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Chapter 1

Carbon Nanotubes in a Fluidic Medium: Critical Analysis

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Additional information is available at the end of the chapter

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1. Introduction

Under the current energy and climate change scenario, the implementation of measures that simultaneously aid resource preservation and environmental protection have gained a significant priority at a global scale. The continuous growth of fossil fuel price and the intensification of natural events severity are different but concurrent indicators of mankind’s dangerous proximity to a point of no return, as far as long-term sustainability and environmental conservation are concerned. Over the past few decades, scientists and engineers have proposed and successfully employed all kinds of improvements in most industrial areas, however, progress still needs to be made.

Heat exchangers are widely used as a part of most mechanical systems. They are a basic component in industrial plants, transportation equipment and even buildings. The last 20-30 years have witnessed a continuous rise in heat transfer exchange necessities together with a sustained tendency to the equipment miniaturization, leading to notorious heat transfer intensification needs. Although heat transfer intensification has been mostly a core engineering need, it may be regarded as an indirect way to improve systems sustainability. Intensified heat transfer processes require smaller heat exchangers, less heat transfer fluids, lower pumping energy requirements and consequently more sustainable systems. With a perspective of passively increase heat exchanging thermal performance through its intensification, the use of colloidal dispersions of solid nanoparticles in common base fluids (nano-fluids) has recently been proposed. Experimental studies have demonstrated that, compared to the base fluids alone, specifically tailored carbon nanotubes (CNT) based nanofluids may...
show significantly increased heat transfer capabilities, making them very promising from an intensification point of view and consequently from the system sustainability point of view.

Nanofluids can be categorized as a function of the nanoparticle material and shape, which are typically dispersed in an engineering base fluid such as water, ethylene glycol, oil or even a mixture of these. The thermo physical properties of a nanofluid, besides the expected variation with pressure and temperature, will also depend on the considered nanoparticle, base fluid and nanoparticle concentration. In order to predict the performance of their use in industrial applications, a precise understanding of nanofluid thermophysical properties is essential. To that effect, a large amount of studies have been reported in the literature, most of them focus on spherical particle based nanofluids. The majority of the research work in this area has been centred on the quantification of the thermal conductivity enhancement via two approaches: experimental measurement and/or theoretical formulation. The most consensus feature of these studies is that the addition of nanoparticles does increase the effective thermal conductivity of common fluids and that tubular particle nanofluids exhibit the highest enhancements. However, the mechanisms responsible for such anomalous behaviour remain unknown and theoretical models can only match experimental data for specific situations, at short margined parameter values. Among the proposed mechanisms of enhancement, the most accepted are the thermal conductivities of the solid particles and base fluids, particle volume fractions, nano-layer formation, particle clustering and Brownian motion. In the case of nanotube suspensions, the percolation effect is an additional widely accepted heat conductivity enhancement mechanism. Despite the current understanding of the possible mechanism behind the observed behaviour, the exact influence of each parameter is yet to be quantified.

Significantly less attention has been conceded to investigating the convective heat transfer involving nanofluids and possible enhancement factors, an essential requirement in enabling the practical application of nanofluids, e.g., in heat exchangers. The limited available studies report the enhancement of the convective heat transfer coefficient which is explained with the increase of the thermal conductivity expected for the respective nanofluids. Virtually all experimental studies of convective heat transfer, typically studying nanofluid flow through circular tubes, agree that the particle volume fraction is influential to the thermal performance increases.

However, higher particle concentrations contribute to higher pressure drop of the fluid flow, which bares the inconvenience of increased pumping requirements. Another noted trend, though not as well agreed upon, is the dependence on the fluid flow state, most authors reporting convective heat transfer increases as function of growing Reynolds numbers. Several authors also found that the thermal enhancement occurred in the tube entry region, proposing the low boundary layer thickness as a possible culprit.

Most of the experiment model validations, as well as theoretical studies, apply the single-phase approach in nanofluid behaviour predictions. This approach treats the solid particle suspension in a liquid as a single-phase fluid, enabling the employment of classic corre-
tions for convective heat transfer. Despite its reduced application namely due to a higher complexity, authors using the alternative two-phase approach have boasted better agreement with the experimental data. Still, no consensual model has been defined the responsible mechanisms, as well as their levels of influence are yet to be known. Research attempts to test the thermal performance of alternative heat exchanger types have been found, but these are still quite unique and lack proper validation.

Numerical studies of nanofluid heat transfer performances are the scarcest amongst the available literature, most conducted to evaluate forced convection in circular tubes, as the majority of experimental investigations. Here, the influence of the definition of boundary conditions and the associated theoretical assumptions selected are essential. Most studies employ the constant wall heat flux condition and are theoretically based on modifications of classical correlations for laminar and turbulent flow, whenever applicable. With regard to the mentioned anomalous nanofluid behaviour, exhibited in the tube entrances, some authors have employed finer meshes in the region, creating a non-uniformity of overall tube elements. In order to predict and understand the flow and thermal behaviour of nanofluids, further numerical investigation is still required.

2. Heat transfer fluids

The main limitation of the heat transfer enhancement techniques effectiveness is the poor thermal performance of the employed fluids, obstructing increases in performance and compactness of heat exchangers [1]. In what regards heat transfer performance, the fundamental thermo-physical properties of fluids are convective heat transfer, thermal conductivity, viscosity, and specific heat at constant pressure [2].

Table 1 presents the thermophysical properties of the conventional heat transfer fluids commonly used in cooling processes. As shown, water is the most efficient, having a higher thermal performance than glycols or engine oil and being more inexpensive. When freeze conditions or the need to increase the fluid boiling point exist, the addition of ethylene or propylene glycol is frequent, providing freeze and burst protection. Glycols have inferior thermal transfer properties than water and superior densities, resulting in higher flow-rates or heat transfer surface areas, leading to increased pressure drop, energetic requirements and equipment wear [3]. Engine oils can accumulate various functions specific to individual parts of engines, including heat dissipation, friction reduction, detergency and area sealing [4]. Oils also have inferior thermal transfer properties than water, being most suitable for heat transfer duties in which the fluid has increased boiling point requirements. The success rate of engine oils depends on the complex additives that are blended into these, being categorized as chemically active, with the capacity of interaction with metals at low oxidation and degradation costs, and chemically inert, which improve physical properties and effective performance [4, 5].
### Table 1. Thermophysical properties of the conventional heat transfer fluids [6].

