

Review

Review on Synthesis, Thermo-Physical Property, and Heat Transfer Mechanism of Nanofluids

Mahesh Suresh Patil ¹, Jae-Hyeong Seo ², Suk-Ju Kang ^{3,†} and Moo-Yeon Lee ^{1,*,†}

¹ Department of Mechanical Engineering, Dong-A University, Hadan 840, Saha-gu, Busan 604-714, Korea; msp692@gmail.com

² Research and Development Division, Nano Thermal Fusion Technology Company (NTF TECH), Hadan 840, Saha-gu, Busan 604-714, Korea; cheonchw@naver.com

³ Department of Electronic Engineering, Sogang University, 35 Baekbeom-ro, Mapo-gu, Seoul 04107, Korea; sjkang@sogang.ac.kr

* Correspondence: mylee@dau.ac.kr; Tel.: +82-51-200-7642

† These authors contributed equally to this work.

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Abstract: Nanofluids are suspended nano-sized particles in a base fluid. With increasing demand for more high efficiency thermal systems, nanofluids seem to be a promising option for researchers. As a result, numerous investigations have been undertaken to understand the behaviors of nanofluids. Since their discovery, the thermo-physical properties of nanofluids have been under intense research. Inadequate understanding of the mechanisms involved in the heat transfer of nanofluids has been the major obstacle for the development of sophisticated nanofluids with the desired properties. In this comprehensive review paper, investigations on synthesis, thermo-physical properties, and heat transfer mechanisms of nanofluids have been reviewed and presented. Results show that the thermal conductivity of nanofluids increases with the increase of the operating temperature. This can potentially be used for the efficiency enhancement of thermal systems under higher operating temperatures. In addition, this paper also provides details concerning dependency of the thermo-physical properties as well as synthesis and the heat transfer mechanism of the nanofluids.

Keywords: nanofluid; heat transfer; heat transfer coefficient; thermal conductivity; synthesis

1. Introduction

Heat transfer is a basic and significant phenomenon in many industrial processes and thermal systems. In the design of thermal systems, the development and research of technologies for the improvement of the thermal properties of the working fluid for the enhancement of the overall heat transfer efficiency are crucial. Conventional fluids used in various thermal systems have poor thermal properties, which eventually causes systems to operate at lower efficiency. Along with that, advanced fluids for the enhancement of the heat transfer efficiency of various thermal systems have been required for global competition and the environmental challenges associated with the miniaturization of systems. The macro-level understanding of heat transfer has been comprehensively considered with the flow regimes and patterns of working fluids, including phenomena like laminar or turbulent flow, with applicable heat transfer mechanisms. Based on earlier literature reviews, many researchers have studied the application of the high thermal conductivity of metals in a base fluid using mini- and micro-level-sized metal particles. Nanofluids are a new class of fluids which have gathered attention owing to their superior thermal properties, having superior stability with lower erosion problems compared to micrometric suspensions. Additionally, nanofluids have a large surface area with less particle momentum and high mobility, which makes them a potential candidate

for suspension in working fluids. Sidik et al. [1] summarized the methods used by various researchers for the preparation of stable nanofluids. The authors also suggested methods to make nanofluids homogeneous and long-term stable. Koblinski et al. [2] mentioned the poor characterization of a nanoparticle suspension in a base fluid, and the lack of knowledge of the mechanism involved in the heat transfer of the nanofluids are major hindrances to the development of the nanofluids. Contradictory results have been published on the properties of nanofluids. So, the international nanofluids property benchmark exercise (INPBE) was conducted by 34 organizations around the world to compare thermal conductivity data obtained by different experimental approaches for identical samples for various types of the nanofluids [3]. Torri et al. [4] experimentally investigated the heat transfer performances of an aqueous suspension of graphene oxide nanoparticles, and showed enhancements to the heat transfer performance with some pressure losses as compared to a pure water. You et al. [5] demonstrated enhancements of boiling heat transfer through nanofluids and nanoparticle coatings. Numerous studies on nanofluids firstly introduced by Choi et al. [6] have been investigated for usage of working fluids in various research and application fields. The published articles have mostly considered the various parametric effects on the thermo-physical properties of nanofluids. However, the sparse results show disorderliness and sometimes contradictions. Nanofluid synthesis methods with different conditions could alter the physical and chemical properties of the final product, and various parameters could influence the thermal properties of nanofluids, indicating the creation of a large data base for precise application. Additionally, a deeper understanding of heat transfer mechanisms, such as Brownian motion, ballistic phonon transport, layering, and clustering phenomena is crucially required. Namely, the understanding of nanofluid synthesis, thermo-physical properties, and heat transfer mechanisms for the development of more stable and advanced nanofluids requires further research in many industrial processes and thermal systems for the improvement of heat transfer. Therefore, in this paper, the research trends and discussions on nanofluid synthesis, thermo-physical properties, and the heat transfer mechanism are surveyed, and especially, a review of the related papers published between 1993 and 2016 has been conducted in order to provide a state-of-the-art review.

2. Nanofluid Synthesis

It was observed long ago that the inclusion of solid particles in the working fluid could be advantageous for the enhancement of the heat transfer efficiency, considering the enormous thermal conductivity of metals compared to base fluids. Earlier attempts to disperse millimeter/micrometer-sized particles in working fluid have resulted in clogging and sedimentation issues. Compared to this, nanofluids have been found to be more stable due to good suspension and lesser clogging. Even though advancements have been made in nanofluid preparation, there is still the challenge of particle agglomeration in the base fluid, which may be due to high surface area and activity [7]. To achieve stable nanofluids, numerous investigations have been carried out on particle motion and sedimentation for different flow analysis. In order to hinder the agglomeration, various surfactants have been used to create a repulsive force, thereby decreasing the amount of agglomeration.

