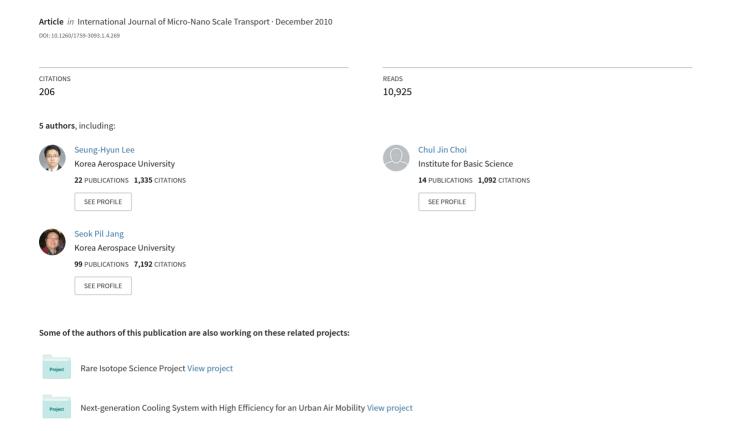
# A Review of Thermal Conductivity Data, Mechanisms and Models for Nanofluids



# A Review of Thermal Conductivity Data, Mechanisms and Models for Nanofluids

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#### **ABSTRACT**

Numerous studies have shown that nanofluids have superb physical properties, among which thermal conductivity has been studied most extensively but remains controversial. In this review article, we first present important milestones in experimental studies that show new features of the thermal conductivity of nanofluids, together with those that show no such special features. After a brief review of the physical mechanisms proposed to explain the thermal conductivity of nanofluids we present a critical review of the classical and new models used to predict the thermal conductivity behavior of nanofluids. We discuss some controversial issues such as data inconsistencies, the sufficiency and suitability of classical and new mechanisms, and the discrepancies between experimental data and model predictions. At the end of our review, we give some directions for future research in nanofluids and to aid researchers in resolving the controversial issues we are still facing in developing nanofluids with superior thermal properties and performance for high heat flux cooling and high efficiency applications.

**Keywords:** nanofluids, thermal conductivity, classical mechanisms, new mechanisms, static model, dynamic model

# **NOMENCLATURE**

- a Radius
- C Constant
- $C_f$  Heat capacity per unit volume of the fluid
- C Heat capacity of a nanoparticle
- c Specific heat
- $\vec{D}_{o}$  Diffusion coefficient
- d Diameter
- *e* Electric charge
- *f* Factorial function
- geq Equilibrium pair distribution function

  Convective heat transfer coefficient
- k Thermal conductivity
- $k_p$  Boltzmann constant
- The average distance for a particle to travel along one direction without changing its direction due to the particle Brownian motion

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- *l* Mean free path
- *n* Number density of nanoparticles
- Pr Prandtl number
- q Heat flux
- Re Reynolds number
- $R_{\rm g}$  The radius of gyration
- $R_{\kappa}$  Kapitza resistance
- r Position
- T Temperature
- t Time
- V Volume

#### **Greek symbols**

- $\alpha$  Thermal diffusivity
- $\delta$  Nanolayer thickness
- $\phi$  Volume fraction (or volume concentration)
- $\mu$  Dynamic viscosity
- $\rho$  Density
- *τ* Particle relaxation time
- Ψ Interparticle potential

#### **Subscripts**

- ag Aggregate
- bf Base fluid
- cl Nanoparticle cluster
- e Equivalent
- eff Effective
- int Particles in the aggregate
- K Kapitza
- layer Interfacial layer (nanolayer)
- p Particle
- pB Caused by Brownian motion of the nanoparticles
- pe Equivalent particle
- peff Effective contribution of the particles
- x Along transverse axesz Along longitudinal axes

# **Superscripts**

eq Equilibrium

# 1. INTRODUCTION

Cooling technology plays a critical role that controls the performance of industrial, consumer, and medical devices and systems. For example, very high density devices (i.e., those with 8-nm features) are anticipated to generate local heat fluxes as high as 10<sup>5</sup> W/cm<sup>2</sup> and the heat fluxes at the die level of 10<sup>3</sup> W/cm<sup>2</sup>, 10 times those of present-day CMOS devices [1]. Inefficient dissipation of the immense amount of heat generated in dense electronics and electronic systems would reduce or limit their performance. Therefore, the thermal management of electronics and electronic systems has been the most important contemporary technology driver for thermal scientists and engineers. Similarly, innovations in the thermal management of the power electronics must be achieved for hybrid electric vehicles [2]. Besides the need for enhanced cooling performance, the increasing demand for energy-savings and emissions reduction makes energy efficiency a pressing issue in the buildings, transportation, power generation, manufacturing, and many other sectors. However, the inherently poor thermal properties of

conventional heat transfer fluids, such as water, oil, and ethylene glycol, are a major barrier to innovations in thermal management and energy efficiency. The development of nanoscale materials provided enormous opportunities across a wide spectrum of critical technologies. In the area of heat transfer fluids, nanoparticles can provide new innovative technologies with potential to tailor the heat transfer fluid's thermal properties through control over particle size, shape, composition, and others. Realizing the unique properties of nanoparticles and their potential to overcome the intrinsic limitation of conventional heat transfer fluids, Choi conceived the concept of nanofluids [3]. The term *nanofluids*, coined by Choi, is defined as a new class of nanotechnology-based heat transfer fluids that are engineered by stably suspending nanosized particles, fibers, sheets, or tubes with average sizes below 100 nm in traditional heat transfer fluids in low volume concentrations (≤1 vol.%) [4].

Numerous experimental studies have shown that nanofluids significantly enhance thermal conductivities [5-13], the convective heat transfer coefficient [14-19], and other properties such as wetting and spreading of nanofluids [20] and heat absorption rate [21]. Because of these unique thermal transport properties and superior performance that are unavailable in traditional heat transfer fluids or conventional particle fluid suspensions, nanofluids have been of great scientific interest to researchers worldwide over the past decade [4]. These novel nanofluids show great promise as next-generation heat transfer fluids for innovative applications in industries such as nuclear power generation, buildings, transportation, aerospace, electronics, tribology, and medicine among others [4, 22]. Besides enhanced thermal properties, nanofluids have other potentially useful properties, such as the formation of nanoporous structures on heated surfaces. Therefore, today's nanofluids technology can be useful to broader applications of nanofluids as nanostructured materials.

In this review paper, we first give an overview of the unique features and major mechanisms of the thermal conductivity, k, of nanofluids (NFs). We then focus our review on the models proposed for enhanced heat conduction in NFs. We also discuss some major issues and challenges related to experimental data, mechanisms and models for NFs from selected works. We present both sides of controversial issues such as data inconsistencies, the sufficiency and suitability of classical and new mechanisms, and the discrepancies between experimental data and model predictions. Finally, we present future research directions in order to address some controversial issues and challenges.

