Thermophysical aspects of nanofluids with carbon nanotubes suspensions-A Review

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Abstract

This article focuses on a comprehensive review in summarizing on the recent research developments regarding the theoretical and experimental investigations about the thermophysical characteristics of carbon nanotubes-nanofluids with mass concentration varying from 0.1 to 1wt% and at the temperatures of 10-60°C. Carbon nanotubes are promising new materials for their mechanical, electrical, thermal, optical and surface properties. The current study explores how several factors those strongly affecting thermal conductivity, viscosity, specific heat and density of carbon nanotube-nanofluids include particle concentration, temperature, particle size, particle type, particle shape, different base fluids, surfactant and ultrasonic time. In addition, different apposite models contributing augmentation of thermal conductivity and decaying of viscosity of carbon nanotubes-nanofluids are introduced. Further, significant heat transfer mechanisms namely Brownian motion, nanoclustering, thermophoresis, and interfacial nano-layer responsible for significant role in augmenting the heat transfer capabilities of carbon nanotubes-nanofluids are well discussed. The viscosity of SWCNT nanofluids shows a non-Newtonian shear-thinning behavior due to the alignment of nanotubes clusters and agglomerates with increasing shear rate. The results reveal that the thermal conductivity, viscosity and density of CNT-nanofluids are higher than that of the base fluid, and enhances with rise in nanotubes concentration. Specific heat peters out with rise in particle loadings and upgrades with increase in temperature. Thermal conductivity of CNT-nanofluids upsurges, whereas the viscosity and density of CNT-nanofluids diminish with rise in the temperature. Finally, the challenges for the future are conveyed.

Key words: Carbon Nanotubes Nanofluids; Synthesis; Nanoclustering; Interfacial nano-layer; Sonication.

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1. Introduction

In the history of progress of nanotechnology in the twenty-first century, carbon nanotubes (CNTs) possessing outstanding electrical, thermal, mechanical, chemical and optical properties (e.g. high thermal conductivity, electrical conductivity, high hardness and stiffness, light weight, special electronic structure, high surface to volume ratio and high chemical stability etc) are being considered as prime candidate materials in multidisciplinary fields including material science, automotive, optical, electrical, aerospace, bio-medical and energy conversion for nano-scale applications. CNTs are long, thin cylinders of carbon atoms with diameter ranges 0.7–50 nm. CNTs are tubular in shape as they are composed of cylindrical sheet form with carbon which is rolled up in a tube like structure with the appearance of lattice work fence. There are three types of CNTs for instance single walled, double walled and multi walled. Single-walled carbon nanotube (SWCNT) consists of one cylindrical graphite sheet whereas multi-walled carbon nanotube (MWCNT) contains multiple layers of graphene sheets.\(^1\)

The nanofluids (nfs) are novel type of fluids in which nanoparticles [nano meter-sized particles (smaller than 100 nm)] such as copper (\(\text{Cu}\)), nickel (\(\text{Ni}\)), aluminum (\(\text{Al}\)), Silver (\(\text{Ag}\)), titanium oxide (\(\text{TiO}_2\)), aluminum oxide (\(\text{Al}_2\text{O}_3\)), copper oxide (\(\text{CuO}\)), iron oxide (\(\text{Fe}_3\text{O}_4\)), etc. are mixed with the base fluids/conventional fluids such as water, kerosene, ethylene glycol, light oil etc. through proper dilution and suspension. Simply, we may say that nanofluid (nf) is a suspension of solid nanoparticles (1-100 nm) in conventional fluids. Choi\(^2\) was the pioneer who invented the nanofluid experimentally through proper suspension and dilution of nanoparticles (nps) with base fluids in 1995 at Argonne National Laboratory, USA. By using nfs highest possible thermal properties at the smallest possible concentrations (<1% volume fraction of nps) by uniform dispersion and stable suspension of nps in base fluids can be accomplished. By mixing nanoparticles in the base fluid, thermal conductivity (TC) of the fluids provides dramatic improvement (TC values of about 20-150% higher) in the HT capability compared to that of the traditional/conventional/base fluids\(^3\text{-}^5\).

The study of HT has vital role in industries for determining the quality of final products with desired characteristics which greatly depends on the rate of HT /rate of cooling between the fluid and solid surface. In view of diversified industrial needs, conventional fluids have received much attention by many vibrant researchers in the last quarter century. However, they do not have enough heat transfer capability. Such drawbacks of base fluids restrict their use as cooling agent in many heat flow devices include electronics devices, material processing, solar thermal collectors etc. From the research it is well known that micron-size particles mixed with base fluids lead to poor stability and sedimentation of the micron-size particles, erosion, clogging of the channels, and the enhanced fluid pumping power in heat transfer systems. Such drawbacks impede the microfluids in HT applications. In contrast, nfs concept has emerged to overcome these experienced problems. Various methods of preparation, addition of surfactants for enhancement of stability and use of ultra sonication along with proper dispersion (dilution and suspension) of nano-size particles that lead to the formation of nfs (where nano-size particles exhibit more stability, larger surface area to volume ratio and the higher surface energy resulting aggregation and sedimentation) of remarkable thermo-physical properties, superior transport properties and significant enhancement in HT capability. One of the most important determining factors of nfs is the higher TC/enormous HT capability (compared to that of conventional base fluids) leads to high performance with respect to improved efficiency, reduction in size and fabrication cost and better safety margin of HT equipments/thermal systems-favours the nf being served as best suitable coolants in the ever increasing applications of the present growing industrial world\(^6\text{-}^9\). Such applications include as coolants are in cancer therapy, safer surgery, heat exchangers, micro-channel heat sinks and several electronic devices for use in military systems, vehicles and transformers, in designing the waste heat removal equipment, major processing industries associated with
materials and chemicals, oil and gas, food and drink, paper and printing, textiles, polymer extrusion, heat exchangers, micro-channel heat sinks, glass blowing, rapid spray cooling, cooling of microelectronics, wire drawing and quenching in metal foundries and as refrigerant/lubricant mixtures enabling to chill or cool buildings. Nanofluids along with biotechnological components bring forth many potential applications in cancer therapy, biological sensors, pharmaceuticals, and safer surgery by cooling. Magneto-nanofluids are vital in applications include optical modulators, magneto-optical wavelength filters, tunable optical fibre filters and optical switches and bio-medical applications viz. wound treatment, sterilized devices, gastric medications, asthma treatment, targeted drug release (drug delivery), synergistic effects in immunology, elimination of tumors with hyperthermia, magnetic cell separation and contrast enhancement in magnetic resonance imaging. Taking the above relevance into mind, numerous researchers have been motivated and extended their interest to investigate several aspects of flow and HT of nfs associated with different configurations.

