Review

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Review

Why Carbon Nanotubes Improve Aqueous Nanofluid Thermal Conductivity: A Qualitative Model

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Abstract: Media thermal conductivity is important in various heat-transfer processes. Many conventional fluid conductors suffered low conductivity and environmental issues. Therefore, researchers developed efficient aqueous nanofluid conductors. Carbon nanotubes (CNTs) are widely studied to reach efficient, stable, low-cost and environmentally-friendly aqueous-nanofluids. This review provides a clear understanding of how CNTs improve thermal conductivity of aqueous nanofluids. A qualitative model is presented to explain literature mechanisms behind improvement. CNT type effects are discussed with other factors such as aspect ratio, Reynold number, dispersion quality, composition, temperature and additives. CNT functionalization is described. Relations to estimate nanofluid thermal conductivity are discussed. The model will help specialists to tailor CNT aqueous nanofluids as desired.

Keywords: carbon nanotubes (CNTs); thermal conductivity enhancement of water; heat transfer fluids; CNT aqueous nanofluids

1. Introduction

1.1. General

Thermal conductivity is a crucial property in engineering because it dictates how effectively a material can transfer heat. In many systems, we need to use highly insulating materials to slow down heat transfers. On the other hand, materials with high thermal conductivity are needed to speed up heat transfer between two systems with a temperature gradient [1]. In industry, like energy production, food production, energy storage, microelectronics, heat sinks, air-conditioning and heating, efficient fluids need to be used. Good thermal conductors help in maintaining desired temperature levels & reducing energy consumption. Water is one of the efficient heat transfer fluids with low cost and environmental friendliness. Unfortunately, water has limitations in high freezing point, relatively low heat conductivity and corrosive properties. Fortunately, these challenges can be overcome by adding special materials, while keeping the merits. Nanomaterials, including carbon nanotubes (CNT), were experienced to boost the thermal properties of water [2]. CNT aqueous nanofluids have recently shown promising potential in improving the thermal properties of water and enhancing heat transfer. Therefore, extensive research has been conducted on the incorporation of CNTs in water-based Nanofluids to enhance their thermal conductivity. The discovery of CNTs dates back to 1991 [3]. In 1993 they also reported the single-walled CNT synthesis with a diameter of 1 nm. Tremendous studies were reported on CNT materials from various aspects, including preparation methods, characterizations, physical properties, stabilities, chemical inertness, and others.

Literature showed how CNTs inclusion improves water Nanofluids thermal conductivity. The literature described how the nanofluid thermal conductivity is affected by various CNT parameters. CNT particle size expressed in the so-called aspect ratio (CNT length divided by diameter) affected thermal conductivity [4]. Functionalized CNT Nano-fluids exhibited higher thermal conductivity than non-functionalized counterparts [5]. Fluids of single walled CNTs (SWCNT) exhibited higher conductivity than multi walled CNTs (MWCNT) counterparts [6]. Adding other components, such as gibberellic acid, to the fluid may further improve its thermal conductivity [7]. Literature shows that more studies are needed to find more boosters for the thermal conductivity and better results in CNT water Nanofluids.

1.2. Scope and Relevance

This review specifically aims at providing a comprehensive understanding of how thermal properties of aqueous nanofluids are improved by suspending CNTs. A qualitative model is presented to explain the underlying mechanisms behind this enhancement. The study is based on reviewing earlier literature. These are the boundary limits of the present review.

Tremendous technical articles, related to CNT aqueous nanofluids are available in literature. Researchers described CNTs from various aspects, such as preparations, characterizations, and various applications, including CNT nanofluids [8-10]. Based on SCOPUS [11], since 2020, more than 830 review articles related to CNTs and applications were published in specialty journals. Among these, only 5 review articles related to multi-walled carbon nanotubes (MWCNTs) in water nanofluids, concerning thermal conductivity improvement, were published, as described below. No reviews, related to single-walled carbon nanotubes (SWCNTs) in aqueous nanofluid thermal conductivity improvement, can be found.

Researchers reviewed modeling the thermal conductivity of carbon nanotube (CNT) nanofluids and nanocomposites in general [12]. Kumar [13], experimentally investigated the influence of low nanoparticle concentration on specific volume, viscosity and thermal conductivity [13]. Ali and Tugolukov experimentally reported the effect of unfunctionalized CNTs on thermal conductivity of nanofluids [8]. Chemical and physical methods, to produce stable CNT-aqueous nanofluids, with various pathways to reach highly stable suspensions, were reviewed [14]. Devarajan et al. experimentally studied the thermophysical properties of carbon nanotubes (CNT) and CNT/Al_2O_3 hybrid nanofluids for heat transfer applications [15]. Several thermal conductivity measurement techniques employed to study factors affecting the thermal conductivity of nanofluids in general, were reviewed [16]. Ali and Tugolukov reviewed the augmentation of heat transfer and thermal conductivity of traditional fluids by incorporating CNTs and other mixed CNTs to produce nanofluids [17]. Ahmadi et al. [14] reviewed nanofluid thermal conductivity, and showed how temperature, form of nanoparticles, concentration and other parameters influence the thermal conductivity of the nanofluid. Increasing the temperature and concentration of nanoparticles typically increased thermal conductivity of nanofluids. Methods to improve thermal conductivity, such as using binary fluids, were also described. However, the review was not devoted to CNT aqueous nanofluids but was too general and involved various types of materials. In another review [18] thermal conductivity enhancement by material phase change, for thermal energy storage purposes was described. That was to understand thermal conduction mechanisms of phonons inside phase change materials (PCMs), together with the morphology effect, manufacturing process and thermal conductivity of composite PCMs. The reference was specifically devoted to phonon mechanistic thermal conductivity. Recent experimental results, measuring techniques, novel ideas and relevant connections, with special attention to dilute suspensions of well-dispersed spherical nanoparticles in water or ethylene glycol, without reference to CNTs, in aqueous nanofluids, were reviewed [19].

Effective thermal conductivity models of nanofluids, with comparison between experimental results and theoretical predictions were reviewed [20]. The study was general and showed considerable disparities between the available experimental results and theoretical model predictions. Heat transfer augmentation for commercially available nanofluids was demonstrated to reach 15-40% range, with a few cases culminating in orders of magnitude enhancement as reviewed earlier [21]. The study was general and did not focus on the CNT aqueous nanofluids.

Based on earlier literature, it can be noted that CNT aqueous fluids with improved thermal conductivity was not widely reviewed before, even in general terms. Specifically, SWCNT aqueous nanofluids were not reviewed. Why CNT inclusion improves aqueous nanofluid thermal conductivity was not specifically reviewed. In fact, the theoretical basis of such improvement is necessary as it helps making the best decisions in future CNT nanofluid research and design with the highest performance, but was not reviewed before. To the best of our knowledge, the present article is the first review that gives theoretical foundations, at a qualitative level, for this specific subject.

2. Methodology

As described above, this review is focused on rationalizing how the thermal conductivity of water can be improved by inclusion of CNTs. To acquire the necessary data, literature was heavily investigated. The literature search was restricted to journals cited in SCOPUS only. The search was made with a special focus on key words relevant to the subject, such as CNT, aqueous nanofluids, thermal conductivity enhancement and other related terms. Literature involved full research articles, short communications, reviews, and patents. The number of publications related to CNT in general was too big to consider in a single review article. Refinement was then made keeping in mind the title of this study. Therefore, results that are directly related to the theory of CNT effect on water thermal conductivity, were given special priority. Other results that describe special characteristics of CNTs, such as physical characteristics, types of CNTs, dimensions and others were also considered. Reports showing CNTs in various types of nanofluids, including conventional ones, were also considered. Attention was paid to experimental and theoretical results describing how CNTs affect thermal conductivity of water, concerning effects of CNT type (be SWCNT or MWCNT), dimensions, edge type, concentration. Literature showing mathematical relations to explain earlier findings was also given high priority.

3. Modeling and theory

3.1. General

A qualitative model is presented here to describe why the CNTs improve the thermal properties of aqueous nanofluids. The study will answer the following questions: How did literature explain the effect of the CNTs? What are the main theories being considered in thermal conductivity in nanofluids? What parameters are involved in thermal conductivity enhancement? Such questions will be answered here with help from earlier mathematical relations and models.

3.2. Concept of Thermal Conductivity

Heat transfer occurs in three different methods, radiation, convection, and conduction. In the subject matter here, the discussions are restricted to conduction only. Hence, the term thermal conductivity is being used. Thermal conductivity (k) is the ability of the material to transfer energy (in the form of heat) between two systems with a temperature gradient. It is measured in Watts per unit length Kelvin (W/m.K). Since the W unit is defined as Joules per second, higher thermal conductivity means faster overall heat transfer through the material, while materials with lower thermal conductivity are used in insulation. Knowledge of thermal conductivity k is important in heat transfer processes.