# 2. EXPERIMENTALLY DISCOVERED FEATURES OF THE THERMAL CONDUCTIVITY OF NANOFLUIDS

Thermal conductivity is the most studied property of nanofluids because it is of great theoretical and practical interest to scientists and engineers. Pioneering researchers have discovered that the heat conduction behavior of nanofluids has novel features that are completely lacking in conventional suspensions of micro- or millimeter-sized solid particles. Moreover, the unprecedented thermal transport phenomena in nanofluids surpass the fundamental limits predicted by effective medium theory (EMT), in which thermal diffusion is the only heat conduction mechanism. In contrast to these pioneering discoveries, this unexpected heat conduction behaviors are not observed in some experimental studies. In this section, representative experimental studies from both sides will be presented.

# 2.1. Anomalously high thermal conductivity at low concentrations

Lee  $et\ al.$  [23] and Wang  $et\ al.$  [24] produced oxide nanofluids using a two-step method and showed that the k of oxide nanofluids is slightly greater than that of base fluids or than that predicted by EMT. Therefore, this study did not generate significant interest in oxide nanofluids. Although Eastman  $et\ al.$  [25] and Xuan and Li [26] were the first investigators to make metallic nanofluids containing Cu nanoparticles, using a two-step method the k of their nanofluids was not superior to that of oxide nanofluids. However, researchers took notice when Eastman  $et\ al.$  [5] demonstrated for the first time that copper nanofluids produced by a single-step method show a dramatic enhancement in thermal conductivity (up to a 40% at a particle concentration of 0.3 vol.%) compared to oxide nanofluids produced by a the two-step method. Conventional particle-liquid suspensions require high concentrations (>10%) of particles to achieve such dramatic enhancement. Furthermore, they showed that Cu nanofluids have an anomalous enhancement in thermal conductivity far beyond the predictions

of conventional effective medium theory even at very low volume concentrations (<1 vol.%). Patel *et al*. [7] produced gold nanofluids using single-step chemical methods and observed anomalous enhancements in thermal conductivity at vanishing concentrations. Liu *et al*. [27] synthesized Cu nanofluids using a chemical reduction method with no surfactant and observed that the thermal conductivity was enhanced by up to 23.8% at 0.1 vol.%. Jana *et al*. [12] observed that Cu-water nanofluids show a 74% increase in conductivity at 0.3 vol.%, far exceeding the previous record of 40% [5].

More recently, Garg *et al.* [28] measured the thermal conductivity of Cu nanoparticles in ethylene glycol and also found an anomalous increase, i.e., the measured increase in conductivity was twice the predicted value by the MG theory [29]. These studies show that metallic nanofluids truly stand out as high quality nanofluids. Schmidt *et al.* [30] also reported that the thermal conductivity of  $Al_2O_3/decane$  nanofluids have an anomalous enhancement in thermal conductivity (11% at 1 vol.%) and Philip *et al.* [31] reported very exciting results that the thermal conductivity enhancement of  $Fe_3O_4$  nanofluids under a magnetic field can reach up to 216% at 4.5 vol.%.

In contrast, no anomalous enhancement in thermal conductivity was observed with nanofluids produced by other groups [for example, see 32-36]. These contradictory *k* data highlight the need for more controlled syntheses and accurate characterization and thermal conductivity measurements of nanofluids.

In Figure 1, the thermal conductivity ratio  $k_{eff}/k_{bf}$  is plotted for several kinds of nanofluids from different sources as a function of  $\beta\phi$ , where  $\beta \equiv [k_p - k_{bf}]/[k_p + 2k_{bf}]$  [37] and  $\phi$  is the volume fraction of nanoparticles, and compared with the prediction from the Maxwell model for dilute nanofluids of spherical nanoparticles. The very fact that there are huge differences in k as shown in Figure 1 infers that there are huge differences in the quality of nanofluids. Although a number of data can be predictable, some other experimental results [for example, 5, 10, 24, 38-40] show anomalously high thermal conductivity compared with the predictions of the classical EMT-based model. In general, nanofluids produced by one-step methods have well dispersed and stably suspended nanoparticles and higher thermal conductivities compared to those produced by two-step methods, as shown in Figure 2. Therefore, good dispersion and stable suspension of nanoparticles in the host liquids are prerequisites

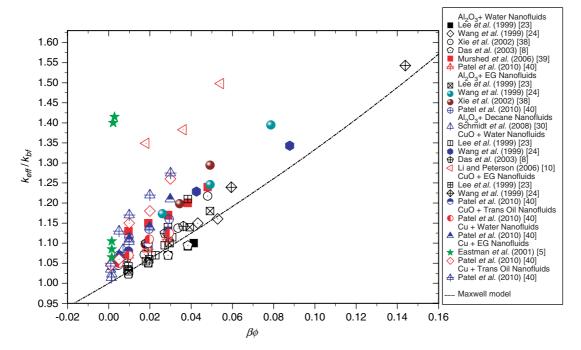
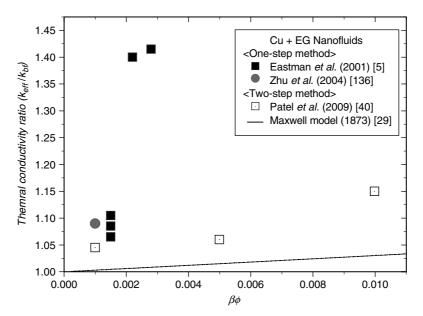
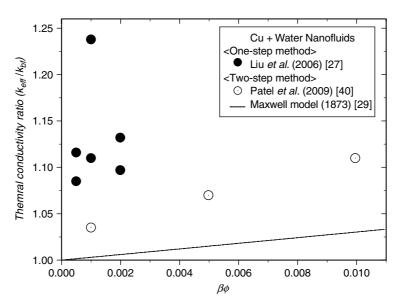


Figure 1. Experimental data on the ratio of thermal conductivity of nanofluids to that of the base fluid as a function of  $\beta\phi$ , where  $\beta\equiv[k_p-k_{bf}]/[k_p+2k_{bf}]$ ,  $\phi$  is the volume fraction of nanoparticles.



(a) Experimental results of thermal conductivity ratio of Cu-EG nanofluids



(b) Experimental results of thermal conductivity ratio of Cu-water nanofluids

Figure 2. Comparison of the thermal conductivity ratio for nanofluids produced using one-step and two-step processes.

for the study of nanofluids properties as well as for their applications. This requirement can be achieved using various dispersion and stabilization methods. However, it is important to keep in mind that some nanofluids containing uniformly dispersed and stably suspended nanoparticles do not have any conductivity enhancement for presently unknown reasons.

