts are shown to increase with molar mass due to an increase in number of translational, vibrational and rotational modes\textsuperscript{365}.

5.3.3 Effect of Nanoparticle Size on the Specific Heat Capacity of Nanofluids

The variation of specific heat capacity and the normalized specific heat capacity of nanofluids with temperature with respect to particle size is shown in Fig. 5.7 (a & b). From the Fig. 5.7 it is clearly seen that the specific heat capacity ratio decreases with increase in particle size. A similar trend was reported by Xiong et al.\textsuperscript{229} for Ag nanoparticles of size ranging from 5 to 50 nm suggesting that the enhanced \(C_p\) in smaller sized nanoparticle is caused by the larger atomic thermal vibrational energies of surface atoms. Wang et al.\textsuperscript{223} reported that the specific heat capacity of nanoparticle increases with decrease in size of the particle in the case of CuO nanoparticle of size ranging from 3.4 to 50 nm.
Figure 5.7: (a) Specific heat capacity of kerosene based Fe$_3$O$_4$ nanofluids with different average particle sizes and (b) the corresponding specific heat capacity ratio.

The major contribution to the specific heat capacity above ambient temperature is determined by the vibrational degrees of freedom, and the peculiarities of surface phonon spectra of nanoparticles are responsible for the anomalous behavior of specific heat capacity. The vibrational states with lower frequencies make a larger contribution to heat capacity.\textsuperscript{366} Studies on the effect of nanoparticle size on the specific heat capacity by Dudda et al.\textsuperscript{50} showed 8, 12, 19 and 27 % enhancement of specific heat capacity for the SiO$_2$ nanoparticle size of 5, 10, 30 and 60 nm, respectively. Novotny et al.\textsuperscript{367} reported a decrease in the specific heat capacity with increase in the nanoparticle size which is attributed to the absence of low frequency modes and the increase in the specific heat capacity at low temperatures was attributed to the additional vibrational mode of surface phonon. More heat is required to raise the temperature of surface atoms because of larger vibrational amplitude of surface atoms, compared to the bulk atoms.\textsuperscript{368}
Aluminum-Ruthenium (AlRu) nanoparticles of size ranging from 7 to 12 nm, with large atomic-level strain, showed a specific heat increase of ~20%, which was attributed to the large changes in the vibrational and configurational part of the entropy.\textsuperscript{353}

5.3.4 Effect of Shape of Nanostructures on the Specific Heat Capacity of Nanofluids

![Graph showing specific heat capacity vs. temperature for PAO based Al2O3 nanofluids with different morphologies.]

\textbf{Figure 5.8:} Variation of specific heat capacity as a function of temperature for PAO based Al2O3 nanofluids with spherical and rod shaped particles of concentration 0.01 wt%.

\textbf{Fig. 5.8} shows the variation of $C_p$ as a function of temperature for PAO based Al2O3 with different particle morphologies. A concentration of 0.01 wt% was used in the case of spherical Al2O3 and rod shaped Al2O3 in PAO. For both the nanofluids, $C_p$ increases with temperature. At the same concentration (0.01 wt%), the specific heat capacity of the
nanofluid containing spherical particles was more compared to that of rod shaped Al₂O₃ nanoparticles. In the present case, the aspect ratio of the nanorods was ~ 8 (80 x 10 nm²), while the nanospheres diameter was 10 nm. The surface area to volume ratio for nanorods is 425×10⁶ while that of nanospheres (diameter 10 nm) is 600×10⁶. Therefore, the surface atoms are more in the case of nanospheres compared to that of nanorods. This means more heat is required to raise the temperature of surface atoms by one degree.

![Diagram](image)

**Figure 5.9:** Schematic representation of the effect of (a) smaller d, (b) larger d, (c) spherical particle and (d) non spherical particle on the specific heat capacity and thermal conductivity of the nanofluid.

Therefore, the observed larger specific heat capacity of nanospheres than that of nanorods is in good agreement with surface atomic consideration. This study hence shows that the
particle morphology also plays a major role in the specific heat capacity of nanofluids. The observed reduction in $C_p$ with increasing aspect ratio of nanoparticles is in sharp contrast with the increase in thermal conductivity in several nanofluids. The schematic representation of the effect of particle size and morphology on the specific heat capacity and thermal conductivity of the nanofluid is shown in Fig. 5.9.