When two systems, with temperature gradient, come into direct interfacial contact with one another, energy (heat) transfer spontaneously occurs from the higher temperature system to the lower temperature one. Assuming no insulation (perfectly conducting) materials, the transfer process occurs faster with higher temperature gradient. Assuming liquid phases, in both systems, molecules randomly move with kinetic energies distributed according to the Maxwell-Boltzmann distribution curve. Therefore, molecules in the warmer system have higher average kinetic energy than those in the colder system. Assuming similar molar masses, the average molecular speed in the warmer system should be higher than in the colder system, since the average kinetic energy is related to molar mass and kelvin temperature, as shown in Equations (1) and (2):

$$KE = \left(\frac{1}{2}\right) Mv^2 \quad (1)$$

$$KE = \left(\frac{3}{2}\right) RT \quad (2)$$

where K.E. is kinetic energy, M is molar mass, v is average molecular speed between collisions, R is the gas constant (8.12 J/mole. K), and T is the Kelvin temperature.

Combining Equations (1) and (2) yields Equation (3) which shows how molecular speed increases with temperature:

$$v = (\frac{3RT}{M})^{1/2} \qquad (2)$$

Figure 1. summarizes how heat conductivity occurs. T_1 describes a liquid with higher temperature, and T_3 is a system with a lower temperature. T_2 is a heat carrier fluid medium. The solid lines represent the container walls, which are assumed to have no effect for simplification. Upon elastic collisions, molecules T_1 with higher kinetic energy relay parts of their energy to other molecules from T_2. The medium T_2 is then responsible for energy transfer to T_3. Heat transfer inside T_2 occurs via molecular elastic collisions, in addition to convection. The speed at which heat transfer occurs inside T_2, is called the thermal conductivity of the medium, being termed here as fluid.

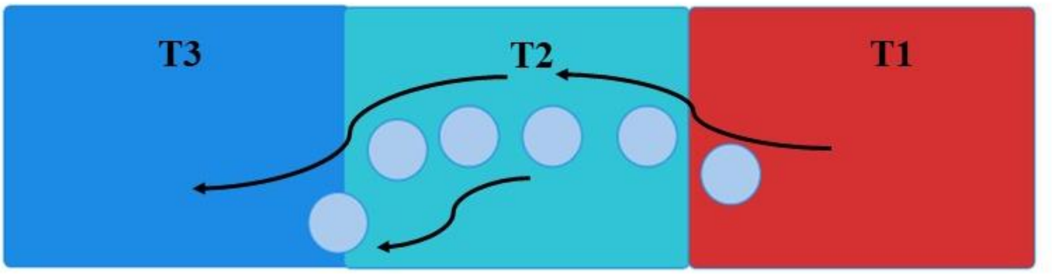

Figure 1. Schematic diagram of how heat conduction occurs from the wormer system to the colder system through a medium (thermal conductor) by molecular elastic collision.

The discussions above describe heat transfer in the most commonly used liquid media. Other phases may also be used. In gaseous media the same molecular elastic collision concept is understandable. In solid conductors, where molecular motion is restricted, things may be different. For instance, in solids molecular (atomic) vibrations should be considered. Moreover, in solid metals free electrons freely move inside energy bands and undertake thermal conduction from one point to another as seen in Figure 2.

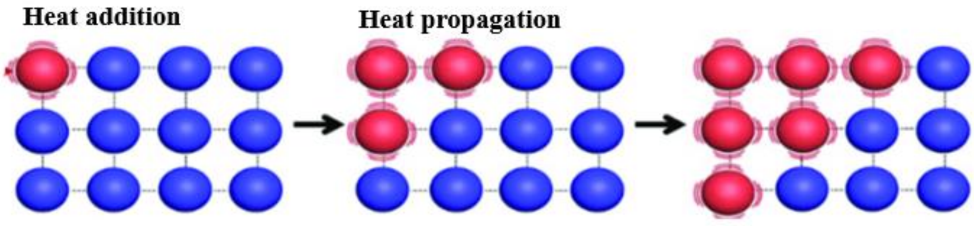

Figure 2. Heat transfer by conduction in solid metals. Drawn based on general literature.

Based on these basic physical concepts, different materials have different thermal conductivities, as they have varieties of phases, electronic structures, bond strengths, intermolecular interactions, molar masses, polarities, viscosities, melting points, boiling points, and purities. Conductivity of a given substance may also vary depending on conditions such as phase and purity. Laser flash analysis is frequently used to measure thermal conductivity. Temperature of the substance also affects its conductivity in a rather non-linear relation [22] . Table 1 shows a number of thermal conductivity values for various pristine materials. As can be seen in Table 1, CNTs have especially high thermal conductivity values. This is due to their unique structures. CNTs consist of single- or multi-layers of carbon atoms arranged in cylindrical shapes at nanometer scale width with various lengths. The carbon atoms are bonded together to form hexagonal rings that involve conjugated double (π) bonds [8-11]. Within the CNT particle, conjugated double bonds form energy bands in which single electrons may move freely, in a similar fashion to other metal conductors. In fact, such free electrons may be responsible for relatively large electrical conduction of the CNTs. However, while the free electrons may be partly involved with thermal conduction in CNTs, another major reason is also proposed. If one part of the CNT is heated its covalent bonds undergo vibrations, like other solids. Therefore, the intra-particle heat transfer may occur via two concurrent processes, free electron motion and bond vibration. This presumably explains the high intra-particle conductivity in CNTs compared to other systems, like Al, Cu, Fe and others. CNTs also have much higher thermal conductivity than pure water, since conduction in the former is intra-particle type while in water it is inter-particle type. CNTs also have higher conductivity than diamond (1000 W/m.K) presumably due to the presence of conjugated (π) bonds in the former.

Table 1. Thermal conductivity values for a number of common materials at room temperature atmospheric pressure.

Phase	Material	Thermal conductivity [W/m·K]	Ref.
Liquid	Water	0.5918-0.609	[23]
	Ethylene glycol	0.246	[24]
	Engine oil	0.145	[24]
	Water	0.51	[23]
	Castor oil	0.18	[23]
	Ethanol	0.171	[23]
	Acetic acid	0.193	[23]
	Phenol	0.19	[23]
Solid	Snow (dry)	0.050–0.250	[23]
	Aluminum	237	[23]
	Ductile steel	80	[23]
	Stainless steel 304	16.2	[25]
	Carbon steel	54	[26]
	Gold	320	[23]
	Aluminum nitride	321	[23]
	Beryllium	209–330	[23]
	Bismuth	7.97	[23]
	Boron arsenide	1300	[23]
	Copper (pure)	401	[23]
	Diamond	1000-2300	[23]
	Germanium	60.2	[23]
	Polyurethane foam	0.03	[23]
	Expanded polystyrene	0.033–0.046	[23]
	Manganese	7.810	[23]
	Ice	2.22	[25]
	Silica aerogel	0.02	[23]
	Silicon nitride	90-177	[23]
	Silver	406	[23]
	SWCNT	<6000	[27]
	MWCNT	<3000	[27]

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The type of the CNT affects its intrinsic thermal conductivity, Table 1. In some literature, pristine SWCNT have superior thermal conductivity (up to 6000 W/m.ºK) compared to MWCNTs (up to 3000 W/m.K) [28-30]. However, when composited with other materials, things may change and the MWCNTs may exhibit higher thermal conductivity than their SWCNTs [31]. The fact that SWCNTs have higher values indicates the effect of vibrations as a major factor in determining the thermal conductivity. This is because MWCNTs involve more conjugated π-bonds with more free moving electrons than in SWCNTs. Based on conjugation only, MWCNTs should have higher conductivity. Therefore, vibrations are the major factor for SWCNT higher conductivity.

3.3. Impact of CNTs on Aqueous Nanofluid Thermal Conductivity

CNT nanomaterials possess exceptional mechanical, electrical and thermal properties, making them ideal additives for various applications. Because CNTs have higher thermal conductivity values than water, the thermal conductivity of aqueous CNT suspensions is expected to be higher than pure water. CNT concentration should also affect the suspension thermal conductivity. The effects of suspending solid nanoparticles on nanofluid conductivity, in various solvents were mathematically described. Researchers tried to mathematically describe how thermal conductivity, in various nanofluid, depends on various factors, including base fluid thermal conductivity. Bruggeman [32] proposed relation (4) to analyze the interactions between particles and fluid in a homogenous suspension that best works for spherical particles. The relation is shown in Equation (4).

$$\emptyset((K_p + K_{eff})/(K_p + 2K_{eff})) + (1 + \emptyset)\left(\frac{K_p+K_{eff}}{K_p+2K_{eff}}\right) = 0 \quad (3)$$

where K_{eff} is effective thermal conductivity, K_p is particle thermal conductivity, and $\emptyset$ is the concentration.