# 2.2. Nonlinear relationship between conductivity and concentration

Choi et al. [6] made the first carbon nanotubes (CNT)-based nanocomposite material with the highest

thermal conductivity enhancement ever achieved by dispersing CNTs in a liquid matrix of PAO and discovered that the measured thermal conductivity of the CNT nanofluids is nonlinear with nanoparticle volume fraction at low volume fractions of CNTs. This is another anomalous feature of the k of nanofluids, since predictions by classical EMT show a linear relationship. In an attempt to confirm these results, Xie  $et\ al.$  [41] and Wen and Ding [42] made CNT nanofluids and measured the thermal conductivity of their CNT nanofluids but found smaller enhancements compared to the data by Choi  $et\ al.$  [6]. Finally, Shaikh  $et\ al.$  [43] independently confirmed the previous results on both the large magnitude of enhancements and the nonlinear trend in the thermal conductivity of the CNT-PAO oil nanofluids Choi  $et\ al.$  [6] reported six years ago as shown in Figure 3. This shows that it is neither straightforward nor speedy to reproduce high-quality nanofluids and their anomalous thermal properties. Interestingly, Murshed  $et\ al.$  [44], Hong  $et\ al.$  [45] and Chopkar  $et\ al.$  [11] showed that NFs containing spherical NPs also have strong nonlinear behavior, thereby demonstrating that nonlinear relationship is not limited to CNTs with a high aspect ratio, with which the new phenomenon was first discovered.

## 2.3. Temperature-dependent thermal conductivity

Das *et al.* [8] were the first to show that nanofluids containing spherical nanoparticles have strongly temperature-dependent thermal conductivity. They found that the conductivity enhancement of  $Al_2O_3$  or CuO nanofluids is two to four times that of the base fluid over a temperature range between 20°C and 50°C. Li and Peterson [10] found that the temperature effect is stronger compared to the data of Das *et al.* [8]. This new discovery was confirmed by other research groups [for example, see 7, 46-53]. Temperature dependent thermal conductivity of nanofluids is significant for engineering applications of nanofluids because it raises an exciting possibility to develop "smart" nanocoolants that "sense" their thermal environment and tune their heat conduction property to prevent hot spots. In contrast, other research groups [33, 35, 54-56] measured thermal conductivity of nanofluids and showed no dependence on

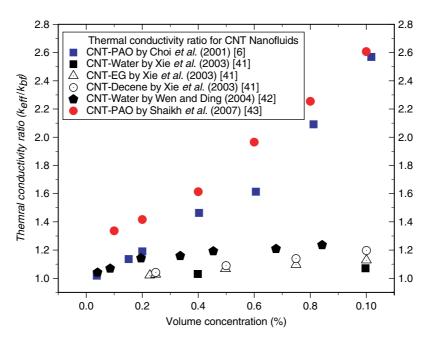


Figure 3. Comparison of the thermal conductivity ratio for CNT nanofluids produced by four groups. Shaikh *et al.* [Shaikh *et al.*, 2007] independently confirmed the magnitude of enhancements and nonlinear trend in the thermal conductivity of the CNT-PAO oil nanofluids Choi *et al.* reported six years ago.

temperature.

# 2.4. Size-dependent thermal conductivity

It has been known that the properties of monodisperse suspensions depend on the particle size [57]. However, Chopkar *et al.* [11] were the first to show experimentally that the effective thermal conductivity of  $Al_{70}Cu_{30}$  nanofluids strongly depends on the nanoparticle size. This is a significant feature of nanofluids. In addition, their study shows a nonlinear relationship between the effective thermal conductivity and the particle size in the particle diameter range of 10–80 nm. Their data clearly show a steeper size dependence in the small particle size range. Size-dependent thermal conductivity of nanofluids also has been observed by Chon *et al.*, [46] and Hong *et al.* [9]. More recently, Kim *et al.* [58] showed that the thermal conductivity of nanofluids increases linearly with decreasing particle size and stated that no existing empirical or theoretical correlation can explain the linear behavior. Strong size effects in nanofluids are significant in practical applications of nanofluids. In contrast, several research groups have shown that the thermal conductivity of nanofluids increases with increasing particle size [for example, see 59, 60].

More recently, Patel *et al.* [40] measured the thermal conductivity of nanofluids to obtain a comprehensive dataset for parameters such as the nanoparticle volume fraction and size and temperature of nanofluids. Their results reconfirmed that the thermal conductivity of nanofluids displays abnormal enhancement that cannot be predicted by Maxwell model, strong temperature dependency, and inverse particle size dependency.

## 2.5. pH-dependent thermal conductivity

Xie *et al.* [38] and Lee *et al.* [61] studied the k of nanofluids under varying pH conditions. Xie *et al.* [38] are the first to show that the thermal conductivity of  $Al_2O_3$  nanofluids increases gradually as the difference between the pH value of nanofluids and the isoelectric point of  $Al_2O_3$  nanoparticle increases. Lee *et al.* [61] found that the k of CuO nanofluids increased by a factor of 3 as pH decreases from the point of zero charge (PZC) of 8 to 3, indicating that CuO nanofluids have a strongly pH-dependent k.

# 2.6. Tunable thermal conductivity under external fields

Philip *et al.* [62, 63] observed that the thermal conductivity of kerosene-based nanofluids containing 6.3 vol.% of magnetite particles has increased up to four times that of the base fluid under an applied magnetic field. Most recently Shima *et al.* [64] showed that the ratio of thermal conductivity to viscosity can be tuned from 0.725 to 2.35 in magnetically controllable nanofluids containing only 0.078 vol.%. These findings demonstrate that magnetically controllable nanofluids can behave like a multifunctional "smart" material that functions both as a coolant and a damper, offering exciting applications in microfluidic devices, MEMS/NEMS, and other nanotechnology-based miniature devices.

# 2.7. High k nanofluids containing surface-modified nanoparticles and/or no dispersants

Because the addition of chemical dispersants and stabilizers could adversely influence the properties of nanofluids, a few research groups produced nanofluids without any dispersants or with surface-modified nanoparticles [8, 23, 65, 66]. Recently, Yu *et al.* [67] made stable nanofluids by dispersing plasma-treated diamond nanoparticles with no surfactants and showed ~20% increase in thermal conductivity at 0.15 vol.% of diamond nanoparticles. This work shows the importance of particle surface treatment. This work also illustrates that methods for making nanofluids without using any dispersants are preferred, especially for reference nanofluids. When dispersants and stabilizers are used, their role in altering the microstructure and properties of nanofluids should be studied.

In summary, the unique features of the thermal conductivity of nanofluids such as anomalously enhanced thermal conductivity at low particle concentrations, a nonlinear relationship between thermal conductivity and particle volume fraction, and temperature- and size-dependent thermal conductivity have been observed in most of the experimental studies carried out over more than 10 years. Nearly all

of the anomalous features have been confirmed by multiple groups. However, there are other groups who have observed no anomalous conductivity with their nanofluids. As a result, whether the anomalous features of the k of nanofluids are real or not has become an issue that has sparked controversy in the nanofluids community. Considering the various synthesis methods and process parameter variations and the experimental difficulties in accurately measuring thermal conductivity of nanofluids, it is understandable that we have this controversy.