There are two major methods for the preparation of nanofluids. The first is a one-step method, and the second is a two-step method. In the preparation of nanofluids, the two-step method is the most commonly used economical method [8,9]. In this method, the nanoparticles, nanofibers, nanotubes, or other nanomaterials are first produced as a dry powder by chemical, physical, or laser methods. As a second step, intensive magnetic force agitation, ultrasonic agitation, high shear mixing, ball milling, etc. is used to disperse nanoparticles into a base fluid. Agglomeration is considered as one of the major issues in the preparation of a nanofluid [10]. The strong interparticle van der Waals force is considered to affect the stability of nanofluids, as this enhances the aggregation between nanoparticles. Although this method might have some disadvantages, the large-scale production of nanofluids using the two-step method is recognized as economical [11]. Ultrasonic vibrators or mixing devices are used to stir the nanopowder with base fluid to decrease particle agglomeration [12].

Several studies have used the two step method for the synthesis of nanofluids [13–16]. Some researchers have advocated that the two step method is advisable for the synthesis of oxide particles suspended in a nanofluid rather than metal particles suspended in a nanofluid [17]. A significant area of research and application in nanofluids centers around the preparation of a fluid that is stable for a longer duration [18]. Although the two-step method is economical, this method poses the problems of drying, storage, and transportation. Additionally, the stability and thermal conductivity of the produced nanofluids are not optimal. Poor stability due to the agglomeration is the major drawback of the two-step method. In order to overcome this issue, the one-step method has been introduced. The one-step method is the process of simultaneously making and dispersing the particles in the fluid. It consists of direct evaporation and condensation, the submerged-arc nanoparticle synthesis system (SANSS), and laser ablation [11,19,20]. In these methods, metals are vaporized using physical processes and then cooled into liquids to synthesize nanofluids. These physical methods have admirable control over the size and stability of nanofluids, the nanoparticles are uniformly distributed in the base fluid, and there is a reduction in production costs, making these one-step methods an attractive option.

Different dielectric liquids with different thermal conductivities (influencing different morphologies) are used in vacuum-SANSS method. Nanoparticles display different types of morphologies, such as needle-like, polygonal, square, and round shapes, with reasonably good avoidance of particle aggregation [8]. Meanwhile, residual formation due to an incomplete chemical reaction is the major drawback, as the residual remains in the prepared nanofluid, creating an undesirable impurity effect. A newly-developed chemical solution method (CSM) attempts to produce nanofluids with better stability and thermal conductivity. A distinguishable advantage of employing a one-step method is that parameters affecting the synthesis process, such as temperature, pH, reactant and additive types, and concentration can be varied, and desired micro-structures can be targeted. However, overall, for large scale production, the one-step method is less suitable [21–23].

Hwang et al. [16] conducted experimental investigations of homogeneous dispersions of nanoparticles in nanofluids. They tested the effect of different techniques for the dispersity and stability of nanoparticles in nanofluids. To inspect the usefulness for nanofluid synthesis, different physical treatments based on the two-step method have been verified and tested. The study indicated that out of stirrer, ultrasonic bath, ultrasonic disruptor, and high-pressure homogenizer, the homogenizer was the most effective method for breaking the agglomeration. Lo et al. [20] prepared Cu-based nanofluids using submerged arc nano-synthesis by selecting copper as the electrode and using different dielectric liquids. They discussed the effects of experimental parameters and dielectric liquids on the characteristics of the final product (Table 1). Drzazga et al. [24] studied the influence of nonionic surfactants (Rokanol K7 and Rokacet 07) on the particle size distributions, zeta potential, nanofluid flows, and thermal properties. It was found that the addition of small amounts of nonionic surfactant reduced the Darcy friction factor of nanofluids for smaller Reynolds numbers.

Table 1. Effect of process parameters on the composition and morphology of particles obtained by the submerged-arc nanoparticle synthesis system (SANSS) [20].

Sample Code	A	B	C	D	E
Current (A)	9	9	9	6	4.5
Voltage (V)	220	220	220	220	220
Pressure of chamber (Torr)	30	30	30	30	30
Pulse duration (ms)	12	12	12	25	25
Pulse-off time (ms)	12	12	12	25	25
Dielectric liquids	De-ionized water	30% ethylene glycol	50% ethylene glycol	70% ethylene glycol	Pure ethylene glycol
Temperature of dielectric liquid (°C)	2	2	2	2	2
Composition	CuO	Cu ₂ O	Cu ₂ O	Cu ₂ O	Cu
Morphology	Needle-like	Polygon	Polygon, square	Square	Ball-like

This section deals with studies related to nanofluid synthesis. The one-step method and the two-step method for nanofluid preparation were discussed, highlighting the advantages and issues associated with each method. The two-step method has a major stability issue which arises due to agglomeration, while the one-step method may create impurities if the reaction remains incomplete, forming residuals. Based on the published article reviews, the above results indicate that the thermo-physical properties and heat transfer performances depended on the stability, dispersity, and the method of preparation. Research related to keeping nanofluids active and stable for longer durations is one of the areas requiring immediate attention. Additionally, future research on the performance of nanofluids, focused on the advancement of techniques to prepare more stable nanofluids, is also expected.