<table>
<thead>
<tr>
<th>Fluid Property</th>
<th>Water</th>
<th>Ethylene Glycol</th>
<th>Engine Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity @ 300K (W/mK)</td>
<td>0.613</td>
<td>0.258</td>
<td>0.145</td>
</tr>
<tr>
<td>Dynamic viscosity @ 300K (N.s/m²)</td>
<td>0.798x10⁻³</td>
<td>4.8x10⁻³</td>
<td>319x10⁻³</td>
</tr>
<tr>
<td>Kinematic viscosity @ 294K (m²/s)</td>
<td>0.801x10⁻⁶</td>
<td>17.8x10⁻⁶</td>
<td></td>
</tr>
<tr>
<td>Density @ 298K (Kg/m³)</td>
<td>995.7</td>
<td>1096.78</td>
<td>1114.62</td>
</tr>
<tr>
<td>Specific heat capacity @ 295K (KJ/(Kg.K))</td>
<td>4.179</td>
<td>2.36</td>
<td>2.3927</td>
</tr>
</tbody>
</table>

#### 3. Nanofluids

For heat transfer enhancement, the alternative to the conventional approach of increasing device size or altering component geometry is improving fluid performance. As was observed in Table 1, conventional fluids have poor thermal properties that constitute a paramount limitation in heat transfer enhancement. Following a general trend for system miniaturization with improved heat transfer requirements, experimental studies into the application of particles, with higher thermal performance, to these fluids have taken place. This has led to the development of nanofluids, nano-sized solid particles suspended in conventional fluids (base fluids) with the purpose of increasing the heat transfer performance of the fluids.

It is well known that solid materials tend to have much higher thermal conductivities than fluids [7], as it can be observed in Figure 1. Therefore, it is expected that fluids containing suspended solid particles, millimetre and micrometer sized, display significantly enhanced thermal conductivities, as compared with conventional fluids, due to their large surface areas. However, its usage has not been reported on practical applications due to sedimentations, erosion, fouling and increasing pressure drops for pumping the fluid. Modern material processing technologies provided the possibility of nano-scaled material production, which has originated the emergence of nanofluids, at a time in which heat transfer requirements are summiting. Due to the smaller size, nanoparticles exhibit higher mobility and less particle interaction, allowing for improved stability and heat transfer. Such factors are significant in reducing pumping power, fluid inventory and eliminating clogging issues, thus increasing global interest in nanofluid research.
The application of different types of metallic and oxide nanoparticles has been investigated by several researchers. The most widely studied nanoparticles are the Al₂O₃ and CuO. In the last decade, carbon nanotubes (CNT) have attained a great interest from researchers, due to their exceptional physical properties, namely their enormous thermal and electrical conductivity [8]. The possibility to incorporate a small amount of CNTs into base engineering fluids in order to enhance its thermal conductivity has been studied.

However, the major drawback of using CNTs lies with its poor dispersability and homogeneity into the base fluid [9] (pristine CNTs tend to aggregate). The aggregation of carbon nanotubes may cause their settlement, the clogging of the flow channels and the decay of the overall effective properties.

### 3.1. Nanofluid tailoring

Nanofluid preparation is a complex process due to a number of factors with a high degree of difficulty in maintaining under control. Masuda et al. [10] found that particle instabilities resulted in agglomerations while Grimm [11] had to conduct experiments in an accelerated manner due to imminent particle settling. Nowadays, nanofluid development is based on two methods: the one-step method and the two-step method, the latter being the one employed in earlier investigations. The most important features when considering a massive nanofluid production are the nanoparticle materials and the host liquids. It is vital that nanoparticles show an high dispersability and stability and chemical compatibility with the selected host fluid.

![Figure 1. Thermal conductivities of common solids and liquids, at room temperature [7].](http://dx.doi.org/10.5772/51965)
Particle agglomeration can be prevented by balancing attractive forces between the nanoparticles within the fluid, obtainable through the employment of two common mechanisms: electrostatic stabilization (also known as mechanical or physical) or steric stabilization (chemical) [12, 13]. Mechanic stabilization generally includes ultrasonication, i.e., different pressure wave generation which induces cavitation and consequent particle deagglomeration. It consists of the placement of an electric charge on the particle surfaces with the purpose of to force kinetic stability. The absorption of ions to the electrophilic metal surface during the process creates an electrical multi-layer, resulting in repulsive electric forces between nanoclusters [14, 15]. Electrostatic stabilization is pH sensitive and of limited use, therefore steric stabilization is being most frequently applied [12].

This chemical methodology consists in the addition of a bulky material layer, such as a polymer or surfactant, to the nano particles, which provides a steric barrier enabling cluster prevention [16-18]. An alternative mechanism of stabilization, involving the addition of charged nanoparticles to microspheres, has recently been reported. The stabilization is obtained through the addition of small charged nanoparticle concentrations which repel Van der Waals attraction forces [19].