The effective thermal conductivity depends on the particle thermal conductivity and concentration, but not on the fluid thermal conductivity itself. The relation is too simple and general for particles not for nanoparticles or nanofluids, but formulated a basis for other more successful models.

In 1962 Hamilton & Crosse [33] introduced a more accurate relation for liquid mixtures of non-spherical particles. The shape factor was first introduced, as denoted by n =3ψ . For a given particle, with a given shape, the sphericity (ψ) is defined as the ratio between the surface area of a sphere (with the same volume) to the actual area of that particle [34]. The relation is described in Equation (5) below, and involves the base fluid thermal conductivity expressed as K_b, and $\emptyset$ is the concentration or volumetric fraction. The particle shape factor is also involved. Inclusion of particle concentration further brings the approximations to the accurate values. Unfortunately, the model is not specific for nanosized particles.

$$K_{eff} = \frac{K_p+(n-1)K_b-(n-1)(K_b-K_p)\emptyset K_p}{K_p+(n-1)K_p+\emptyset(K_b-K_p)} \quad (4)$$

Yamada and Ota relation in 1980 was one of the early attempts to bring various variables together, Equation (6). The fluid effective thermal conductivity is a function of the base liquid thermal conductivity (K_f), the particle thermal conductivity (K_p), particle aspect ratio R/L, and particle concentration ($\emptyset$). The aspect ratio for a general particle was introduced for the first time, as a higher aspect ratio induces higher thermal conductivity. The concentration was also included in the correlation together with the thermal conductivity of the base fluid and the particles. Again, the relation was not specific for nanoparticles as they were not widely used at the time.

$$K_{eff} = \frac{K_f\left(1+\left(\frac{K_{fl}}{K_pR}\right)\emptyset 0.2+\left(1-\frac{K_f}{K_p}\right)\emptyset L/K_p(\emptyset)\right)^{0.2}}{1+\frac{K_fL\emptyset 0.2}{K_pR}-(1-\frac{K_f}{K_p})\emptyset} \quad (6)$$

In 1981, Maxwell [35] introduced a relation for colloidal suspensions thermal conductivity K as described in Equation (7) below, including particle thermal conductivity (K_p), fluid thermal conductivity (K_f), volume fraction of particles or concentration ($\emptyset$), where K_p>>K_f and ($\emptyset$) <<1. Maxwell predicted a linear dependence on particle concentration, Equation (8).

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$$\frac{K}{K_f} = K_p + 2K_f + \frac{2\emptyset Kf\left((K_p - K_f\right)}{Kp + 2K_f - \emptyset(K_p - K_f)} \quad (5)$$

$$\frac{K}{K_f} \sim 1 + 3\emptyset \quad (6)$$

In 2003, Yu and Cho [36] introduced a modified Maxwell relation considering the nanolayer effect in thermal conductivity and utilizing the Schwartz effective medium theory in Equation (9).

$$K_{pe} = \frac{[2(1-\gamma) + (1+\beta)(1+2\gamma)\gamma]K_p}{-(1-\gamma) + (1+\beta)^3(1+2\gamma)} \quad (7)$$

where γ is $\frac{K_{lyer}}{Kp}$, $\beta = \frac{h}{r}$ (layer thickness/radius of particle), then the final modified Yu and Choi model can be written as in Equation (10) .

$$K_{eff} = \frac{K_{pe} + 2K_{bf} + 2K_{pe} - K_{bf})(1-\beta)\text{^}3\ \emptyset K_p}{K_{pe} + 2K_{bf} - \left(K_{pe} - K_{bf}\right)(1+\beta)^3\ \emptyset} \quad (8)$$

In 2012, Maxwell introduced his model for estimating the thermal conductivity of the nanofluids for heterogenous as shown in Equation (11)

$$\frac{K_{eff}}{K_{bf}} = 2K_p + K_{bf} + \frac{\emptyset(K_p - K_{bf})}{2K_{pe} + K_{bf} - 2\emptyset(K_{pe} - bK_{bf})} \quad (9)$$

where K_{eff} is the effective nanofluid thermal conductivity, K_{bf} is medium thermal conductivity, K_p is particle thermal conductivity and particle concentration $\emptyset$.

A modified relation [36] to calculate the effective thermal conductivity of the nanofluid (K_{eff}), depending on the particle thermal conductivity K_p, medium thermal conductivity K_{bf} and particle concentration $\emptyset$, was proposed as a special case of Hamilton crosser model, Equation (12)

$$\frac{K_{eff}}{K_{bf}} = \frac{(K_p + 2K_{bf} - 2\emptyset(K_{bf} - K_p)}{(K_p + 2K_{bf}) + \emptyset(K_{bf} - K_p)} \quad (10)$$

In 2015, a different correlation considering the water thermal conductivity, particle thermal conductivity K_p, water K_w , water density ρ_w, particle concentration ø, effective thermal conductivity of the nanofluid K_{eff} and fluid temperature T_f, was proposed. The terms αp and αw denote thermal diffusivity of particle and water, respectively, as seen in Equation (13) [37].

$$K_{eff} = K_w[0.8938(1 + \left(\frac{\emptyset}{100}\right)^{1.37}\left(1 + \frac{T_f}{70}\right)^{0.2777}\left(1 - \frac{\rho_w}{150}\right)^{-0.0366}\left(1 - \frac{\alpha_p}{\alpha_w}\right)^{0.01737}] \quad (11)$$

Navaei et. al. [38] introduced a new more realistic relation that combines the Brownian and the static thermal conductivities together in one correlation. All the previous relations in Equations (4-13) can be considered as static. Equations (14-16) summarize the relations in which K_{eff} is the effective thermal conductivity, K_{static} is the static thermal conductivity, $K_{Brownian}$ is the thermal conductivity considering the Brownian motion of particles. Other factors are as defined above, like K_f is the base fluid thermal conductivity is the nanoparticle thermal conductivity, K_{eff} is the nanofluid thermal conductivity, ø is the nano particle concentration, ρ_f is the fluid density, ρ_{np} is the nanoparticle density, £ is liquid thermal resistance and C_p is the particle specific heat.

$$K_{eff} = K_{static} + K_{Brownian} \quad (12)$$

$$K_{static} = K_f\left[\left(K_{np} + 2K_{bf}\right) - 2ø\left(K_{bf} - K_{np}\right)\right]\left[\left(K_{np} + 2K_{bf}\right) + ø\left(K_{bf} + K_{np}\right)\right] \quad (13)$$

$$K_{Brownian} = 5 \times 104\beta ø\rho p C_p £\sqrt{(kT\backslash(2\rho npR_{np}))(£(T,ø))} \quad (14)$$

Jang and Choi [39] introduced a relation that considers Brownian motion of a nanoparticles in nanofluids considering the convective effect at the nanoscale as observed in Equations (17-19).

$$J = -h\delta r\ \frac{dt}{dz}\left(1 - \emptyset_{eff}\right) \quad (15)$$

$$h = \frac{K_{bf}}{d_p \boldsymbol{Re}.{d_p}^2 \overset{2}{Pr}} \quad (16)$$

$$K_{eff} = K_{bf}\left(1 - ø_{eff}\right) + BK_p ø_{eff} + C_{pco}\left(\frac{d_{bf}}{d_p}\right)K_{bf}{Red_p}^2\ ø_{eff} \quad (17)$$

where B is the Kapitza resistance per unit area, C_{pco} is a proportionality constant, and Reynolds number is defined by Equation (20) below

$$Re_{dp} = \frac{D_0\, d_p}{l_{bf}\,\mu_{bf}} \quad (18)$$

where D_0, l_{bf} and μ_{bf} are the diffusion coefficient, the liquid mean free path and the dynamic viscosity of the base fluid, respectively.

This relation focused on heat transfer between particles and base fluid, which was not directly related to the heat transfer. The relation accounts for particle size, temperature, and particle volume fraction. The Brownian effect was also considered since the high temperature-dependent features might be induced by Brownian motion.

It should be noted that the reported relations may not fully explain the observed increased thermal conductivity in fluids. The molecular-level layering of the liquid at the liquid/particle interface (nanolayer), Brownian motion of the nanoparticle, clustering, nanoparticle size, pH, temperature, and the nature of heat transport in the nanoparticles are all factors that may influence the thermal conductivity of nanofluids. None of these factors appears to be solely responsible for the increase in thermal conductivity, and all should be considered. More research is needed to develop relations showing all factors in nanofluid behaviors. Furthermore, experimental data from diverse research do not compare well for seemingly identical settings, making development not easy. More study is also needed to understand the nature of heat transmission in cases of nanoparticles. However, the Maxwell relation, which is suitable for solid-liquid suspensions comprising millimeter or micrometer-sized spherical particles at low concentrations and ambient conditions, was used to approximately analyze the thermal conductivity of nanofluids.