Experimental and theoretical studies have ensured that TC of cylindrical structured nps is higher than that of spherical nps. In is well found that spherical nps are the metallic and oxide nanomaterials such as aluminium and aluminium oxide have TC of 237 W/m K and 40 W/m K respectively. In contrast, CNTs have TC in a range of 2000-6000 W/m K. Estimations confirm that the values for TC of single walled carbon nanotube (SWCNT), double walled carbon nanotube (DWCNT) and multi walled carbon nanotube (MWCNT) are 6000 W/m K, 3986 W/m K and 3000 W/m K, respectively. The TC of DWCNT and MWCNT decays respectively due to the increase of nanotube wall layers. In view of high TC, large specific surface area (SSA), high aspect ratio and low specific gravity, CNTs have been chosen by researchers as best suitable nanoparticles to improve the overall TC and therefore the performance of existing HT system. The pioneering study regarding CNT nf was conducted by Choi et al. by dispersing MWCNT nanoparticles in synthetic poly oil base fluid. They found 160% augmentation in TC for 1.0 vol% of MWCNT nanoparticles. According to literature, no further studies have reported such improvement in TC using MWCNT nanofluid. CNT nanofluids are expected to exhibit excellent thermal features, long term stability and rheological properties compared to traditional working fluids. Ding et al. reported in their study that TC of CNT based aqueous nanofluid upsurges significantly with the temperature by 15% at 20°C, 30% at 25°C and by 79% at 40°C for the same volume fraction. Xie et al. dispersed 1.0 vol% MWCNT nps in three different base fluids and found the augmentation of TC as 7.0%, 12.7%, and 19.6% for distilled water (DW), ethylene glycol (EG), and decene (non polar liquid) respectively. Nevertheless, a small amount of CNT nps in nf is capable of upgrading TC significantly, the CNT nps is vulnerable to agglomeration due to hydrophobic nature of CNTs, high surface area and the van der waals forces. Sonication is the most common method used by the researchers to improve the stability of CNT nfs by breaking the agglomerations of nps. Beside sonication, various surfactants such as sodium dodecyl sulfate (SDS), sodium dodecyl benzene sulfonate (SDBS), cetyltrimethyl ammonium bromide (CTAB), hexamethyldisoxane (HMDS), sodium deoxycholate (DOC), poly-vinyl pyrrolidone (PVP) and gum Arabic (GA) have been used to accomplish desired stability of sample nfs. Functionalization of CNT nfs is another way to obtain better stability with higher TC. Further, Lotfi et al. found from his investigation that HT enhances in the presence of multi-walled nanotubes in comparison with the pure water. Kathiravan et al. considered MWCNT as nps for pool boiling to investigate the HT behaviour of the nf. The MWCNT nanoparticles were dispersed by 0.25, 0.5 and 1.0 vol% with water and also with the suspension of water and SDS. The HT coefficients of nf were enhanced 1.7 times compared to water. Park and Kim investigated hydroxyl radicals combined with oxidized multi-walled CNTs (MWCNTs) to upgrade the HT utility of the heat pipe in a solar collector using nanofluids. It is visualized that the TC is 12.6% higher at 90°C than that of the base fluid and the viscosity is 11% lower due to oxidation. Therefore, oxidized MWCNT nf imparts high operating temperature range in a heat pipe of a collector. CNT nf is considered as an excellent working fluid for direct absorption solar collector (DASC) due to
high TC, good optical properties, and dispersion stability. The TC is mainly dependent on temperature than the volume concentration which is a great advantage for solar collector applications. Therefore, they reported CNT nanofluid as a very suitable working fluid for augmenting overall efficiency of DASC (See Karami et al.\textsuperscript{62}). Chougule\textsuperscript{63} carried on a study on FPC involving heat pipe and compared the performance using water and CNT nanofluid. The performance of collector using nf found to be better. The average collector efficiencies using water and nf for tilt angle $31.5^\circ$ are 25% and 45%, for tilt angle $50^\circ$ are 36% and 61% respectively. The maximum instantaneous efficiency achieved by using CNT nf is 69% for tilt angle. Moreover, thermodynamic effect in Darcy–Forchheimer nf flow of a single-wall carbon nanotube/multi-wall carbon nanotube suspension due to a stretching/shrinking rotating disk using Buongiorno two-phase model was investigated by Nayak et al.\textsuperscript{64}. In their study they explored how the utilization of both porous media and nfs with CNTs as nps can augment the thermal efficiency of typical physical systems significantly.

From the literature survey it is observed that it is demonstrated there is a substantial augmentation of the HT performance of different CNTs-nfs in comparison to their base fluids. Specifically, SWCNT nps exhibit higher TC and better optical properties such as Raman, fluorescence and absorption spectra compared to DWCNT and MWCNT nps. Therefore, it is inevitable to carry on more studies on SWCNT nf to find out their suitability in various HT applications. More investigations on the study of SWCNT nfs are yet to be done. Therefore, the present study aimed to investigate the thermophysical aspects (density, specific heat, viscosity, TC and Rheology) of SWCNT nf to bridge the research gap by utilizing methods like surfactant addition, ultrasonication, nanoclustering, particle loading etc.

2. Rheology of CNT nanofluids:

Rheological behavior of nfs has vital role on the stability and flow behavior of the nfs. The viscosity of SWCNT nfs of different concentrations as a function of shear rate is envisioned in Fig. 1. A shear thinning behavior is visualized for all np concentrations yielding progressive diminution in viscosity with enhancing shear rate. A shear thinning behavior can achieved due to de-agglomeration of clustered nanotubes or realignment in the direction of the shearing force which decays the resistance to the flow thereby generating less viscous fluids. Garg et al.\textsuperscript{65} and Nanda et al.\textsuperscript{66} have explored similar shear thinning behavior for MWCNT and SWCNT nfs respectively. In order to verify the rheological behaviors of SWCNT nfs, relation between shear rate and shear stress for different volume concentrations of nps at $20^\circ$C was investigated. The Rheology of SWCNT nf is illustrated at Fig. 2. The shear stresses of the nf upsurge almost linearly with increasing shear rate for all volume concentrations.

![Fig. 1 Rheological behavior of SWCNT nanofluids (viscosity as a function of shear stress)](image-url)
SYNTHESIS of CNTs nanofluids:

The development of stable carbon nanotube suspension involves two steps. The first step represents the breaking the agglomeration by mechanical processes and the second step deals with stabilizing the suspensions. High pressure ultrasonic homogenizers are most frequently used to overcome the strong cohesion forces between CNTs. The CNTs in the suspension segregate and settle down under gravitational forces due to the hydrophobic character without any surfactant. In order to get a stable suspension of CNTs and water, SDS surfactant that provides hydrophilic character to CNTs are utilized. Two-step method was implemented to develop SWCNT nfs of five desired volume concentrations. The suspension of SWCNTs, SDS and DW was then sonicated by a high pressure ultrasonic homogenizer for one hour as shown in Fig. 3.

Fig. 2 Rheological behavior of SWCNT nanofluids: shear stress as a function of shear rate

Fig. 3 Sonication of (SWCNT-SDS + DW) suspension (Sabiha et al.1)
The desired concentrations used in this study include 0.05, 0.1, 0.15, 0.2 and 0.25 vol%. The nps and the base fluid respectively; whereas \( \rho_{np} \) and \( \rho_{bf} \) are the density of nps and base fluids respectively. It is obvious that the highly agglomerated nps were able to be easily broken by the combination of strong shear force and cavitations generated by the high-pressure homogenizer. The SWCNT nfs preparation conditions are incorporated in Table-1.

Table 1. Nanofluids preparation conditions (Sabiha et al.\(^1\))

| Base fluid       | Water             |
|------------------|-------------------|
| Nanoparticle     | SWCNT             |
| Nanoparticle type| Cylindrical       |
| Surfactant       | SDS               |
| Volume concentration (vol%) | 0.05, 0.1, 0.15, 0.2, 0.25 |
| Ultra-sonicator  |                   |
| Time(min)        | 60                |
| Power(W)         | 500               |
| Frequency(kHz)   | 20                |
| Pulse(s)         | 2                 |
| Term(s)          | 2                 |

3. Experimental studies on thermophysical behavior of CNT nanofluids

Density

The density of SWCNTs nfs at different temperatures in the concentration range of 0-1wt% is well illustrated in Fig. 4. It clearly visualized that the density of DIW and the SWCNTs nfs diminishes with the rise in temperature at the same concentration. With the rise of temperature from 10°C to 60°C the density of DIW decays from 999.61 to 984.12 \( \text{Kgm}^{-3} \). Specifically, the density of the 0.1 wt% SWCNTs nf reduces from 1000.13 to 984.65 \( \text{Kgm}^{-3} \) and the density of the 1 wt% SWCNTs nf falls from 1004.88 to 989.46 \( \text{Kgm}^{-3} \) as the temperature rises from 10°C to 60°C. Furthermore, it is understood that the density of SWCNTs-nf enhances with the rise in the mass fraction of SWCNTs. The variation of density is 0.52-0.54% at the mass concentration of 1wt% for the different temperatures of SWCNTs nanofluid. As a result, the infusion of SWCNTs influences the density of the base fluid.