5.4. Conclusions
The thermophysical properties of nanofluids with different types of nanoparticles as a function of concentration, shapes, size and base fluids are studied. The present work concludes that the nanoparticle concentration, shape and size play a major role in specific heat capacity of nanofluid. In the Fe$_3$O$_4$ nanofluids, the specific heat capacity is found to decrease with increasing particle concentration while an increase in the specific heat capacity is observed in Al$_2$O$_3$/PAO based nanofluid. This suggests that PAO molecules strongly modify the interfacial thermal characteristics of Al$_2$O$_3$ nanoparticles. The size dependent studies on specific heat capacity suggest that the $C_p$ increases with decreasing dispersed nanoparticle size. The study shows that the particle morphology also plays a major role in specific heat capacity of nanofluids and the $C_p$ decreases with increasing aspect ratio of nanoparticles due to reduced surface atomic contributions.
Chapter VI

Tunable Thermal Transport in Phase Change Materials Using Inverse Micellar Templating and Nanofillers

6.1. Introduction

The use of organic phase change materials as heat transfer media has attracted much attention in the recent years due their ability to freeze without much supercooling.\textsuperscript{232} The crystallization of the n-alkane chain releases a large amount of latent heat, which is the key to heat transfer applications. Another material of focus, for such cooling applications over the past one decade, was dispersions of nanomaterials, popularly known as nanofluids\textsuperscript{38}. The intense research on various nanofluids led to the conclusion that traditional nanofluids show only modest thermal conductivity enhancement.\textsuperscript{40, 147, 182, 246, 278} During the last decade, several new promising approaches to achieve extremely large thermal conductivity enhancement using carbon nanotubes,\textsuperscript{376} graphene,\textsuperscript{337, 369, 377, 378} magnetic materials\textsuperscript{276, 331, 379} and composites\textsuperscript{191, 373, 377, 380} have been demonstrated.

The recent finding of reversible tuning of electrical and thermal conductivities using first-order phase transitions in percolated composite materials\textsuperscript{236-238, 243} have attracted much interest among nanofluid research community because of their important applications in heat management in various industrial sectors. Zheng et al.\textsuperscript{237} have observed large contrasts in the electrical and thermal conductivities at the phase transition temperature in graphite/water and carbon nanotube/hexadecane suspensions, which was attributed to the modulations in the electrical and thermal contact resistances due to the internal stress generated during the phase transition. Harish et al.\textsuperscript{238} reported a large enhancement in the thermal conductivity in the solid phase (~250 \%) of an alkane (n-octadecane) containing 0.25 wt\% of single-walled carbon nanotubes, compared to the nominal enhancement in the liquid state (~10 \%).
Schiffres et al.\textsuperscript{243} demonstrated tunable electrical and thermal conductivities by controlling the crystal growth through freezing rate control in solution-based nanocomposites where nanoparticles are driven into concentrated intercrystal regions to increase the percolation pathways and to reduce the interparticle resistance. Sun et al.\textsuperscript{236} studied the room temperature electrical and thermal switching in CNT/Hexadecane composites and found 5 orders of electrical and 3 times of $k$ variations at the phase change point of hexadecane. Though significant enhancement in thermal and electrical conductivities are observed in nanocomposites during phase change, the reversible switching under long repeated cycling is strongly affected due to the agglomeration of nanomaterials because of the strong van der Waals interaction and the high reactivity of nanomaterials. Also, aggregation not only hampers the long term stability of such nanocomposites but also reduces their switching time. Here, a novel strategy is disclosed to overcome these difficulties by templating alkanes with inverse micelles. Since agglomeration issue is negligible in micellar systems due to steric interactions, such systems offer promising heat transfer applications. For these studies, soft systems of inverse micelles of size ranging from 1.5 to 6 nm, with different head groups were prepared. The $k$ tunability of the micellar systems with dispersions of multiwalled carbon nanotubes and graphite nanofibers in n-hexadecane under identical experimental conditions were compared and the effect of functionalization of nanomaterials on stability, agglomeration and thermal conductivity enhancement was studied.
6.2 Materials and Methods

6.2.1 Materials
The surfactants OA, AOT and Span 80 were used in this study. The critical micellar concentrations (CMC) for OA, AOT and Span 80 are 0.72, 0.077 and 0.019 mM, respectively. For the studies, stock solutions of OA, AOT and Span 80 surfactants were prepared in n-hexadecane from which different concentrations were prepared. The structures of these three surfactants are shown in Fig. 2.1. The n-Hexadecane is chosen as the phase change material and graphite nanofibers and multiwalled carbon nanotubes are used as nanoinclusions. Preparation method to produce dispersion of MWCNT and GNF in hexadecane is discussed in Chapter 2.

