Temperature Dependent Heat Transfer Performance of Multi-walled Carbon Nanotube-based Aqueous Nanofluids at Very Low Particle Loadings

Investigating the mechanism of thermal conductivity enhancement

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Aqueous suspensions of multi-walled carbon nanotubes (MWCNTs + deionised water) have been synthesised. Carbon nanotubes (CNTs) were derived by chemical vapour deposition (CVD). Transmission electron microscopy (TEM) measurements show the formation of MWCNTs. Three samples of CNT-based aqueous nanofluids having MWCNT concentrations of 0.01 vol%, 0.03 vol% and 0.05 vol% were prepared with the help of ultrasonic irradiation. A very small amount of sodium dodecyl sulfate (SDS) was used as a surfactant to minimise the agglomeration of the MWCNTs. An effective enhancement in thermal conductivity was observed at different temperatures. The obtained results are explained with percolation theory.

1. Introduction

Heat transfer management is becoming increasingly critical in the infrastructure, industry, transportation, defence and aerospace sectors. Several cooling methods have been investigated recently to meet the heat transfer requirements of 21st century high-technology, high density heat producing industrial equipment. Water, ethylene glycol and mineral oil have been used as conventional coolants for different industries. Conventional heat transfer systems used in a wide range of applications, including petrochemicals, refining, power generation and microelectronic devices, are rather large and involve a significant amount of heat transfer fluids in comparison to biomedical engineering based applications (1). Managing high density heat generation in microelectronic industries is a good example (2, 3).

Modern, small scale cooling applications require very effective coolants. Existing heat management systems can be improved by enhancing the performance of heat transfer fluids through the use of nanofluids, resulting in lower heat exchange surface area, lower capital costs and higher energy efficiencies (4). Several techniques have been investigated to enhance the thermal exchange performance of the fluids. Out of many tried methods,
one is to add a very small percentage of nanoparticles having high thermal conductivity into heat transfer fluids to improve their overall thermal conductivity (5–8). Such additives may include novel metals, metal oxides and carbon nanostructures. Nanoparticles may possess either spherical, cylindrical, fibril or sheet-like structures. Cylindrical carbon nanostructures (4, 9, 10) or CNTs have very high thermal conductivity of the order of 3000 W m$^{-1}$ K$^{-1}$ (11). MWCNTs have very exotic physical properties and are relatively easy to synthesise. They have been shown to be promising additives in conventional heat transfer fluids for diverse heat transfer applications (9, 12). Several researchers have tested different combinations and permutations of CNTs, the effects of their aspect ratios (diameter and length) and base fluids on thermal conductivity in CNT-based nanofluids (13). For a more uniform dispersion of CNTs, the effects of different quantities of surfactant materials on thermal conductivity have also been studied (14). However the addition of a large weight percentage of filler in a fluid affects its viscous properties. Higher viscosity does not support better heat conduction due to the need for higher pumping power as well as changes in other fluidic properties.

The present work is focused on the preparation of nanofluids by dispersing MWCNTs in deionised water and measuring the temperature dependent thermal conductivity of the nanofluids at very small particle loadings. The experimental observations regarding thermal conductivity enhancements can be explained with the help of appropriate theoretical models. It has now been established that when CNTs are suspended in conventional heat transfer fluids, anomalous enhancements in thermal conductivity are observed (15, 16). The motivation behind the present study is to find the mechanism of thermal conductivity enhancement at very small concentrations of MWCNTs in suspension and the effects of MWCNT aqueous nanofluids on thermal performance at a range of temperatures. It is assumed that the viscous properties of the base fluid do not change with the inclusion of very low CNT loadings.

2. Materials and Methods

Deionised water and MWCNTs were used to produce nanofluids. The MWCNTs were synthesised by CVD using nickel salen \([N,N’\text{-ethylene-bis(salicyldieneiminato)}\]-nickel(II); \(\text{Ni(C}_{16}\text{H}_{12}\text{N}_{2}\text{O}_{2})\) as a catalyst. The details of the CNT growth are described elsewhere (17). Ni salen was found to produce CNTs via a tip-growth mechanism. Small Ni particles were observed at the tips of the CNTs which were otherwise free of Ni. Since Ni is used as a catalyst in relatively small amounts and is embedded inside the CNT tips, its contribution to the thermal conductivity enhancement can be ignored. The MWCNTs have an average outside diameter of 30 nm, and a length of several micrometers, as observed by electron microscopy (field emission scanning electron microscopy (FE-SEM) and TEM) (Figures 1(a) and 1(b)).