Fig. 4 Density of SWCNT nanofluid as a function of mass fraction (Xing et al.\(^6\))
**Specific heat:**

The effect of temperature on specific heat of SWCNT nfs at different volume concentrations is shown in Fig. 5.

![Fig. 5: Specific heat of SWCNT nanofluid as a function of temperature and particle volume concentrations (Sabiha et al. 1)](image)

It is noticed that the specific heat of SWCNT nfs upgraded with temperature, for instance the values of specific heat obtained in the experiment for 0.05 vol% are 3.66, 3.72, 3.79, 3.83 and 3.90 kJ/kg at temperature 20, 30, 40, 50 and 60°C respectively. However, the specific heat decayed gradually with rising volume concentration. It implicates that lower heat is required to increase the temperature of the nanofluid with higher particle volume concentration. According to the experimental results, when the temperature is fixed at 20°C, the specific heat values 3.66, 3.43, 3.27, 3.11 and 2.97 kJ/kg.K are for volume concentrations of 0.05, 0.1, 0.15, 0.2 and 0.25 vol% respectively. It is also envisioned that the specific heat of SWCNT nf is lower than that of water. It is so because when the specific heat of nanoparticles is less than the base liquid, the specific heat of suspension belittles. Fig. 6 shows the comparison between the experimental results of specific heat and the theoretical results obtained by using the following expression

\[
C_{\text{nf}} = \frac{(1-\phi)(\rho C_p)_{\text{bf}} + \phi(\rho C_p)_{\text{np}}}{(1-\phi)(\rho)_{\text{bf}} + \phi(\rho)_{\text{np}}}
\]  

(2)

where \(C_{\text{nf}}\) is the specific heat of SWCNT nf, \(\phi\) is the volume concentrations, \(\rho\) is the density, \(C_p\) are respectively the specific heat of SWCNT nps and base fluid.
It is found that the experimental values of specific heat are lower compared to the theoretical values and the average deviation is found to be 14.08%. There is no available equation in literature to determine the specific heat of CNT nfs. Therefore, deviation is observed as (2) is valid to determine the specific heat of any homogenous mixtures and ignored the crucial factors such as surfactant effect, particle size and aspect ratio of CNT nps.

**Viscosity:**

In 1991, Sumio Lijima\(^6\) discovered CNTs. Because of excellent properties CNTs have been attracted by diversified sectors\(^7^0\). In the beginning, multi walled carbon nanotubes (MWCNTs) in carbon soot were produced by an arc discharge method (Lijima\(^7\) in 1991. Two years later, he observed the single walled carbon nanotubes (SWCNTs). Dispersion of CNTs in the base fluid is challenging due to the tendency of nanotubes to agglomerate. Stable CNT nfs can be synthesized physically by ultrasonication, high shear mixing, ball milling, and/or chemically by functionalization through altering the surface chemistry of the nanotubes covalently, and the addition of surfactants which adsorb onto the nanotubes surfaces non-covalently. Functionalization over the other surfactant free method provides good fluidity, long-term stability, significant HT (Aravind et al.\(^7\)). Functionalized CNTs are used as advanced HT fluids in thermal energy/heat exchange engineering systems. They evaluated the viscosity of four groups of CNTs nanofluids at a very low volume fraction of 0.005% and 0.03% with water and EG as base fluids, respectively. The results conveyed that the relative viscosity of CNTs nfs is not sensitive to the base fluid type but influenced by the temperature since the relative viscosity at 70°C was higher than that at 30°C. A functionalization method to stabilize CNT nfs was developed by Esumi et al.\(^7\). In this method, 1 g CNT was dispersed and treated in a mixture of concentrated nitric acid and sulfuric acid (1:3 volume ratio) for 30 mins and refluxed at 40°C. Having washed with deionized water till pH = 7 nanotubes were dried at 100°C in vacuum and then 0.01g of dried samples were suspended in 30ml of different liquids. Ultrasonication was applied to the latest suspensions about 4hrs. The resultant nanotubes were well dispersed.
into individual fibers in base fluids. This established method has been applied by many researchers in their experiments. The colloidal stability of functionalized MWCNT-based nfs was examined by Lamas et al., where he suggested that functionalization of CNTs helps greatly in the formation of highly stable nfs. The thermophysical properties of water-based SWCNTs nfs with varying nanotubes concentrations in the range of 0.1–1 wt% and at a temperature range of 10–100°C was studied by Xing et al. They declared from their study that viscosity and density of nfs incremented with the rise in nanotubes concentration. An increased viscosity of 35.9% at 1 wt% nanotubes loading at 60°C was reported.

Ding et al. used a variety of surfactants in stabilizing CNT-water nfs. Surfactants such as sodium laureate (SL), sodium dodecyl benzene sulfonated (SDBS) and Gum Arabic (GA) can stabilize CNTs in the suspension for over 1 month without any visual sedimentation. They reported linear shear thinning behavior of their nfs whereas their base showed nonlinear shear thinning nature. Sabiha et al. prepared a water-based SWCNTs nf with addition of SDS to stabilize the suspensions and with sonication for 1h. Increment of viscosity by 82.01% was the expected result. Singh et al. investigated the viscosity of CNT-EG nfs. Before CNTs being dispersed into ethylene glycol and sonicated for 1.5h, those were functionalized by acid treatment. The outcome of the study was that viscosity increased with CNT concentration but exponentially decayed with temperature. Chen et al. examined the viscosity of CNTs-water nfs and found that increment of temperature from 6 to 65°C can greatly reduce the viscosity of nfs but has little effect on the relative viscosity. With the addition of very slight amount of CNTs, such as 0.2vol.% can unexpectedly reduce the viscosity of base fluid. This implicates that the nf has a lower viscosity compared to the base fluid. This is due to the lubricating effect of nanoparticles. Besides the particle loading and temperature effect, the shear rate effect is more extensively studied. CNTs nfs exhibit non-Newton behavior. Ko et al. synthesized two types of water based CNTs nfs by acid treatment and by surfactant treatment, respectively. Their results showed that both kinds are non-Newton fluids and exhibit noticeable shear thinning behavior at all kind of concentrations. The viscosities of CNTs nfs prepared by both acid and surfactant treatment (TCNT) are lower than that of pristine CNTs nanofluids (PCNT). Further, the viscosities of CNTs nfs developed by the acid treatment are obviously lower than the ones developed with surfactant. Garg et al. measured the viscosity of CNTs nfs prepared by different period of ultrasonication. They disclosed that CNT nfs showed a typical non-Newtonian behavior in accordance with the Power Law viscosity model. The initial sonication will induce growth in viscosity of nfs. The rationally behind is that the clusters of CNT bundles by sonication improve the dispersion. However, the longer time sonication breaks the CNTs into shorter ones which in turn destroy the networking of CNTs and weaken the dispersion situation there by decreasing in viscosity. The impact of particle loading and temperature on the viscosity of CNT nfs was reported by Halelfadl et al. The results revealed that the nfs exhibited Newtonian behavior at lower particle loading but a shear thinning behavior at higher loading. The viscosity greatly increases at high particle loading owing to the aggregates of CNTs. Temperature has impact on the absolute viscosity but has little effect on the relative viscosity of nfs at high shear rate.

Many others discussed in the related areas. Ding et al. analyzed the viscosity of CNT water nfs under different particle loading, temperature and pH values. In their study, they observed that the viscosity of water-based nfs of MWCNTs as a ratio of the shear rates in different volume fractions and temperatures. Their report reveals that at all shear rates, the viscosity of nf enhances with rise in the volume fraction and reduces with incrementing the temperature. They also revealed the Newtonian behavior for a nf without surfactant. With adding Arabic gum as a surfactant, they observed a thin shear behavior for lower shear rates and a thick shear behavior for shear rates over 200s⁻¹. The experimental results focused in Fig. 7 represents that the viscosity of
CNT nfs upsurge with the rise of particle content and fall in temperature. It is also shown in Fig. 8 that how the viscosity varies with temperature for nfs made with water and ethylene glycol as base fluids and with multi walled carbon nanotubes as nanoparticles. A shear thinning behavior in nfs was noticed. Such characteristic is applied to tubular geometry because the lower viscosity and better lubrication appear at the wall region. They also showed that the viscosity of pure gum Arabic fluid is much lower than that of the CNT nf. They also eliminated the doubt that the gum Arabic dispersant produce the shear thinning behavior since the viscosity of pure gum Arabic fluid is much lower than that of the CNT nf (Fig. 9).