CNT nanofluids have been found to have a greater instability than spherical particle nanofluids, a consequence of the tendency to assemble into bundles or ropes which results from the stronger Van der Waal attractive forces between carbon surfaces, intensified by the higher nanotube specific areas [13, 20]. Nanotube morphology and attractive forces between tubes are highly influential in successful dispersions [21]. CNTs are usually suspended with the assistance of steric stabilization though surfactant employment or other functionalization techniques, which generally involves nanotube treatment with acids at high temperatures [13, 22]. Functionalization also aids in effectively preventing nanotube aggregation [23]. As with the spherical nanoparticles, electrostatic (or physical) stabilization is typically avoided, as it has also been found to cause the CNTs destruction [24]. According to Hilding et al. [21] the most important challenges in CNT nanofluid production are the chemical and morphological purification of the nanotubes, the uniform and reproducible dispersion and the orientation of the nanotubes in liquid and melt phases. The use of the mentioned surfactants is advantageous in interface absorption and accumulation in supra-molecular structures, thus aiding a uniform dispersion [20]. Nasiri et al. [13] experimentally concluded that functionalized suspensions present better stability, dispersion and thermal conductivity than suspensions obtained through ultrasonication, resulting in a lower propensity for agglomeration and precipitation. The same authors also found that the thermal conductivity of all suspensions decrease with time, the reduction rate varying with the preparation method. However, an experimental study using plasma coating on MWCNT nanoparticles to improve stability was successfully conducted by Kim et al. [25]. A desired nanotube orientation can be obtained through shear flows, elongation flows or by electric and magnetic field application [21].
4. Conductive heat transfer

Being below the critical length scale, the physical properties of nanoparticles differ from conventional bulk solids, serving as motivation for a large number of studies on nanofluid behaviour. Most of these studies echo higher heat transfer performances than that of the base fluids alone, though some contradictory results have been reported [26]. Experiments have shown that the thermal conductivity of nanofluids depends on a large number of parameters, but an accurate, consensual prediction of its variation with these parameters is yet to be established [27].

Measurement of the thermal conductivity of liquids can be a difficult task, this due to the necessity of establishing a steady one-dimensional temperature field. The measurements should be taken in a reduced timeframe, so that convection currents cannot develop, while liquid heating should take place from above to facilitate heat conduction in a layer wise manner. The most common measurement methods are the transient hot-wire method, cylindrical cell method, temperature oscillation method and 3-omega method.

The transient hot-wire technique is the most employed method, consisting in the measurement of temperature and time response of a platinum wire, acting as a probe, subjected to an abrupt electrical pulse [27, 28]. The wire, heated resistively, usually employing a Wheatstone bridge resistor setup, is suspended in the nanofluid with the purpose of increasing its temperature [27, 29]. The temperature increase of the fluid, measured by the wire, depends on its thermal conductivity, which is calculated from the temperature-time profile of the wire [28-32]. This method has several advantages, the most significant being the capacity to eliminate experimental errors associated to natural convection, as well as the relatively accelerated measurement process [27]. The main drawback is the need for a chemical wire coating for measurements in electrically conducting fluids [28, 29].

Over the last decade, a large number of experimental studies investigating the enhancement in thermal conductivity of nanofluids have been conducted. Most have shown increases in thermal conductivity of nanofluids, even at diminutive particle volume fractions, when compared to base fluids, in most cases exceeding the predictions of theoretical models developed for suspensions of larger particles. The studies have also revealed that the thermal conductivity depends on several parameters and that these dependencies cannot be discarded when investigating heat transfer mechanisms of nanofluids [33-36].

Eastman et al [37] has shown an increase in thermal conductivity of about 60% for the nanofluids consisting of water as base fluid with 5%vol of CuO nanoparticles. Wang et al [9] measured the thermal conductivity of Al₂O₃ and CuO nanoparticles dispersed in distilled water (DW), ethylene-glycol (EG) and engine oil (EO). The increase of thermal conductivity was different for each base fluid, suggesting an effective thermal conductivity dependent on the base fluid thermophysical properties. Xuan et al. [38] studied the thermal conductivity enhancement for Cu-DW nanofluid. The result was the increase of 56% for the thermal conductivity with a 5% of volume fraction. Xie et al. [39] investigated the effects of pH value of the suspensions, the specific surface area of the nanoparticles and the thermal conductivity
of the base fluid. The enhancement observed seemed to increase with the decrease of pH values, and with the increase of nanoparticles specific surface area. Das et al. [40] investigated the influence of the temperature in the enhancement of thermal conductivity of nanofluids based on Al₂O₃ and CuO. The experimental results have shown that the thermal conductivity rise with an increase in temperature. Murshed, et al [31] reported a maximum of 33% enhancement on thermal conductivity for 5% volumetric loading of TiO₂ nanoparticles in water based nanofluids.

In the last decade, carbon nanotubes (CNT) have attained a great interest from researchers, due to their exceptional physical properties, such as its enormous thermal and electrical conductivity [41]. The possibility to incorporate a small amount of CNTs into base fluids, in order to enhance its thermal conductivity has been studied. Effective thermal conductivity measurements of dispersed CNTs in synthetic poly-oil were carried out [42] and it was found out a 160% increase in the thermal conductivity of oil at 1% volume fraction of CNTs. Thermal conductivity of Cu-ethylene-glycol nanofluids was assessed [43], and it was observed a 40% enhancement containing approximately 0.3% vol. of Cu nanoparticles with a mean diameter of 10 nm. A thermal conductivity increase of 35% to 79% for 0.5 to 1.0% vol. of carbon nanoparticles in water was also observed [44]. The viscosity of CNT nanofluids as a function of shear rate was also measured at different temperatures and concentrations, at pH=6. It was observed a shear thinning behaviour, at low shear rates, but a slightly shear thickening is seen at shear rates greater than 200 s⁻¹. It was observed that the thermal conductivity enhancement reaches up to 17.8% at the volume fraction of 0.01 (1%vol.) for CNTs – ethylene glycol base nanofluids [45]. At low volume fractions (<0.4 %vol.), nanofluids have lower viscosities than the corresponding basefluid, due to the lubricative effect of the nanoparticles. Various nanoparticles were studied [46], such as multiwalled carbon nanotubes (MWCNT), fullerene, copper oxide, silicon dioxide (SiO₂) and silver, and used it to produce nanofluids with enhancing thermal conductivity and lubrication. As basefluids, distilled water (DW), ethylene glycol (EG), silicon oil and poly-α-olefin oil (PAO) were used. These authors observed the highest thermal conductivity enhancement in MWCNT water based nanofluids, whereas the lowest one was observed for silicon dioxide (SiO2). They have also concluded that the higher thermal conductivity enhancement can be obtained for basefluids with the lower thermal conductivity.

At present there are no general and precise analytic models able to predict the thermal conductivity of nanofluids. Most of the tentative proposals in this field underestimate the nanofluid thermal conductivity when compared to experimental results [1, 47].