The lack of an agreement between experimental data from different groups can be due to differences in sample quality, the dependence of thermal conductivity on many factors, and differences in measurement uncertainties. There are several ways to reduce data inconsistencies due to differences in sample quality. It appears that the primary causes of the significant discrepancies in all nanofluid k data are vast differences in quality between samples that are supposedly identical or at least similar in ingredients and concentrations and uncertainty in characterizing nanoparticles including the size, shape, surface properties, and agglomeration of nanoparticles. Since these characteristics are determined in the production process, the first step in investigating the causes of these data discrepancies as well as in evaluating any physical mechanisms and theoretical models is to produce nanofluids of high quality in terms of stability and thermal conductivity, containing the same concentrations and ingredients, preferably without any dispersants or stabilizers especially for reference nanofluids, using the same processes for making nanofluids. When dispersants and stabilizers are used, their role in altering the microstructure and properties of nanofluids should be understood. Nanofluids produced in this way for thermal conductivity measurements should then be characterized, including particle size and size distribution, shape, surface properties, and structures such as levels of agglomeration/clustering of nanoparticles.

In addition to the differences in sample quality, another major cause of the large discrepancies in the k data is the fact that the k of nanofluids depends on a great number of parameters, some of which are coupled. Experimental studies have shown that the k of nanofluids is determined by parameters related to (1) nanoparticles—e.g., concentration, size [7, 38, 46], shape [5, 7, 68—for spherical; 6, 41—for nonspherical], agglomeration (fractal-like shapes) [8, 23, 26, 44, 61, 69], surface charge [70] and thermal conductivity; (2) base fluids—e.g., thermal conductivity and viscosity; (3) nanofluids—e.g., temperature [7, 8, 10]; (4) the interfacial chemical/physical effect or interaction between the particles and base fluid [41, 61]; and others. Therefore, for meaningful comparison between measured data and critical evaluation of models, it is necessary to measure the k of completely characterized nanofluids including the suspension stability as a function of one variable while the others are fixed. However, this is challenging as indicated by Bang and Heo [71], who have applied axiomatic design theory [72] to the design of nanofluids. Some of the parameters are coupled, and ideas to decouple them are needed.

Another way to reduce data inconsistencies due to differences in sample quality and differences in measurement uncertainties is to conduct round-robin tests using identical test samples and accurate methods and apparatuses for measuring the thermal conductivity of nanofluids. Recently, an international nanofluid property benchmark exercise (INPBE) [73] was launched to validate nanofluid thermal conductivity measurement methods and to resolve the large discrepancies in the k data. The main findings of the exercise are that the thermal conductivity enhancement was consistent between various measurement techniques and that the generalized effective medium theory was in agreement with the measured thermal conductivity data, suggesting that no anomalous enhancement of thermal conductivity was achieved in the nanofluids they tested [73]. It appears that the nanofluids tested in the exercise are not considered high quality. For example, the highest average thermal conductivity ratio of 20% was achieved at 31 vol.% of silica nanoparticles in water. This is much smaller than the theoretical predictions of the EMT of Maxwell or Bruggeman [74]. In contrast, Lee et al. [75] produced ethylene glycol-based ZnO nanofluids containing no surfactant by a one-step physical method, conducted roundrobin tests on thermal conductivity measurements of three samples of surfactant-free nanofluids, and demonstrated that the measured thermal conductivities are beyond the lower and upper bounds calculated using the models of the Maxwell and Nan et al. [76], with and without the interfacial thermal resistance. Therefore, it is highly desirable to make high-quality nanofluids with both suspension stability and high conductivity for use as reference nanofluids as a way to resolve issues such as the anomalous k behavior of nanofluids.

#### 3. MECHANISMS FOR ENHANCED HEAT CONDUCTION IN NANOFLUIDS

As shown in Figure 1, the classic Maxwell effective medium model that assumes the thermal diffusion mechanism underpredicts the magnitude of the thermal conductivity enhancement of most of the nanofluids. Maxwell's model shows that the thermal conductivity of nanofluids depends only on the volume fraction of nanoparticles when the volume fraction is low and the thermal conductivity ratio of nanoparticles to fluid is high. However, the majority of the experimental data described in the previous section shows that the thermal conductivity of nanofluids depends on a number of other parameters such as particle size and fluid temperature and acidity. This implies that classical effective medium theories cannot predict some of the new features of the thermal conductivity of nanofluids. Regarding the hypothesis that some fundamental mechanisms that are missing in classical effective medium theories could change the traditional understanding of how heat is conducted, several investigators proposed new concepts and mechanisms behind the thermal conductivity behavior of nanofluids.

The proposed heat conduction mechanisms in nanofluids can be categorized into static mechanisms and dynamic mechanisms. Static mechanisms, which assume that nanoparticles are motionless in nanofluids, include nanolayer, aggregation and percolation, interface thermal resistance, and fractal geometry. Dynamic mechanisms, which are based on the assumption of randomly moving nanoparticles in nanofluids, include Brownian motion and nanoconvection. These mechanisms are developed on a microscopic level. In this section we present the proposed heat conduction mechanisms in nanofluids from a broader perspective by including microscopic mechanisms such as nanolayer, aggregation, collision of Brownian particles, nanoconvection and macroscopic mechanisms such as dual-phase-lagging conduction. The mechanisms of heat conduction in nanofluids are discussed in more detail in recent reviews by Chandrasekar and Suresh [77], Yu et al. [78], and Wang and Fan [22].

# 3.1. Microscopic static mechanisms

## 3.1.1. Nanolayer of ordered liquid molecules at nanoparticle-liquid interface

Yu *et al.* [79] showed experimentally the existence of an ordered layer of liquid molecules at the solid-liquid interface that had been predicted for years [80]. This nanolayer structure was introduced by Keblinski *et al.* [81] and Yu and Choi [82] as the first static mechanism to explain the enhanced thermal conductivity of nanofluids. Figure 4 shows that the basic concept of nanolayer. Keblinski *et al.* [81] estimated the upper limit for the thermal conductivity enhancement with nanolayer effect by assuming that the thermal conductivity of the liquid nanolayer is the same as that of the solid nanoparticle. Yu and Choi [82] proposed the concept that a nanolayer acts as a thermal bridge between a nanoparticle and a bulk liquid. Based on this new mechanism of a thermal bridge nanolayer, Yu and Choi developed a renovated Maxwell model for the effective thermal conductivity of nanofluids containing spherical nanoparticles with an ordered nanolayer. They extended the concept of the thermal bridge nanolayer to nonspherical particles and renovated the Hamilton-Crosser model [83].