3. Thermo-Physical Properties

3.1. Thermal Conductivity

Before the discovery of nanofluids, many researchers tried to enhance thermal conductivity (thereby increasing the heat transfer) by mixing nanoparticles into the working fluid. Lee et al. [25]—while a conducting experiment on Al_2O_3 and CuO nanoparticles—suggested that particle size and shape are dominant in improving the thermal conductivity of nanofluids. Pryazhinikov et al. [26] conducted systematic measurements of the thermal conductivity coefficients of more than fifty nanofluids based on water, ethylene glycol, and engine oil, with different nanoparticle suspensions of SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , CuO , and diamond. The authors concluded that there is no direct correlation between the thermal conductivity of the nanoparticle material and the thermal conductivity of the nanofluid containing these particles, which is a quite different and important finding, considering the various attempts made by researchers to postulate the existence of such a relationship. The authors also showed that Maxwell theory is insufficient to calculate the thermal conductivity of nanofluids, as nanofluid properties are functions of particle size, material, type of base fluid, and concentration. Masuda et al. [27] studied the alterations in the thermal conductivity using fine powders of Al_2O_3 , SiO_2 , and TiO_2 . They reported that the thermal conductivity increased in the case of Al_2O_3 and TiO_2 , but did not change greatly in the case of SiO_2 . Xie et al. [28] prepared and measured the thermal conductivity of nanosized SiC (silicon carbide) in deionized (DI) water. They reported the effects of morphologies (size and shape) on the enhancement of the thermal conductivity of the nanoparticle suspension. For a SiC -26 particle suspension in $\text{DI-H}_2\text{O}$, the authors found a 15.8% enhancement in thermal conductivity at the volume concentration of 4.2%. Similarly, for a SiC -600 particle suspension in $\text{DI-H}_2\text{O}$, a 22.9% increase was noted at a volume concentration of 4.0%. Eastman et al. [17] investigated the thermal conductivity of ethylene glycol with Cu nanoparticle size of 10 nm. The thermal conductivity at the volume concentration of 0.3% was improved up to 40% in a dispersion of Cu nanoparticles in ethylene glycol. Paul et al. [29] synthesized Al-5 wt% Zn nanoparticles and investigated the thermal conductivity of nanofluids after dispersing them in ethylene glycol as a base fluid. They found an enhancement of 16.0% in thermal conductivity for nanoparticle dispersions at a volume concentration of 0.1%. They also reported that the thermal conductivity ratio of Al-5 wt% Zn dispersed in ethylene glycol decreased as the crystalline/grain size of the particles increased. Eastman et al. [30] carried out an investigation of water-based nanofluids containing CuO nanoparticles. They found a 20% enhancement of effective thermal conductivity when CuO nanoparticles were added to the water at a volume concentration of 5.0%. They also reported a 15% improvement in the heat transfer coefficient of the water under dynamic flow conditions when CuO nanoparticles at a volume concentration of 1.0% were added to the water. Das et al. [31] investigated the thermal conductivity of two different nanofluids with Al_2O_3 and CuO nanoparticles suspended in the water using a temperature oscillation technique. They showed drastic increases in the thermal conductivity over the temperature ranges of 21 °C to 51 °C.

Since the invention of the nanofluids, many researchers have studied the enhancement of the thermal conductivity of the working fluids of thermal systems. Choi et al. [32] conducted experiments on nanotube-in-oil suspensions, and found that thermal conductivity increases anomalously greater than theoretical predictions, and that the increase is nonlinearly dependent on concentration. The authors found that nanotubes showed the highest thermal conductivity enhancement of around 2.5 times the base fluid thermal conductivity, and that the size and shape of the nanotubes play a vital role (aspect ratio ~2000).

Liu et al. [33] conducted experiments on carbon nanotube (CNT)-based nanofluids, and for CNT–ethylene glycol suspensions, a 12.4% increase in thermal conductivity for 1 vol% was reported, while for a CNT–synthetic engine oil suspension, a 30% enhancement was observed at a volume fraction of 2 vol%. The increase was much larger than in CuO-based nanofluids, and the authors reasoned that Brownian motion at the nanoscale level is responsible for controlling the thermal conductivity of nanofluids. Hwang et al. [34] investigated the thermal conductivity of four different nanofluids using a transient hot wire method; namely, water-based multi-walled carbon nanotubes (MWCNT), CuO nanoparticles, SiO₂ nanoparticles, and ethylene-based CuO nanoparticles. Among these four, MWCNT-based nanofluids showed the highest increase of 11.3% in thermal conductivity at a volume concentration of 1.0 vol%. Xing et al. [35] reported a study on the thermal conductivity enhancement of water-based nanofluids with different types of CNTs. Table 2 shows the properties of short single walled nanotubes (S-SWNTs), long-single walled nanotubes (L-SWNTs), and multi-walled nanotubes (MWNTs) with different aspect ratios and special surface area. At 0.48 vol%, when temperature was increased from 10 to 60 °C, the thermal conductivity values increased from 0.604 to 0.707, 0.580 to 0.654, and 0.627 to 0.760 W/m·K, respectively, for S-SWNTs, L-SWNTs, and MWNTs. The authors argued that the values of the thermal conductivity enhancement were different from literature because of the different sizes of CNTs and the preparation process. At a constant temperature of 30 °C and a volume concentration of 0.24 vol%, the relative increments of thermal conductivity were 7.54%, 3.33%, and 2.75% for L-SWNTs, S-SWNTs, and MWNTs. The authors concluded that L-SWNTs are a promising option for the enhancement of the thermal conductivity of water-based nanofluids, advocating that the higher aspect ratio was advantageous for the thermal conductivity enhancement and that a higher surface area provides a larger contact area, which may result in a decrease in interfacial contact resistance. Farbod et al. [36] concluded that the length of CNTs reduces due to the functionalization, and because of this, the thermal conductivity increases. This is in contrast with [35], which concludes that the thermal conductivity of SWNTs increases with length. Xing et al. [37] concluded that the SWCNTs exhibit good thermal performance in the laminar flow regime, whereas in the turbulent flow regime, viscosity increase offsets thermal conductivity enhancement, indicating a need for the selection of operational temperature and concentration of SWCNTs for better thermal performance under the turbulent flow regime.

Table 2. Properties of carbon nanotubes (CNTs) [35]. S-SWNT: short single-walled nanotubes; L-SWNT: long single-walled nanotubes; MWNT: multi-walled nanotubes.

Properties	S-SWNTs	L-SWNTs	MWNTs
Outer diameter (nm)	1–2	1–2	10–30
Inner diameter (nm)	0.8–1.6	0.8–1.6	0.8–1.6
Length (um)	1–3	5–30	~30
Aspect ratio	500–3000	2500–30,000	1000–3000
Special surface area (m ² /g)	>380	>380	>100
Thermal conductivity	~4000	~4000	~2000
Pure density (g/cm ³)	2.1	2.1	2.1
Purity	>90%	>90%	>90%

