

## Synthesis and investigation of thermal conductivity carbon nanotubes: MWCNT and SWCNT

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**ABSTRACT:** In this study, Bio-based carbon nanotubes (CNTs) have received considerable research attention due to their comparative advantages of high level stability, simplistic use, low toxicity and overall environmental friendliness. New potentials for improvement in heat transfer applications are presented due to their high aspect ratio, high thermal conductivity and special surface area. Phonons have been identified as being responsible for thermal conductivities in carbon nanotubes. Therefore, understanding the mechanism of heat conduction in CNTs involves investigating the difference between the varieties of phonon modes and knowing the kinds of phonon modes that play the dominant role. In this review, a reference to a different number of studies is made and in addition, the role of phonon relaxation rate mainly controlled by boundary scattering and three-phonon Umklapp scattering process was investigated. Results show that the phonon modes are sensitive to a number of nanotube conditions such as: diameter, length, temperature, defects and axial strain. At a low temperature (<100K) the thermal conductivity increases with increasing temperature. A small nanotube size causes phonon quantization which is evident in the thermal conductivity at low temperatures.

**Keywords:** *Carbon nanotubes; Low temperature; Phonons; Thermal conductivity; Umklapp process*

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### INTRODUCTION

Since their discovery in 1991, research on carbon nanotube (CNTs) has emerged, branching open new discoveries and opportunities. CNTs have wonderful heat and electrical transfer properties which makes them a sort of wonder material. The diversity in property which is an advantage stems from their abilities to be rolled up in different tube axis based on different helicities (Das, *et al.*, 2007) and this is determined by a vector, called a chiral vector which discriminates CNTs into "zigzag",

"armchair", and "chiral" forms. Carbon nanotubes are one-dimensional cylinders and can be single or multiple layers of carbon. Nanotubes with a single layer are called single wall carbon nanotubes (SWCNTs) while carbon nanotubes with more than one wall are called multi-wall carbon nanotubes (MWCNTs). The diameters of the tubes are in the range of a few nanometers (0.4-1.4 nm) and a length in micrometers, which confers high aspect ratios. MWCNTs are easier to synthesize when compared to SWCNT because they can be

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grown from most hydrocarbons at a low temperature (600-900°C). SWCNTs are usually synthesized by incorporating transition metals in catalytic amounts in the arc-discharge process while being able to grow from selected hydrocarbons (Gheisari, *et al.*, 2015). Earlier studies determined that CNT immersed in suitable base fluids had the ability to reduce erosion and clogging which is seen in micro particles and this has led to significant energy savings and high efficiency in micro-channels (Choi and Eastern, *et al.*, 2005). The knowledge of the thermal conductivity of CNTs is very useful in the design of microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) used for efficient thermal transport system in electrical, mechanical and chemical applications, solar energy systems and central air conditioning systems. It is also necessary in the development of molecular theories in nanofluids and nanofluid mixtures. Low thermal conductivity is a primary limitation in developing energy-efficient heat transfer fluids required for ultrahigh performance cooling .

Nanofluids however, are seen to have high thermal conductivities which depends not only on forces acting on nanoparticles but also on particle motion and interaction with turbulent eddies which leads to an astonishing reduction in heat exchanger pumping power. After reviewing previous works, we find that the reported thermal conductivities of CNT are as high as 3000W/mK (Choi, *et al.*, 1998). For bio-based CNT on the other hand, there is less literature available. Recently, the thermal conductivity of bio-based phase change (PCM) was enhanced by adding carbon nanotubes and the thermal conductivity reported is 0.557W/mK (Jean, *et al.*, 2013). In comparison to tested carbon black, studies by (Qi, *et al.*, 2007) revealed a 36% in the thermal conductivity of carbonized ball milled lignin after synthesis by ball-milling. This review presents the various methods of synthesis of carbon nanoparticles and equally important, an investigation of the thermal conductivity measurements of MWCNT and SWCNT. The effects of temperature, length, substrate and diameter of the nanotubes have been analyzed. The current trend towards miniaturization and the global need for a renewable and sustainable heat transfer source has motivated this study.

## SYNTHESIS OF CARBON NANOPARTICLES

The tube diameter (d) and the helical angle  $\theta$  are the two factors that describe the structure of a nanotube, not to forget the helical vector  $C = na_1 + ma_2$  (where  $a_1$  and  $a_2$  are the graphene sheets). Tubes are characterized by (x,y) notation depending on how they are rolled. The diameter and helical angle of nanotubes can be found from x and y and given in (Eq. 1) and (Eq. 2).

$$d = \frac{c}{\pi} = \frac{\sqrt{3r_{c-c}}(y^2 + xy + x^2)^{1/2}}{\pi} \quad (1)$$

$$\theta = \tan^{-1} \frac{\sqrt{3m}}{(y + 2x)} \quad (2)$$

$r_{c-c}$ : The c-c distance of the graphene layer (1.421 )

### Length of the chiral vector

From a broad view, there exist three methods of synthesizing carbon nanotubes (Qi, *et al.*, 2007):

- Formation of single-walled nanotubes (SWNT) by the incorporation of transition metals in catalytic amounts in the arc-discharge process;
- Laser evaporation which results in the formation of rope-like structures; and
- Chemical vapour deposition.