As stated above, the thermal conductivity of nanofluids is affected by many factors including the thermal conductivity of the suspended particles, thermal conductivity of the base liquid, concentration, heat capacity, diffusivity, particle shape, particle volume fraction, temperature, and other variables as described in above Equations. Other attempts were also made [40-42]. To include other significant elements, other relations were proposed [42, 43], and the influence of interfacial nanolayers was considered. Convective heat transfer, generated by Brownian motion, were also described [44, 45]. Other researchers [46-48] studied the effect of nanoparticle clustering. Detailed analysis of theoretical prediction for the thermal conductivity of nanofluids was reported [49].

All reported relations are only useful approximations. The thermal conductivity of CNT nanofluids is affected by many factors such as CNT concentration, length, added surfactants, temperature, and functionalization, allowing customization to suit specific applications. It is not easy to propose a totally comprehensive relation that involves all variables with accuracy. Moreover, the effect of the type of the suspended nanoparticle itself has not been quantified. For instance, in case of carbon nanotubes, the number of walls in SWCNTs and MWCNTs were not described. Therefore, there is need for more experimental and theoretical study in nanofluid thermal conductivity, especially on the CNT aqueous nanofluids.

3.4. Proposed Model and Postulates

Suspending nanoparticles into a liquid improves its thermal conductivity, to various extents depending on various parameters, as quantitatively described in the above relations. It is time to propose a simple model to specifically rationalize how adding CNTs improves the thermal conductivity of aqueous fluids. Typically, aqueous nanofluids are colloidal suspensions consisting of a base fluid (e.g., water) and nanoparticles (e.g., CNTs) with sizes ranging from 1 to 100 nm. The postulates are:

(1) A CNT is a long nano-wide tube.
(2) When suspended in water, the CNT may interact with water molecules via weak interactions to keep the tubes suspended. The interactions vary depending on type and structure of the CNT. The interactions are further improved by functionalizing the tube with other polar groups such as -COOH or -SO_3H.
(3) Due to its directional structure, the CNT tube, together with bonded water molecules, forms a cluster that moves freely inside the nanofluid through the Brownian random motion.
(4) A number of clusters may interact together to form a network of clusters that freely moves through the Brownian random motion.

(5) Heat moves through a given cluster from one end (with the higher temperature) to another end (with lower the temperature) in a directional manner. The cluster behaves as a conducting channel.
(6) The network also carries heat from the higher temperature side of fluid to the lower temperature side, through the Brownian motions. This process provides an additional path of heat transfer through convection.
(7) The cluster and network formation induce various effects on the base liquid physical properties, such as viscosity, surface tension, interface characteristics with the container walls, and others. Such variations may further affect thermal conductivity of the nanofluid.

These postulates are made based on earlier literature results, including theoretical and mathematical correlations, as described above. The model rationalizes the influence of CNT addition on aqueous nanofluid thermal conductivity through the proposed mechanisms.

3.5. Mechanisms of Thermal Conductivity Increase in Aqueous Nanofluids

3.5.1. Conductive Network Formation

Due to its 1-dimensional tube structure, CNT interact with a number of water molecules to form a cluster. The clusters form conductive networks in the fluid. In case of non-functionalized CNTs, only weak interactions occur by virtue of weak London forces. This explains the instability of non-functionalized nanofluids that precipitate with time. In case of functionalized CNTs, the functional groups may interact with water molecules through relatively strong dipole-dipole interactions. H-bonding may also occur in CNTs functionalized with carboxylic group -COOH. Such bonds are responsible for the stability of the CNT aqueous nanofluids as reported earlier [50]. The strong bonds help form stable conductive networks in forming stable 1-dimensional clusters, which are responsible for 1-dimensional thermal conduction from one end to the other. With their high intrinsic conductivity, the CNT blocks increase the overall conductivity within the frameworks, as shown in Figure 3 below. Moreover, the networks move through the nanofluid by the Brownian motion and help transfer heat from higher temperature to lower temperature regions by convection.

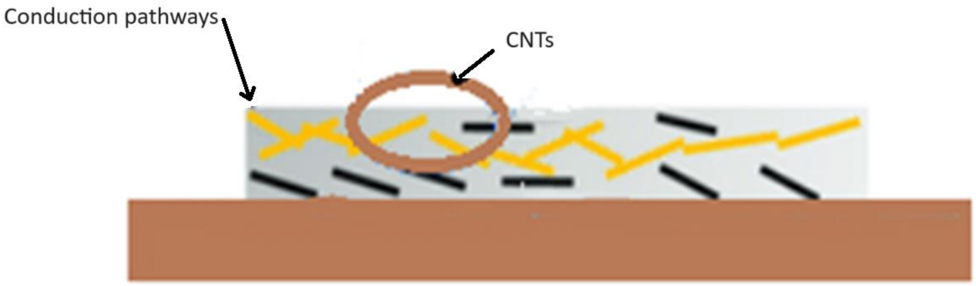

Figure 3. Schematic describing CNT conductive network formation in water.

CNTs may behave as nanoscale channels within the fluid, which serve as extra pathways for heat conduction [51]. The extent of improvement may vary based on factors such as CNT concentration K_eff, alignment and the properties of the CNT used.

3.5.2. Boundary Layer Disruption

CNT presence disrupts the boundary layer surrounding the particles, allowing for better heat transfer between the fluid and solid phases. This affects the interaction between the CNT surface and water molecules, Figure 4. This can be improved by CNT functionalization [52].

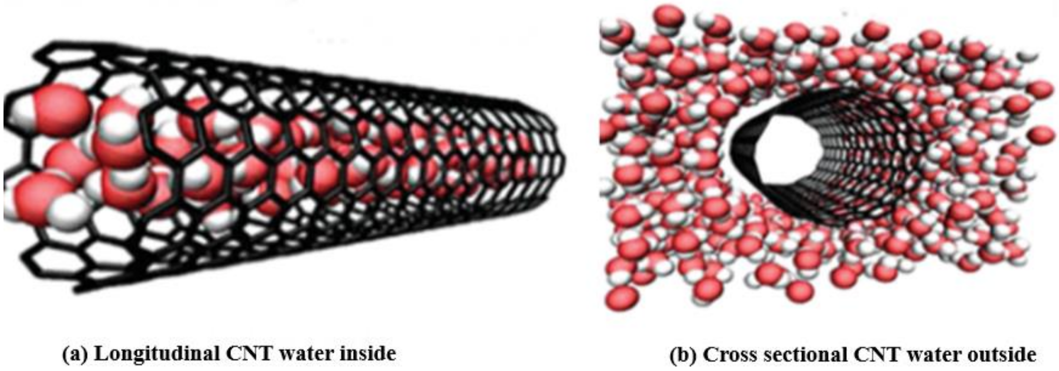

Figure 4. Schematic showing how water molecules interact with CNT armchair surfaces. (a) Longitudinal CNT water inside and (b) cross sectional water outside CNT armchair views. Reproduced with permission from ACS [52].

3.5.3. CNT Contact Resistance Reduction

Normally speaking, heat transfer across an interface between two systems encounters thermal resistance that inhibits the transfer. In CNT aqueous nanofluids, the CNTs are intimately boned to water molecules, especially in functionalized systems, to form conductive networks. This lowers the thermal resistance at the interfaces, allowing more efficient heat transfer at the CNT/water interface on one hand, and at the CNT/CNT interface on the other hand. The result is reduced thermal boundary resistance at the interface between the CNTs and the liquid. CNTs are easily recognized due to their high aspect ratio. In the base liquid, they aggregate or come into touch with one another. Aggregation is one of the major processes that explains the high thermal conductivity of nanofluids [53, 54]. Contributions of additional possible pathways to thermal conductivity increase, such as Brownian motion and the interfacial nanolayer, should be considered.

3.5.4. Lowered Phonon Scattering

In solids, heat gain is expressed in terms of phonons. A phonon is a unit of vibrational energy that arises from oscillating atoms within a crystal. Thus, the phonon is a quantized energy packet associated with the crystal vibration. Phonons can travel relatively freely in CNTs, with low phonon scattering by defects, impurities, or interfaces. This explains the conductivity within the CNT itself. Within the nanofluid, the low scattering concepts is also useful. As described in A above, the nanofluid is understood as a network of particles interconnected with tubes, such tubes furnish extra channels for heat transfer along the fluid and increase thermal conductivity [55].