# 3.1.2. Aggregation of nanoparticles

Clustering or aggregation is an inherent property of nanoparticles whether they are in liquid or dry powder form due to van der Waals forces. Keblinski  $et\ al.\ [81]$  conceptualized clustering of nanoparticle as a mechanism of enhanced k of nanofluids, assuming that clustered nanoparticles provide local percolation-like paths for rapid heat transport and increase the effective nanoparticle volume fraction. Wang  $et\ al.\ [84]$  developed a fractal model for predicting the k of nanofluids containing nanoparticle clusters. Prasher  $et\ al.\ [85,\ 86]$  studied the effects of aggregation on the k of nanofluids and showed that the aggregation time constant decreases rapidly with decreasing nanoparticle size and that the k enhancement increases with increasing level of aggregation, leveling off after the optimum level of aggregation is reached. However, Xuan  $et\ al.\ [69]$  simulated Brownian motion and aggregation of nanoparticles and showed that nanoparticle aggregation reduces the k of nanofluids because the random motion of aggregates is slower than that of a single nanoparticle.

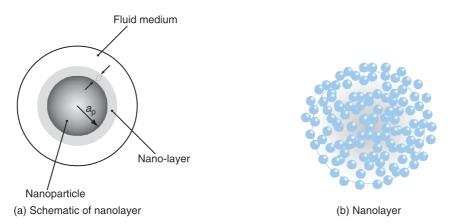


Figure 4. Single spherical nanoparticle with nanolayer (or interfacial layer) in the base fluid.

#### 3.2. Microscopic dynamic mechanisms

Effective medium theories assume that particles are stationary in a fluid. Thus, effective medium theories with the microscopic static mechanisms described above cannot explain the k behavior such as temperature- and particle-size-dependent thermal conductivities of nanofluids. A suspension of nanosized particles is different from that of micro- or millimeter-sized particles in that the latter are static and the former is dynamic because nanoparticles are constantly in random motion, even if the bulk fluid is stationary. So it is expected that there will be a fundamental difference in the mechanisms of heat transport in nanofluids due to dynamic effects in nanofluids.

There are two kinds of Brownian motion in nanofluids: collision between Brownian nanoparticles and convection induced by Brownian nanoparticles. Figure 5 shows the basic concept of Brownian-particle-induced convection.

#### 3.2.1. Collision between Brownian nanoparticles

Collision between nanoparticles due to Brownian motion of nanoparticles is the first dynamic mechanism studied for enhanced k of nanofluids. However, Wang  $et\ al$ . [24] and Keblinski  $et\ al$ . [81] have shown that the k enhancement due to collision between Brownian nanoparticles is negligible because Brownian nanoparticle diffusion is much slower than thermal diffusion.

#### 3.2.2. Nanoscale convection induced by Brownian nanoparticles

Realizing that nanoparticle diffusion has little effect on the k of nanofluids because it is orders of magnitude slower that thermal diffusion, Jang and Choi [87] proposed the hypothesis that Brownian nanoparticles induce convection at the nanoscale level and that Brownian-motion-induced nanoconvection is a key mechanism to explain the temperature- and size-dependent thermal conductivity of nanofluids. As discussed in section 4.3.1, the Jang and Choi model [87] captures both the temperature- and size-dependent features of the thermal conductivity of nanofluids whereas EMT-based models fail to capture any features. Koo and Kleinstreuer [88] extended the concept of nanoconvection to include the effects of fluids dragged by a pair of nanoparticles and mixing. Prasher  $et\ al.$  [89] extended the concept of nanoconvection by considering the effect of Brownian-motion-induced convection from multiple nanoparticles. Patel  $et\ al.$  [90] used nanoconvection induced by Brownian nanoparticles and the specific surface area of nanoparticles in their micro-convection model. Ren  $et\ al.$  [91] considered kinetic-theory-based microconvection and liquid layering in addition to liquid and particle conduction.

However, the nanoconvection mechanism has been questioned. Evans *et al.* [92] and Vladkov and Barrat [93], among others, used MDS to show that the contribution of nanoconvection to the thermal conductivity enhancement is negligible. However, Sarkar and Selvam [94] also used MDS to show that

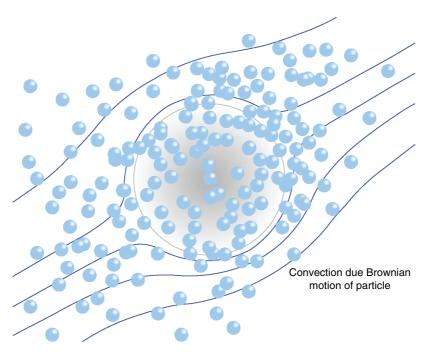


Figure 5. Microscale convection effect due to the Brownian motion of the particle.

the thermal conductivity enhancement is mostly due to the increased movement of liquid atoms in the presence of nanoparticles. Li and Peterson [95] simulated the mixing effect of the base fluid directly adjacent to the nanoparticles and showed that Brownian-motion-induced microconvection and mixing significantly enhance the macroscopic heat transfer in nanofluids. Eapen *et al.* [34] showed experimentally that microconvection does not enhance the thermal conductivity of silica and Teflon suspensions. Therefore, the debate over the nanoconvection mechanism will continue until it is resolved experimentally at the nanoscale.

# 3.3. Macroscopic mechanisms

#### 3.3.1. Dual-phase-lagging conduction

Wang and Wei [96] and Wang and Fan [22] investigated the nature of heat conduction in nanofluids by developing a macroscopic heat conduction model from first principles. The Wang group proposed dual-phase-lagging heat conduction as a macroscopic mechanism that comes from the presence of nanoparticles in nanofluids and showed the possibility of thermal waves and resonances that could enhance the thermal conductivity of nanofluids more than those observed so far.

In summary, a number of microscale and macroscale mechanisms have been proposed to explain the magnitude and trend of the thermal conductivity of nanofluids because effective medium theories based on the underlying assumption of diffusive conduction and motionless nanoparticles cannot predict new features of the thermal conductivity of nanofluids. New models based on the proposed heat conduction mechanisms in nanofluids can predict both the magnitude and trend of the thermal conductivity of nanofluids. However, they cannot accurately predict experimental data. The controversy regarding the proposed mechanisms of the thermal conductivity of nanofluids is far from over [for example, see 92, 97-99] The controversy comes primarily from a lack of understanding of the scientific basis for the mechanisms of enhanced thermal conductivity of nanofluids [77, 100]. Therefore, the proposed concepts and mechanisms behind the thermal conductivity behavior of nanofluids remain to be validated. More systematic experiments with well-dispersed, well-characterized nanofluids and a better understanding of the physics of fluid flow and heat transfer at the nanoscale are needed to establish the

fundamental mechanisms of heat conduction in nanofluids. Understanding these mechanisms is essential for the development of models that can accurately predict the k behavior of nanofluids.

#### 4. THERMAL CONDUCTIVITY MODELS FOR NANOFLUIDS

There are a number of different types of models developed to predict the newly observed thermal conduction behavior of nanofluids. In this paper, we have classified thermal conductivity models into five groups by the main underlying mechanism employed in the models. Five groups of mechanism-based k models for NFs include those based on (1) classical effective medium theory; (2) nanoscale layer; (3) Brownian motion; (4) agglomeration; and (5) other mechanisms. Each group of mechanism-based k models has been further broken into several subcategories.