Bio-based carbon nanoparticles are a promising substitute for the metal based nanoparticles. Past studies on CNTs have shown increase in thermal conductivity, latent heat, thermal resistance, environmental friendliness, renewability and overall thermal efficiency. The precursor used during synthesis is very important in controlling the morphology and yield of carbon nanoparticles. Precursors such as graphite powders, petroleum pitch, carbon rich polymers, and other types of hydrocarbons have been successfully used in synthesizing CNT and research is still ongoing in this area. However due to toxicity and environmental hazards that can be caused, it is important to produce nanomaterials which are free from amorphous carbon. They should be obtained from green sources

that would pose no harm to humans and the environment. (Arai, *et al.*, 2011) reviewed greener routes used for nanoparticle production. Greener routes sourced from plant extracts and natural products used in past research were studied. These natural products, some of which were used as reductants and capping agents during synthesis have proven to assist with problems relating to environmental contamination, while using non-toxic solvents like water. Plant parts such as the leaf, roots, fruits, seeds and stem are being used for metal nanoparticle synthesis. This is identified to be due to the presence of polyphenols because they are stable in acidic solutions and they also modulate the oxidative defense system in cells. The bio-molecules present in plant are reported to reduce metal ions or act as capping agents to nanoparticles in a single-step green synthesis methods developed by (Choi, *et al.*, 1998). The authors emphasized their advantages of being rapid, readily conducted at room temperature and easily scaled up. Micro-organisms have been used to produce nanoparticles but the rate at which synthesis occurred was found to be slow and only limited number of sizes and shapes are amenable compared to that of plant-based. The polyphenols present in tea extracts can act as both chelating and reducing agents which prevents agglomeration in nanoparticle formation and consequently leads to an increase in stability and longevity.

(Gheisari, *et al.*, 2015), synthesized carbon nanoparticles from glucose and alkali or acid additives. However the former carried out their experiments under ultra-sonication condition, while the latter utilized hydrothermal synthesis. From their results, the method based on ultrasonic synthesis was more efficient in terms of particle size agglomeration as the particle size obtained (5 nm) as opposed to the particle sizes from which were 70-100 nm. Ultrasound has been known to generate alternating low-pressure and high-pressure waves in solution, leading to the formation and collapse of small vacuum bubbles. (Qi, *et al.*, 2007) have also applied a simple hydrothermal method using L-ascorbic acid as a carbon source. There were no acidic additives and there was no need for any surface modification. However, the addition of ethanol improved the surface state of the carbon nanoparticle. (Prasek, *et al.*, 2011) reported the synthesis of bio-based carbon

nanoparticle using lignin as the carbon source. The freeze drying process was used in order to avoid lumps or aggregates formed from carbonization. It was observed that there was an increase in thermal stability with a corresponding increase in KOH. This was as a result of the influence of KOH on the particle size as lignin samples modified with KOH yielded ultrafine particles even though it forms agglomeration at higher concentrations of 15%. To avoid the problem of lump formation (agglomeration) which usually arises from carbonization, thermal pyrolysis method was recently used by (Prasek, *et al.*, 2011) to synthesize bio-based nanoparticles from coconut milk. The authors used the pyrolysis method because it does not involve any acid treatment or any surface passivating agent. The result however shows a large size range (20-50 nm) which could be due to non-homogeneity in the pyrolysis method adopted. Apart from the chemical methods used for synthesis, physical approaches are also being used for synthesis of nanoparticles (Prasek *et al.*, 2011). Physical methods include: ball milling and mechanical grinding. A bottom-up mechano-chemical approach using milling of inorganic precursors was also presented by (Dai *et al.*, 2002) conventionally; ball milling is a top down approach because the particles are broken down into nanometer sized particles.