6.2.2 Methods
The $k$ of the dispersion was measured by using a hot wire probe. An inverted phase contrast microscope was used to obtain the microscopic images of the nanofluids. Details of these equipments are discussed in Chapter 2.

6.3 Results and Discussion

6.3.1 Effect of Inverse Micellar Templating on $k$ Contrast in Hexadecane under Freezing

Fig. 6.1 shows the variation of $k/k_f$ and the percentage of increase in $k$ as a function of temperature for different volume fractions of oleic acid in hexadecane. Here, $k_f$ is the thermal conductivity of hexadecane. The surfactants are amphiphilic molecules with hydrophilic and hydrophobic parts. They exist as unimers at concentrations below the critical micellar
concentration and form spherical inverse micelles just above the CMC. The hydrophobic force and entropy are the driving forces for the inverse micelle formation.

![Graph showing variation of effective thermal conductivity and the percentage of increase in thermal conductivity as a function of temperature for different volume fractions of oleic acid in hexadecane. Inset shows the magnified view of region I (23 to 27 °C).](image)

**Figure 6.1**: Variation of effective thermal conductivity and the percentage of increase in thermal conductivity as a function of temperature for different volume fractions of oleic acid in hexadecane. Inset shows the magnified view of region I (23 to 27 °C).

In a normal micelle, the surfactant molecules are oriented in such a way that the hydrophobic hydrocarbon chains (tails) face towards the interior of the micelle, leaving the hydrophilic groups (head) in contact with the aqueous medium. In the case of non-polar solvent, the hydrophilic groups are sequestered in the micelle core and the hydrophobic groups extend away from the center. The CMC for OA is 0.72 mM (i.e. $\phi = 0.0002$). The diameter of the oleic acid inverse micelle is ~ 6 nm. All the concentrations studied here are well above the CMC and hence inverse micelles are present in all these cases.
**Fig. 6.1** can be divided into two regions, I and II, where region I ($T > 22 \, ^\circ C$) corresponds to the liquid phase and region II ($T < 18 \, ^\circ C$) corresponds to the solid phase. The $k$ increases with increase in OA concentration in both regions I and II. In the liquid state, the $k$ enhancement was nominal, i.e., from 1 to 6.9 \%, as the $\phi$ of the OA is increased from 0.017 to 0.223. In the solid state, immediately after freezing, the $k$ enhancement increases from 188 to 277 \% as the OA $\phi$ increases from 0.017 to 0.223. With further decrease in temperature, beyond the freezing point, the $k$ is found to decrease a little and then becomes constant for all the concentrations of OA. In the solid phase, a larger enhancement of 277 \% is observed immediately after freezing of the base fluid ($T = 16 \, ^\circ C$) for a $\phi$ of 0.223. With further decrease in temperature below freezing point, the $k$ decreases and reaches ~150.9 \% at $T = 10 \, ^\circ C$ and remains constant thereafter. The $k$ of nanofluids increases with the micellar loading in both the regions, which can be understood as follows:

The critical micellar concentration for oleic acid is 0.72 mM$^{381}$ corresponding to a volume fraction 0.0002. As the concentration of oleic acid in the present study is much above the CMC, inverse micelles are present in the solutions. The increase in $k$ with the concentration of OA in both the regions indicates that the presence of inverse micelles increase the $k$ of the alkane. The $k$ of pure hexadecane and OA are 0.144 and 0.164 W/m-K, respectively. To check the universality of micellar templating on $k$ enhancement during freezing transitions, the experiments in two other inverse micellar systems were also performed.