Nanofluids were prepared using a two step method. First the required amounts of MWCNTs and deionised water needed for the sample preparation were determined. Then a very small amount of surfactant (SDS) was dissolved in the liquid matrix, followed by appropriate amounts of MWCNTs for synthesis of different concentrations of nanofluids. SDS was used to minimise the agglomeration of nanotubes in the base fluid. The samples having MWCNTs were stirred using a magnetic stirrer and were ultrasonicated for 20 minutes with 100 W intensity at 20 kHz ultrasonic frequency (Sonics VC 505). As the probe sonicates within a limited conic volume, to facilitate uniform dispersion, sonication was followed by 10 minutes magnetic stirring. According to the density data provided by Jana et al. (18), 0.026 g, 0.078 g and 0.130 g of CNTs were dispersed in 100 ml of deionised water to prepare nanofluids with 0.01 vol%, 0.03 vol% and 0.05 vol% CNTs. 100 ml suspensions of each composition were prepared.

Thermal conductivity of the synthesised nanofluids was measured with a Hot Disk TPS 500 Thermal Constant Analyser which works on the temperature coefficient of resistance principle. The transient plane source (TPS) method is an updated version of the transient hot wire (THW) technique (19). The uncertainty in the measurements in this method is ±4%. TPS overcomes many of the drawbacks of THW due to its sensor structure and shape. TPS has a computer controlled temperature controller for accurate temperature settings and precise results at typical temperatures. The TPS based instrument can be used to measure thermal constants such as conductivity and diffusivity via a Ni sensor, using the temperature coefficient of resistance. Inside the instrument, the TPS element behaves both like a temperature sensor and a heat source. TPS uses the Fourier law of heat conduction as its fundamental principle for measurements.
3. Results and Discussion

Thermal conductivity measurements were taken for all the nanofluid samples at temperatures from 10ºC to 80ºC. The experimental data for thermal conductivity of the nanofluid samples are presented in **Figure 2**. For comparison, the temperature dependent thermal conductivity data of the base fluid (water) are also given. It can be seen that there is no significant increase in the thermal conductivity with the suspension of 0.01 vol% MWCNTs. On the other hand, there is a significant anomalous increase in the thermal conductivity of water with suspension of 0.03 vol% CNTs. Thus, it can be claimed that the percolation threshold exists below 0.03 vol%, leading to the conclusion that the CNTs do not have continuous chains from one end to the other below a certain particle loading, as predicted by Sastry et al. (20).

Although a number of models based on different mechanisms are available currently in the literature, no theoretical model is able to explain the anomalous thermal conductivity enhancement observed experimentally due to controlled and uncontrolled parameters in the experimental setup (21). Some models, for example the Sastry model, are in reasonable agreement with the experimental data under different assumptions and conditions. A critical analysis of the theoretical models has been carried out by Lamas et al. (21) who concluded that the available models show a negative effect of temperature on thermal conductivity enhancement in these systems. However, this is contradictory to the available experimental results. The agreement of theory and experiment was achieved by adjusting parameters such as the CNT geometry (22) and the value of interfacial conductance (23). These theoretical models had various degrees of empiricism and provided a limited physical insight into the experimental observations. In past studies, experimental data have showed that the dispersion technique and interaction between the CNTs and the base liquid also play a strong role, causing the enhancement to vary by as much as 7%–40% for water-MWCNT nanofluid (24).

For the present study, very low concentrations were chosen for two reasons. Firstly, to maintain the fluidic...
or viscous properties of the base fluid; and secondly to investigate the existence of a percolation threshold to explain anomalous thermal conductivity enhancements as predicted by Sastry and his coworkers. A number of physical mechanisms have been proposed to explain the thermal conductivity enhancement of a nanofluid.

An early concept was interfacial layering: the formation of a solid-like, liquid molecular layer close to the CNT interface, which has much higher thermal conductivity than the bulk liquid itself (25). Alternatively, due to the high aspect ratio of CNTs, interaction between them is thought to be highly probable resulting in the formation of a network. The phenomenon is often termed percolation. The formation of a highly conductive heat flow path in the liquid by the percolation network can potentially explain the enhancement due to concentration of CNTs in relatively low temperature zones where Brownian motion is not dominant. A critical volume fraction of MWCNT loading, called percolation threshold, was thought to exist above which the electrical conductivity of the MWCNT nanofluid would abruptly increase multifold. However, initial experiments did not show any such sudden rise in the effective thermal conductivity of the nanofluid. Thus it was concluded that there is no percolation threshold in thermal transport in those experiments (25, 26), a view that was contradicted recently (20). Sastry et al. considered percolation without specifically approaching it from a threshold perspective (20). Their approach relies on the basic premise of three-dimensional MWCNT chain formation in the liquid (percolation) and consideration of a thermal resistance network with higher resistance contact points of CNTs and very low resistance CNT channels. Random CNT orientation and CNT-CNT contacts are introduced by probability density function. They considered a cubical volume of nanofluid formed by dispersion of CNTs. The fundamental basis of the model is an interaction between the CNTs touching each other to form percolating chains in the suspension. In this mechanism, resistive points are formed at the contact centres of the CNTs. Thus, a series of resistive contact points offer resistance in the thermally conductive medium of a CNT chain. The net resistance has been calculated by Sastry et al. (20) as given in Equation (i): 