#### ***Effects of synthesis parameters on CNT growth***

The parameters involved in the synthesis of CNT play an important role on the final characteristics of the CNT structures. The influence of synthesis time on CNT yield from literature increases with increasing time. This is evident from studies by (Das, *et al.*, 2007) where at 2 minutes, short and isolated SWCNT with poor quality and high defects were obtained while CNTs with lesser defects were achieved for synthesis carried out in 30 minutes. Conversely, it has been observed that CNTs obtained after much longer synthesis time were likely to possess weaker crystallinity. This report stated that increasing the reaction time of synthesis led to a constant inner diameter while the outer diameter increased (Xie, *et al.*, 2007). The effect of temperature on synthesis of CNT using nickel substrates generated results which indicate a major formation of multi-walled carbon nanotubes at lower temperature and nickel thickness. The temperature

was varied between 900°C, 800°C and 700°C and the fine tuning of the temperatures produced radical results in the CNT structure obtained. The study showed that higher temperatures promotes core-shell configuration and for decreasing temperature, the formation of CNT is enhanced. (Prasek, *et al.*, 2011) showed that when the temperature of synthesis is lower than 750°C, CNT formation was lesser; however CNT formation was higher for higher temperatures (>900°C). The best temperature for CNT growth occurred between 800°C and 900°C and the optimum growth temperature was at 850°C, while obtained an optimum growth of ~99.99% at 900°C. Apart from synthesizing from high temperatures, carbon nanotubes can also be synthesized from carbonaceous solids at low temperature (450°C). In the chemical vapour deposition method (CVD), a hydrocarbon gas which is the carbon source is used together with a metal catalyst which acts as seed for the growth of CNTs. CVD takes place at a lower temperature (500-1000°C) (Choi, *et al.*, 1995). Synthesis of CNTs is usually followed by purification, deposition and suspension in an organic solvent (Qinet, *et al.*, 2010). Using CVD method of synthesis allows more precision control of CNT orientation, lower cost and more defined product(s). Selecting a proper precursor, catalyst and suitable vapour pressure optimizes the yield of growth rate and quality of produced CNTs (Choi, *et al.*, 2005).

The choice of catalyst and substrate is important for the successive growth and desired orientation of CNTs. The use of transition metals as catalyst for CNT synthesis have been reported by (Prasek, *et al.*, 2011). The most common transition metal catalysts used are Fe, Co, and Ni due to their high solubility and carbon diffusion rate. They are desirable due to high melting points and strong adhesion qualities. Higher quality nanotubes growth is obtained when Fe is used as catalyst during synthesis compared to Co and Ni. This has been attributed to its greater carbon solubility. Increasing the Fe loading decreased the quality of the nanotubes synthesized due to extensive agglomeration of the Fe particles (Choi, *et al.*, 2005). It was concluded that lower metal loading percentage is preferable for the growth of better quality CNTs with uniform diameters. MgO and Mo have also been identified to be a suitable catalyst support for Fe as it produces nano-

tubes with better graphitization, smaller and more uniform nanoparticles. A uniform diameter CNT was synthesized using Mn12 as a catalyst precursor (Xie, *et al.*, 2007). The diameter grown is  $1.5 \pm 0.31$  nm and the result indicates that an adhesion strength exists which can determine the diameter of as-grown SW-CNT needed for controlled synthesis. (Choi and Eastman, 1995), revealed that the amount and dimension of the catalytic particles dispersed on the support was useful in controlling nanotube shape. A novel method of synthesis was reported by the authors using an improved floating catalyst approach produced by catalytically pyrolyzing benzene at 1100°C-1200°C.

Solid organo-metalloenes have been used due to their metal liberating qualities which catalysis hydrocarbon deposits efficiently. Alloy of metals also play a substantial role in catalyzing the growth CNTs and through them a better yield of CNTs are derived. As more research continues on enhancing the growth of CNTs, noble metals have been discovered to effectively synthesize CNTs. However, they are most effective when their particle sizes are very small (<5 nm). A robust and cost effective method of CNT synthesis was reported by (Choi, *et al.*, 1998), in which catalytic particles solution and carbon sources were atomized without the use of a special heating system. This method of synthesis proved more effective than thermal pyrolysis based catalytic vapour deposition (CVD) in which there is difficulty in controlling the quantity of particles entrained in carrier gas due to steep temperature gradient between furnaces. The method also proved more effective than aerosol pyrolysis. Catalytic pyrolysis involving annealing of carbonaceous solid containing cobalt has been used to synthesize MWCNT. The cobalt is used as a catalyst to decompose carbonaceous solid, form carbon gas species and eventually growth of CNTs. Cobalt precursors however, have disadvantages which consist of the availability of high pressure to achieve adequate SWCNT yield to overcome equilibrium limitations at atmospheric pressure. The use of cobalt can also lead to the deposition of carbon at high temperatures and are hazardous. This mentioned downside of cobalt and other transition metals motivated to use a systematic approach based on catalyst loading, pre-treatment and selection of the right operating conditions for the im-



provement of a monometallic catalytic system for the growth of SWCNT. High quality SWCNTs with high yield was achieved by using a 2 wt. % Fe-MgO catalyst with diameters ranging from 0.8-2.0 nm.