Hajjar et al. [38] conducted experiments on graphene oxide nanofluids at temperatures of 10, 20, 30, and 40 °C, with varying concentrations of 0.05, 0.10, 0.15, 0.20, and 0.25 wt%, and concluded

that a maximum thermal conductivity enhancement of 47.54% was observed for 0.25 wt% graphene oxide at a temperature of 40 °C. Kamtchi et al. [39] conducted experimental studies on a graphene oxide–water nanofluid and reported thermal conductivity enhancements of 0.82%–3.51%, 1.58%–6.71%, and 3.96%–10% for concentrations of 0.01, 0.1, and 0.3 g/L, respectively. The authors pointed out that these enhancements were higher compared to aqueous Al₂O₃, CuO, and diamond nanofluids for the same concentrations, and reasoned that this may be due to enhanced Brownian motion. Many researchers have developed analytical models to predict the thermal properties of nanofluids [40–42]. In these models, the requirement of the empirical determination of a few parameters on a case-by-case basis makes it less suitable for using it for the design and optimization of new or existing materials. Wang et al. [43] developed a 3-D numerical model to predict the thermal conductivity enhancement of carbon fiber composites using a lattice Boltzmann scheme to solve governing energy transport equations, which requires no empirical parameters. However, this model predicted slightly lower values than experiment data, probably due to non-consideration of convective heat transfer in fiber–oil suspension.

The above discussion concluded the significance of thermal conductivity in nanofluid applications in various areas. The thermal conductivity is affected by the concentration of the nanoparticle, the size of the nanoparticle, and operating temperature. The increase of the thermal conductivity with an increase of the temperature is an interesting phenomenon which could be potentially used for the efficiency enhancement of thermal systems under higher operating temperatures.

3.2. Viscosity

Pak et al. [44] investigated the turbulent frictions and heat transfer behaviors of Al₂O₃ and TiO₂ nanoparticles suspended in water, and conducted viscosity measurements using a Brookfield viscometer. They announced that the relative viscosities (dimensionless) of Al₂O₃ and TiO₂-based working fluids with 10% volume concentration were 200 and 3 times larger than that of water, respectively. These viscosity results are significantly larger when compared with the predictions of the classical theory of suspension rheology. Sabiha et al. [45] found that the viscosity of SWCNT nanofluids increased with nanoparticle concentration, whereas it decreased with increasing temperature. Viscosities of SWCNT nanofluids were reported to be 1.18, 1.21, 1.23, 1.26, and 1.28 mPa s for nanoparticle concentrations of 0.05, 0.1, 0.15, 0.2, and 0.25 vol%, respectively, at a constant temperature of 20 °C. For temperatures of 20, 30, 40, 50, and 60 °C, the viscosities were 1.18, 0.95, 0.81, 0.75, and 0.67 mPa·s, respectively, at a constant volume concentration of 0.05 vol%. These results indicated the non-linear variation of viscosity with volume concentration and temperature. Esfahani et al. [46] found that the increases in viscosity of graphene oxide nanofluids at 0.01 and 0.5 wt% (T = 25 °C, shear rate 100 s⁻¹) were 38% and 130%, respectively, and attributed it to the formation of agglomerations in suspension.

Hussein et al. [47] experimentally investigated the thermal properties of different types of nanoparticles (Al₂O₃, TiO₂, and SiO₂) dispersed in water. Figure 1 shows the effect of the nanoparticle volume concentration on the viscosity. They computed the effect of the nanofluid concentration on the friction factor. They concluded that the viscosity increased with the concentration, the highest being at a volume concentration of 2.5%. Lee et al. [48] conducted experiments on Al₂O₃–water nanofluids. They found that the viscosity significantly decreased with increasing temperature. Table 3 shows the enhancement in the effective viscosity of Al₂O₃ nanofluid at various nanoparticle concentrations at 21 °C. The viscosity variations were nonlinear, even for low nanoparticle concentrations. Meanwhile, the variations of the thermal conductivity with nanoparticle concentration were linear.

The above discussions indicate the significance of viscosity as a crucial property for defining nanofluid behavior. It is found that the viscosity of nanofluids increases with the particle concentration, and decreases with increasing temperature.

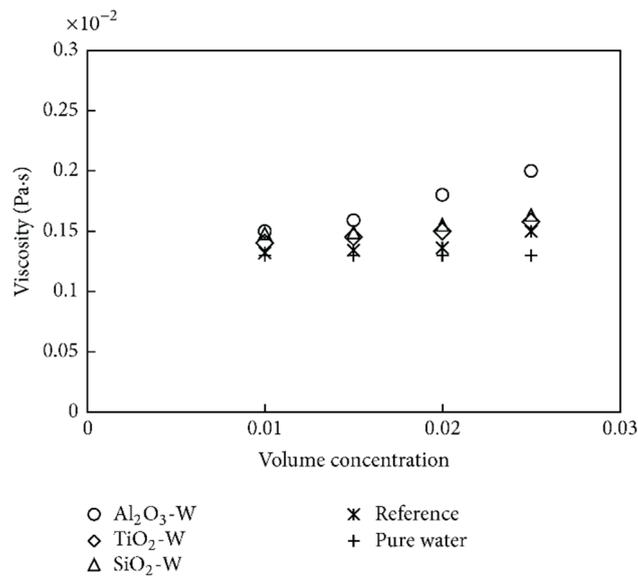


Figure 1. Viscosity of nanofluid and base fluid at different volume concentrations [47].

Table 3. Enhancement in the effective viscosities of Al_2O_3 nanofluids at various nanoparticle concentrations at 21 °C [48].

Concentration (%)	0.01	0.02	0.03	0.1	0.2	0.3
Enhancement (%)	0.08	0.11	0.89	1.74	2.51	2.9

3.3. Heat Transfer Coefficient

It is believed that a significant reason for heat transfer enhancement for nanofluids—apart from the anomalous increment in thermal conductivity—are eddy or turbulence magnification, Brownian motion, and boundary layer modifications. Xual et al. [49] investigated the convective heat transfer coefficient and the friction factor of water based nanofluids with Cu nanoparticles under turbulent flow. They concluded that the suspended nanoparticles improve the heat transfer, with nanofluids having a better heat transfer coefficient compared to the basic working fluid. They proposed a heat transfer correlation and also affirmed that there was no pumping loss for nanofluids containing a low volume fraction of suspended nanoparticles. Ding et al. [50] studied the heat transfer of a water-based nanofluid with multi-walled carbon nanotubes (MWCNTs) in a horizontal tube. They found that the improvement in heat transfer depended on the Reynolds number, CNT concentration, and pH. They also discussed the enhancement in heat transfer as a function of the axial distance from the inlet (Figure 2a). Figure 2b shows the variations of the heat transfer coefficient with respect to the axial distance. While studying the variations of the effective thermal conductivity when CNT concentration was varied at different temperatures, they found a discrepancy with previously published results at 30 °C [32,51–53]. They suggested that the discrepancy might be associated with the thermal properties and the aspect ratio of CNT used, as well as the liquid–CNT interfacial resistance. While discussing the effect of pH, they concluded that the heat transfer coefficient was larger at pH = 6 than at pH = 10.5. Figure 3 shows the effect of pH on the convective heat transfer.