**Fig. 6.2** shows the variation of $k/k_f$ and the percentage of increase in $k$ as a function of temperature for different $\phi$ of AOT in hexadecane. The AOT forms inverse micelles in hexadecane above $\phi > 2.1 \times 10^{-5}$ (i.e., 0.077 mM)$^{382,383}$ The $\phi$ values used in our experiments
were well above the CMC which ensure inverse micelles in the system. The linear length of the AOT molecule is 1.2 nm and the typical inverse micellar size of AOT is 1.5 nm. The $k$ increases with concentration of AOT in both the regions as observed in the case of OA.

**Figure 6.2:** Variation of effective thermal conductivity and the percentage of increase in thermal conductivity as a function of temperature for different volume fractions of AOT in hexadecane. Inset shows the zoomed view of region I (23 – 27 °C).

In the liquid state, the $k$ increases from 4.8 to 7.6 % as the $\phi$ of AOT is increased from 0.072 to 0.189. In the solid phase, the $k$ enhancement increases from 133 to 170 % as the $\phi$ of AOT is increased from 0.072 to 0.189, immediately after freezing. With further decrease in the temperature, the $k$ is found to decrease slightly and then remains constant. This can be explained in terms of the variations in the aspect ratio of the needlelike crystals formed. It
has been shown by Schiffres et al.\textsuperscript{243} that rapid cooling can result in a larger aspect ratio of the needles and a larger $k$ enhancement.

![Graph showing variation of effective thermal conductivity and percentage enhancement as a function of temperature for different volume fractions of Span 80 in hexadecane]

**Figure 6.3**: Variation of effective thermal conductivity and the percentage of increase in thermal conductivity as a function of temperature for different volume fractions of Span 80 in hexadecane. Inset shows the zoomed view of region I (23 – 27 °C).

**Fig. 6.3** shows the variation of $k/k_f$ and the percentage of enhancement in $k$ as a function of temperature for different volume fractions of Span 80 in hexadecane. The $k$ values of pure hexadecane and Span 80 are 0.144 and 0.182, respectively. The CMC value of Span 80 is approximately 0.019 mM\textsuperscript{384} which corresponds to a $\phi$ of 6.24×10\textsuperscript{-6}. The typical inverse micellar size of Span 80 is 5 nm.\textsuperscript{387} Like in the previous two cases, the $k$ increases with $\phi$ in both the regions. In the liquid state, the $k$ enhancement increases from 2.7 to 7.3 % as the $\phi$
increases from 0.079 to 0.205. In the solid state, the $k$ enhancement increases from 124 to 196% as the $\phi$ is increased from 0.079 to 0.205, immediately after freezing. With further decrease in temperature beyond freezing point, the $k$ is found to decrease a little and attains a constant value. In solid phase a larger enhancement of 196% is observed immediately after freezing of base fluid ($T = 16^\circ C$ and $\phi$ of 0.205). With further decrease in temperature, the $k$ decreases and reaches 103% and remains constant at $T \leq 10^\circ C$.

The aggregation number is the ratio of micellar core volume to the volume of one chain. The presence of surfactant micelles may have affected the freezing/melting point of hexadecane due to thermodynamic effects and also due to the different crystal structures formed. Studies show that the dispersed oil droplet size has an effect on the freezing point of hexadecane (bulk freezing point of hexadecane is $18^\circ C$) in agreement with the Gibbs–Thomson equation. On the contrary, in the presence of normal micelles, $k$ decreases with increase in concentration of micelles, and the mechanism of conduction of heat through normal micelle is discussed in Chapter 3. The molecular dynamics simulations studies show that the interfaces of organic liquids with surfactant tail groups are highly conductive. The large conductance of the organic liquid-surfactant interface was attributed partly to the penetration of alkane molecule into the surfactant tail regions, which is more prominent for linear surfactant molecules. The very similar molecular and vibrational structures of the surfactant tails and the alkane molecules lead to the optimization of the van der Waals interactions between the chains in the two species.

The composite system has a matrix of alkane base fluid with surfactant micelles dispersed. As the net thermal resistance of inverse micelle is much lower than that of the alkanes
because of the highly ordered packing of the linear chain surfactant within the sphere, the effective interfacial resistance along the conduction path should be much lower than that of pure alkane. Further, the cores of the micelles have polar head groups, which might entrap hydrophilic moieties (e.g. moisture, ions etc.) within the cores, which is again more thermally conducting than the alkane (e.g. water has a thermal conductivity of 0.6 W/m-K compared to 0.12 W/m-K for alkanes). With increase in oleic acid concentration, the numbers of inverse micelles in the system will also increase which in turn reduces the effective interfacial thermal resistance along the heat conduction pathways. The observed increase in $k$ with increase in volume fraction of the micelles is in very good agreement with the above hypothesis.