Understanding the growth and controlling the diameter of CNT facilitates the study of fundamental properties and the exploration of new applications (Choi, *et al.*, 2005). The key role of a catalyst in defining the nanotube diameter produced by CVD is evident from the analysis of the diameter distribution which shows a close correlation between diameters of nanocluster catalyst and nanotubes. This discovery was made when the authors (Choi *et al.*, 2005) prepared iron nanoclusters having three distinct average diameters which were used to grow carbon nanotubes with similar average diameters. Diameter-controlled synthesis of SWCNT using Mn<sub>12</sub> cluster as a catalyst precursor by means of mist flow CVD has also been reported by (Kim *et al.*, 2001). The mist flow CVD was reported to be effective for the diameter controlled growth of SWCNTs. Site selective synthesis based on CVD is able to grow CNTs at controllable locations and with desired orientations on surfaces (Dai, *et al.*, 2002). CVD are described to be effective in the preparation of hybrid materials based on CNT on different supports where surface located growth is required. The study was on the utilization and comparison of natural nontronites and synthetic haematites as interface modification nanoparticles for local growth of CNT at required support.

## THERMAL CONDUCTIVITY OF CARBON NANOTUBES

### *Thermal conductivity in a base fluid*

Thermal conductivity and heat transfer of nanofluids depends not only on the forces acting on nanoparticles, but also on particle motion and interaction with turbulent eddies (Choi, 1995). Convective heat transfer can be passively improved by altering the boundary conditions, flow geometry or by increasing the thermal conductivity of the base fluid. Decrease in diameter of nanoparticles brings about a more uniform temperature distribution. However, there is a corresponding increase in cost and complexity of nanoparticle production (Vollebregt, *et al.*, 2013). Previous

study reveals that the effective thermal conductivity of suspensions with spherical particles increases with the volume fraction of the particles and also increases with the ratio of the surface area to volume ratio of the particle. It has also been pointed that since heat transfer takes place at the surface, nanoparticle with a wide surface area should be used. Compared to millimeter and micrometer sized particles suspensions, nanofluids possess better long term stability and rheological properties which makes them have higher thermal compatibility. Carbon based nanoparticles are being used to enhance the thermal conductivity of their applications. The high conductivity, high aspect ratio of CNTs and also their special surface area is responsible in making them suitable for heat transfer purposes in nanofluids. The enhanced thermal conductivity is due to the nature of heat conduction in nanotube suspensions and an organized structure at the solid/liquid interface. Brownian motion has also been suggested to be a major phenomenon in controlling a nanofluids thermal conductivity. The study by (Jeong, *et al.*, 2013) considered the preparation of thermal enhanced bio-based phase change materials (PCM) by using vacuum impregnation method with exfoliated graphite nano-platelets. The results shows a 375% increase in thermal conductivity. There was also an increase in the latent heat and thermal resistance. The thermal conductivity of ethylene glycol and synthetic engine oil were improved by dispersing multi-walled carbon nanotubes and was measured using the transient hot wire method. The authors reported an increase in thermal conductivity with an increase in volume fraction. Thermal conductivity enhancements up to 12.4% was achieved for CNT-ethylene glycol suspensions at a volume fraction of 1 vol% when compared to CuO based nanoparticles. In addition, up to 30% enhancement in thermal conductivity was achieved for CNT-engine oil suspension with 2 vol%. These results clearly indicate that the enhanced thermal conductivity ratios increase with a corresponding increase in the volume fraction of CNTs and it is nearly non-linear.

### *Thermal conductivity of multi-walled carbon nanotubes*

The need to measure the intrinsic thermal properties and thermal conductivity of individual carbon nano-

tubes in order to get an accurate estimation prompted the study by (Kim, *et al.*, 2001, Wang, *et al.*, 2007) and (Choi, *et al.*, 1998). The studies of the thermal properties of MWCNTs by taking bulk measurements had a disadvantage of yielding an ensemble average over different tubes in a sample. This is as a result of the existence of various tube-tube junctions which can be an obstacle to thermal transport in bundle nanotubes. These tube-tube interactions are primarily caused by van der Waals forces except for special instances when local charge introduces additional electrostatic fields. The interaction between confined nanotubes in bundles can partially decrease their rotational and vibrational freedom, lead to extinguishing of phonon modes which also decrease the thermal conductivity. To achieve high thermal conductivity in long MWCNT, it was proposed that the nanotubes should touch each other over less than 2-3% of their total length. A micro-fabricated suspended device hybridized with MWCNT to probe thermal transport was developed (Aliev, *et al.*, 2010).

A mechanical approach was used to place MWCNT on the device and this approach produced a nanotube device that can be used to measure the thermal conductivity of individual MWCNT. The thermal conductivity reported is over 3000W/mK at room temperature. On the other hand (Choi, *et al.*, 1998) have used a combination of electric fields with an alternating current (ac); direct current (dc) to place a single CNT across the electrodes for thermal conductivity measurements using 3- $\omega$ .