# 4.1. Classical effective medium theory based models

The classical models for the thermal conductivity of composite materials are static models with the assumptions of motionless particles and diffusive heat transfer in both continuous matrix phase and dispersed phase. The parameters of these static models include the thermal conductivities of the components; the volume fraction, shape, and distribution of particles; and particle-particle interaction in dense suspensions. Whereas the classical EMT based models can predict thermal conductivity of suspensions of particles with a size of a micrometer or larger, they fail to predict most thermal conductivity data for nanofluids. Nevertheless, a number of EMT-based models have been used to compare with the k data for nanofluids as described below. However, all of these models are essentially equivalent because they predict almost identical k for dilute nanofluids. Therefore, the Maxwell model has been used widely as representative of all classical EMT-based models.

The simplest model based on the EMT was first developed by Maxwell for a dilute suspension of non-interacting spherical particles [29]. The Maxwell model [29] and Maxwell-Garnett model [101] predict well the thermal conductivity of dilute solid-liquid mixtures of relatively large (micro-and millimeter-size) particles. The effective thermal conductivity can be expressed as

$$k_{eff} = \left[ \frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\phi}{k_p + 2k_{bf} - (k_p - k_{bf})\phi} \right] k_{bf}$$
 (1)

This mathematical model shows that the effective thermal conductivity of nanofluids depends on the thermal conductivities of the spherical particle and the base fluid and the volume fraction of the solid particles.

Bruggeman [74] developed a model based on the symmetrical EMT. For a binary mixture of homogeneous spherical inclusions, the symmetrical Bruggeman model can be written as

$$\phi \left( \frac{k_p - k_{eff}}{k_p + 2k_{eff}} \right) + (1 - \phi) \left( \frac{k_{bf} - k_{eff}}{k_{bf} + 2k_{eff}} \right) = 0$$
 (2)

The Bruggeman model has no limitations on the concentration of spherical particles. For low particle concentrations, the predictions of thermal conductivity from the Bruggeman model and the Maxwell model are identical. But as the particle concentration and thermal conductivity ratio increase, the discrepancy between the two models increases.

Hamilton and Crosser [102] extended the Maxwell model to take into account irregular particle geometries by introducing a shape factor. When the thermal conductivity of the particles is over 100 times larger than that of the base fluid  $(k_p/k_{bf} > 100)$  the thermal conductivity can be expressed as

$$k_{eff} = \left[ \frac{k_p + (n-1)k_b - (n-1)(k_{bf} - k_p)\phi}{k_p + (n-1)k_{bf} + (k_{bf} - k_p)\phi} \right] k_{bf}$$
 (3)

where n is the empirical shape factor  $n = 3/\psi$ , and  $\psi$  is the particle sphericity, defined as the ratio of the surface area of a sphere with the same volume as the particle equal to the surface area of the particle. When the sphericity of the particles is one, the Hamilton-Crosser model reduces to the Maxwell model for spherical particle mixtures.

Hashin and Shtrikman [103] derived theoretical bounds for the effective thermal conductivity of suspensions. The Hashin and Shtrikman (HS) bounds can be written as

$$\frac{k_p + 2k_{bf} + 2\phi(k_p - k_{bf})}{k_p + 2k_{bf} - \phi(k_p - k_{bf})} \le \frac{k_{eff}}{k_{bf}} \le \frac{3k_f + 2\phi(k_p - k_{bf})}{3k_p - \phi(k_p - k_{bf})} \frac{k_p}{k_{bf}}$$
(4)

When the particle thermal conductivity is higher than that of base fluid, the HS lower bound is consistent with Maxwell model. In this case, the upper bound is derived by simply exchanging the values for the properties and volume fraction of the particles and the base fluid. Keblinski et al. used the HS bounds to show that the well-established effective medium theories are capable of explaining nearly all the published thermal conductivity data for nanofluids without resorting to new mechanisms [104]. As they mentioned, the HS upper bound corresponds to large pockets of fluid separated by linked chainforming or clustered nanoparticles [104]. It describes suspensions with long wire-like structures of nanoparticles aligned with the heat propagation direction. Such structures of nanoparticles are seldom realizable with dilute nanofluids containing well-dispersed nanoparticles. Therefore, the upper bound given by the HS model is not applicable to dilute nanofluids. More realistic upper and lower bounds for nanofluids having low concentration of well-dispersed nanoparticles are given by Buongiorno et al. [36]. Using the classical Maxwell model without thermal resistance as an upper bound of the thermal conductivity of dilute nanofluids, it is clear from Figure 1 that the thermal conductivity enhancements of most nanofluids are larger than the upper bound of the Maxwell model. Therefore, models based on new mechanisms as well as the classical diffusion mechanism are necessary to predict thermal conductivity data for nanofluids.

Jeffrey [37] developed a theoretical model assuming the conduction of heat through a stationary and random and statistically homogeneous suspension of spherical particles in a matrix of uniform conductivity. Jeffrey [37] also assumed that the volume fraction of particles is small. His mathematical model can be written as

$$k_{eff} = \left[1 + 3\beta\phi + \phi^2 \left(3\beta^2 + \frac{3\beta^3}{4} + \frac{9\beta^3}{16} \frac{\chi + 2}{2\chi + 3} + \frac{3\beta^4}{2^6} + \cdots\right)\right] k_{bf}$$
 (5)

with

$$\chi = \frac{k_p}{k_{bf}}$$
 and  $\beta = \frac{k_p - k_{bf}}{k_p + 2k_{bf}} = \frac{\chi - 1}{\chi + 2}$  (6)

Davis [105] developed a theoretical model for calculating the effective thermal conductivity of a composite material containing spherical inclusions. He assumed that the surface of a large heated body kept at a uniform temperature is in contact with a composite material of infinite extent that has a lower temperature far from the heated body. He used Green's theorem to compute the rate of heat transfer from the heated body to the composite material. The resulting formula is

$$k_{eff} = \left[1 + \frac{3(C-1)}{\{C+2-(C-1)\phi\}} \{\phi + f(C)\phi^2 + O(\phi^3)\}\right] k_{bf}$$
 (7)

with

$$f(C) = \sum_{p=6}^{\infty} \left[ \left( B_p - 3A_p \right) / (p-3) 2^{p-3} \right]$$
 (8)

where C is the ratio of the thermal conductivity of the spherical inclusions to that of base fluid and  $A_p$  and  $B_p$  are the known functions of C. This model is more relevant than prior works, since higher-order terms are taken into consideration [105].