Earlier theoretical models are derived from the Maxwell model (1881), a semi-empiric correlation used to describe the effective thermal conductivity (kₑₑ) of larger scale spherical solid suspensions in liquids, with emphasis on the conductivity of the solid particles (kₚ) and base liquids (kₒ) used, as well as the volume fraction (φ) of solid particles [1, 48, 49]. However, despite working best for low concentrations of solid particles, the Maxwell model was rapidly found to under-predict effective thermal conductivities of smaller nano-scaled suspensions, also failing for non-spherical particle suspensions [1, 49].
In 1935, Bruggeman proposed a similar model that didn’t present the low volume fraction constraint of its predecessor, satisfactorily agreeing with early experimental data [49, 50].

$$k_{\text{eff}} = \frac{k_p + 2k_b + 2(k_p - k_b)\phi}{k_p + 2k_b - \phi(k_p - k_b)}$$  \hspace{1cm} (1)

Later, the Hamilton and Crosser model (1962) introduced an empirical particle shape factor \(n\), dependent on sphericity, to account for its effect, obtaining the same result as the Maxwell model for spherical particles [1, 49].

$$g = \left(\frac{k_p - k_{\text{eff}}}{k_p - 2k_{\text{eff}}(1 - \phi)}\right)$$

$$= \frac{k_p - k_{\text{eff}}}{k_p - 2k_{\text{eff}}(1 - \phi)} = 0$$  \hspace{1cm} (2)

This model was the first to reveal the importance of the geometrical shape of the dispersed particles. However, since it is based on Maxwell model, this is only valid for heterogeneous systems where the interaction between the particles is negligible. Such heterogeneous mixtures are known as dispersed phase distributions. Although, for specific volume fractions and shape of the particles, the mixture phase distribution may modify for aggregate structure or percolation-like structure.

The percolation theory predicts the existence of a critical particle concentration threshold, characterized by the formation of a continuous solid path, formed by highly conducting nanotubes coming into contact with each other, thus assisting the increase in thermal conductivity of several orders of magnitude [23, 51-53] consider heat percolation as one of the main culprits for the higher thermal conductivity exhibited by CNTs.

Xie and Chen [54], producing CNT nanofluids via ball milling, found that longer milling times lead to higher aggregation levels, which promote percolation, having concluded that the positive influence of aggregation surpasses the negative effect of aspect ratio deterioration that results from excessive milling. The percolation threshold of CNTs depends on nanotube dispersion, alignment, aspect ratio and surface modifications [23].

Munson-McGee [55] found that a reduction of the threshold can be obtained with an increase in aspect ratio, demonstrating that the critical volume of cylindrical particles can vary from less than 1% to just over 20%, whereas Biercuk, et al [56] indicated that the threshold for SWCNTs is approximately equal to the inverse of the aspect ratio, which was roughly 1000 in value, and that the percolation network formation occurs at inferior loadings, even for randomly oriented nanotubes.
Martin et al. [52] established that the threshold for MWCNTs could be controlled by diffusion during particle dispersion. The same authors also consider that reported inconsistencies between experimental observation and the statistical percolation theory are owed to the lack of considerations with regard to inter-particle interactions, neglecting the effects of Van der Waals forces and Coulomb interactions due to static particle charging, and kinetic effects, such as particle Brownian motion. They also predicted that aging high aspect ratio nanotube dispersions would lead to lowered percolation thresholds.

Lamas et al. [51] backed by theoretical studies of Biercuk et al. [56] and Nan et al. [57], indicate thermal conductivity discontinuities, attributed to Kapitza resistances and the anisotropy thermal properties of the CNTs, credited to play a significant role in defining the percolation threshold. These interfacial thermal resistances were recognized to depend on the bonding strength between CNTs and the surrounding medium, as well as low functionalization levels [58, 59]. The dependence of the Kapitza resistance on the strength of liquid-solid interactions was found to exhibit two distinct regimes: an exponential dependence for weak bonding and a power law dependence for strong bonding, in which thermal resistance is inversely proportional to the solid-liquid connection strength [59]. Shenogin et al. [58] found that the functionalization of SWCNTs leads to significant decreases of the referred thermal resistances, but they also witnessed drops in thermal conductivity with increases in functionalized atom fractions. They used the effective medium theory to predict that this dependence could be eliminated for highly functionalized CNTs.

The previously mentioned Hamilton and Crosser model (1962) was the first to enable the prediction of the effective thermal conductivity of non-spherical particles. However, this classic model was formulated for larger sized particles than the nano-sized ones employed in nanofluids, being found to under-predict the effective thermal conductivity of CNT nanofluids.

Nan et al. [57] presented a simple formula based on Maxwell’s effective medium model, accounting for high particle aspect ratios and volume fractions. However, the model was later found to over-predict the thermal conductivity, explained by not accounting for the influence of the interfacial thermal resistances [51]. These conclusions led the authors to propose a modified model the following year, formulated to include, to some extent, the interface thermal resistance effect on the thermal conductivity [60]. According to the revised model, the effective thermal conductivity enhancement is a function of the volume fraction ($\phi$) and $\beta$ coefficients along the transverse direction ($\beta_x$) and the longitudinal direction ($\beta_z$). These coefficients depend on the thermal conductivities in each direction ($k_{11}$ and $k_{22}$), in turn influenced by the particle thermal conductivity ($k_p$), nanotube diameter (d) and length (L), as well as the radius in which Kapitza resistance is influential ($a_k$). The Kapitza radius is a function of interface thermal resistance ($R_k$) and base fluid thermal conductivity ($k_b$). Although the increasing complexity, the revised model was found to lack precision for increasing volume fractions and also doesn't account for percolation effects, CNTs assumed to be isolated from each other [61].
Xue [61] proposed a theoretical model which incorporates interfacial thermal resistances using an average polarization theory, as well as simultaneously considering the effects of nanotube dimensions and concentrations. The deduced expression leads the author to state that increases in thermal conductivity can be obtained via an increase in nanotube length, regardless of the corresponding diameter, which indicates that thermal variations along the transversal direction can be neglected. Same author also proposed a Maxwell-based model to account for the effect of the nanotube orientation distribution, founded on the discontinuity theory of dispersions in a continuous phase [62]. Once again, the effect of percolation was overlooked and the model only predicts increases in effective thermal conductivity for increases in particle volume fraction [51].