The phonon scattering is minimized by the high aspect ratio associated with CNTs. As heat moves within a CNT, it keeps moving for long distances with no scattering. This is contrary to other nanoparticles, where heat flow is subject to interruptions by various interfaces.

3.5.5. Increased Contact Points

As described in A above, upon dispersion in water, the CNT particles create a network framework. The framework involves contact points so-called percolation paths. These paths facilitate heat transfer between adjacent nanotubes themselves, and between nanotubes and the surrounding water molecules[56]. The CNTs act as thermal bridges within water, facilitating the transfer of heat from one location to another. This bridging effect enhances the overall thermal conductivity [5].

3.5.6. Brownian Random Motion

CNT networks undertake continued Brownian motion inside the liquid. This is facilitated by their light weight and flexible nature. The Brownian motion encourages heat transfer through the extra pathways in addition to convection. It also helps remove insulating layer formation. While moving, the networks undergo collisions with other species, and provide extra pathways for heat conduction.

3.5.7. Thermal Diffusivity

CNTs enhance the thermal diffusivity of water, allowing for faster and more efficient heat propagation through the nanofluid. Thermal diffusivity α is related to thermal conductivity k, specific heat capacity C_P, and density ϱ through Equation (21), [56].

$$\alpha = \frac{K}{\rho Cp} \quad (19)$$

For CNT aqueous suspension, changes in thermal diffusivity affect thermal conductivity. With higher diffusivity and dispersion, the interactions with water molecules are improved leading to increased thermal conductivity.

3.5.8. Surface Tension and Viscosity

Surface tension is defined as "*the propensity of liquid surfaces to statically shrink to the minimum surface area*". It describes the ability of a liquid to keep a minimal surface area. Surface tension at liquid/air interfaces is caused by the higher intermolecular attractions in the liquid (cohesion) compared to molecule attraction with air (adhesion) [57]. There are two main active systems. The first is an inward strain on the surface molecules, the second is a tangential force parallel to the liquid surface.

The tangential force is commonly known as surface tension. Thus, the liquid surface behaves as elastic membrane. However, this parallel should not be laterally true, since the tension is a feature of the liquid-air or liquid-vapor interface. Water has a surface tension of 72.8 milli Newtons per meter (mN/m) at 20 °C, that is higher than many liquids. This is due to unusually high intermolecular attractions in water, via a web of hydrogen bonds. Surface tension is also more commonly expressed in terms of energy per unit area [58, 59], as shown in Equation (22). Typically, CNTs do not significantly affect water surface tension due to relatively weak interactions between water molecules and CNTs. However, functionalized CNTs can lower the surface tension of water, like surfactants. The carbon nanotubes thus disrupt the hydrogen bonding between water molecules [60] yielding lower surface tension.

$$\gamma = \frac{F}{L} = \frac{E}{A} \quad (20)$$

where L is the length, F is force, E is energy, A is area and γ is surface tension.

Other reports showed that the water surface tension may increase by adding CNTs, depending on concentrations, types and other additions [61]. Water viscosity (μ) is also affected by adding CNTs depending on their nature and concentration [62]. The viscosity of CNT water nanofluids depends on factors like CNT concentration, temperature, and fluid composition. Generally, viscosity increases with CNT concentration. That is due to interactions and entanglement of CNTs within the fluid, Figure 3. CNTs undergo agglomeration, which may lower the mobility and decrease thermal conductivity by convection. Moreover, viscosity increases the thickness of the thermal boundary layer which slows down heat transfer. On the other hand, the CNTs increase agglomeration instead of single particle dispersion. With higher viscosity, water molecule random motion slows down, which inhibits random mixing of various parts of the nanofluid. This allows the directional heat motion through the CNT networks (channels) to continue. The presence of CNTs may also lower the viscosity of aqueous nanofluids when dispersed properly. This reduction in viscosity promotes better flow and lowers pumping requirements. In a very dilute system, with a volume fraction $\lesssim$0.02%, interactions between the suspended particles can be ignored. In such a case one can explicitly calculate the flow field around each particle independently, and combine the results to obtain effective viscosity. For spheres, this results in Einstein's effective viscosity formula.

Higher concentrations of the CNT increase fluid viscosity. The solid particle shape also affects the viscosity of the suspension. Particle concentration and viscosity were mathematically expressed. Hussein et. al.2013 introduced Equation (23) [63] where the effective viscosity depends on the particle concentration (K_eff), particle diameter and nanofluid temperature.

$$\frac{\mu_{nf}}{\mu_f} = \left(1 + \frac{\mathrm{K\_eff}}{100}\right)^{11.3} \left(1 + \frac{T_{nf}}{70}\right)^{-0.038} \left(1 + \frac{\mathrm{K\_eff}_{dp}}{170}\right)^{-0.061} \quad (21)$$

Sidik and Mamat 2015 introduced Equation (24) [64], where the effective viscosity depends on the particle concentration

$$\mu_{nf} = \mu_{\mathrm{f}}/(1 - \mathrm{K\_eff})^{2.5} \quad (22)$$

Kumar [13] proposed Equation (25), where the effective viscosity again depends on the concentration.

$$\mu_{nf} = \mu_b(123\emptyset^2 + 7.3\emptyset + 1) \quad (23)$$

As seen, surface tension and viscosity are not directly related to fluid properties, despite being related in the context of CNTs water fluids. The relation between viscosity and surface tension is complex and depends on different experimental conditions and other factors. Examples are CNT functional groups that influence the viscosity of nanofluids, altering the surface chemistry of CNTs and affecting their interactions with the surrounding fluid, but the specific impact depends on the type, density and distribution of the functional groups. These factors should be considered to improve the dispersion of CNTs in the fluid, reducing aggregation and potentially decreasing viscosity.

The addition of CNTs may alter the surface properties and disrupt the hydrogen bonding to water, affecting surface tension. Simultaneously, the interaction of CNTs within the fluid can impact viscosity, especially if they lead to entanglement or aggregation. However thermal conductivity has a broad range and a nonlinear relationship. CNT volume and enhancement fraction cannot be satisfactorily predicted by these relationships as earlier determined [5].

3.5.9. Type of Carbon Nanotube

In their pristine solid forms, single-walled carbon nanotubes (SWCNTs) tend to have higher thermal conductivity (6000 W/m.K)compared to multi-walled carbon nanotubes (MWCNTs) (2000-3000 W/m.K) [65]. As described above, within a CNT, heat moves from the higher temperature end to the lower temperature end by either or both two mechanisms: vibrations or free π-electron motions. SWCNTs have higher conductivity due to their higher flexibility which allows more vibrations. MWCNTs have higher densities of free π-electrons, which are known to help conduct heat [66], but the particles are more rigid and have less vibrational ability. Overall, in the pristine dry state, SWCNTs have higher conductivity than MWCNTs.

Therefore, logically speaking, SWCNTs should increase nanofluid thermal conductivity more than MWCNTs. However, this needs not necessarily be true. In nanofluids, other factors are involved such as the aspect ratio, the aggregation and the heat channels described above. MWCNTs generally have higher aspect ratios than SWCNTs. As a result, MWCNs are more likely to increase nanofluid dispersion and thermal conductivity than SWCNTs. This is also due to other factors such as particle aggregation, nanolayer, ballistic (surface to air) phenomena [67].

3.5.10. CNT Concentration

The relationship between functionalized CNT concentration (up to certain limits) and thermal conductivity lies in the formation of higher numbers of conductive networks within the nanofluid. Quantitative relationships were made, allowing to optimize CNT concentrations for specific applications. Most relations described above considered the effect of nanoparticle concentration on the fluid thermal conductivity. In addition to conductive networks, the Brownian motion and percolation paths increase with higher CNT concentration [2, 68-70] It should be noticed that the addition of CNTs typically has little effect on the boiling point of water [71]. However, they affect the water freezing point by hindering the formation of ice crystals, resulting in freezing point lowering “depression”. This behavior is useful in aqueous nanofluid applications

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4. Results and Discussion

Numerous publications confirmed improvement in the thermal conductivity of water by suspending CNTs inside. The qualitative model presented above, with its assumptions and related modes of actions, are used here to rationalize earlier literature results. The improvement arises from the high thermal conductivity of the CNTs and their interaction with the water molecules. There are several factors affecting the thermal conductivity, as described above, which will be used to rationalize results using the qualitative model presented above:

4.1. CNT type

CNTs are divided into single-walled (SWCNTs) and multi-walled (MWCNTs). Double walled (DWCNTs) are also known. CNTs exhibit extraordinary properties in mechanical and electrical fields, such as stiffness, low gravitational weight, lower density, strength, elasticity, good electrical and thermal conductivity, high modules of elasticity, stability, and corrosion resistance.