Fig. 7 Viscosity as a function of shear rate for CNT nanofluids (Ding et al.\textsuperscript{81})

Fig. 8 Viscosity changes with temperature for Water-based and EG-based nanofluids containing MWCNTs (Khodadadi et al.\textsuperscript{88})
In another study, Yang et al.\textsuperscript{89} used polyisobutylene succinimide surfactant for the production of a nf of MWCNTs in oil. They also used the ultrasonic methods for homogenization and stabilization. They showed that this surfactant well controlled the viscosity of nfs, especially at low shear rates. The Newtonian behavior is observed for very low volume fractions of CNTs while the non-Newtonian behavior is observed at low shear rates. Kinloch et al.\textsuperscript{90} studied the rheological behavior of water nanofluid-oxidized carbon nanotube. He observed a thin shear behavior for all nfs volume fractions. They also observed augmented viscosity by increasing the volume fraction. Vakili-Nezhaad and Dorany\textsuperscript{91} determined the suspension of single-walled CNTs in lubricating oil at temperature ranging from 25\textdegree C to 100\textdegree C and obtained that increase of 33% viscosity of this nf in a 0.2% volume fraction. Ruan and Jacobi\textsuperscript{92} examined the rheological properties of nf produced by considering MWCNTs as nps and ethylene glycol with a volume fraction of 0.5 as base fluids with ultrasonic effects. They disclosed that at a constant shear rate, the viscosity initially increased and then decreased, with rising ultrasonic time. Table 2 conveys some studies conducted on nfs made with different CNTs.

Fig. 10 illustrates the viscosity of SWCNT nfs, as a function of temperature and various volume concentrations. It reveals that an increase in viscosity is attained due to incremented nanoparticle concentration. However, the viscosity belittles with rising temperature. For instance, at 20\textdegree C, the viscosities of SWCNT nfs are 1.18, 1.21, 1.23, 1.26 and 1.28 mPa for 0.05, 0.1, 0.15, 0.2 and 0.25 vol% respectively.
Table 2 Some studies on nanofluids made with carbon nanotubes

| Authors            | CNTs/base fluid | Rheology                      | Key results/remarks with influence ranks                                                                 |
|--------------------|-----------------|-------------------------------|-----------------------------------------------------------------------------------------------------------|
| Yang et al. 93     | MWCNTs/Oil      | Newtonian and shear thinning  | At $\varphi = 0.34\text{ vol\%}$ $\tau = 10\text{ Pa}$ $\mu_{eff} = 1570$ $\tau = 50\text{ Pa}$ $\mu_{eff} = 30.20$ |
| Garg et al. 65      | MWCNTs/ Water   | Non-Newtonian shear thinning  | A number of mechanisms related to boundary layer thickness, micro-convective effects, particle rearrangement, effect due to viscosity |
| Chen et al. 94      | MWCNTs/ Water   | -                             | At $\varphi < 0.4\text{ vol\%}$ $T < 55^\circ\text{C}$ $\mu_{eff} < 1$ (decreasing) $T=55^\circ\text{C}$ $\mu_{eff} > 1$ (increasing) |
| Xie and Chen 95     | MWCNTs/ Silicon oil | Newtonian                    | At $\varphi = 0.54\text{ wt\%}$ $\mu_{eff} < 1$ (decreasing)                                            |
| Phuoc et al. 84     | MWCNTs/ Water   | Non-Newtonian                 | At $\varphi = 0.5\text{ wt\%}$ $\mu_{eff} = 0.8$ (decreasing)                                           |
| Harish et al. 96    | SWCNTs/ Water   | -                             | At $\varphi = 0.3\text{ vol\%}$ $\mu_{eff} = 1.3$                                                        |
| Estelle et al. 97   | MWCNTs/ Water   | Newtonian and shear thinning  | At $\varphi = 0.55\text{ vol\%}$ $\mu_{eff} = 5.2$ with SDBS $\mu_{eff} = 1.5$ with lignin               |
| Sadri et al. 98     | MWCNTs/ Water   | Newtonian and shear thinning  | Nanofluids viscosity increased up to 7 min of sonication and then decreased with more rise in sonication time |
| Maillaud et al. 99  | CNTs/ Water     | Shear thinning                | Nanofluids viscosity augmented with TX100 and CNT loading                                               |

Fig. 10 Specific heat of SWCNT nanofluid as a function of temperature and particle volume concentrations (Sabiha et al.)
As particle concentration improves, the internal viscous shear stress uplifts as shown in Fig. 1 which yields higher fluid viscosity. However, the viscosity belittles with rising temperature. This is because the rising temperature peters out the intermolecular forces of the particles and fluid itself. This is due to the fact that the shear effect of nfs is strongly influenced by the increase in the concentration of nps. In other words, the internal viscous shear stress uplifts due to rise in particle concentrations. However, the adhesion of nps as well as water molecules is decreased as a result of increasing temperature. At 0.05 vol%, the viscosities of SWCNT nfs are 1.18, 0.95, 0.81, 0.75 and 0.67 mPa s for 20, 30, 40, 50, and 60°C respectively. The first study conducted by Masuda et al. to investigate the concentration and temperature dependence of viscosity of aqueous nfs containing $\text{Al}_2\text{O}_3$, $\text{TiO}_2$ and $\text{SiO}_2$. They declared that the viscosity enhances with concentration while undermines with temperature in non linear fashion. Many reported in their studies substantial or nonlinear decrease of viscosity with increasing temperature regarding viscosity of nfs.

The experimental values are then compared to the existing correlations at Fig. 11. The experimental values are found to be higher than theoretical values of Brenner and Condiff as well as Timofeeva et al.

**Fig. 11** Experimental results of relative viscosity compared to existing correlations (Sabiha et al.)

*Thermal conductivity of Carbon Nanotube Nanofluids:*

The TC of SWCNT nf for volume concentration ranging from 0.05 to 0.25 vol% with respect to temperature is demonstrated in Fig. 12.

**Fig. 12** Thermal conductivity of SWCNT nanofluid as a function of temperature and particles volume concentrations
From the above figure it is well understood that the enhancement of TC is low at temperature 20-30°C but larger enhancement is the result for temperatures above 30°C compared to distilled water. Brownian motion accounts for the deviations in thermal conductivities with temperature, higher aspect ratio of the particle, the effects of particle agglomeration, the change of viscosity with temperature, and the enhanced surface area of suspended nanostructures contribute to the temperature dependence of SWCNT nf. Increment in TC observed with the increase in the volume concentration is due to the inherent high HT capacity of SWCNT nps.

The highest enhancement in TC at 60°C is attained to be 9.36%, 13.66%, 23.93%, 30.76% and 36.39% compared to water for 0.05, 0.1, 0.15, 0.2 and 0.25 vol% SWCNT respectively. Keblinski et al. proposed that the micro or nano-convection due to Brownian motion, formation of nanolayer around particles, and near field radiation are the mechanisms behind the augmentation of TC of nfs.

Some recent studies have revealed that the growth of cluster size has significant impact on the augmentation of TC, however, excessive clustering yields sedimentation which is an adverse effect to the TC augmentation. From the experimental result as shown in Fig. 13, it is noticed that higher augmentation in TC is availed for higher volume concentration and larger cluster size is the result for higher loading of nps. Therefore, the nanoparticle clustering also accounts for the TC augmentation.