Sastry et al. [63] presented a model based on percolation and the contact resistance in the consequent thermal resistance network. A dimensionless parameter was introduced to represent the effect of percolation, it being a function of conductance between CNTs (G), CNT length (L_f) and particle volume fraction (ϕ). According to their model, the effective thermal conductivity depends on the number of parallel CNT chains (M), the number of connected segments (N) over a distance (X), CNT diameter (d) and the heat transfer area (A),

\[
k_{eff} = \frac{X}{A} \left\{ \frac{2 \pi k_d}{d} + \frac{1}{M} \right\}^{-1} + \frac{2 \pi k_d d^2}{G_d L_f} ; M = \frac{4 \pi X^3}{\pi d^2 LN}
\] (5)

Based on the Sastry et al. model [63], Koo et al. [64] proposed a revised model which takes the non-linear conductivity enhancement with particle concentration increases into account using the excluded volume concept, where the excluded volume is the volume surrounding an object in which the centre of an identical object should be missing in order to avoid object inter-penetration. According to their model, the role of percolation is represented not only by the Sastry et al. dimensionless parameter, but also by the number of contacts per cylinder (N_c) of randomly oriented cylinders, quantified by the product of the excluded volume and the CNT volume fraction, as follows:
Patel et al. [53] derived a model for CNT nanofluids based on a spherical particle conductivity model previously proposed by Kumar et al. [65], announcing a reasonable enhancement trend prediction for both oil and water based CNT nanofluids. Additionally, two paths for heat flow are assumed: one through the base liquid and another through the CNTs; both considered to be acting in parallel to each other. According to the model, the effective thermal conductivity is a function of the base liquid molecular size ($r_b$), the average CNT diameter ($d$) and the CNT volume fraction ($\phi$).

$$k_{eff} = \left(1 + \frac{k_{\eta\phi}}{k_b[1-\phi]}\right)k_b$$

(7)

With a view to predict the effects of anisotropy, aspect ratio, non-straightness, CNT volume fraction and interfacial thermal resistance on the effective thermal conductivity, Deng et al. [66] and Deng and Zheng [67] proposed several analytical formulas. The most significant of these models takes into account a non-straightness of CNTs ($\eta$), a high thermal anisotropy of CNTs ($k_{11}/k_{33} < 1$), a random CNT orientation and a tube-end thermal resistance. The model also assumes the formation of CNT thermal cables, while the role played by the aspect ratio ($p = L/d$) is reflected by parameter $H$, as follows,

$$k_{eff} = 1 + \frac{\eta \phi}{3} + H(\eta \phi)k_b$$

(8)

$$H = \frac{1}{p^2} \left[ \frac{p}{\sqrt{p^2 - 1}} \ln \left( p + \sqrt{p^2 - 1} \right) - 1 \right]$$

5. Convective heat transfer

In order to employ nanofluids in concrete applications, a full understanding of their convective heat transfer features is essential. When compared to the reported studies of thermal conductivity, convective heat transfer research is scarce, little attention having been given to determining the convective heat transfer characteristics of nanofluids [34, 68]. However, in recent years this mode of heat exchange has gained more awareness, result of a necessary comprehension for practical application. Convective heat transfer can be divided into two categories: closed flows forced convection, with induced fluid flow through confined re-
regions such as pipes and channels, and natural convection, with fluid motion due to buoyancy both in closed and opened flow conditions [33].

5.1. Forced convection

Of the limited available literature, most studies are focused on the forced convective heat transfer of nanofluids in circular tubes. The convective heat transfer coefficient depends on thermal conductivity, specific heat capacity, viscosity, flow rate and density of fluids [29]. The fluid flow nature is of up most importance, studies being conducted for both laminar and turbulent flows. The reported investigations characterize the heat transfer with emphasis on the convective transfer coefficient (h) or more frequently, in a non dimensional approach, by the Nusselt number (Nu), as a function of the Reynolds number (Re) and the Prandtl number (Pr), also non dimensional numbers. The Nusselt number presents the ratio between convective and conductive heat transfer and is given by

$$Nu = hL/k_f$$

where L is the characteristic length, $k_f$ is the thermal conductivity of the fluid and h is the convective heat transfer coefficient.

A Nusselt number close to one, namely convective and conduction of similar magnitude, is characteristic of “slug flow” or laminar flow. A larger Nusselt number corresponds to more active convection, with turbulent flow typically in the 100-1000 range.

These parameters are dependent of the nanofluid thermal transport properties, most significantly the viscosity ($\mu$) and the thermal conductivity ($k$), that are a function of the temperature. As a result, most experimental procedures involve the measurement of the fluid temperature in different regions along the tube. In experimental procedures, laminar flow convective heat transfer studies are frequently validated using the predictions of the Shah equation, whereas turbulent flows are typically validated by the Gnielinski or the Dittus-Boelter equations, defined in terms of the Nusselt number [69].

Shah equation for laminar flows (D, tube diameter and x, axial position along tube axis):

$$Nu = \begin{cases} 1.953 \left( \frac{Re Pr}{D} \right)^{1/3}, & \frac{Re Pr}{D} \geq 33.3 \\ 4.364 + 0.0722 \frac{D}{x} \frac{Re Pr}{D}, & \frac{Re Pr}{D} < 33.3 \end{cases}$$

$$f = 0.078 \left( \frac{Re}{Nu} \right)^{1/4}$$

$$Nu = hL/k_f$$
Dittus-Boelter equation for turbulent flows:

\[ Nu = \frac{f}{\frac{f}{2} \left( \frac{1}{Re} \right) Pr} \left( 1 + 12.7 \left( \frac{f}{2} \right)^{1/2} \left( \frac{Pr^{2/3}}{Re^{1/4}} - 1 \right) \right) \]  

(11)

Dittus-Boelter equation for turbulent flows:

\[ Nu = 0.023 Re^{0.8} Pr^{0.4} \]  

(12)

5.1.1. Laminar flow

Ding et al. [44] studied the heat transport properties of MWCNT/water nanofluids along a uniformly heated copper tube. The experimental data demonstrated good agreement with the Shah equation for laminar flows under the constant heat flux boundary condition. The convection coefficient was found to increase significantly with nanoparticle concentration and the Reynolds number, both for spherical and elongated particles (MWCNT). The highest values of the convective coefficient were witnessed in the tube entrance region, leading the authors to indicate the creation of multiple artificial entrances along tubes, to maximize the heat transfer via boundary layer degradation, for future studies. However, the most significant enhancement occurred in the vicinity of the tube midway point (110 times the tube diameter), about 375% at Re=800, for 0.5wt% CNTs.