The type of added CNT affects the nanofluid in different ways: suspension in water is better for multi-walled CNT than that for SWCNT. Although pristine SWCNTs have higher thermal and electrical conductivity (6000 W/m.k), in nanofluids things may vary depending on other factors like type, concentration, suspension and bonding, functionalization, as described above. CNTs suspended in water, interact with water molecules via weak interactions to keep the tubes suspended. These interactions depend on the type and structure of the CNT. The interactions are further improved by functionalizing the tube with other polar groups such as -COOH or -SO_3H. In case of functionalized CNTs, the functional groups may interact with water molecules through the relatively strong dipole-dipole interactions. H-bonding may also occur as will be described.

The presence of CNTs disrupts the boundary layer surrounding the particles, allowing for better heat transfer between the fluid. For example, MWCNT has half the thermal conductivity (3000 W/m.K) of SWCNT (6000 W/m.K), but in water, MWCNT suspensions may have better thermal conductivity than SWCNT suspension. This can be explained by the fact that MWCNT has better suspension thus better conductive networks rather than SWCNT which usually have lower dispersion thus agemate and sinks after time. Similarly, functionalized CNTs may have better effective thermal conductivity in water than non-functionalized. However, these issues are not unequivocal as literatures showed otherwise.

Literature revealed that the thermal conductivity of the CNT nanofluid is greatly influenced by the length of the CNTs and the number of walls, as shown in Figure 5. The concentration and type are also involved as discussed in Section 4.2. The aspect ratio, where MWCNT normally have higher values than SWCNT, will be discussed in Section 4.3 as well. As a result, the researchers have carefully examined this criterion [72] and used various types of CNT (SWCNT, MWCNT, and functionalized MWCNTs) with the same purity of 95%. The study confirmed that SWCNT exhibited the highest thermal conductivity. However, the conductivity dropped due to low stability. On the other hand, MWCNTs, especially ones with higher aspect ratios, showed higher thermal conductivity, as described in Figure 5. This is consistent with other literature, as in Equations (3-7), researchers considered the shape effect on thermal conductivity of the nanofluid.

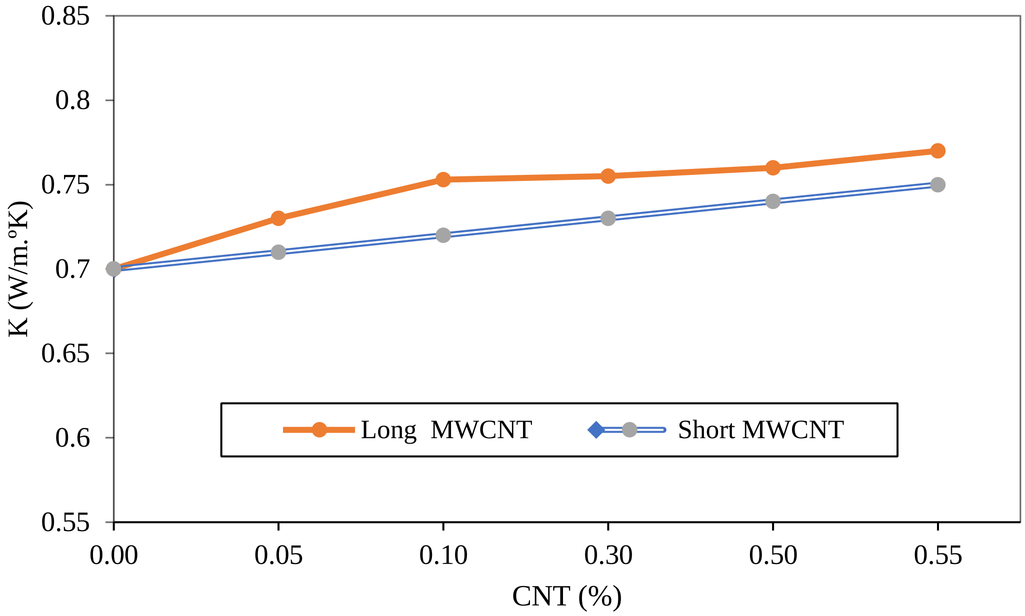

Figure 5. Effect of MWCNT length on normalized thermal conductivity of nanofluid. Plots show conductivity vs. concentration at 40 ºC. Drawn based on literature [7].

4.2. CNT Concentration

Comparative studies between CNT aqueous nanofluids and pure water have consistently shown significant improvements in thermal conductivity when CNTs are present. Literature showed that with increased CNT concentration in water, the fluid thermal conductivity increases. The concentration was expressed in various forms in literature, where some used the volume fraction. With higher CNT volume fraction, thermal conductivity increased. Reports [73-77] confirmed earlier proposed relations, such as those of Maxwell-Eucken and Hamilton-Crosser, and considered the concentration of particles. The quantification of the relationship between CNT concentration and thermal conductivity enhancement allows for the optimization of CNT concentration for specific application. Chaichan et al. [78] showed that CNT nanofluid thermal conductivity increased with increased MWCNT concentration, Figure 6a. The results are also in congruence with simulation results reported earlier [79], Figure 6b.

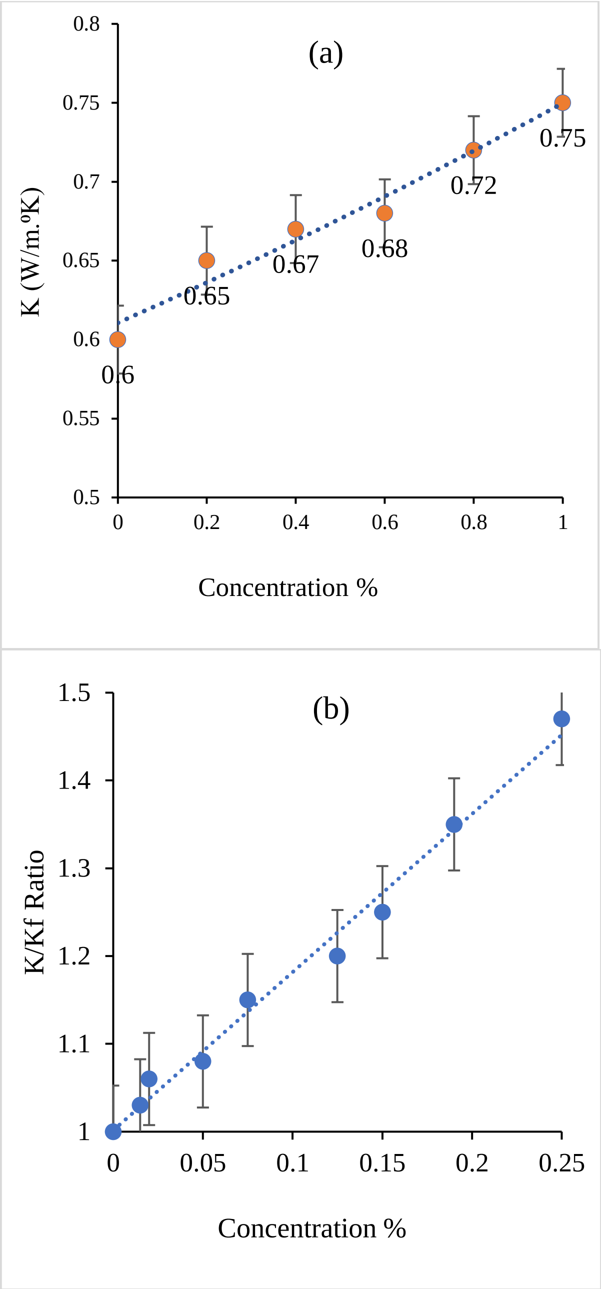

Figure 6. Effect of CNT concentration on aqueous nanofluid thermal conductivity. (a) Thermal conductivity values vs. MWCNT concentration, reproduced with permission from ACS [78]. (b) Simulated thermal conductivity improvement compared to water value, reproduced with permission from Hindawi open access [79].

Despite the differences between researchers, the CNT concentration affects the fluid thermal conductivity. This can be explained as follows. When CNTs are dispersed in water, they tend to agglomerate due to van der Waals forces. At low concentrations, these agglomerates are sparse and do not form continuous networks, resulting in limited thermal conductivity enhancement. With higher CNT concentration, the probability of agglomerates to come into contact, and form a percolating network, increases, as described in Figure 3 above. This percolating network facilitates the heat transfer through the nanofluid, leading to significant enhancement in thermal conductivity. P. Estellé [7] also showed that the effective thermal conductivity increases by increasing the concentration of CNT in water. The studies compared different models in the literatures and samples taken by the author at 20 ^{0}C

However, there are upper limits for CNT concentrations, beyond which thermal enhancement starts to decrease. This is attributed to the excessive agglomeration of CNTs that hinders the formation of effective conductive networks and destabilizes the suspension. In applications where, moderate thermal conductivity improvement is needed, lower CNT concentrations should be considered. When higher conductivity is needed, higher CNT concentrations should be considered, up to certain limits. Therefore, CNT concentration should always be chosen based on demand while minimizing material and processing costs.