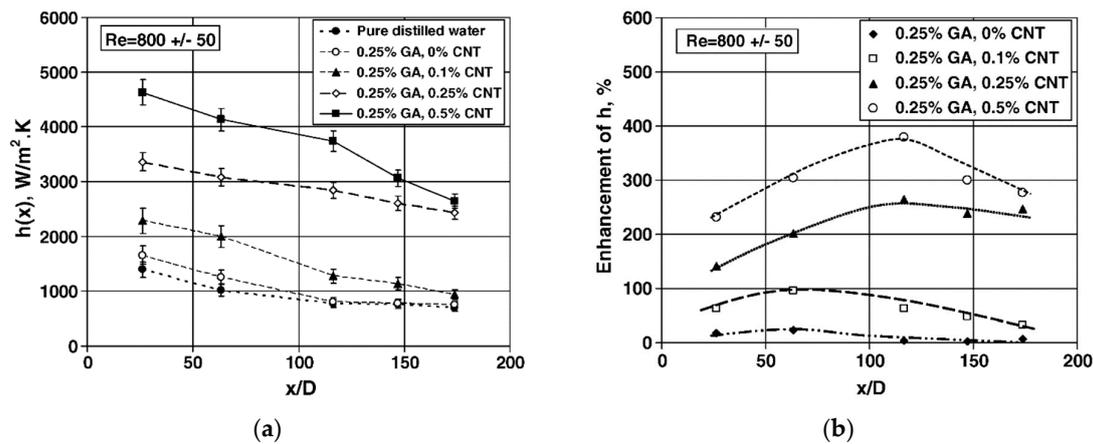


Figure 2. Viscosity of axial profiles of heat transfer (a) coefficient and enhancement of heat transfer coefficient (b); for different CNT concentrations ($pH \approx 6$) [50].

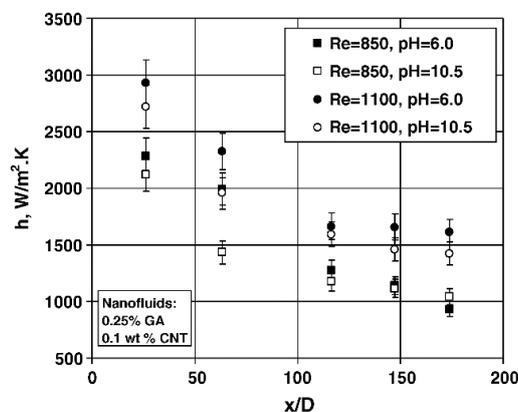


Figure 3. Effect of pH on the convective heat transfer [50].

Some researchers have studied the potential of using nanofluids in heat exchangers as the working fluid. Sarafraz et al. [54] conducted experimental studies on MWCNT nanofluids inside a plate heat exchanger, and found that at volumetric concentrations of 0.5 and 1 vol%, the Nusselt number increased to $\sim 7\%$ and $\sim 14\%$ respectively, while for 1.5 vol%, the Nusselt number suddenly decreased compared to 0.5 and 1 vol%, indicating that viscosity enhancement could outweigh the thermal conductivity enhancement at higher concentrations. Duangthongsuk et al. [55] investigated the heat transfer coefficient and the pressure drop of TiO_2 -water nanofluids in a horizontal double tube counter-flow heat exchanger with turbulent conditions. They reported that the convective heat transfer coefficient of nanofluids was 6%–11% larger than the base fluid, with a small penalty in the pressure drop. They also concluded that the heat transfer coefficient improved with the mass flow rate of the nanofluids and increased with the decrease of the nanofluid temperature. Figure 4a shows the effect of Reynolds number on the heat transfer coefficient. It is evident from the figure that the convective heat transfer coefficient of the nanofluids is larger than the base fluid at any Reynolds number. The enhancement observed may be due to the increase in the thermal conductivity due to nanoparticle suspension and the large energy exchange due to chaotic movements of nanoparticles. Figure 4b shows the pressure drop comparison between the nanofluids and the water at a volume concentration of 0.2 vol%. It can be seen that there is little difference in the pressure drop of nanofluids when compared to the pressure drop of the base fluid for the given conditions. Another interesting aspect to note is the reduction in the pressure drop when the temperature of the nanofluids is increased. This indicates that the operation of nanofluids at higher temperatures has the dual advantage of higher thermal conductivity along with a reduced pressure drop.

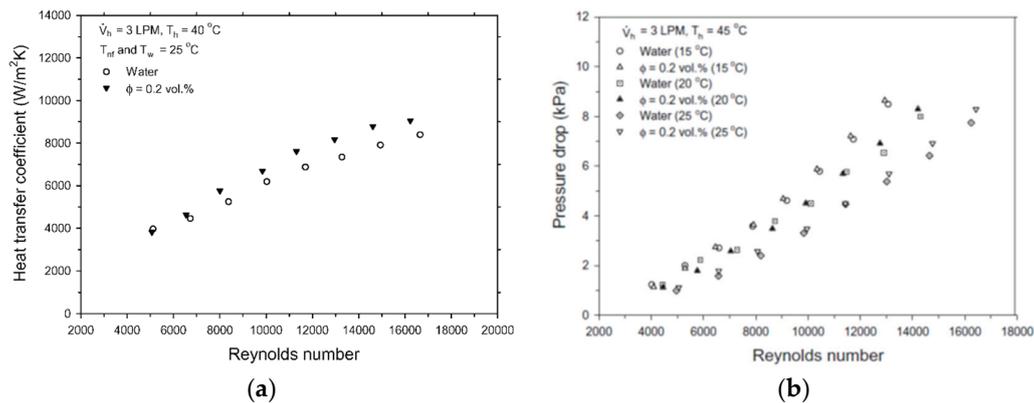


Figure 4. (a) Comparison of heat transfer coefficient obtained from water and that from the 0.2 vol% TiO₂ nanoparticles dispersed in water; (b) Comparison of 0.2 vol% nanofluid pressure drop and water pressure drop [55].