This approach is based on selective deposition technique which has a benefit of permitting the control of single nanotube placement. The thermal conductivity was reported as 650 and 830 W/mK respectively. The technique is reported to operate on a narrow-band detection technique and is said to give better signal-to-noise ratio. In order to produce reliable data on the thermal conductivity of various sizes of nanotubes, a novel measurement technique was developed based on the four-point-probe third-harmonic (3- $\omega$ ) method with assistance of a focused ion beam (FIB) for electric field supply. As compared to the two points probe 3- $\omega$  method used by (Choi, *et al.*, 1998), the accuracy of the measurement is significantly enhanced by eliminating the contact contribution in the measurement

which was previously done by annealing the nanotube samples at 600°C. The measured value for the CNTs investigated by the authors is 300±20 W/mK. The variation in thermal conductivity is likely to depend on the type and size of carbon nanotube utilized which gives rise to different mean free paths of the energy carriers.

The 3- $\omega$  technique of measuring thermal conductivity recently used by (Choi, *et al.*, 1995) was employed to determine the thermal conductivity for a low temperature grown vertical MWCNT bundles. This is important because CNT bundles which are required to obtain a low electrical and heat resistance applications need to possess low thermal conductivity. The thermal conductivity reported was 1.7-3.5 W/mK. The disadvantage of this method is a low quality sample arising from a low growth temperature. The notable technical difficulty in fabricating devices used by the authors from literature motivated the research by (Prasek, *et al.*, 2011). The authors estimated the thermal conductivity of an individual CNT from the obtained thermal diffusivity measurement of MWCNT array based on a laser flash technique. The following correlation was used to determine the thermal conductivity:

$$\lambda = \alpha\rho C_p \quad (3)$$

Where:

$C_p$ : Specific heat

$\rho$ : Density

$\alpha$ : Thermal diffusivity of CNT

The thermal conductivity at room temperature was reported to be about 750W/mK and it increased smoothly with an increase in temperature (Aliev, *et al.*, 2010). Measuring the thermal conductivity of a film of MWNTs using pulsed photo-thermal reflectance technique was used by (Samani, *et al.*, 2012, Arai, *et al.*, 2011). This non-contact method is said to have an advantage of having no boundary scattering due to reservoir junction which has been observed in electrical junction (Aliev, *et al.*, 2010). The thermal conductivity for CNT bundle length of 10–50  $\mu\text{m}$  and diameter 40-100 nm was measured and was found to be about 15W/mK while (Snowdman, *et al.*, 2014), reported a thermal conductivity of 2586 W/mK for an

individual CNT of length 2  $\mu$ m and diameter 150 nm. The high thermal conductivity of the individual MW-CNT by (Snowman, *et al.*, 2014), has been proposed to arise from the existence of ballistic flux of long-wave acoustic phonon, which originates from all the walls having equal contribution to thermal transport. These phonons enable heat transport in MWCNT, and are therefore an essential factor of the thermal conductivity. For novel materials for which quantitative measurements cannot be carried out, simulations involving molecular dynamics are applied. The need to understand the lattice thermal transport properties of carbon nanotubes for nano-electromechanical systems (NEMS) and microelectromechanical systems (MEMS) devices prompted the study by (Choi, *et al.*, 1998, Che, *et al.*, 2000, Berber, *et al.*, 2000). The MD approach is essential to observe the theoretical predictions of the thermal conductivity of CNT and the influence of various defects. One major concern of using MD however, is the size effect of the simulation box due to periodic boundary simulations. The thermal conductivity is extracted from the Green-Kubo relationship in (Eq. 4).

$$\Lambda(\omega) = \frac{1}{2K_B T^2 V} \widehat{C}_{ij}^q(\omega) \quad (4)$$

$k_B$ : Boltzmann constant;  
 V: Volume;  
 T: Temperature of the sample; and  
 $C_{ij}^q$ : Quantum canonical correlation function

The thermal conductivity obtained was 950 W/mK along the tube axis and 5.6 W/mK in the direction perpendicular to the tube.

### Thermal conductivity in single-walled carbon nanotubes

The thermal conductivity of SWCNTs from most studies in literature have been seen to depend on several CNT parameters ranging from nanotube length, simulation method for free boundary and periodic boundary conditions temperature, axial strain, radius and chirality of the tube and interaction between the nanotube with the substrate. Several other studies also