**Fig. 13 Average particle size in SWCNT nanofluids as a function of volume concentration**

The measurement of TC was carried on by using NETZSCH laser flash apparatus (Range: 0.1–2000W/mK; Accuracy: ±5%). The TC of PCM are summarized in Table 3.

| Sample | Weight Fraction (wt.%) | Thermal diffusivity (mm²/s) | Specific heat (kJ/kg.K) | Density (Kg/m³) | Thermal conductivity (W/m K) | Enhancement ratio (%) |
|--------|------------------------|-----------------------------|-------------------------|-----------------|-----------------------------|---------------------|
| DM     | -                      | 0.578                       | 1.528                   | 1480.01         | 1.308                       | -                   |
| DM-CNT | 0.1                    | 0.626                       | 1.511                   | 1480.53         | 1.401                       | 7.10                |
|        | 0.2                    | 0.655                       | 1.505                   | 1480.87         | 1.460                       | 11.62               |
|        | 0.3                    | 0.748                       | 1.482                   | 1481.22         | 1.642                       | 25.53               |
|        | 0.4                    | 0.783                       | 1.459                   | 1481.67         | 1.695                       | 29.41               |
|        | 0.5                    | 0.818                       | 1.432                   | 1482.36         | 1.738                       | 32.87               |
From the table, it is revealed that TC of composites augmented with the weight fraction of additives. The TC upsurges from 1.308W/mK pure DM to 1.401W/mK and 1.738W/mK for 0.1% and 0.5% DM-CNT composites. In fact, a linear trend is observed between TC value of composites and weight fraction of additives. The TC augmentation of DM-CNT for 0.1–0.5% nanocomposites were obtained by 7.1–32.8% as compared to pure DM. Formation of network structure in the nanocomposites may be the sole reason for augmentation of TC. It is also known that augmented TC of nanocomposites with CNTs is due to a network of continuous quasi 2D bundles or due to high heat transport pathways created by self-organized bundles of CNT and due to the ability of CNTs to induce strong crystalline networks and possibility of molecular chain to get absorbed on the CNT surface and align themselves parallel to the axis of CNT.

4. Theoretical studies on thermophysical behavior of CNT nanofluids
4.1 Role theoretical models on viscosity of CNT nanofluids

Frequently used theoretical model to predict the viscosity of the solid-liquid mixture is the Einstein model\(^\text{117}\). The correlation is expressed as follows:

$$\frac{\mu_{nf}}{\mu_{bf}} = 1 + 2.5\phi$$

where \(\mu_{bf}\) and \(\mu_{nf}\) are the viscosity of base fluid and nf respectively. Einstein’s formula was found to be restricted to low volume concentrations \((\phi < 2\%)\).

Considering the shape of the particles, the viscosity of nf with arbitrary shape and low volume concentrations is expressed as\(^\text{118}\):

$$\frac{\mu_{nf}}{\mu_{bf}} = 1 + K\phi$$

where \(K\) is the shape factor, the value become bigger as the particles is more asymmetrical as shown in Table 4.

| Shape               | Sphere | Oval | layered structure | rodlike |
|---------------------|--------|------|-------------------|---------|
| \(K\)               | 2.5    | 4.8  | 53                | 80      |

The viscosity ratios \(\frac{\mu_{nf}}{\mu_{bf}}\) of SWCNTs-nf at different temperatures are shown in Fig. 7.

Fig. 14 Viscosity ratios \(\frac{\mu_{nf}}{\mu_{bf}}\) of SWCNTs-nanofluids at different temperatures.
It is obvious that the viscosity ratio upsurges as the particle volume concentration increases. In addition, the viscosity ratios have a slight enhancement with the rise in temperature and it becomes exact as the concentration rises, as shown by the experimental results. The maximum deviation of viscosity ratio is 7.43\% between 10°C and 60°C at the concentration of 1wt\%. The viscosity ratios attain almost constant values at different temperatures for a fixed concentration indicating that it is temperature independent.

4.2 Role theoretical models on thermal conductivity of CNT nanofluids:

After a huge gap Maxwell’s model was modified by a noteworthy researcher named Hamilton and Crosser\textsuperscript{119} to determine the effective TC of non spherical particles with implementation of a shape factor (n). The developed equation is

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

where n is the shape factor, \( n = \frac{3}{\psi} \) (\( \psi \) is the sphericity). Sphericity is defined as the ratio of surface area of a sphere with volume equivalent to that of the average particle, to the surface area of the particle. \( \psi = 1.0 \) and \( \psi = 0.5 \) correspond to spherical and cylindrical shapes, respectively. When \( \psi = 1 \), the Hamilton and Crosser model reduces to Maxwell’s model and well agrees with experimental data for \( \phi < 0.3 \).

Xue\textsuperscript{120} established a model for calculating the thermal conductivity of CNT nf, which is

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

The above novel type models comprise the conventional factors such as particle type, loading and base fluid type.

Using the same method, Murshed \textit{et al.}\textsuperscript{121} proposed a TC model for nanotube based nfs with an interfacial layer. Their model is expressed as:

\[
k_{\text{eff}} = \left( k_p - k_{tr} \right) \phi_p k_{tr} \left( \beta_1^2 - \beta^2 + 1 \right) + \left( k_p + k_{tr} \right) \beta_1^2 \phi_p \beta^2 \left( k_{tr} - k_f \right) + k_f
\]

Jiang \textit{et al.}\textsuperscript{122} studied the heat conduction process along the radial direction of a CNT with an interfacial layer and established a model on TC of CNT based nfs. The model is expressed as:

\[
k_{\text{eff}} = k_f \left( k_p + (n-1)k_f + (n-1)\phi(k_{pe} - k_f) \right)
\]
\[
k_{pe} = k_f \left( \frac{2k_p + \left( \beta^3 - 1 \right) \left( k_p + k_{lr} \right)}{2k_{lr} + \left( \beta^3 - 1 \right) \left( k_p + k_{lr} \right)} \right)
\]

\[
k_{lr} = \frac{k_p R \left( 1 + \frac{t}{R} - k_f \right) \ln \left( 1 + \frac{t}{R} \right)}{t k_f \ln \left( \frac{1 + \frac{t}{R}}{k_p} \right) k_f}
\]

where \( \beta = 1 + \frac{t}{R} \), and \( k_{pe} \) is the equivalent TC of the nps.

5. Factors influencing the thermophysical behavior of CNT nanofluids
5.1 Particle Concentration

TC enhancement could be achieved due to volume loading of nps. Earlier many researchers robustly analyzed and revealed that the enhancement in TC increases with particle concentration (\( \phi \)). In fact, small amount of well-dispersed metal or advanced material nps could contribute considerable increment of TC of nfs. Assael et al.\(^{123}\) carried out investigation using MWCNT and DWCNT–water nfs, where CTAB and Nanosperse AQ were considered as dispersants, and the maximum TC enhancement of 34% was achieved at 0.6 vol.%. Wen and Ding\(^{124}\) prepared CNT–water nf with sodium dodecylbenzene sulfonate nfs (SDBS) used as a dispersant and visualized that the enhancement of TC has been achieved ~23.7% for CNT concentration of 0.84%, at 20\(^\circ\)C and the enhancement increases to ~31% at 45\(^\circ\)C. Ding et al.\(^{81}\) prepared CNT–water nfs with 0.25 wt.% of gum arabic (GA) as dispersant. It appears that the effective TC escalates with rise in temperature and concentration. TC of different types of nps such as MWCNTs, CuO and SiO\(_2\) dispersed in water and EG was considered in the preparation of nfs\(^{125}\). The highest TC enhancement was found for an MWCNT–water nf: 11.3% at \( \phi = 1 \) vol.%. Xie et al.\(^{77}\) made nfs by dispersing CNTs into polar liquids like distilled water, EG into non polar fluid like decene with oleylamine as surfactant. An enhancement of 19.6% in TC was recorded for \( \phi = 1 \) vol.%, CNT nps in decene. Chen et al.\(^{126}\) found in his study that TC enhancement of 17.5%, 16.0%, and 12.0% was observed for CNT nfs dispersed in EG, Glycerol, and DW, respectively at \( \phi = 1 \) vol.%. Further, Liu et al.\(^{127}\) prepared EG based CNT nfs and showed a TC enhancement of 12% at \( \phi = 1 \) vol.% and synthetic engine oil based CNT nfs showed a 30% TC enhancement at \( \phi = 2 \) vol.%. The TC of polyethylene and polypropylene particles dispersed in a mixture of silicon oil and kerosene was studied by Shin and Lee\(^{128}\). They have observed that the TC enhancement of 13% at \( \phi = 10 \) vol.%. Similar study was performed by Choi et al.\(^{129}\) using a CNT in oil mixture.