When the alkane undergoes first order phase transition during cooling, it forms crystals\textsuperscript{237} of different morphologies, whose aspect ratio can vary from micro to millimeter scale depending on the rate of cooling.\textsuperscript{243} This suggests that, during the freezing transition, the nanosized frozen inverse micelles with highly packed linear chain surfactant within the sphere are pushed to the inter crystal boundaries, thereby filling the heat conduction path that reduces the effective thermal resistance.\textsuperscript{238} Studies show that the presence of surface active species in long-chain alkanes can induce or alter surface freezing to become oriented chains.\textsuperscript{390} An earlier study suggests that the internal stress generated during freezing also improves the conduction among the crystals.\textsuperscript{237} Molecular dynamics simulations of the structure of paraffins in solid and liquid states shows that, upon crystallization, the $k$ doubles due to the formation of nanocrystallites paraffin.\textsuperscript{242}
Among the three micellar systems studied, oleic acid based templating showed the highest $k$ enhancement. The matched alkyl chain length (or vibrational spectrum) of both oleic acid and hexadecane seems to optimize the van der Waals interactions between the chains in the two species, thereby lowering the interfacial thermal resistance, in agreement with earlier theoretical predictions. Simulations results further show that penetration of alkane molecules in the tail region of a straight chain surfactant is more (with less thermal resistance) compared to less-ordered unsaturated, kinked surfactant or double-tailed lipid molecules. The molecular surface structure of liquid alkanes changes with alterations in a solvent’s molecular structure due to surface free energy considerations. In the presence of inclusions, the surface structure is altered due to changes in the van der Waals interactions between adjacent solvent molecules and the net ordering of liquid molecules at an interface due to intrinsic interfacial anisotropy. The greater efficiency of thermal vibration waves (phonons) through straight and densely packed chains are expected to provide a better heat conduction. Molecular dynamics simulations predict a larger interfacial thermal resistance for dissimilar structured base fluid (alkane) and surfactant molecules. Based on our experimental results, the conclusions drawn are graphically illustrated in Fig. 6.4 (a-d).
Figure 6.4: (a&b) The atomic structure of alkanes without and with inverse micelles, respectively. The magnified views of a single hexadecane molecule and the inverse micelles are shown by arrows. Figure 6.4 (c&d) shows the configuration of the crystals without and with inverse micelles, respectively.

Fig. 6.4 (a) and (b) shows the atomic structure of alkanes without and with inverse micelles, respectively. The magnified view of a single hexadecane molecule and the inverse micelles are shown by arrows. Fig. 6.4 (c) and (d) shows the configuration of the crystals without and with inverse micelles, respectively. During freezing transition, the inverse micelles are pushed to the microcracks and the intercrystal boundaries, leading to a better heat conduction path. The alkane molecules may also undergo some ordering around the inverse micelles, which can restrict translational diffusions of alkane molecules. These findings are consistent with the ice-templating and nanoparticle-induced molecular alignment of alkane. In order to compare the micellar templating to that of nanofillers, the temperature dependent \( k \)
measurements are carried out using MWCNTs and GNF. Also, effect of nanomaterial type and their aggregation on $k$ enhancement under freezing conditions are studied.

### 6.3.2 Effect of Graphite Nanofiber Inclusions on $k$ Contrast in Hexadecane under Freezing

![Graph showing effective thermal conductivity and percentage enhancement](image)

**Figure 6.5:** Variation of effective thermal conductivity and the percentage of increase in thermal conductivity as a function of temperature for different volume fractions of GNF in hexadecane. Inset shows the zoomed view of region I (23 – 27°C).