Timofeeva et al. [56] investigated the heat transfer properties of the synthetic oil (Therminol 66) with a suspension of silica particles of 15 nm. They have discussed the effect of the nanoparticle and surfactant concentrations on the nanofluids' properties, such as the thermal conductivity, the viscosity, and the total heat absorption. For an efficient heat transfer, the surfactant-to-nanoparticle (SN) ratio was optimized. Figure 5a shows the non-linear variations of the viscosity with particle concentration. Nanofluids with a suspension at a volume concentration of 1.2 vol% showed Newtonian behaviors, but showed non-Newtonian behaviors at a volume concentration of 3.6 vol%. It can be observed that—particularly for the case of 7.0 vol% nanofluids—an uninterrupted increase in viscosity above 65 °C was indicative of an inadequate low surfactant concentration. Non-polar fluids and inorganic nanoparticles are non-miscible in nature, and Brownian collisions at higher temperatures lead to agglomeration and higher viscosity. Figure 5b shows the linear increment in thermal conductivity with increases of the volume concentration of the nanoparticle. In addition, the authors discussed the effects of SN ratio on thermal conductivity and viscosity. The authors argued that, although a strong agglomeration was observed in the concentrated SiO₂/TH66 nanofluids, no anomalous increase in thermal conductivity was observed. This is contradiction with many studies, which report that agglomeration in nanofluids leads to an abnormal increase in thermal conductivity.

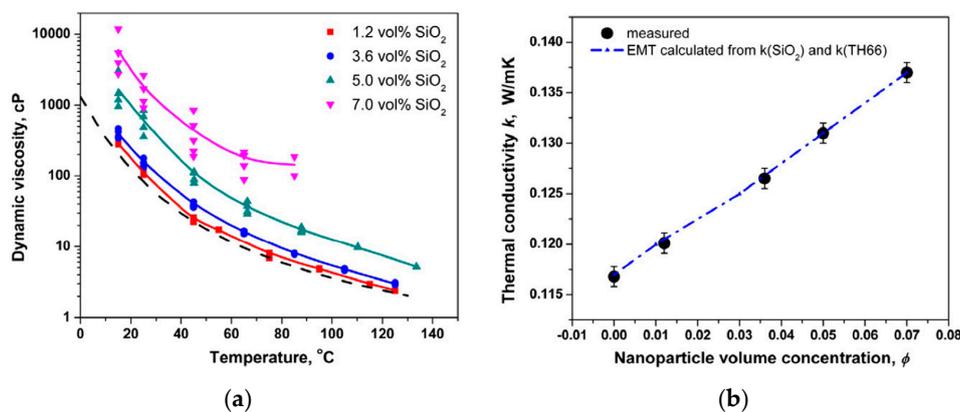


Figure 5. (a) Temperature dependence of the dynamic viscosity of TH66-based nanofluids at various SiO₂ concentrations with ~0.12 M of BAC (Benzalkonium chloride) surfactant. Multiple symbols of the same type and color represent the viscosity at shear stresses from 10 to 40 D/cm² with higher viscosity at lower shear stress; (b) Thermal conductivity of SiO₂ suspensions in TH66 with various particle concentrations and ~0.12 M BAC surfactant. Dashed-dotted line represents the thermal conductivity values calculated from EMT (effective medium theory) equation [56].

Figures 6 and 7a,b show that the effects of SN ratios, and the optimal SN mass ratios were observed to be between 0.5:1 and 1.25:1 for 15 nm SiO₂ nanoparticles. When the solid–liquid or liquid–air interfaces become saturated, it leads to the development of micelles using surfactant. This effect causes enhanced viscosity for suspended particles. The critical micelle concentration (CMC) can be calculated based on minimum viscosity and higher SN ratio at any particular temperature. CMC is dependent on temperature, as it can be seen that the SN ratio corresponding to minimum viscosity changed from less than 0.25:1 at 15 °C to 1.25:1 at 130 °C.

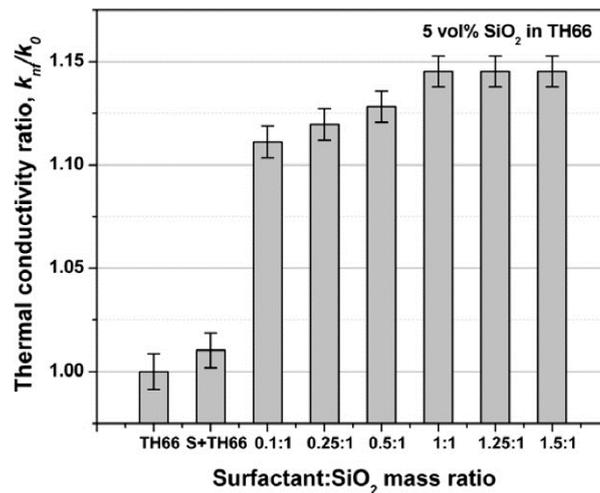


Figure 6. Enhancements in thermal conductivity of 5 vol% SiO₂/TH66 suspensions at various surfactant-to-nanoparticle (SN) ratios. S + TH66 indicates the thermal conductivity measured in a base fluid with the highest surfactant concentration used in the series (i.e., a 1.5:1 ratio) [56].