Most of the experimental studies on nfs deal with the effect of particle volume concentration on viscosity. Many researchers agreed with the consensus that the increase in the particle concentration upsurges the viscosity\(^{130}\) and belittles the stability. Therefore, researchers carried out studies on nfs by keeping the particle concentration at a limit usually below 10 wt. It is universally concluded that the enhancement in volume fraction leads to augmentation in viscosity. The most appropriate models considering the effect of particle volume fraction are enlisted in Table 5.
Table 5 Summary of viscosity models for given types of nanofluids in different researches

| Authors                  | Nanofluids  | Volume fraction range (%) | Expressions of viscosity models |
|--------------------------|-------------|---------------------------|--------------------------------|
| Brenner and Condiff      | CNT-Water   | -                         | $\frac{\mu_{nf}}{\mu_f} = (1 + n\mu)$ |
| Boboo et al.             | MWCNT-Water | 0.0-1.0                   | $\frac{\mu_{nf}}{\mu_f} = 1 + a\phi + b\phi^2$ |
| Vakili-Nezhaad et al.    | SWCNT-lubricant | 0.01-0.2               | $\frac{\mu_{nf}}{\mu_f} = 0.2T^2 - 30.3T + 1048$ |

5.2 Particle size:

The general trend of theoretical as well as experimental results implicates that the viscosity greatly depends on the particle size in the sense that viscosity of nfs increases with increasing particle diameter.

5.3 Surfactants addition:

Usually, the purpose of using additives is to achieve better stabilization of nfs and prevent them from agglomeration. For instance, water as a base fluid is polar while oil non-polar. Also, oxide nps are hydrophilic whereas CNTs are hydrophobic in nature. Thus, the addition of surfactants can be regarded as most appropriate method to upgrade dispersion of nps in the base fluids like dispersion of CNTs in water or oxide particles in the oil. Surfactants act as a bridge to attach nps to the base fluids in order to avert particles aggregation (lowers the viscosity). Surfactants are the products used in the chemical industries, detergents, pharmaceuticals, drilling muds etc. These are widely used for developing even dispersion of nps in the base fluid. Surfactants are oil soluble as well as water soluble. Therefore, the selection of surfactant depends on the nature of the base fluid. Surfactants can be negatively charged (anionic), positively charged (cationic), neutral (non-ionic) or both negatively and positively charged (amphoteric) based on the charge on its head group. Mainly, the nanoparticles’ surface charge and the base fluid considered determine the surfactant to be selected. This is because the use of surfactants may be unfavorable for the applications at elevated temperatures.

Most of the research outcomes reveal that an optimum concentration of additives will upgrade the TC of nfs. Additive develops an insulation layer around nps and could help them to be dispersed in the base fluid however performances might be deteriorated at high temperature. Assael et al. developed nfs by dispersing CMWNT and CDWNT in water, where CTAB and Nano-sperse AQ employed as surfactants. The maximum TC enhancement obtained was 34% for a 0.6 vol.% CMWNT suspension in water with CTAB. The summary of previous studies on CNT nfs influenced by particles volume concentration, particle size and surfactant addition are highlighted in Table 6.
| References                  | Nanofluid        | Particle size          | Surfactant               | Concentration            | Sample preparation and Measurement method | Findings                                                                                                                                                                                                 |
|-----------------------------|------------------|------------------------|--------------------------|--------------------------|--------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Estellé et al.\(^{136}\)   | MWCNT/DI water   | D 9.2-11.4 nm          | SDBS Lignin              | 1 wt.% nanotube 2 wt% surfactant | Two step KD2 pro                         | - Very low volume concentration of nanoparticles is able to enhance TC  
- TC enhancement is weakly affected by CNT aspect ratio and surfactant type                                                                                                                                       |
| Sadri et al.\(^{78}\)      | MWCNT/DW         | D 20-30 nm L 10-30 μm  | SDS SDBS GA              | 0.25 wt.% 0.5 wt.%        | Two step TC-KD2 Pro Viscosity-rotational Rheometer | - TC increased 22.31%  
- MWCNT nanofluid containing GA exhibits higher TC than SDS and SDBS.                                                                                                                                                                                               |
| Wusiman et al.\(^{137}\)   | MWCNT/DW         | D 5-20 nm L ~5 μm      | SDBS SDS                 | 0.5 wt.% CNT with 0.25 wt.% SDBS (pH ≈ 9) | Two step THWM                           | - MWCNT nanofluid containing SDBS performs better TC than SDS  
- TC increased 2.8%                                                                                                                                                                                                                                               |
| Wusiman et al.\(^{138}\)   | MWCNT/DW + EG    | D 20-30 nm L 10-30 μm  | Chitosan dispersant      | 0.1 wt.% 0.2 wt% 0.3 wt.% | Two step KD2 Pro Viscosity meter for viscosity and DSC for specific heat | - TC ratio increased 35.1-40.2% compared to EG/DW and viscosity ratio increases by 3.8-5.1%  
- TC increased 35.4-45.5%  
- TC increased 40.4-49.6%  
- Viscosity ratio increased 4.8-6.4%  
- Specific heat increased with temperature but decreased with increasing concentrations                                                                                                                                 |
| Kumaresan et al.\(^{139}\) | MWCNT/DI water   | D 30-50 nm L 10-20     | SDBS (0.1 vol%)          | 0.15 vol% 0.3 vol% 0.45 vol% | TC-KD2 Pro Bohlin CVO                      | - Heat transfer coefficient enhanced by 92% for 0.15 vol% MWCNT                                                                                                                                          |
| Author(s)                        | Base Material          | Diameter/Length | DOC Concentration | Rheometer Type          | TC Increase (Temp) |
|---------------------------------|------------------------|-----------------|-------------------|-------------------------|--------------------|
| Haris et al.                    | SWCNT/ DW              | 0.8-1.6 nm      | 0.3 vol%          | DSC (TA Q200)           | 287.5% at 60°C     |
|                                 |                        | 0.1-0.6 μm      |                   |                         |                    |
|                                 | EG (30 vol%)           | μm              |                   | Rheometer               |                    |
|                                 |                        |                 |                   |                         | Heat transfer coefficient enhanced by 150% for 0.45 vol % MWCNT |
|                                 |                        |                 |                   |                         |                    |
| Haris et al.                    | SWCNT/EG               | DOC             | 0.2 vol.%         | THWM                    | -TC increased 14.8% |
|                                 |                        |                 |                   |                         |                    |
| Wavekar et al.                  | MWCNT/ EG              | D 20 nm         | 0.35 wt% SDS      | Two step THWM           | -TC increased 21%  |
|                                 |                        | L 35 μm         |                   |                         | MWCNT/GA 0.05 vol% |
|                                 |                        |                 |                   |                         | -TC increased 37.4% at 25 °C  |
|                                 |                        |                 |                   |                         | -TC increased 287.5% at 60°C  |
| Kumaresan and Velraj            | MWCNT/ DI water        | D 30-50 nm      | 0.15 vol% SDBS    | TC -KD2 Pro Bohlin CVO  | -TC increased by    |
|                                 | (70 vol%) / EG(30vol%) | L 10-20 μm      | 0.3 vol%          | Rheometer Specific heat-| maximum 19.73% at  |
|                                 |                        |                 | 0.45 vol%         | DSC(TA instrument, Q200)| 0.45 vol%          |
|                                 |                        |                 |                   |                         | -The enhancement in specific heat is maximum for lower concentration |
|                                 |                        |                 |                   |                         | -Viscosity increases with increasing vol% but decreases when temperature increases |
| Aravind et al.                  | MWCNT/ DW/EG           | Function-       | 0.03 vol%         | Two step Lambda         | -TC of water and EG |
|                                 |                        | alized CNT      |                   | Instruments             | increased up to 33% |
|                                 |                        |                 |                   |                         | and 40% respectively |
| Kim et al.                      | Plasma coated MWCNT/   |                 | 0.01 vol%         | Two step THWM           | -TC increased 255%  |
|                                 | DW                    |                 |                   |                         |                    |
| Garg et al.                     | MWCNT/ GA              |                 | 1.0 wt%           |                         | -TC increased 20%   |
|                                 |                        |                 |                   |                         | at 30 °C           |
| Chen and Xie                    | MWCNT/ SO              | HMDS/functional- | 1.0 vol%          | Two step TSHWM          | -TC increased 19%   |
|                                 |                        | ization         |                   |                         |                    |
| Authors          | Type    | Treatment | Concentration | Method | Temperature Increase |
|------------------|---------|-----------|---------------|--------|----------------------|
| Jiang et al.     | CNT/R13 | None      | 1.0 vol%      | One step thermal constant analyzer | -TC increased 10.4% |
| Nanda et al.     | SWCNT/EG/PAO | GA      | 3.0 wt%       | Transient planar source technique | -TC increased for EG 35% and for PAO 12% |
| Glory et al.     | MWCNT/W | GA        | 3.0 wt%       | Steady state | -TC increased 64%    |
| Chen et al.      | MWCNT/EG | Surface treatment | 1.0 vol.% | Two step THWM | -TC increased 17.5%  |
| Amrollahi et al. | SWCNT/EG | None     | 2.5 vol%      | Two step steady method | -TC increased 20%    |
| Hwang et al.     | MWCNT   | D 10-30 nm L 10-50 μm | SDS | 1.0 vol% | -TC increased 7.0% MWCNT/Oil 0.5 vol% -TC increased 8.7% |
| Ding et al.      | MWCNT/GA | D 20-60 nm L few ten μm | 1.0 wt% | | -TC increased 79% (30°C) |
| Hwang et al.     | MWCNT/W | DS S      | 1.0 vol.%     | Two step THWM | -TC increased 11.3%  |
| Assael et al.    | MWCNT/W | CTAB Triton X-100 | 0.6 vol% | Two step THWM | -TC increased 34% -TC increased 13% |
| Hwang et al.     | MWCNT/W | SDS       | 1.0 vol%      | THWM | -TC increased 7%     |
| Assael et al.    | MWCNT/W | CTAB      | 0.6 vol%      | THWM | -TC increased 34%    |
| Liu et al.       | MWCNT/EG | D 20-50 nm | 1.0 vol% 2.0 vol% | Modified THWM | -TC increased 12.4% -TC increased 30% |
| Assael et al.    | MWCNT   | D 100 nm L 50 μm | SDS | 0.6 vol% | THWM | -TC increased 38%    |
5.4 Interfacial Nano-layer:

Nanolayer is the solid-like structure formed in between the surface of base fluid molecules and nps\textsuperscript{155}. The fact that interfacial layer in nfs is considered as a nano scaled shell surrounding the particles. It comprises of liquid molecules but behaving as solids. Because the interfacial layer is located at the liquid-solid interface, it acts as an intermediate physical state with complex interface electrostatic effects and hence acts as an important thermal bridge between the nps, and base fluid. The thickness of this liquid layer is of the order of nanometer. This nanolayer is to play an important role in heat transport from solid to the adjacent liquid. Although many existing TC models greatly underestimate the TC of nfs when compared with the existing experimental results, an effective, well-grounded and prevailing method to enlarge the theoretically determined value of TC models is to consider the effect of interfacial nanolayer. Leong \textit{et al.}\textsuperscript{156} implemented the effect of the interfacial layer on the TC of a spherical particle based nf and established a TC model. An analytical solution of a partial differential equation in spherical coordinates built for the thermal conduction process of a single spherical particle with an interfacial layer in a bulk liquid resulted into the development of this model. Jiang \textit{et al.}\textsuperscript{122} carried out their study on the heat conduction process along the radial direction of a CNT with an interfacial layer and proposed a model on the TC of CNT based nfs. In effect, the method of considering the interfacial nanolayer definitely augments the theoretical determined value of conventional models. This is because it enhances the volume fraction of particles especially at low particle size. However, the pitfalls of the models involving the effect of the interfacial layer is that the exact thickness and TC of the interfacial layer are set hypothetically because at present it cannot be obtained by experimental or theoretical methods. Therefore, the measurements on the thickness and TC of nanolayer are very important for the model development and usefulness.

5.5 Particle Temperature

According to researchers’ view temperature and TC are closely intimated i.e. when temperature rises, TC of nf gets augmented. Temperature plays a significant role in augmentation of TC in nfs, as the base fluid and nanoparticle thermal conductivities are a strong function of temperature. Many researchers studied on the effect of temperature on the viscosity of nanofluids along with the effects of other factors. Duangthongsuk and Wongwises\textsuperscript{157} studied titanium oxide-water nanofluid in a temperature range of 15° C to 50° C and a volume of 0.2–3% and found that a decrease in viscosity causes an increase in temperature. The influence of temperature on enhancement of TC of CNT nfs was studied by Ding \textit{et al.}\textsuperscript{151}. When temperature grows from 20° C to 30° C, the enhancement of TC augmented from 10% to 79% for 0.49% nanofluid. Ghozatloo \textit{et al.}\textsuperscript{158} observed that the TC of water based surface modified CNT increases with increase in temperature.

5.6 Particle loading:

Halelfadl \textit{et al.}\textsuperscript{86} found that the CNT nanofluids exhibit Newtonian behavior at lower particle loading and a shear thinning behavior at higher loading.

5.7 Nanoclustering

Because of Van der Waals forces, some nano-clusters are developed. As a result, a passageway with lower thermal resistance is established for the heat transfer\textsuperscript{159}. The nanoclustering phenomenon offers a negative effect on nanofluids from two aspects. By creating large masses, this phenomenon can result instability
of the suspension and also reduces the heat transfer by creating areas with no nps in the liquid and enhancing the thermal resistance. Clustering leads to an augmentation in the local volume fraction which in turn yield greater the viscosity of nfs.  

5.8 Ultrasonication

Due to inter-particle adhesion forces, nanoparticles get agglomeration and their settlement takes place under the influence of the gravity forces. The presence of np aggregates accounts for the dispersion stability decaying with time. For enhancement of the stability time of TC, ultrasonication has been widely used, and has been considered as an inevitable method in the development of nfs. This is because ultrasonic vibration is a possible way to break up cluster formation of nanoparticles and help to scatter the nanoparticles into base fluids. Ultrasonication process is categorized as direct sonication-as the immersion of ultrasonic probe or horn into the mixture, and indirect sonication-where the sample inside a container that submerged into a bath having liquid (mostly water) over which ultrasonic wave is transmitted.

Amrollahi et al.\textsuperscript{161} used the ultrasonic disrupter and observed that the size (1-4 nm) of agglomerated CNT particles and number of primary particles in a particle cluster was significantly reduced. The TC augments with augmented ultrasonication time (0-20 h) is the result of their study. The TC of MWCNT nanofluids (10-30 nm) grow nonlinearly with an increment in sonication (0-23 h) specific energy input. TC augments with sonication time/energy because the effect on breaking agglomerates was more significant than the effects related to reduction in the MWCNT lengths (Ruan and Jacobi\textsuperscript{162}). Ultrasonication baths or probes are commonly used to physically disperse nanoparticle clusters. Sound energy at an ultrasonication level of 20 kHz and above is applied for a predetermined period of time to disperse nanoparticles into a base fluid and to break clusters of nanoparticles\textsuperscript{92}. Sezer and Koc et al.\textsuperscript{163} studied the effect of ultrasonication time on viscosity and HT performance of MWCNT nanofluid.