4.3. Aspect Ratio

The aspect ratio of carbon nanotubes, which refers to their length-to-diameter ratio, affects thermal conductivity. Figure 5 showed that longer MWCNTs yield higher thermal conductivity in nanofluids. Figure 7 also shows how the CNT aspect ratio, in both MWCNTs and SWCNTs, affects aqueous nanofluid thermal conductivity. The results are consistent with Equation 9 above, which described how shape factor affects fluid thermal conductivity. Researchers varied CNT length at fixed diameter. The results showed higher thermal conductivity enhancement with longer CNTs. In addition to length, the diameter of CNTs has also been investigated [5]. A smaller diameter coupled with a longer length (higher aspect ratio) further enhanced thermal conductivity [17] as seen in Figure 7b below.

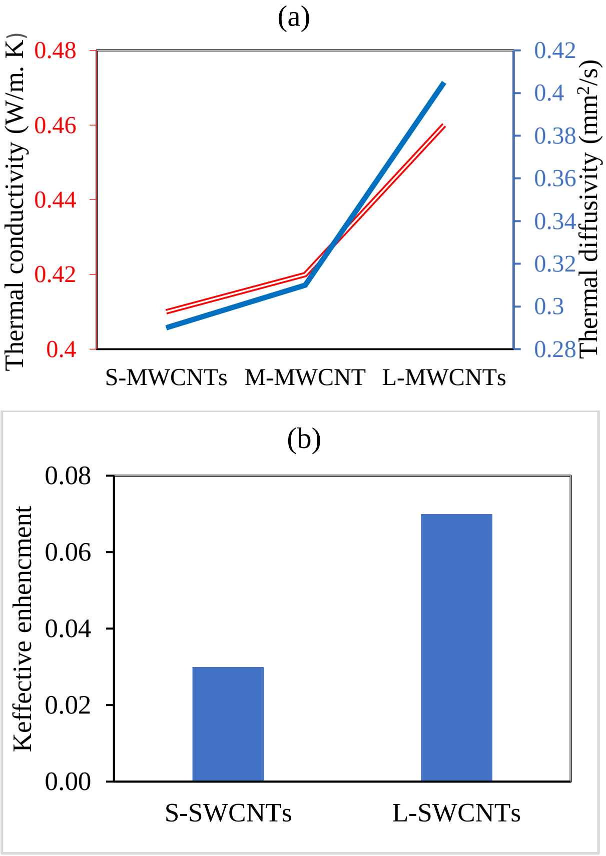

Figure 7. Effect of aspect ratio on CNT aqueous nanofluid thermal conductivity. (a) MWCNT length effect (having 10% concentration), reproduced with permission from MDPI open access [31]. (b) Thermal conductivity enhancement by using SWCNTs (short vs. long tubes), reproduced from Yildiz Technical University open access [17].

The CNT aspect ratio plays a vital role in nanofluid thermal conductivity improvement, as confirmed by other literature [80]. The effect of aspect ratio on thermal conductivity is rationalized by the present model. Longer CNTs have higher aspect ratio values. Longer nanotubes provide more efficient pathways for heat conduction, resulting in higher thermal conductivity enhancement. The interface between the CNTs and water molecules increases, with higher contact areas and more contact points, allowing more efficient heat transfer. The alignment of CNTs within the water nanofluid is influenced by the CNT particle length. Longer CNT particles are more uniformly aligned in the fluid and create continuous pathways for heat conduction [81]. However, in some literature, the effect of aspect ratio on thermal conductivity is not guaranteed [82].

Reynold number also affects the nanofluid thermal conductivity. Reynold number is defined as the "ratio of the inertial forces to viscus forces within the desired fluid subject to the relative internal movements resulted from different fluid velocities", Equation (26).

$$Re = \frac{\rho u L}{\mu} \quad (24)$$

where Re is Reynold number, ϱ is the density of the fluid, u is the flow speed, μ is the dynamic viscosity of the fluid and L is the characteristic linear dimension.

Because higher velocities increase turbulence, which means stronger dispersibility and better heat transfer, a higher Reynold number means higher thermal conductivity. Liu et al. [81] stated that the chillers capacity was optimum at a flow rate 100 l/min corresponding to 13200 Reynold number under turbulent conditions. MWCNTs consist of multiple layers of graphene tubes, unlike SWCNTs with one layer only, which gives better mechanical properties and allows more interfaces and defects. This hinders the efficient transition of heat by creating phonon scattering and increasing the thermal resistance of MWCNTs in dry state. In the dispersed state, the thermal conductivity of MWCNTs is improved by their higher aspect ratio and better contact with water due to higher surface areas. Several possible mechanisms, for increased nanofluid thermal conductivity, have been proposed in literature, including particle aggregation, nanolayer, ball-stic transport and nonlocal effects, near-field radiation and nanoparticle thermophoresis [67].

4.4. Dispersion Quality

Dispersion quality involves how much the suspension is uniformly distributed. It also involves how stable the suspension is with time. These characteristics are dominated by the following main parameters.

4.4.1. Functionalization

Chemical functionalization is a modification of the CNT walls by attaching other additives to them. In chemical functionalization, functional groups are anchored to CNT surface C atoms by genuine chemical bonds, as summarized in Figure 8. Other non-covalent functionalization modes are known, as described in the Figure.

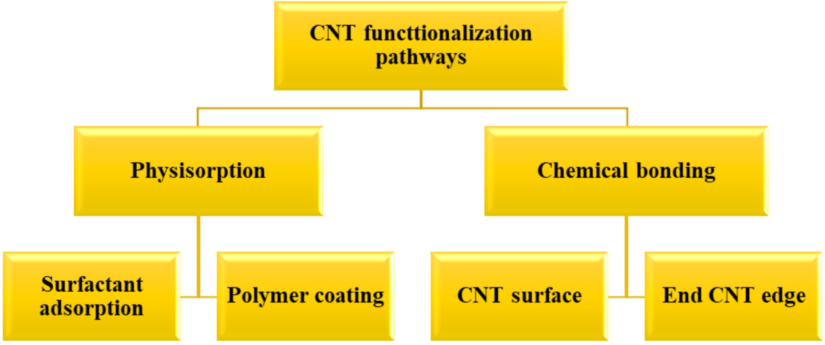

Figure 8. Types of CNT functionalization. Drawn based on literature [83].

By providing new ways of interaction between the CNT and water molecules, functionalization improves the dispersion quality and stability of the CNT aqueous nanofluid. However, both experimental observations and simulations showed that over functionalization significantly lowers CNT heat transport properties of nanofluids. The influence of functional groups, on the thermal conductivity of CNT nanofluids, was revealed by analyzing the effect of pristine CNT thermal conductivity, hydrogen-bond formation, mean-square displacement of water molecules and interlayer thermal resistance at CNT/water interface. Such lowering was documented in literature [70]. In practice, both fluid stability and thermal conductivity enhancements are needed. Therefore, over functionalization should be avoided. On the other hand, nanofluid stability could be achieved at moderate degrees of functionalization by using other additional methods such as sonification, aspect ratio control and concentration. Better dispersion is needed as it yields better alignment of particles and better bonding with water molecules.

In terms of boundary layer, stronger bonding disrupts the boundary layers, which further improves thermal conductivity along the networks and channels. Stronger bonds also give better Brownian motion which affects thermal conductivity. In addition to the thermal conductivity of the suspension, stability is also very important for application purposes. Therefore, CNT functionalization is necessary to keep the CNTs suspended, despite its negative impact on conductivity, and a balance should be made.

4.4.2. Sonication

Sonication is very useful in suspension stabilization. Surfactants are also added to the suspension to keep CNT dispersed in water. Sonication involves using ultrasonic waves to agitate particles and improve their dispersion in water. Literature confirmed improved suspension stability by sonication [84-86]. Wave frequencies higher than 20 kHz are normally used. Both bath type and probe type sonicators were described.

Sonication time also affects fluid stability and consequently thermal conductivity. With longer sonication time, conductivity improvement occurred up to a limit, after which no effect was observed. Table 3 summarizes literature findings for sonification time effects. Asadi [86] reported the effect of sonication time on CNT suspensions of 0.3% concentration. Good stability was observed in sonication times up to 60 min.