Fig. 6.5 shows the variation of $k/k_f$ and the percentage of increase in $k$ as a function of temperature for different volume fractions of GNF in hexadecane. As the volume fraction of GNF increases, the $k$ also increases in both the liquid and solid phase. This observation was in agreement with the earlier reports.\(^\text{236, 237, 243}\) In liquid state, the $k$ enhancement increases from 4.5 to 11% whereas in the solid state the $k$ enhances from 136 to 245% as the F-GNF
concentration increases from 0.0008 to 0.0039. With further decrease in temperature beyond freezing point, the $k$ decreases a little and remains constant for all concentration of GNF. In solid phase, a larger enhancement of 245 % is observed immediately after freezing of the alkane basefluid ($T = 16 ^\circ C$) at a GNF loading of $\varphi = 0.0039$. With a further decrease in temperature, the $k$ decreases and reaches 161 % at $T \leq 10 ^\circ C$. Earlier study in graphite/HD suspension\textsuperscript{237} shows that the $k$ increases to 220 % in the solid state with a graphite loading of $\varphi = 0.008$. The large contrast observed in the $k$ in the solid state was attributed to the effective transfer of heat through percolation structures and the internal stress generated during freezing. Schiffres et al.\textsuperscript{243} demonstrated the tuning of electrical conductivity and $k$ by varying freezing rate control between $10^2$ and $10^{-3} ^\circ C/min$, where they achieved a thermal conductivity contrast ratio varying between 2.3 and 3.0 for a $\varphi$ of 0.01 in multilayer graphene suspended in hexadecane at solid-liquid transition while $k$ varies between 2.1 and 2.6 in pure hexadecane. The larger $k$ contrast at slower cooling rate was attributed to the formation of larger crystals and the accumulation of more nanoparticles at the intercrystal regions thereby creating additional percolation pathways for heat transport. Harish et al.\textsuperscript{238} observed a 250 % enhancement of $k$ in the solid state with a SWCNT loading of 0.25 wt%. It was suggested that the alkane molecules surrounding the nanotubes, when frozen to solid phase, exhibit a tendency to form lamellar layers along the nanotubes axis leading to a 2D structural ordering in the planes perpendicular to the nanotube axis which is similar to the crystalline polymer.\textsuperscript{238}
**Figure 6.6**: Effective thermal conductivity of GNF nanofluids as a function of volume fraction in the solid and liquid state. EMT fit is shown by the solid line.

**Fig. 6.6** shows the \( k/k_f \) of GNF nanofluids as a function of volume fraction in the solid and liquid state. The Maxwell model is shown by the solid line. At room temperature, the thermal conductivity of the GNF and the base fluid (hexadecane) are ~ 1500 W/m-K\(^{392}\) and 0.144 W/m-K, respectively. The theoretical fit shows that at room temperature the experimental data are well above the Maxwell’s theory. These results show an extremely large thermal conductivity enhancement in both liquid and solid phase in the presence of F-GNF nanoinclusions. Similar enhancement beyond the EMT predictions are observed in multilayer graphene suspended in hexadecane\(^{243}\) in hexadecane based graphite and CNT dispersions\(^{237}\), \(^{393}\) and in n-octadecane based single-walled carbon nanotube dispersions\(^{238}\). **Table 6.1** shows the comparison of the thermal conductivity results in nanofluids with different phase change materials and the dispersed materials.
Table 6.1: Comparison of the thermal conductivity values in nanofluids with different phase change materials and dispersed materials.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Dispersed phase</th>
<th>Dispersed medium</th>
<th>Volume fraction</th>
<th>k/k_f</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Liquid (25 °C)</td>
<td>Solid (4 °C)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Multilayer graphene</td>
<td>Hexadecane</td>
<td>0.01</td>
<td>-</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>Functionalized MWCNT</td>
<td>Hexadecane</td>
<td>0.01</td>
<td>1.42</td>
<td>3.93</td>
</tr>
<tr>
<td></td>
<td>Original MWCNT</td>
<td></td>
<td>0.008</td>
<td>1.07</td>
<td>2.71</td>
</tr>
<tr>
<td>3</td>
<td>Graphite</td>
<td>Hexadecane</td>
<td>0.01</td>
<td>2.9</td>
<td>8.57</td>
</tr>
<tr>
<td>4</td>
<td>SWCNT</td>
<td>Octadecane</td>
<td>0.001</td>
<td>1.1</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Exfoliated graphite nanoplatelets</td>
<td></td>
<td>0.0004</td>
<td>1.43</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.002</td>
<td>1.14</td>
<td>2.71</td>
</tr>
<tr>
<td>5</td>
<td>Oleic acid</td>
<td>Hexadecane</td>
<td>0.223</td>
<td>1.069</td>
<td>2.85</td>
</tr>
<tr>
<td></td>
<td>AOT</td>
<td></td>
<td>0.19</td>
<td>1.076</td>
<td>2.19</td>
</tr>
<tr>
<td></td>
<td>Span 80</td>
<td></td>
<td>0.205</td>
<td>1.03</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>F-GNF</td>
<td></td>
<td>0.0039</td>
<td>1.11</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>F- MWCNT</td>
<td></td>
<td>0.0039</td>
<td>1.13</td>
<td>2.05</td>
</tr>
</tbody>
</table>