Amrollahi et al. [70] conducted a similar experiment for both laminar and turbulent flows, using functionalized MWCNT nanofluids. Their experiment resulted in less significant values for the convective heat transfer enhancement (33-40% at Re=15920) when compared to the previous study.

Chen et al. [45] investigated the heat transfer behaviour of TiO$_2$ nanotube suspensions in water, through a tube, under the constant wall heat flux boundary condition. The convective heat transfer enhancement varied minimally for different nanotube loadings, decreasing along the tube length.

Garg et al. [71] prepared an experimental study to evaluate the influence of the ultrasonication extent, during MWCNT/water nanofluid preparation, on the heat transfer performance. To that effect, four distinct samples, with ultrasonication times ranging from 20 to 80 minutes, were prepared. The convective heat transfer was analysed along a copper tube, under a constant heat flux condition, with Reynolds numbers varying between 600 and 1200. As with previous studies, the convection coefficient was highest in the tube entry region but its maximum enhancement was found to occur in the developed boundary layer region. Surprisingly, the increase in Reynolds numbers resulted in a decrease of the convective heat transfer coefficient. The authors found that the optimum ultrasonication time was 40 minutes, above which the tube breakage rate increased, and that the viscosity of nanofluids increases with ultrasonication times.
Silva and Abreu et al. [72, 73] conducted similar experiments to evaluate the convective heat transfer of low particle concentration MWCNT/water nanofluids along a stainless steel tube, under the constant wall heat flux boundary condition. In both investigations the convection coefficient enhancement was greatly superior to that observed for the thermal conductivity, reported to be maximum in the tube entry region. Table 2 resumes the main experimental studies of forced convection heat transfer, under laminar flow, of tubular particle nanofluids. Greater attention will be paid to these studies further on, as these will act as an experimental basis for numerical model development and validation.

<table>
<thead>
<tr>
<th>Author</th>
<th>Nanofluid</th>
<th>Nanotube Loadings</th>
<th>Test Tube Dimensions</th>
<th>Heat Transfer Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>[44]</td>
<td>MWCNT/Water</td>
<td>0.1-0.5wt%</td>
<td>L=0.96m d=4.5mm</td>
<td>375% for h at 0.5wt% and Re=800</td>
</tr>
<tr>
<td>[71]</td>
<td>MWCNT/Water</td>
<td>0.2wt%</td>
<td>L=0.914m d=1.55mm</td>
<td>32% for h at Re=600; 29% at Re=900</td>
</tr>
<tr>
<td>[74]</td>
<td>MWCNT/Water</td>
<td>0.2vol%</td>
<td>L=1.8m d=5mm</td>
<td>10% for k at Re=1200</td>
</tr>
<tr>
<td>[70]</td>
<td>MWCNT/Water</td>
<td>0.1-0.25wt%</td>
<td>L=1m d=11.4mm</td>
<td>12% for h at 0.12wt%; 40% at 0.25wt%; Re=1592</td>
</tr>
<tr>
<td>[72]</td>
<td>MWCNT/Water</td>
<td>0.25vol%</td>
<td>L=1.2m d=6mm</td>
<td>105% at Re=2060</td>
</tr>
<tr>
<td>[73]</td>
<td>MWCNT/Water</td>
<td>0.25-0.5vol%</td>
<td>L=1.2m d=6mm</td>
<td>94% for h at 0.5vol% and Re=2061</td>
</tr>
</tbody>
</table>

Table 2. Summary of experimental studies of forced convective heat transfer, under laminar flow, of tubular particle nanofluids.

5.1.2. Turbulent flow

Despite extensive research, limited experimental investigations of tubular shaped particle based nanofluids were found. Amrohalli et al. [70] evaluated the convective heat transfer enhancement of functionalized MWCNT/water nanofluids for both laminar and turbulent flow modes. The convection coefficient in turbulent flows displayed a greater increase than the values obtained for laminar flows and the enhancement decreased with increasing temperatures. The coefficient was found to become constant with increasing the Reynolds number in the tube entry region.

Liu and Liao [75] studied the heat transfer behaviour of CNT dispersions in an aqueous solution of cetyltrimethyl ammonium chloride (CTAC), intentionally used to reduce drag. The heat transfer enhancement was found to be greater with higher temperatures, even when the drag reduction is insignificant, and higher particle loadings. The dependence of the convection coefficient on the Reynolds number was noticed to be minimal. Table 3 resumes the
main experimental studies of forced convective heat transfer, under turbulent flow, of tubular particle nanofluids.

<table>
<thead>
<tr>
<th>Author</th>
<th>Nanofluid</th>
<th>Nanotube Loadings</th>
<th>Test Tube Dimensions</th>
<th>Heat Transfer Enhancement</th>
</tr>
</thead>
<tbody>
<tr>
<td>[70]</td>
<td>MWCNT/Water</td>
<td>0.1-0.25wt%</td>
<td>L=1m d=11.4mm</td>
<td>25% at 0.12wt% and Re=4778</td>
</tr>
<tr>
<td>[75]</td>
<td>CNT/CTAC</td>
<td>0.5-4wt%</td>
<td>L=1.08m d=25.6mm</td>
<td>70% for h at 2wt%; 40% increase at 4wt%; Re~45000</td>
</tr>
</tbody>
</table>

Table 3. Summary of experimental studies of forced convective heat transfer, under turbulent flow, of tubular particle nanofluids.