5.9 Effect of Particle Type

In fact, there are some advanced structural material nps such as graphene, CNTs, etc. accounts for extremely high enhancement on the TC of the nfs. Hwang et al.\textsuperscript{125} used the np such as MWCNTs, CuO and SiO\textsubscript{2} as dispersants in water and EG to prepare nfs and concluded that the highest TC enhancement was found for an MWCNT–water nf compared to any other nps. That is why MWCNTs possess the highest TC of ~ 3000 $Wm^{-1}K^{-1}$ compared to other nps.

5.10 Effect of Base Type Fluid :

Nevertheless, TC of the base fluid affects the HT enhancement of nfs the Brownian motion is affected by the viscosity of the base fluid which in turn affects the TC\textsuperscript{164}. Based on the published experimental results, a conclusion was drawn that a larger disparity between the base fluids and nps could accomplish a higher enhancement. TC ratio was highest for EG, followed by water, engine oil, and vacuum pump oil. Liu et al.\textsuperscript{165} investigated by dispersing MWCNT in EG and synthetic engine oil. An enhancement in TC of 30% was found for CNT–EO at 2 vol.%, and for CNT–EG nfs the TC enhancement was 12.4% at 1 vol.%. Xie et al.\textsuperscript{77} used MWCNT nps as dispersants in three different base fluids such as: distilled water, EG, and decene to prepare nfs. They observed that the TC enhancement grows with the increment in nanotube loading, but was decayed with increase the base fluid.
5.11 Effect of Aspect Ratio:

Survey on previous researches confirmed that an increase in TC enhancement was due to increase in particle aspect ratio. For the particle loading of 1 vol.%, the CNT nfs with an aspect ratio of 666.7 showed a \( k/k_f \) of 2.04, whereas CNT with an aspect ratio of 18.8 showed a \( k/k_f \) of 1.43.

6. Challenges and opportunities:

Nevertheless, the characteristics and application of nfs have been investigated tremendously in wide range for the last couple of decades the research on nf is still facing a lot of challenges and opportunities. The investigations performed on TC of nfs confirmed that the effect of Brownian motion of nps and the formation of clusters in fluids are two key mechanisms which lead to the augmentation of TC, but studies focused on detailed analysis of mechanisms are not available in the literature. The researches on time-dependent property, for instance TC of nfs find deficiency. The time-dependent properties of nfs are unpredictable and to be focused.

Flow characteristics like enhancing rate of heat transportation in the thermal systems associated with complex porous matrix have been found at greater scale in filtration processes, combustion systems, geothermal energy extraction systems, oil and gas production, hazardous waste isolation process, and sustainable urban drainage system etc. Carbon nanotubes (CNTs) are ubiquitous due to its exceptional tremendously high thermal and electrical conductivities, strength, stiffness and toughness characteristics. The utilization of both porous media and nfs with CNTs as nps can augment the thermal efficiency of typical physical systems significantly. Darcy’s law is not enough for the porous space having large pore radius. The implementation of Darcy-Forchheimer model to handle the thermal systems with complex porous matrix and accomplish to control the HT at the boundary surfaces is a challenge of the future study.

The effects of surfactant on TC of nfs are not clear. Many researches confirm that although suitable surfactant can improve the dispersion, it causes growth in viscosity and drop in TC. However, other studies convey that some surfactant can improve dispersion and enhance TC, but not increase the viscosity greatly and even produce drag reduction. The use and evaluate the benefit of surfactant is another challenge in the future study. To test the effect of multi-wall carbon nanotubes as high TC additives and its usage in medium-temperature latent heat energy storage applications is a great challenge in the future study.

New models and methods of preparation for the remarkable augmentation of TC of nfs may be introduced. More influencing physical parameters and mechanisms (with detailed analysis) that uplift the TC of nfs may be studied. Numerous opportunities are there that can be predictable in the future studies of nanofluids. The enhancement in TC of some advanced and precious materials such as Graphene, diamond, isopropanol \( \text{Al}_{2}O_{3} \), CNT, Au, Ag is promising one. In addition, the clustering of nps is very important factor for both the enhancement in TC and sedimentation. However, the investigations on it are rare. The control of the clustering of nps to accomplish a high TC with less sedimentation is a great challenge ahead. A shift from developing traditional materials such as metals, ceramics, polymers and composites to a more revolutionary trend of developing nanostructures which are functionalized, self-assisting and occasionally even self-healing materials is an eye-catching challenge for the future study.

Above challenges and opportunities are of great significance for further studies on the determination of thermophysical aspects of nanofluids.

Conclusion

CNTs have been envisioned as important materials capable of dominating the 21st-century revolution in nanotechnology. The real value of CNTs vests in their range and breadth of properties, namely, their electrical,
thermal, magnetic and optical properties that impart additional benefits enabling development of multifunctional, structural materials. A comprehensive review on the experimental and theoretical studies on the thermophysical aspects such as density, specific heat, viscosity and TC of nfs has been carried out. The present study presents many appropriate models involving adequate pertinent physical parameters, suitable HT mechanisms for the enhancement of TC of nfs. The major remarkable outcomes of the present study are as follows:

- Various established theoretical models namely Maxwell, Hamilton and Crosser, Xue, Murshed, Jiang, Timofeeva and Buongiorno models enhance thermal conductivity of nanofluids.
- Several factors such as solid volume fraction, temperature, particle size, particle shape and different base fluids influence the TC of nfs. Enhancement in particle concentration and temperature augments the TC of nfs appreciably. Smaller size of the particle accounts for higher augmentation of nfs of nf. The augmentation of TC depends strongly on the shape of the nps in the sense that cylindrical nps accounts for higher TC enhancement than spherical nps. Effective TC ratio belittles due to augmentation in the TC of base fluid.
- Viscosity of CNT nfs upsurge with the rise of particle content and fall in temperature.
- Particle loading uplifts the viscosity and TC of nfs.
- Most experimental results ensure that a Newtonian behavior is the result at lower concentrations of below 4%.
- Well known heat transfer mechanisms such as Brownian motion, thermophoretic motion, clustering and layering enhance the TC of nfs. Brownian motion and clustering are two important mechanisms contributing outstanding augmentation of heat transportation of nfs.
- The material type has significant influence on the TC of nfs. The rationale behind this is that the TC of Graphene, CNTs, Au, Ag etc. nfs is greater than that of \( \text{TiO}_2 \), \( \text{SiC} \), \( \text{SiO}_2 \) etc. nfs.

Abbreviation

CNT: Carbon nanotube
SWCNT: Single walled Carbon nanotube
MWCNT: Multi walled Carbon nanotube
DWCNT: Double walled Carbon nanotube
nps: Nanoparticles
nfs: Nanofluids
TC: Thermal conductivity
HT: Heat transfer
SSA: Specific surface area
SDS: Sodium dodecyl sulfate
SDBS: Sodium dodecyl benzene sulfonate
CTAB: Cetyltrimethyl ammonium bromide
HMDS: Hexamethyldisilo xane
DOC: Sodium deoxycholate
PVP: Poly-vinyl pyrrolidone
GA: Gum Arabic
DASC: Direct absorption solar collector
DW: Distilled water
DIW: De-Ionzied water
EG: Ethylene glycol
Scope of Future Research:

Some suggestions for future works may be incorporated as follows:
- Introducing Darcy-Forchheimer model to exhibit the inertia effects for the fluid flow with high velocities.
- Microrotation mechanism may be considered into the CNT flow pattern.
- Entropy optimization due to heat transfer on flow of CNT nanofluids may be taken into account.

Applications:

Flow and heat transfer of CNT nanofluids have widespread applications in micro and nano-electronics, flat panel displays, conductive plastics, gas storage, technical textiles, ultra-capacitors, sensors, biosensor and several others.

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