Table 3. Stability improvement values measured for various nanofluids after optimal sonication times.

No.	Sonication time	Particle	Stability	Nano fluid	Ref.
1	60 min	MWCNT 5-15 μm functionalized	80 days	CNT Water	[84]
2	60 min	MWCNT	30 days	CNT Water	[86]
3	45 min	Various types	117 days	CNT-water	[72]

4.4.3. Addition of Surfactant:

Proper dispersion of CNTs in water is crucial to produce stable nanofluids. This can be achieved by sonification and/or functionalization as described above. Surfactants also influence the interfacial characteristics between CNTs and the surrounding medium affecting fluid stability and thermal transport, Figure 9. Some surfactants may form a stable coating on CNTs while others may impact the interactions between CNTs and water molecules, influencing thermal properties. Table (4) below shows examples of commonly used surfactants in SWCNT water suspensions.

Dispersion of CNTs in water, by surfactants, occurs through the interaction between surfactant hydrophobic tail and CNT hydrophobic surface. Surfactant hydrophilic head group interacts with water molecules. This enhances the contact between water molecules and CNTs in a way that increases the dispersion stability and thermal conductivity of the suspension. Surfactant addition thus helps stabilize nanofluids. Without surfactants, the thermal conductivity of nanofluids dropped fast after manufacturing, due to instability. Literature [87] described stable thermal conductivity in nanofluids containing sodium dodecyl sulfate (SDS) as a surfactant. High thermal conductivity enhancement was observed when sodium dodecyl sulfate (SDS) dispersant was used at 38.0% y mass of SDS to nanofluid with 0.6 vol% CNT loadings [88]. The surfactant type also affected thermal conductivity. Hexadecyl trimethyl Ammonium bromide (CTAB) showed higher performance than other surfactants [88].

While the surfactant may improve the nanofluid stability, it may also lower thermal conductivity, as reported by [81]. This is because surfactants act as dispersing agents and prevent CNT network formation.

In summary, surfactants may improve or lower nanofluid thermal conductivity. The conductivity enhancement is presumably due to improved Brownian random motion in the stable suspension. The conductivity lowering is also understandable as individual CNTs are isolated inside micelles, away from one another. CNT networks are not encouraged by the surfactant, which lowers nanofluid thermal conductivity through the thermal channels. Therefore, surfactant type and concentration should be carefully optimized to reach the best balance between stability and conductivity.

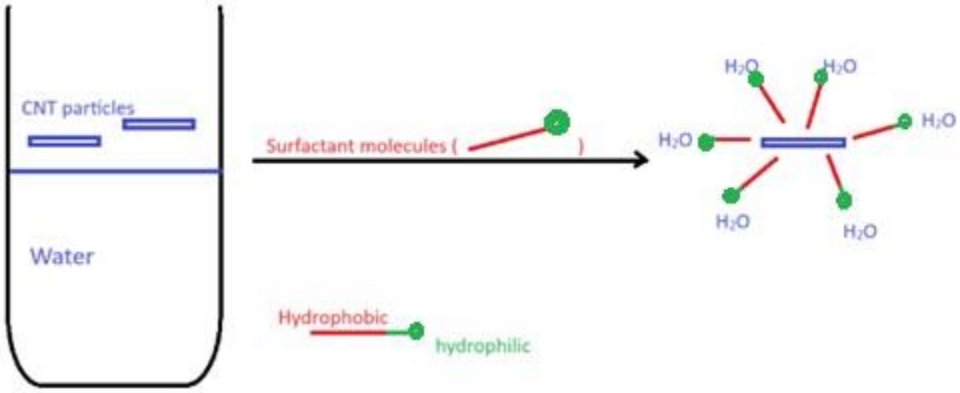

Figure 9. Role of surfactant molecules (with hydrophilic and hydrophobic terminals) in suspending hydrophobic CNT particles inside water by micelle like formation. Based on common literature [89].

Table 4. Common surfactants used in nanofluids [90].

Surfactant	Surfactant
Cetyltrimethylammonium bromide (CTAB).	Sodium dodecyl benzene sulfonate (SDBS),
Anionic (SDS)(Sodium Dodecyl Sulfate	sodium dodecyl sulfate (SDS)
Cationic (CTAB) Cetyltrimethylammonium bromide	Tween 80 polysorbate 80
Nonionic (LAE-7) Shazand Petrochemical complex	Tergitol NP-10
Amphoteric (CHAPS) Nonionic surfactants	Poly-Vinyl-Pyrrolidone (PVP)
Hydropalat 5040 Sodium polyacrylate in aqueous solution	Gum Arabic (GA)
Aerosol OT-70 PG	Hexadecyl-Trimethyl-Ammonium-bromide (CTAB)
Oleic Acid	Antiterra 250
Laurate salt	Disperbyk 190
Sodium dodecyl sulfate (SDS)	Hypermer LP1
Disponil A 1580	Aerosol TR-70
	Aerosol TR-70 HG

4.5. Temperature

Literature shows that the thermal conductivity of nanofluids increases as temperature rises. The effects of temperature on nanofluid conductivity were investigated by several researchers as summarized in Table 5.

Table 5. Effect of temperature on nanofluid thermal conductivity.

No.	Temperature range ºC	Thermal conductivity enhancement%		Ref.
		Lower temperature	Higher temperature	
1	60-80	15.0	35.0	[91]
2	30 - 50	7.2	9.8	[92]
3	60 - 80	25.0	45.0	[91]

The results are further corroborated by Table 6, [93]. The results are also in congruence with other reports [75]. The explanation for this is the liquid–solid interface as described earlier [94]. Table 6 shows that the thermal conductivity of pure water remains steady with increased temperature. When CNT is added, the thermal conductivity increases with increased temperature. Moreover, thermal conductivity is further increased by increased CNT concentration, in congruence with discussions in Section 4.2.

Table 6. Effects of CNT concentration and working temperature on CNT aqueous nanofluid thermal conductivity, data are based on literature *[93].*

Working temperature (ºC)	Thermal conductivity (W/m.K) for various CNT concentrations (mass%)					
	(0.00) pure water	0.01	0.02	0.04	0.08	0.1
20	0.6	0.6	0.64	0.65	0.66	0.7
30	0.6	0.7	0.66	0.7	0.75	0.8
40	0.6	0.9	1.2	1.5	1.7	1.9
50	0.6	1.25	1.5	1.7	1.9	2.2
60	0.6	1.5	1.7	1.9	2.1	2.5

Literature [2] showed that the temperature indirectly affects nanofluid thermal conductivity. The temperature increases nanofluid thermal conductivity by increasing Brownian motion which leads to improved CNT dispersion in water and higher thermal conductivity [42, 95, 96]. Equations (6) and (7) summarize the effect. Based on kinetic energy, Equation (2), by increasing the temperature the phonon phenomenon is more active.

On the other hand, at higher than 45 ºC, the effect of temperature becomes smaller [93]. This is due to temperature effect on the CNT network. Higher temperatures may break the network into smaller fragments, which lowers the thermal conduction through the channels. Therefore, temperature indirectly affects CNT nanofluid thermal conductivity, and the working temperature should be carefully observed.

5. Conclusion

The need for effective, stable, low cost and environmentally safe nanofluids is a de facto. In many processes, where efficient cooling and heating are needed, special fluids are needed to undertake the heat transfer and heat exchange. Based on cost and environmental concerns, water is the best medium for heat transfer and thermal conduction, and should always be considered. However, water needs improvement in thermal conductivity. Suspending carbon nanotubes (CNT) in water is being widely considered for this purpose. Tremendous research is underway aiming at optimizing the thermal conductivity of CNT based aqueous nanofluids. Experimental and theoretical studies investigated the effects of various parameters on the fluid thermal conductivity, including type of the CNT, functionalization, concentration, dispersion quality and aspect ratio. The impact of the CNT properties on various properties of water, such as volume change, viscosity and surface tensions, was studied. Literature findings are not free of contradictions and discrepancies. In many cases various reports show different measured values of thermal conductivity. Mathematical relations were proposed to facilitate the predictions of various CNT nanofluid characteristics. A simple qualitative model is presented here, to rationalize how adding CNTs to water may affect its thermal conductivity. Based on literature findings, the proposed model involves a number of postulates. The postulates are being used to explain various published results in the field. Effects of CNT type (including single-walled and multi-walled types), functionalization, concentration, surfactant addition, surfactant addition and working temperature, on the nanofluid characteristics are being explained by the model postulates. Balancing, between thermal conductivity and nanofluid stability, is strongly recommended, as described here. The review will be helpful to many researchers and industrialists, especially those who are new to the field. The review thus carries both academic and application values to the field of CNT-based aqueous nanofluid technologies.

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