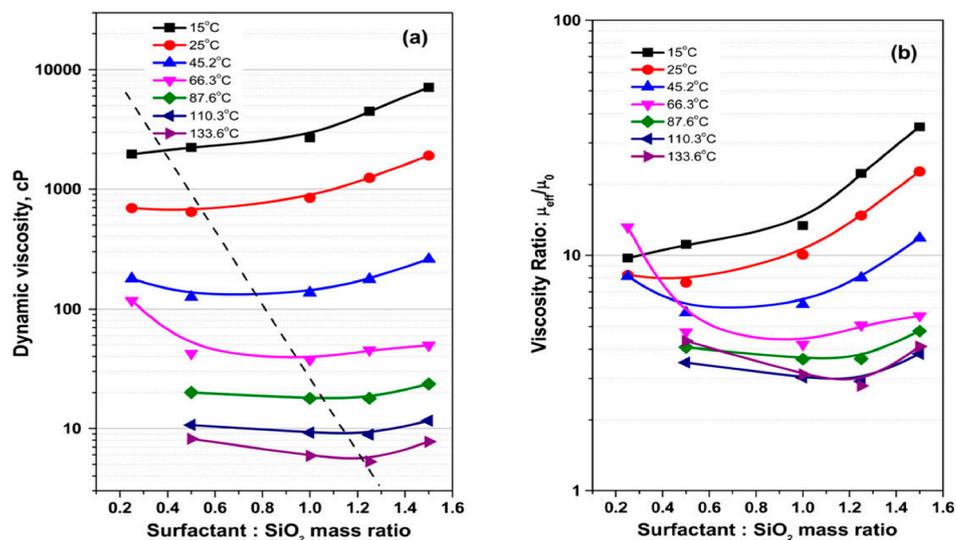


Figure 7. (a) Viscosity; and (b) viscosity ratio of 5 vol% SiO₂/TH66 suspensions at various surfactant-to-nanoparticle ratios. Viscosity values at 20 D/cm² shear stress are used to compare the results at various temperatures and suspension compositions [56].

This section summarized the various parametric effects on the thermo-physical properties of nanofluids. Thermal conductivity, viscosity, and heat transfer coefficient were considered as important properties which influence the heat transfer in nanofluids, eventually deciding the applicability. Among all of the nanofluids, the MWCNT-suspended nanofluids showed higher thermal conductivity, owing to the superior thermal properties of CNTs. The dependence of the thermo-physical properties

of nanofluids on a range of parameters, including size, shape, concentration, SN ratio, temperature, Reynolds number, and many more makes it difficult to compile the data considering specific applications. Contradictory results, such as agglomeration effects increasing or decreasing thermal conductivity, make it difficult to understand the behavior of the heat transfer mechanism. So, the next section discusses studies related to heat transfer mechanisms responsible for enhanced heat transfer in nanofluids.

4. Heat Transfer Mechanism

Developing an efficient thermal system requires an in-depth understanding of physical phenomena concerned with heat transfer and thermodynamics. The challenges in understanding the mechanism responsible for the enhanced thermal properties of nanofluids are mainly due to the difficulties and limitations associated with characterization in experimentation. Previously, the inability to predict this increase in thermal conductivity using theoretical models was due to the fact that earlier models for solid/liquid suspensions are based on only thermal diffusion (Fourier's law of heat conduction) [32]. It seems that, among the various researchers, there is no single mechanism which is universally accepted to account for the complex physical phenomena taking place during heat transfer in nanofluids. Various models have been proposed to explain the heat transfer mechanism in nanofluids, including Brownian motion, ballistic phonon transport, layering, clustering phenomenon, agglomeration, interface thermal resistance, etc., with sometimes contradictory results. Considering nanofluids, Brownian motion is characterized as spontaneous motions of nano-particles in a base fluid which results in micro-convection phenomenon around nano-particles [57,58]. Koblinski et al. [59] evaluated the four specific mechanisms to understand the fundamentals of heat transport in solid nanoparticle colloids under stationary conditions, and suggested that layering at the solid/surface interface, ballistic phonon transport, and clustering may play important roles, rather than Brownian motion. Cui et al. [60] investigated the mechanisms of heat transfer enhancement due to chaotic movements of nanoparticles using molecular dynamics simulations. The authors compared the time periods of nanoparticles moving and diffusing, and deduced that the movements of nanoparticles are effective in transferring heat in nanofluids. Along with translational movements, nanoparticles have rotational movements. The authors also proved that rotational movements and translational movements enhance the heat transfer by comparing rotational Reynolds number Re_w and translational Reynolds number Re_u . Some studies supported the idea that the enhanced thermal behavior of nanofluids is due to Brownian motion [61–63], while some other researchers concluded that the Brownian motion has a less significant effect [59,64–66].

Some studies have reported that nanoparticle aggregation plays an important role in nanofluids' thermal transport [67–71]. Hong et al. [70] used light scattering effects to show the effects of micron-size Fe nanoparticles' aggregation into clusters on a large enhancement in thermal conductivity. Kwak et al. [71] concluded that the large increase in thermal conductivity and viscosity at low nanoparticle volume fraction is an indication of aggregation effects. This has created interest in understanding the clustering phenomenon, and various studies have been conducted in this regard [72–76]. Interestingly, Prashaer et al. [77] combined aggregation kinetics based on colloidal chemistry with the physics of thermal transport, and found that sedimentation is considerably visible due to aggregation, which negatively affects the thermal conductivity of nanofluids. The authors also discussed that—apart from physical properties such as the thermal conductivities, viscosities, and densities of participating components of nanofluids—the effective thermal conductivity also depends on chemical parameters such as the Hamaker constant, zeta potential, pH, and ion concentration. The dimensions of nano-particles are sometimes comparably similar to or smaller than phonon mean free path, which shifts phonon transport from diffusive to ballistic. There are few studies [78,79] which take into account the effect of ballistic phonon motion while evaluating the contributions of various mechanisms for the calculation of heat transfer enhancements. As nanofluids are suspended in a base fluid, they are characterized by a large amount of solid–liquid surface

interaction, which indicates that a thermal boundary may play a significant role in understanding the dynamics of heat transfer in nanofluids.