Hasselman and Johnson [106] derived an expression for the effective thermal conductivity of composites, taking into account the thermal barrier resistance at the interface between the materials and the relations for insertion shapes for spherical, cylindrical, and flat plate for low concentration of dispersions. The resulting expression for spherical particles can be arranged as

$$k_{eff} = \left[ \frac{k_p (1 + 2\kappa) + 2k_{bf} + 2\phi(k_p (1 - \kappa) - k_{bf})}{k_p (1 + 2\kappa) + 2k_{bf} - \phi(k_p (1 - \kappa) - k_{bf})} \right] k_{bf}$$
(9)

where  $\kappa$  is a dimensionless parameter defined as

$$\kappa = \frac{a_K}{a_p} \tag{10}$$

where  $a_K$  is the so-called Kapitza radius defined as

$$a_K = R_K k_{bf} \tag{11}$$

where  $R_K$  is the Kapitza resistance, or thermal boundary resistance. Hasselman and Johnson found that the effective thermal conductivity depends on the volume fraction of the dispersed phase as well as the dispersion size.

Nan *et al.* [76] introduced a methodology for predicting the effective thermal conductivity of composites of arbitrarily shaped inclusions with the Kapitza resistance, using an effective medium approach. Their model can be arranged as

$$k_{eff,11} = k_{eff,22} = \left\{ \frac{2 + \phi \left[ \beta_{11} \left( 1 - L_{11} \right) \left( 1 + \left\langle \cos^2 \theta \right\rangle \right) + \beta_{33} \left( 1 - L_{33} \right) \left( 1 - \left\langle \cos^2 \theta \right\rangle \right) \right]}{2 - \phi \left[ \beta_{11} L_{11} \left( 1 + \left\langle \cos^2 \theta \right\rangle \right) + \beta_{33} L_{33} \left( 1 - \left\langle \cos^2 \theta \right\rangle \right) \right]} \right\} k_{bf}$$
(12)

and

$$k_{eff;33} = \left\{ \frac{1 + \phi \left[ \beta_{11} \left( 1 - L_{11} \right) \left( 1 - \left\langle \cos^2 \theta \right\rangle \right) + \beta_{33} \left( 1 - L_{33} \right) \left\langle \cos^2 \theta \right\rangle \right]}{1 - \phi \left[ \beta_{11} L_{11} \left( 1 - \left\langle \cos^2 \theta \right\rangle \right) + \beta_{33} L_{33} \left\langle \cos^2 \theta \right\rangle \right]} \right\} k_{bf}$$

$$(13)$$

with

$$\beta_{ii} = \frac{k_{ii}^c - k_{bf}}{k_{bf} + L_{ii} \left( k_{ii}^c - k_{bf} \right)}, \qquad \left\langle \cos^2 \theta \right\rangle = \frac{\int \rho(\theta) \cos^2 \theta \cdot \sin \theta d\theta}{\int \rho(\theta) \sin \theta d\theta}$$
(14)

and

$$k_{ii}^{c} = k_{s} \frac{k_{s} + L_{ii} (k_{p} - k_{s})(1 - v) + v (k_{p} - k_{s})}{k_{s} + L_{ii} (k_{p} - k_{s})(1 - v)}, \qquad v = \frac{a_{1}^{2} a_{3}}{(a_{1} + \delta)^{2} (a_{3} + \delta_{K})}$$
(15)

The model is applicable for predicting the effects of particle shape, size, orientation, distribution, volume fraction, and interfacial thermal resistance on the thermal conductivity of composites containing arbitrarily shaped inclusions.

Table 1 summarize the classical effective medium theory based models for the thermal conductivity of nanofluids and shows the model equations and key parameters required for determining thermal conductivity and remarks.

#### 4.2. Nanolayer based models

We categorize nanolayer based models into three submodels: theoretical models, combined models, and computational models.

#### 4.2.1. Theoretical models

Perhaps the earliest example of a nanoscale structure-based model for k of nanofluids is found in the work of Yu and Choi [82]. Accounting for the concept of the nanolayer, Yu and Choi [82] modified the Maxwell model to predict the effective thermal conductivity of nanofluids. Two essential features of the Yu and Choi model are (1) consideration of a new nanoscale structure that has not been considered in classical EMT models and (2) a new assumption that the solid-like nanolayer acts as a thermal bridge between a solid nanoparticle and a bulk liquid in nanofluids, an idea contrary to that in nanocomposite solids, has been made. In order to include the effect of the nanolayer, Yu and Choi assumed that (1) the solid-like layer of thickness  $\delta$  around the particles is more ordered than that of the bulk liquid; (2) the thermal conductivity of ordered layer  $k_{\text{layer}}$  is thus higher than that of the bulk liquid; (3) the nanolayer around each particle could be combined with the particle to form an equivalent particle; and (4) the particle volume fraction is so small that there is no overlap of equivalent particles. Based on the effective medium theory and assumptions (3) and (4), the equivalent thermal conductivity  $k_{\text{pe}}$  of the equivalent particles can be expressed as

$$k_{pe} = \frac{\left[2(1-\gamma) + (1+\beta)^3 (1+2\gamma)\right] \gamma}{-(1-\gamma) + (1+\beta)^3 (1+2\gamma)} k_p$$
 (16)

where  $\gamma = k_{\text{layer}}/k_p$  is the ratio of nanolayer thermal conductivity to particle thermal conductivity, and  $\beta = \delta/a_p$  is the ratio of the nanolayer thickness to the original particle radius. With Equation (16), the Maxwell model can be modified into

$$k_{eff} = \frac{k_{pe} + 2k_{bf} + 2(k_{pe} - k_{bf})(1 - \beta)^3 \phi}{k_{pe} + 2k_{bf} - (k_{pe} - k_{bf})(1 + \beta)^3 \phi} k_{bf}$$
(17)

This model reduces to the Maxwell model when  $\gamma = 1$  or  $\beta = 0$ . The modified Maxwell model