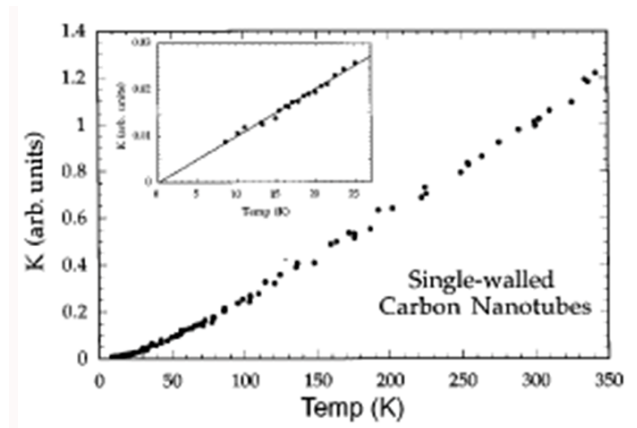


Fig. 1: Thermal conductivity of SWNT as a function of temperature.

emphasized the fact that dependence of thermal conductivity below 30K is reliant on phonons rather than electrons. Therefore, understanding the mechanism of heat conduction in SWCNTs involves investigating the difference between the varieties of phonon modes and to determine which kinds of phonon modes play the dominant role (Lukes and Zhong, 2007, Wang, *et al.*, 2007, Hone, *et al.*, 1999, Cao, *et al.*, 2004, Ren, *et al.*, 2010).

### Temperature dependent thermal conductivity of single-walled carbon nanotubes

The thermal conductivity of SWCNT measured by (Prasek, *et al.*, 2011) was focused on the low temperature range (<100K), which had a linear behavior. At this low temperature, a small diameter most probably affects the phonon properties of single-walled carbon nanotubes. A significant decrease in thermal conduc-

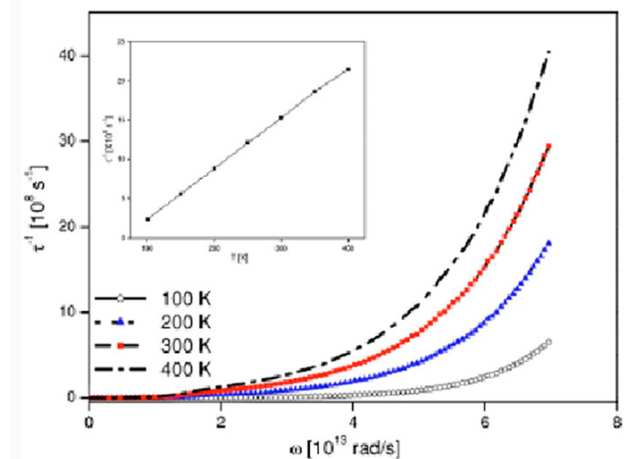


Fig. 2: Relaxation rates of Umklapp process of (6, 0) SW-CNT.

tivity was observed as the temperature decreased (Fig. 1). The results from the studies revealed an intrinsic thermal conductivity of nanotube bundles rather than sample dependent effects like joints between bundles. (Arai, *et al.*, 2011) reported a peak behavior at about 85K accompanied by a rapid decrease in the temperature dependent thermal conductivity which is caused by the Umklapp scattering freezing out. The peak behavior will shift to higher temperatures as diameter increases while neglecting dependence on tube chirality. This is because as the temperature increases, the strong Umklapp scattering becomes more effective due to the thermal population of higher-energy phonons (Fig. 2).

(Jeong, *et al.*, 2013) made an attempt to explain the observed temperature variation of thermal conductivity using a theoretical anisotropic model. The thermal conductivity based on the model is given as:

$$\kappa = \frac{B_c^2 \theta_{D,eff}^2}{h^2 (6\pi^2 n)^{2/3}} \frac{\pi h}{B_c} \theta_{D,eff}^{d-1} \frac{1}{3} \times 1 \quad (5)$$

Where  $B_c$  is the Boltzmann constant,  $h$  is the Planck's constant and  $\theta_{D,eff}$  is the efficient temperature. The anisotropic model is used because other models like Debye and the extended Debye model do not take into account the presence of the anisotropic nature of SWCNT especially at low temperatures below 30K. In addition, the anisotropic model explains well the temperature variation of specific heat in the entire temperature range 2-300K (Yang, *et al.*, 2002). The thermal conductivity involves phonon-phonon scattering and phonon-phonon interaction which produces phonon mean free path or phonon relaxation time  $\tau$ . Fig. 3 shows the thermal conductivity measurements by (Qi, *et al.*, 2010). From the Fig. 3, it can be seen that the highest thermal conductivity was observed at the highest temperature (350°K) and the lowest conductivity at the lowest temperature (8°K).