5.1.3. Theoretical studies

Despite a recent interest boom regarding convective heat transfer intensification by the use of nanofluids, theoretic models of convective heat transfer remain scarce, most are derived from classical correlations, such as the aforementioned Shah or Dittus-Boelter equations for laminar and turbulent flow, respectively. This bares the consequence of only being valid for specific nanofluids over small parameter variations [49].

Pak and Cho [76], following their experimental study of the heat transfer performance of $\text{Al}_2\text{O}_3$/water and TiO$_2$/water nanofluids under turbulent flow conditions, proposed the following correlation, a modified version of the Dittus-Boelter equation.

$$Nu = 0.021Re^{0.8}Pr^{0.5}$$

Xuan and Roetzel [77] derived correlations for the convective heat transfer of nanofluids proposing two different approaches: the first treating nanofluids as single-phase fluids, the second assuming nanofluids as solid-liquid mixtures. The first method assumes that classical correlations for pure fluids, such as, can be applied to convective heat transfer predictions. The second approach continues to treat the nanofluid as a single-phase fluid but also takes into account the heat transfer enhancement due to the thermal dispersion that results from random particle motion. Both approaches indicated that the heat transfer enhancement depends on thermal conductivity increase and chaotic particle motion, which accelerates energy exchanges. For the second approach, the effective thermal conductivity of the nanofluid is given by the sum of the contributions of the single-phase thermal conductivity of the nanofluid ($k_{nf}$) and the thermal conductivity of the dispersion ($k_d$), as follows,

$$k_{ef} = k_{nf} + k_d; k_d = C(\rho C_p)_d \mu_d e_d$$

$$}\text{(14)}$$
Based on the thermal dispersion and their experimental results for Cu/water nanofluids, Li and Xuan [78] proposed a model for predicting forced convective heat transfer of nanofluids inside circular tubes. According to this correlation, the thermal dispersion promoted by micro-convection and micro-diffusion is quantified by the Peclet number (Pe). Based on their experimental data for both laminar and turbulent flows, the following correlations were proposed.

Laminar flows: \( N_u_{nf} = 0.4328(1.0 + 110285\phi^{0.754}Pe_{d}^{0.218})Re_{nf}^{0.333}Pr_{nf}^{0.4} \)

Turbulent flows: \( N_u_{nf} = 0.0059(1.0 + 7.628\phi^{0.6886}Pe_{d}^{0.01})Re_{nf}^{0.9238}Pr_{nf}^{0.4} \)

Ding and Wen [79] focused on particle migration derived from Brownian motion, as well as shear stress and viscosity gradients, indicating a non-uniform property distribution that causes radial variations in thermophysical properties, most notably of temperature and flow velocity, thus being proposed as a possible enhancement mechanism in heat transfer of nanofluids.

A comprehensive study of different analytical approaches was conducted by Mansour et al. [80], in which laminar and turbulent flows, for an Al\(_2\)O\(_3\)/water nanofluid, were considered and common correlations used for nanofluids were evaluated for fully developed streams in a tube subjected to a constant heat flux boundary condition. Their analysis was focused on the determination of the specific heat, the viscosity and the thermal conductivity, followed by pressure drop and heat transfer correlation studies for singular tube conditions using distinct particle volume fractions. The most significant discrepancies were found for the laminar flow cases, some contradictory.

### 5.2. Natural convection

The natural convection of nanofluids having been found to be influenced by liquid unstable density distributions, which result from temperature and particle distribution differences due to particle sedimentation [81, 82].

Few experimental and analytical studies to ascertain the natural convective heat transfer behaviour of nanofluids have been performed. Kang et al. [81] and Putra et al. [83] conducted similar experiments using cylindrical and rectangular vessels, respectively, in which the nanofluid was heated from one side (or wall) and cooled from the other. Kang et al. [81] found that the formation and deterioration of multiple layers around SiO\(_2\) nanoparticles occurred, these influenced by the increase of the temperature gradient between opposite sides. Putra et al. [83] found that the enhancement of the thermal conductivity of CuO/water nanofluids was higher than that of Al\(_2\)O\(_3\)/water nanofluids, both displaying improved convection than that of common slurries but inferior to that of the base fluid. Additionally, both nanofluids’ natural convective heat transfer properties were found to deteriorate with an increase in particle concentration and density, characterized by decreasing Nusselt numbers.

Analytic studies conducted by Khanafer et al. [84] and Kim et al. [85] led the authors to conclude that natural convective heat transfer increased with the particle volume fraction (at any Grashof number), contradicting the experimental conclusions of Putra et al. [83].
6. Numerical studies

The computational analysis of fluid mechanics and heat transfer phenomena (CFD) of nano-fluids requires strong and validated models regarding their thermo physical properties dependency with temperature and pressure. It is also fundamental to establish the physical nature of a nanofluid, namely if it should be considered a single-phase or a multi-phase material, since the numerical modelling approach may depend on that. The lack of knowledge regarding the above mentioned aspects is reflected on the limitations showed by the results of exiting studies focus on nanofluids CFD analysis. Although the referred limitations, CFD analysis of nanofluid systems may be quite important, namely as a support tool to the more fundamental experimental work.

A pioneer study in this area is due to Xuan and Roetzel,[77] the simpler single-phase assumption for nanofluids has been found to be numerically more efficient, result of its reduced computational workloads. The advantage of this approach resides in the assumption that the base fluid and the nanoparticles are in thermal equilibrium as well as equal velocities [86].

Maiga et al. [87] developed a numeric model to simulate the flow of Al$_2$O$_3$/water and Al$_2$O$_3$/ethylene glycol nanofluids, under both laminar and turbulent flows, applying single-phase and constant wall heat flux conditions to a circular tube (L=1m; d=10mm). Flow symmetry was assumed and, for turbulent flow, the semi-empirical $K$ model was used to describe the heat flux of the nanofluids. Results demonstrated a higher heat transfer enhancement of the ethylene glycol based nanofluid, increasing with growing particle loads.