The interfacial thermal resistance (also known as Kapitza resistance) is defined as the ratio of temperature discontinuity (ΔT) at the liquid–solid surface interaction and the heat power transporting across a common surface. Some researchers have suggested that Kapitza resistance can play an influential role in the dynamics of thermal flow [80–82]. In some studies, the Maxwell model had been reworked with some modifications to account for the effect of interface thermal resistance. Huaqing et al. [83] assumed that the thermal conductivity distribution from solid–interface layer–liquid is continuous, where bulk liquid, nanoparticle, and intermediate states between them are considered. It was reported that a comparison of experimental and theoretical data provided good prediction, where the heat conduction equation was solved assuming the layer thickness as 2 nm. Interestingly, however, Koblinski et al. [59] assumed that the thermal conductivity of the layer cannot be more than the nanoparticles, and hence layering cannot increase thermal conductivity of nanofluids above the limit.

Jang et al. [84] developed a theoretical model to explain the fundamental significance of the dynamic nanoparticles in the nanofluid. They pointed out that the developed model predicted the effects of particle concentration, particle size, and temperature on the thermal conductivity of the considered nanofluid. Figure 8 shows the nanoparticle size-dependent thermal conductivity of the nanofluids. The authors [84] concluded that the Brownian motion of nanoparticles at the molecular level was a crucial factor of the mechanism of the thermal behaviors. Contradicting that, Evans et al. [85] analyzed the nanoparticle suspension using kinetic theory and showed the effects associated with Brownian motion. They insisted that the Brownian motion had a negligible effect on the thermal conductivity of the nanofluids. They concluded that the anomalous increase in thermal conductivity was observed due to particle clustering. Wamkam et al. [86] studied the effects of pH on the zeta potential, the particle size distribution, rheology, viscosity, and stability of the nanofluids containing ZrO_2 and TiO_2 nanoparticles. They observed a significant enhancement of the thermal conductivity of nanofluids at a weight concentration of 3.0% for metal oxides of ZrO_2 and TiO_2 nanoparticles. Finally, the experimental results indicated that the stability of the tested nanofluids was influenced by pH.

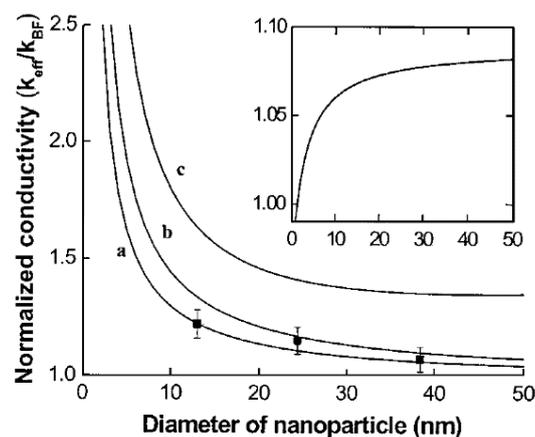


Figure 8. Nanoparticle size-dependent thermal conductivity of nanofluids [84].

Considering the above discussions, it is evident that many theoretical explanations for the anomalous increase in thermal conductivity of base fluids caused by the addition of nanoparticles are provided, but there are many instances where experimental results are quite different than those predicted by existing models. In addition, many contradictory and inconsistent results have been presented by various authors, considering different theoretical models and experimental conditions. Previous studies have mainly argued four different possible mechanisms to explain the heat transfer mechanisms in nanofluids. These are: Brownian motion of nanoparticles, layering phenomenon of liquid at the nanoparticle–liquid interface at the molecular level, ballistic phonon motion, and cluster

phenomenon in nanofluids. Although Brownian motion has limitations, it does have an indirect effect on agglomeration and interface interaction, making it the most eligible mechanism to understand the phenomenon. Many simulation results have shown that layering phenomena fail to address all aspects related to thermal conductivity. The fact that there is little difference in temperature gradient between ordered layer and bulk liquid indicates that layering cannot be the sole reason for heat transfer enhancement. As the nanoparticle size becomes less or comparable to the mean free path of phonons, ballistic motion might be a significant effect. Nevertheless, this cannot be prudent reasoning, as phonons are swifter than ballistic, considering energy transport. The last possible option is clustering phenomena, which can also be observed at low volume fractions, making paths of lower thermal resistance. It is also observed that the evaluation of an optimum loading study is important to maximize thermal conductivity enhancement. Below this optimum loading, there is a large particle free region, thereby not showing maximum enhancement; above this loading, the clusters become more crowded and close packed, which leads to sedimentation.

5. Conclusions

This survey extensively reviewed articles available related to the synthesis, thermo-physical properties, and heat transfer mechanism of nanofluids published in the open literature between 1993 and 2016. Especially, research trends addressing techniques for the synthesis of metal nanofluids, metal dioxide nanofluids, and nanomaterials in fluids, their thermo-physical properties and nanofluids characteristics, such as thermal conductivity, viscosity, heat transfer coefficients, and heat transfer mechanisms were reviewed. Additionally, many parametric effects of nanofluids have been considered. Specifically, parametric effects such as nanoparticle volume concentration, temperature, pH, surfactant–nanoparticle ratio, Reynolds number, and aspect ratio were considered. The heat transfer mechanisms of the nanofluids were discussed, although there is a lack of agreement regarding the heat transfer mechanism and the Brownian effects of the nanofluids. The contradictory reports on the influence of Brownian effects on the nanofluids were especially discussed in an effort to understand the heat transfer characteristics. In addition, this survey is focused on the studies on a single type of nanoparticle with metal, metal dioxide, and nanomaterials such as nanofibers, nanotubes, and graphene dispersed in a base fluid, but more extensive studies could be reviewed on newly-developing hybrid nanofluids, considering parametric effects with thermo-physical explanations in a future article.

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Nomenclature

Φ	Volume concentration (Nanoparticle)
ΔT	Temperature discontinuity
CNT	Carbon nanotube
CSM	Chemical Solution Method
DI	De-ionized
h	Heat transfer coefficient, W/m ² ·K
k	Thermal conductivity, W/m·K
INBPE	International Nanofluids Property Benchmark Exercise
MWCNT s	Multi-walled carbon nanotubes
Re	Reynolds number
SANSS	Submerged-Arc Nanoparticle Synthesis System
SN	Surfactant to nanoparticle ratio

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