At 100K, a clear peak was observed in the study carried out by (Daiet, *et al.*, 2011), which gradually decreases with an increasing temperature till it gets to 200K and from 200K-300K, the temperature becomes constant. This behavior is said to be due to the temperature dependent property of phonon. At low

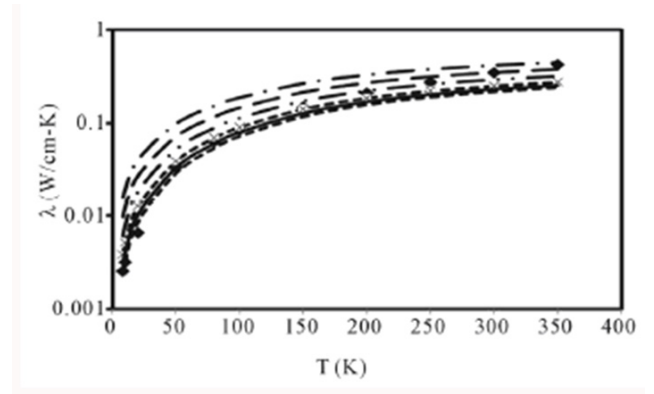


Fig. 3: Thermal conductivity of SWCNT in the temperature range 8-350 at different diameters (0.7, 0.75, 0.8, 0.9, 1, and 1.1).

temperature, the phonon relaxation time is inversely proportional to the temperature which translates into a decrease in thermal conductivity with increasing temperature. However at high temperatures, phonon-phonon scattering contributes to the phonon-decay and shows no temperature dependence (the thermal conductivity is constant).

This peaking behavior is also seen in the studies by (Choi, *et al.*, 1995). It was observed by the authors that the peak shifts to higher temperatures with increasing diameter of nanotube due to the onset of Umklapp scattering, which is said to lower the thermal conductivity at higher temperatures, and also depends of nanotube radius. The peak in this study occurred at 400K and then a drop followed at 500K. Recently a technique known as opto-thermal technique was used to determine the intrinsic thermal conductivity and interfacial thermal conductance on thin nanotube films deposited on silicon substrates as a function of temperature in the range 300-450K. The tube diameter was in the range of 1.2-1.7 nm with a mean length of 1 μm. The value of  $\kappa$  was found to decrease non-linearly by nearly 60%. This was due to the increase of multi phonon scattering at higher temperatures. The thermal conductivity decreased from 26.4 to 9.2W/mK in the temperature range of 300-450K.

The thermal conductivity in higher temperature range of 300-800K has been determined by (Choi, *et al.*, 1998) using reverse fitting based on an existing electro-thermal transport model. The results indicated a restrained decrease in the thermal conductivity of



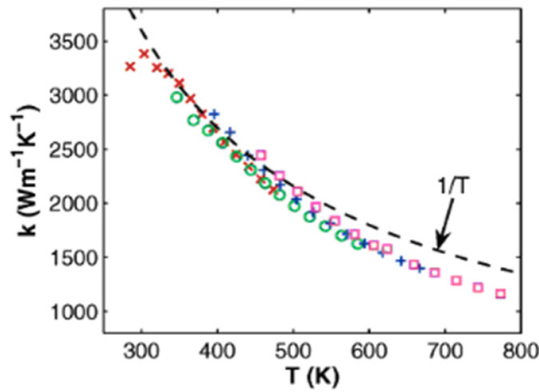


Fig. 4: Thermal conductivity of SWCNT in the temperature range 300-800K.

SWCNT near the upper end of the temperature range which is proportional to  $1/T^2$ . The presence of Umklapp phonon-phonon scattering which gives a temperature dependence of  $1/T$  is seen from the graph. In addition, at the upper end of the graph can be seen a drop in thermal conductivity at a rate steeper than  $1/T$ . The reason given to this is the effect of second order scattering process with scattering rates proportional to  $T^2$ . At the low end of the temperature range, a leveling of thermal conductivity was observed suggesting a transition towards thermal transport limited by phonon boundary scattering due to the finite sample size as seen in Fig. 4.

### THE EFFECT OF SUBSTRATES ON THE THERMAL CONDUCTIVITY OF SWCNT

The question arose on whether the thermal conductivity of SWCNTs was related to the effects of substrates (Das, *et al.*, 2006). This question was answered by carrying out a direct modelling of the heat transfer by means of MD simulations and also by studying the equilibrium multi-particle dynamics based on the Green-Kubo formalism. The study discovered that there was a finite conductivity for nanotubes that were placed on substrates unlike isolated CNT that displayed an anomalous thermal conductivity. The mean free path the heat carries is of the same order or larger than the nanotube length, and for the Knudsen number,  $Kn > 1$ . This shows that the interaction of CNT with a substrate can change dramatically the character of thermal conductivity, due to the appearance of a

narrow gap at the bottom of the frequency spectrum of acoustic phonons.