\[ R_{\text{net}} = \frac{1}{Gd_R^2} \sum_{i=1}^{N} \left( \frac{R_{\text{CNT},p} + 2R_C}{M} \right) \times R_{\text{FIP},p} \]  

(i)

where \( R_{\text{CNT},p} = \frac{L_p}{K_{\text{CNT}} A_{CS}} \); \( R_{\text{FIP},p} = \frac{L_p \sin \phi \cos \theta}{K_{\eta A_{s0}}} \) and \( R_C = \frac{1}{Gd_R^2} \).

Finally effective thermal conductivity can be written as

\[ k_{\text{eff}} = \frac{L_{\text{cell}}}{R_{\text{net}} A_{\text{cell}}} \]; where \( L_{\text{cell}} \) is the length of the cell and \( A_{\text{cell}} \) is the effective area of the cell in which the percolation exists. The thermal conductivity enhancement will not be observed below a certain particle loading, where the formation of chains of CNTs does not occur. The enhancement in thermal conductivity for 0.01 vol% at higher temperatures is due to Brownian motion, which dominates the percolation chain mechanism at high temperatures. The percolation mechanism can be applied for mechanically stable suspensions only. At high temperatures, suspensions become less stable due to Brownian motion.

Figure 3 shows the variation of thermal conductivity enhancement ratio \( (K_{\text{eff}}/K_{\text{liq}}) \) with temperature at different MWCNT loadings. Thermal conductivity ratio is considered as a much more suitable parameter to understand the enhancement in thermal conductivity, irrespective of thermal conductivity of the base fluid or liquid in which MWCNTs are dispersed to form nanofluids. The present experimental study was carried out in the temperature range 10ºC to 80ºC. The thermal conductivity was observed to increase with temperature, contradictory to predictions made by
available theoretical models (21). The temperature effect on thermal conductivity of nanofluids can be explained with the help of Brownian motion. The thermal conductivity of the CNT-water nanofluids was therefore calculated to examine the Brownian motion effect. Prasher et al. (27) developed a model for water based spherical nanoparticle nanofluids. Based on Prasher’s approach, the present experimental observations were modelled for CNT containing water-based nanofluids at high temperatures. Since the CNTs have very small diameters when suspended in the liquid, Brownian movement of the CNTs is quite possible. The root-mean-square velocity \((v)\) of Brownian particles can be defined (18) as Equation (ii):

\[
v_N = \sqrt{\frac{3k_B T}{m_N}} = \frac{1}{d_N} \sqrt{\frac{18k_B T}{\rho_N d_N^3}}
\]

where \(k_B\) is the Boltzmann constant, \(T\) the temperature, \(m_N\) the particle mass, \(\rho_N\) the density, and \(d_N\) the average diameter of the CNTs.

Now we consider the effect of the convection of the liquid near the CNTs due to their Brownian movement. The Reynolds number \(R_e\) based on \(v_N\) given by Equation (ii) can be written as Equation (iii):

\[
R_e = \frac{1}{v} \sqrt{\frac{18k_B T}{\rho_N d_N^3}}
\]

where \(v\) is the kinematic viscosity of the liquid.

The \(R_e\) for 30 nm CNTs in water, \(R_e = 0.0132\), is very small and therefore for convection the flow falls in Stokes regime. If a particle is embedded in a semi-infinite medium of thermal conductivity \(K_m\), then the Nusselt number \((Nu)\) based on the radius of the CNTs can be shown to be \(1\); i.e., \(h = (K_m/\alpha)\). In Stokes regime \(h\) is given (28) as \(h = (K/\alpha)[1 + (1/4)R_e + Pr]\) where \(Pr\) is the Prandtl number, ‘\(\alpha\)’ is the radius of the particle and ‘\(h\)’ is the heat transfer coefficient. Note these relations are derived analytically from first principles. This means that the effective \(K\) of the fluid due to the convection caused by the movement of a single sphere is:

\[
K = K_m[1 + (1/4)R_e \times Pr]
\]