Applying the same theoretical considerations, Roy et al. [6] numerically evaluated the thermal performance and wall shear stress of nanofluids in a radial cooling system, subjected to laminar, uniform velocity flows. The obtained data indicates convection coefficient increases for growing particle volume fraction and Reynolds number. More recently, a similar numerical study was conducted by Saeedi [86] to assess the thermal performance of a CuO/water nanofluid in a tube.

Xuan et al. [88] proposed a thermal Lattice Boltzmann model for flow and energy transport simulation of a Cu/water nanofluid. The distinguishing feature of this model is the hypothesis of particle location at a series of lattices, presenting a Boltzmann distribution within these. Another relevant feature is the temperature independence with regard to particle density distribution. The model predicted a 27% enhancement of the nanofluid Nusselt number over that of water alone.

Following their previously cited experimental investigations with regard to Al$_2$O$_3$/water nanofluids under laminar flow, Heris et al. [89] established a model which employed the thermal dispersion theoretical hypothesis, proposed by Xuan and Roetzel [77]. Simulations indicated that maximal heat transfer enhancements could be gained by the simultaneous effect of volume fraction increase and nanoparticle size decrease.
Employing the two-phase approach, Behzadmehr et al. [90] numerically investigated the turbulent flow of a nanofluid through a tube. The model takes into account both nanoparticle and base fluid molecule velocity gradients and uses a numerical solution to enable the application of the constant wall heat flux boundary condition. The authors performed a simulation using the experimental data gathered by Li and Xuan [78], claiming good agreement for the Cu/water nanofluids, contrary to the single-phase assumption for the same experimental data.

Pfautsch [68] conducted a numerical analysis of the thermal transfer behaviour of Al$_2$O$_3$/water and Al$_2$O$_3$/ethylene glycol nanofluids in a flat PHE assuming fluid and nanoparticle continuity, as well as momentum conservation via the Navier-Stokes equation. Due to a high non-linearity of the governing equations, simulations were performed employing the finite difference method. Results demonstrated that the laminar flow convection coefficient increases dramatically with particle size reduction and volume fraction increase. For well dispersed particles in water the maximum enhancement was predicted to be 130%, whereas for ethylene glycol the enhancement was significantly higher, 275%.

More recently, Mohammed et al. [91] conceived a model of an aluminium square micro-channel heat exchanger (25 channels) with the intent to evaluate the thermal performance of four nanofluids (Al$_2$O$_3$, SiO$_2$, Ag and TiO$_2$) under laminar flow. They assumed single-phase fluids and steady-state flow, while simulations followed the finite volume methodology. Simulations proved the better convective heat transfer performance of the Al$_2$O$_3$ nanofluid and the disadvantageous increase in pumping requirements with increasing Reynolds numbers.

Kalteh et al. [92] proposed a two-phase model to study the behaviour of a Cu/water nanofluid in an isothermally heated parallel plate micro-channel. Once again, the governing mass, momentum and energy equations were solved via the finite volume method using a non-uniform mesh. Perhaps anticipating the more anomalous behaviour reported in experimental studies for singular tube exchangers, the mesh was most refined in the micro-channel entry region. Consequent simulations demonstrated independence between particle viscosity and Nusselt number at Re=100. As with the Behzadmehr et al. [90] model, a comparison with the homogeneous single-phase assumption indicated the higher precision of the two-phase approach.

A unique numerical study was established by Manca et al. [93] in assessing the heat transfer enhancement resultant of an Al$_2$O$_3$/water nanofluid employed in confined slot jet impingement on a heated wall. The single-phase approach was used and the impingement temperature was considered constant. Other relevant considerations included steady-state, turbulent and constant property flow conditions, as well as nanofluid incompressibility.

Heris et al. [94] performed numerical simulations to evaluate the thermal behaviour of Al$_2$O$_3$, CuO and Cu nanoparticle suspensions in water under constant wall temperature boundary conditions when transiting through a square duct, which is less penalizing in pressure drop but limited in heat transfer when compared to the circular profiles. In an analogous approach to that taken by Kalteh et al. [92], the model was composed of a non-un-
form mesh, finer elements packed in the duct entrance region. Of the tested nanofluids, the Cu/water presented the best thermal characteristics, Al₂O₃ displaying the worst.

7. Conclusions

Despite the extensive research on nanofluids, especially spherical particle types, a precise description of the anomalous heat transfer enhancements experimentally displayed is still a paramount limitation. The influential factors, as well as the precise quantification of their contribution to the observed results, remain a source of speculation amongst the scientific community. This is the major issue that currently forbids the employment of nanofluids in practical applications, which could do wonders in reducing fluid inventories and heat exchanger sizes. Obviously, both of these features converge in assisting the achievement of a worldwide goal: sustainable development. Therefore, a full understanding of how nanofluids will perform under real operating conditions is an important goal and a new frontier concerning the sustainable development promotion.

Of the reviewed literature, a limited amount of investigations regarding CNT nanofluids is currently available. A consensual position of the respective authors is that CNT nanofluids exhibit significantly higher thermal properties enhancements than other nanofluids, which indicates that these will promote top efficiencies when used in heat exchanging devices. To this extent, any enlightenment on the possible enhancement mechanisms, as well as the level at which these contribute to such promising behaviour, would be welcome. It can easily be concluded that the lack of experimental and theoretical studies regarding the convective heat transfer behaviour of nanofluids is currently their application in real industrial processes.

In the past few years, with the growing interest concerning nanofluids, some researcher groups have dedicated their attention to the analysis of the thermal properties of CNT based nanofluids, extended to the study of the influence of nanofluid preparation, stabilization and testing conditions, which are time-consuming and expensive tasks. However, with a view to attempting an adequate prediction of the thermal performance of these nanofluids, consistent experimental data is being gathered. This systematic approach is expected to fulfil the imperative requirement of behaviour prediction and allow further progress of these CNT nanofluid studies and some innovative and validated models are expected to be proposed in a near future.

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² Physical and Chemical Properties of Carbon Nanotubes
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