### THE ROLE OF PHONON-PHONON SCATTERING IN CARBON NANOTUBES

Heat conduction by phonons is an inclusive process that incorporates a wide range of physics and plays an essential role in applications ranging from space power generation to LED lighting (Das, *et al.*, 2006). Acoustic phonons play a dominant role in phonon state. Additional phonon mode, scattering process and rolling-up of graphene sheets have significant effects on the temperature dependence of the thermal conductivity both at low temperature and high temperature. In a perfect isolated SWCNT, the physical mechanics of the thermal transport can be analyzed using phonon relaxation rate mainly controlled by boundary scattering and three-phonon Umklapp scattering process. The Umklapp process is made up of the combining process and the splitting process which both contribute to thermal resistance. The total relaxation time can be calculated from Matthiessen's rule and expressed as:

with

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{1}{\tau_U} \tag{6}$$

$$\frac{1}{\tau_U} = \frac{1}{C_p} + \frac{1}{S_p}$$

Therefore the total relaxation rate can be rewritten as:

$$\frac{1}{\tau} = \frac{1}{\tau_B} + \frac{1}{C_p} + \frac{1}{S_p} \tag{7}$$

Where  $\tau_B$  is as the relaxation time for boundary scattering and  $\tau_U$  is as the three-phonon Umklapp scattering process. It was observed that there are very low lying folded phonon branches as the tubes diameter increases which invariably contribute to thermal conductivity (Lu and Yi, *et al.*, 2001). By using the complete dispersion relations for SWCNT, concentrated

on the three-phonon interactions to derive thermal conductivity. (Snowdman, *et al.*, 2014) has shown that the relaxation rate of Umklapp process is derived by the dispersion data and given lattice characteristics. Because the contribution of low frequency phonon is stronger than that of high frequency, the combining process has been assumed to be more important than the splitting process in the evaluation of thermal resistance. The combining process and the splitting process respectively satisfy the selection rule:

$$q + q' = q'' + G \quad (8)$$

$$q = q' + q'' + G \quad (9)$$

Where  $q$ ,  $q'$  and  $q''$  are phonon wave vectors and  $G$  is the reciprocal-lattice vector. From Eq. (9), the relaxation rate of the three-phonon Umklapp process can be given as:

$$\frac{1}{\tau} = \frac{4hy^2}{3\rho\omega^2} \sum_{j=1-N/2}^{N/2} \sum_{p=1}^6 \frac{\omega\omega'\omega''}{v_g} \delta(\delta_\omega) N(\omega', \omega'') \quad (10)$$

And the thermal conductivity calculated for the tube was found to be 474 W/mK at 300K. The effects of orderly functionalization on the thermal conductivity of SWCNT at 300K was carried out by (Snowdman, *et al.*, 2014) using a non-equilibrium molecular dynamics (NEMD) simulations. The simulation was carried out to find the character of the thermal conductivity by means of decorated hydrogen atoms. This was done by calculating the phonon power spectra of the SWCNTs from Fourier transform of the velocity autocorrelation function. From Fourier's Equation, the thermal conductivity is defined thus:

$$J = -\lambda \nabla T \quad (11)$$

Where:  $\nabla T$  is the gradient of the temperature;  $T$  and  $J$  is the resulting heat flux density. The results show that the functionalized CNTs show considerably lesser thermal conductivity than pristine CNT (CNT with attached hydrogen). It was also ascertained that there are more suppressed axial phonon modes of the randomly functionalized SWCNTs than the regular functionalized case. The hydrogen atoms attached to the

CNTs act as a defect which consequently reduces the thermal conductivity. The study of the phonon spectra indicates that the density of phonon modes is significantly changed for functionalized tubes, which leads to a reduction in the phonon scattering length and the suppression of some vibrational modes. This results in the degeneration of thermal conductivity. Below room temperature where the phonon-phonon Umklapp scattering is minimal, phonons have only a few scattering events between the thermal reservoirs and the phonon transport is nearly ballistic. This feature is not present in bulk measurements of MWCNT which is possibly due to additional extrinsic phonon scattering mechanisms such as tube-tube interactions.

## CONCLUSIONS

Carbon nanotubes undoubtedly are an intriguing next generation materials, which are being continuously improved upon for application in diverse areas including chemical, mechanical and electrical systems. Their synthesis, growth and application are an area of active research. From literature, significant milestones have been achieved in the field of CNT synthesis with a focus on CVD. Synthesis parameters have been shown to have a direct output on the shape and morphology of as-grown CNTs. The parameters include precursor, synthesis time, temperature, diameter, among others. The inconsistent heat transfer properties such as thermal conductivity of CNTs are attributed to the various conditions such as temperature, diameter, length, and the morphology of growth of the CNT. The present review validates the similarities in the thermal behavior of MWCNTs and graphite. The thermal conductivity of MWCNTs can be modelled assuming the properties and parameters of graphite, although it is possible that the interlayer coupling in MWCNTs might be slightly different than it is in graphite. It was also shown that phonon confinement effects in MWCNTs are important only at very low temperatures. At low temperatures, the thermal conductivity in SWCNT is dominated by phonon boundary scattering. A linear temperature profile exists at low temperatures less than 80K but shows peak behavior at 85K and falls off at higher temperatures.

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