Note that this is based on a single isolated CNT. In a real system there will be interaction in the convection currents from different CNTs. The value of \(K_m\) is substituted from Equation (iv) in Equation (v):

\[
K = \frac{(1 + 2\alpha) + 2\phi(1 - \alpha)}{(1 + 2\alpha) - \phi(1 - \alpha)}
\]

which is based on the traditional Maxwell-Garnett (MG) model where \(\phi\) is the particle volume fraction, \(\alpha = 2R_bK_m/d_N\), and \(R_b\) is the interfacial resistance. The effective \(K\) of the nanofluid can be written as Equation (vi):

\[
K = \frac{1}{4} \left[ (1 + 2\alpha) + 2\phi(1 - \alpha) \right]
\]

Equation (vi), together with the definition of \(R_e\) given in Equation (iii) has all the necessary ingredients for predicting \(K\), because it includes:

(a) conduction contribution of the CNTs
(b) \(R_b\) between the nanotubes and the water
(c) convection contribution (effective for smaller \(d_N\)).

So far no empiricism has been included in the model. Taking the clue from correlations for particle-to-fluid heat transfer a general correlation for \(h\) of the form:

\[h = (K/\alpha)[1 + AR_e^{\alpha}Pr^{0.333}\phi]\]

is proposed for the Brownian motion induced convection from multiple nanotubes, where \(A\) and \(m\) are constants. Convective heat transfer relations are regime dependent, and so depending on \(R_e\), these relations can change. Therefore it is most likely \(A\) should be independent of the fluid type whereas \(m\) depends on the fluid type. This modification leads to Equation (vii):

\[
K = \frac{1}{4} \left[ (1 + 2\alpha) + 2\phi(1 - \alpha) \right]
\]

If Equation (vii) is valid, \(A\) and \(m\) should be the same for different experimental data for a particular fluid.

Figure 3 shows the semi-empirical model for \(K\) of various water based nanofluids (different \(\phi\)), taking \(R_b = 2.5 \times 10^{-6}\) Km² W⁻¹, \(m = 2.4\) and \(A = 40,000\) (as in similar materials) for the best fit. Here in the model a thermal boundary layer \(\delta_T = 3 \delta_P/Pr\) is arbitrarily defined, where \(Pr\) is the Prandtl number and \(\delta_P\) is the diameter of the base fluid molecule. Here \(Pr = 10\) has been taken. Nusselt number \((Nu)\) is given as \(Nu = R_e^{2} Pr^{2};\) \(\alpha = 2R_bK_m/d_N = 0.967\) has been computed; \(K_m\) is thermal conductivity of water. \(R_e\) has been computed as 0.0132.

It is important to note that in the present case an increase in the viscosity at higher temperature increases Brownian motion. Figure 3 reveals
significant enhancement in the thermal conductivity of water containing a suspension of 0.05 vol% of CNTs at different temperatures, in good agreement with the theoretically modelled curve based on order of magnitude calculations.

The temperature variation of the enhancement of the thermal conductivity ($K/K_0$) on experimental observation is also in good agreement with the theoretical curve within the measurement accuracy of the apparatus. Thus, it may be concluded that convection induced due to Brownian movement of the CNTs is the main cause for the observed enhancement in $K$ of the nanofluid at higher temperatures in the present investigation. The interfacial resistance $R_b$ has also been incorporated as interfacial resistance greatly depends on bonding between the solid and the liquid (27).

The shelf life of the nanofluids was also investigated. In Figure 4 the temporal stability of nanofluid containing 0.03 vol% CNTs is shown at room temperature. The nanofluid is stable for a long time.

4. Conclusions

It can be concluded that the observed thermal conductivity enhancement in prepared nanofluids is due to the suspension of CNTs in deionised water. Sudden enhancement is observed at a concentration of 0.03 vol% CNTs in water at lower temperatures, which is attributed to formation of CNT chains with very high conductivity in the medium. The abrupt enhancement of thermal conductivity at 0.03 vol% can be explained with the help of percolation phenomena. From observations, it can be claimed that the percolation threshold is between 0.01 and 0.03 vol% CNT loadings in base fluid. Thermal conductivity enhancement increases with temperature and concentration of CNTs in the base fluid. The temperature dependence of the thermal conductivity enhancement is explained well with Brownian motion theory as chains of CNTs will not form at higher temperatures due to instability imposed by the temperature increase. These MWCNT + deionised water nanofluids are very stable with time. They therefore show potential to be used as coolants in different fields of industry.

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References

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