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.\textsuperscript{381-384} 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\textsuperscript{207}. 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.

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. \( \phi = 0.0002 \)).\(^{381}\) The diameter of the oleic acid inverse micelle is \( \sim 6 \text{ nm} \).\(^{385}\) 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 $\varphi$ 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 $\varphi$ 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 $\varphi$ 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 $\varphi$ of AOT in hexadecane. The AOT forms inverse micelles in hexadecane above $\varphi > 2.1\times10^{-5}$ (i.e., 0.077 mM)$^{382,383}$ The $\varphi$ 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 of 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 $\varphi$ of $6.24 \times 10^{-6}$. The typical inverse micellar size of Span 80 is 5 nm.\textsuperscript{387} Like in the previous two cases, the $k$ increases with $\varphi$ in both the regions. In the liquid state, the $k$ enhancement increases from 2.7 to 7.3 % as the $\varphi$
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 °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 variation of $k/k_f$ and percentage enhancement as a function of temperature for different GNF concentrations.]

**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. 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$^{237}$ 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.$^{243}$ demonstrated the tuning of electrical conductivity and $k$ by varying freezing rate control between $10^2$ and $10^{-3}$ °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.$^{238}$ 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.$^{238}$
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 $\sim 1500 \text{ W/m-K}$ 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\(^{237}\). 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.

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<th>Dispersion medium</th>
<th>Volume fraction</th>
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<td></td>
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The $k$ changes in hexadecane under repeated freezing and melting cycles for $\phi = 0.223$ of OA, $\phi = 0.189$ of AOT and $\phi = 0.205$ 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) \( \phi = 0.223 \) of OA (c) \( \phi = 0.189 \) of AOT and (d) \( \phi = 0.205 \) of Span 80 after different cycles, closed circles and open circles indicate the \( k/k_f \) measured at 25 \(^\circ\)C and 4 \(^\circ\)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.

![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 $15\,^{\circ}\text{C}$. Further, a decrease in temperature results in a decrease in $k$, to a value of $73\%$, which remains constant at $T \leq 10\,^{\circ}\text{C}$. In the case of HD containing bare graphite nanofibers ($\varphi = 0.0038\,\text{GNF}$), 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. 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.

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 φ 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.

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.$^{394}$ 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.