The k changes in hexadecane under repeated freezing and melting cycles for φ = 0.223 of OA, φ = 0.189 of AOT and φ = 0.205 of Span 80 are shown in Fig. 6.7. During repeated cycles of freezing and melting, the k/k_f in liquid state are found to be 1, 1.069, 1.076 and 1.076 for HD, OA, AOT and Span 80, respectively. The k/k_f of solid states are found to be 1.74, 2.8, 2.19 and 2.11 for HD, OA, AOT and Span 80, respectively. These results show
that the freezing and melting are completely reversible for all the systems studied owing to the monodispersity and non-aggregating nature of micelles.

Figure 6.7: Effective thermal conductivity of (a) pure n-Hexadecane with, (b) $\varphi = 0.223$ of OA (c) $\varphi = 0.189$ of AOT and (d) $\varphi = 0.205$ of Span 80 after different cycles, closed circles and open circles indicate the $k/k_f$ measured at 25 °C and 4 °C, respectively.
6.3.3 Effect of Aggregation of Nanoinclusions on $k$ Enhancement during Freezing

6.3.3.1 Bare, Surfactant Stabilized and Surface Modified GNF

Fig. 6.8 shows the variation of $k$ as a function of temperature for pure alkane, span stabilized GNFs and F-GNFs of $\varphi = 0.0038$. In liquid state, the $k$ of base fluid and nanofluids follows the usual trend.

![Image of graph showing variation of effective thermal conductivity as a function of temperature for pure HD, surfactant stabilized GNFs (GNF+Span80), and F-GNFs. Inset shows the zoomed view of region I.](image)

**Figure 6.8:** Variation of effective thermal conductivity as a function of temperature for pure HD, surfactant stabilized GNFs (GNF+Span80), and F-GNFs. Inset shows the zoomed view of region I.

After freezing, the enhancement of $k$ of the base fluid was 126 % at 15 °C. Further, a decrease in temperature results in a decrease in $k$, to a value of 73 %, which remains constant at $T \leq 10$ °C. In the case of HD containing bare graphite nanofibers ($\varphi = 0.0038$ GNF), the $k$
enhancement was almost the same as that of the base fluid at 15 °C and remains constant with further decrease in temperature. On the other hand, GNF (φ = 0.0039) stabilized with Span 80 showed an enhancement of around 242 % at 15 °C and the value decreases gradually and reaches 155 % enhancement at \( T \leq 10 °C \). F-GNF (φ = 0.0039) also showed an enhancement of around 245 % at 15 °C and decreases gradually and reaches 161 % at \( T \leq 10 °C \). These results suggest that the functionalized nanomaterials provide a higher \( k \) enhancement than that of bare nanomaterials. Among the stabilized ones, the surface modified (F-GNF) gave higher enhancement on freezing. It is known that the dispersibility of nanomaterials improves with functionalization, which should be the main reason for the observed enhancement in stabilized nanofluids.\textsuperscript{148, 331} It is believed that the distribution of GNF’s at the grain boundaries are uniform during the crystallization of alkanes in the case of F-GNF compared to the bundled one in the case of bare GNF. This finding shows that the well dispersed GNF are stable and provides better percolated nanofiber network pathways for the effective heat conduction.\textsuperscript{243}

6.3.3.2 Bare, Surfactant Stabilized and Surface Modified MWCNTs

**Fig. 6.9** shows the variation of \( k/k_f \) as a function of temperature for pure HD, Span 80 stabilized MWCNTs and F-MWCNTs. In the latter two cases the \( \phi \) of MWCNTs is 0.0038. In the liquid state both the surfactant stabilized and the surface modified MWCNTs show a higher \( k \) than that of base fluid. The % of \( k \) enhancement was 8 and 13 % for nanofluids containing Span 80 stabilized and functionalized MWCNTs, respectively. Like the GNF, the F-MWCNTs showed a better \( k \) enhancement than the surfactant stabilized nanofluid. For F-MWCNTs, the maximum enhancement observed is 157 and 69 % at 15 and 10 °C,
respectively. In the case of nanofluid stabilized with Span 80, the % of \( k \) enhancement is 48 and 17 % at 15 and 10 °C, respectively.

![Graph showing variation of effective thermal conductivity as a function of temperature for pure HD, Span 80 stabilized MWCNTs and F-MWCNTs of \( \varphi = 0.0038 \).](image)

**Figure 6.9:** The variation of effective thermal conductivity as a function of temperature for pure HD, Span 80 stabilized MWCNTs and F-MWCNTs of \( \varphi = 0.0038 \).

The reason for the higher \( k \) enhancement in F-MWCNT dispersion is attributed to the better dispersibility of MWCNTs, as evident from the microscopic images, where the percolated nanofibers networks are uniformly distributed, which enables better conduction pathways. The molecular dynamics simulation studies on structural phase transition and crystallization process of alkane molecules in carbon nanotube dispersions show an isotropic-to-nematic or smectic transition with molecules aligned with embedded nanotubes. Under certain situations, the alkane molecules can even form lamellar layers or two-dimensional structure ordering that can affect the translational diffusions and rotation freedom.
Figure 6.10: Phase contrast optical microscopic images of (a) bare GNFs, (b) Span stabilized GNFs, (c) F-GNFs, (d) bare MWCNTs, (e) Span stabilized MWCNTs and (f) F-MWCNTs in hexadecane. In all the cases, the volume fraction is 0.0038. The scale bar corresponds to 50 μm.

To obtain macroscopic evidence for the dispersibility of nanofillers in the PCM matrix and their aggregation under different stabilization conditions, the phase contrast microscopic images of bare GNF, Span 80 stabilized MWCNTs and GNFs and F-MWCNTs and F-GNFs in hexadecane are taken. Fig. 6.10 shows the optical microscopic images of (a) bare GNFs, (b) Span stabilized GNFs, (c) F-GNFs, (d) bare MWCNTs, (e) Span stabilized MWCNTs and
(f) F-MWCNTs in hexadecane. In all the cases, the volume fraction of dispersed nanomaterial is the same $\varphi = 0.0038$ and the microscopy images were taken after sonication for 2 mins. The images confirm the presence of very large aggregates in the case of nanofluids with bare GNFs and bare MWCNTs compared to the other four cases. The Span 80 stabilized and functionalized GNF are fairly well dispersed. Large clusters are observed in the case of Span 80 stabilized MWCNTs nanofluids whereas F-MWCNTs nanofluids showed only a few small clusters, confirming better dispersibility under surface functionalization. Therefore, the observed larger $k$ enhancement in stabilized nanofillers dispersions are indeed due to better distribution of nanofillers in the intercrystal boundaries.

6.4 Conclusions

Extremely large tunable thermal conductivity in a phase change alkane is achieved using inverse micellar templating. The thermal conductivity enhancement between the solid and liquid phase in presence of inverse micelles of size ranging from 1.5 – 6 nm can vary between 111 to 185 %. These results suggest that during the freezing transition, the nanosized frozen inverse micelles with highly packed linear chain surfactant are pushed to the inter crystal boundaries, thereby paving effective heat conduction path. Comparison of results with that of nanofillers in alkanes showed that the $k$ contrast in surface modified graphite and multiwalled carbon nanotube in n-hexadecane at 15 °C for $\varphi \sim 0.0039$ are found to be 161 and 157 %, respectively. The phase contrast optical microscopic images confirm better dispersibility under surface functionalization, which enables better distribution of nanofillers in the intercrystal boundaries and higher thermal conductivity enhancement. Further, these results suggest interesting possibilities of using micellar templated phase
change materials for applications in latent heat thermal storage systems (e.g. solar engineering, seasonal regulation of building temperature, and thermal storage) and new insight into the role of aggregation of nanofillers in $k$ enhancement under freezing conditions.