Table 1. Summary of classical effective medium theory based models

Maxwell (1873). $ k_{eg} = \begin{bmatrix} k_p + 2k_w + 2(k_p - k_y)\phi \\ k_p + 2k_g - (k_p - k_{eg})\phi \end{bmatrix} k_{ig} $ Bruggeman $ \phi \begin{pmatrix} k_p - k_{eg} \\ k_p + 2k_{eg} \end{pmatrix} + (1 - \phi) \begin{pmatrix} k_{ig} - k_{eg} \\ k_{ig} + 2k_{eg} \end{pmatrix} = 0 $ Hamilton and $ k_{eff} = \begin{bmatrix} k_p + (n-1)k_b - (n-1)(k_{ig} - k_p)\phi \\ k_p + 2k_{ig} + 2\phi(k_p - k_{ig}) \end{bmatrix} k_{ig} $ Hishin and $ k_p + 2k_{ig} + 2\phi(k_p - k_{ig}) \leq k_{eff} \leq \frac{3k_f + 2\phi(k_p - k_{ig})}{3k_p - \phi(k_p - k_{ig})} k_{ig} $ Effective medium $ k_p + 2k_{ig} + \phi(k_p - k_{ig}) \leq k_{eff} \leq \frac{3k_f + 2\phi(k_p - k_{ig})}{3k_p - \phi(k_p - k_{ig})} k_{ig} $ Davis (1986) $ k_{eff} = \begin{bmatrix} 1 + 3\beta\phi + \phi^2 \left(3\beta^2 + 3\beta^2 + 3\beta^2 + \cdots \right) \end{bmatrix} k_{ig} $ Hasselman and $ k_{eff} = \begin{bmatrix} 1 + 3\beta\phi + \phi^2 \left(3\beta^2 + 3\beta^2 + 2\beta^2 + \cdots \right) \end{bmatrix} k_{ig} $ Hasselman and $ k_{eff} = \begin{bmatrix} k_p (1 + 2k) + 2k_{ig} - \phi(k_p (1 - k_{ig})) + \beta_{ig} (1 - k_{ig}) \end{bmatrix} k_{ig} $ Nan et al. (1987) $ k_{eff} = \begin{bmatrix} k_p (1 - k_{ig}) + (k_{ig} (1 - k_{ig}) + k_{ig} (1 - k_{ig})) + \beta_{ig} (1 - k_{ig}) + \beta_{ig} (1 - k_{ig}) \end{pmatrix} k_{ig} $ Nan et al. (1997) $ k_{eff-11} = k_{eff-22} = \begin{bmatrix} 2 + \phi \left[\beta_{11} (1 - k_{1i}) (1 + \langle \cos^2 \phi \rangle) + \beta_{ig} (1 - k_{ig}) \langle \cos^2 \phi \rangle \end{bmatrix} \end{bmatrix} k_{ig} $ $ \begin{bmatrix} 1 + \phi \left[\beta_{11} (1 - k_{ig}) (1 - k_{ig}) (1 - k_{ig}) \langle \cos^2 \phi \rangle + \beta_{ig} (1 - k_{ig}) \langle \cos^2 \phi \rangle \end{bmatrix} \end{bmatrix} k_{ig} $ $ \begin{bmatrix} 1 + \phi \left[\beta_{11} (1 - k_{ig}) (1 - k_{ig}) \langle \cos^2 \phi \rangle + \beta_{ig} (1 - k_{ig}) \langle \cos^2 \phi \rangle + \beta_{ig} (1 - k_{ig}) \langle \cos^2 \phi \rangle \end{bmatrix} \end{bmatrix} k_{ig} $		Investigator	Formulation	Key parameter	Remarks
Bruggeman (1935)  Hamilton and Crosser (1962) $k_p + 2$ Hashin and Shtrikman $k_p + 2$ Shtrikman $k_p + 2$ Jeffrey (1973) $k_{eff} = \begin{bmatrix} k_{eff} & k_{eff}$		Maxwell (1873), Maxwell-Garnett (1904)	$k_{eff} = \left[rac{k_p + 2k_{bf} + 2\left(k_p - k_{bf} ight)\phi}{k_p + 2k_{bf} - \left(k_p - k_{bf} ight)\phi} ight]\!$	$\phi$ , $k_p$ , $k_{bf}$	Initial study of effective medium theory (EMT)
Hamilton and Crosser (1962) $k_{e}$ Hashin and Shtrikman $k_{p} + 2$ Shtrikman $k_{p} + 2$ Jeffrey (1973) $k_{eff} = \begin{bmatrix} k_{eff} & k_{$		Bruggeman (1935)	$\phi\left(\frac{k_p-k_{eff}}{k_p+2k_{eff}}\right)+\left(1-\phi\right)\left(\frac{k_{bf}-k_{eff}}{k_{bf}+2k_{eff}}\right)=0$	$\phi$ , $k_p$ , $k_{bf}$	EMT with interparticle interaction
Hashin and Shtrikman $k_p + 2$ Shtrikman $k_p + 2$ Jeffrey (1973) $k_{eff} = \begin{bmatrix} k_{eff} & k_{eff$		Hamilton and Crosser (1962)	$k_{eff} = \left[ rac{k_p + (n-1)k_b - (n-1)ig(k_{bf} - k_pig)\phi}{k_p + (n-1)k_{bf} + ig(k_{bf} - k_pig)\phi}  ight] k_{bf}$	$\phi, k_p, k_{bj'}$ $n = \frac{3}{\psi}$	EMT with shape factor
Jeffrey (1973) $k_{eff} = \begin{bmatrix} k_{eff} = k_{eff} & k_{eff,11} & k_{eff,12} & k_{eff,12} & k_{eff,12} & k_{eff,22} & k_{eff,11} & k_{eff,22} & $	Effective	Hashin and Shtrikman (1962)	$\frac{k_p + 2k_{bf} + 2\phi(k_p - k_{bf})}{k_p + 2k_{bf} - \phi(k_p - k_{bf})} \le \frac{k_{eff}}{k_{bf}} \le \frac{3k_f + 2\phi(k_p - k_{bf})}{3k_p - \phi(k_p - k_{bf})} \frac{k_p}{k_{bf}}$	$\phi$ , $k_p$ , $k_{0f}$	Theoretical bounds of EMT
$k_{eff,11} = k_{eff,22} = \langle k_{eff,21} = k_{eff,22} = \langle k_{eff,22} = \langle k_{eff,22} = k_{eff,22} = k_{eff,22} = k_{eff,22} = \langle k_{eff,22} = k_{eff,22} = k_{eff,22} = k_{eff,22} = \langle k_{eff,22} = k_{eff,22} = k_{eff,22} = k_{eff,22} = k_{eff,22} = \langle k_{eff,22} = k_{eff,22} = k_{eff,22} = k_{eff,22} = k_{eff,22} = k_{eff,22} = \langle k_{eff,22} = k$	medium models	Jeffrey (1973)	$k_{eff} = \left[ 1 + 3\beta\phi + \phi^2 \left( 3\beta^2 + \frac{3\beta^3}{4} + \frac{9\beta^3}{16} \frac{\chi + 2}{2\chi + 3} + \frac{3\beta^4}{2^6} + \cdots \right) \right] k_{ty}$	φ, k <sub>p</sub> , k <sub>bf</sub>	Second order term, EMT with interparticle interaction,
$k_{gf,11} = k_{gf,22} = k_{gf,22} = k_{gf,11}$		Davis (1986)	$k_{_{e\!f\!f}} = \left[1 + \frac{3(C - 1)}{\left\{C + 2 - (C - 1)\phi\right\}} \left\{\phi + f\left(C\right)\phi^2 + O\left(\phi^3\right)\right\}\right] k_{_{b\!f}}$	$\phi$ , $k_p$ , $k_{bf}$	EMT with interparticle interaction
$k_{eff,11} = k_{eff,22} = 4$		Hasselman and Johnson (1987)	$k_{eff} = \left[ \frac{k_p (1 + 2\kappa) + 2k_{bf} + 2\phi(k_p (1 - \kappa) - k_{bf})}{k_p (1 + 2\kappa) + 2k_{bf} - \phi(k_p (1 - \kappa) - k_{bf})} \right] k_{bf}$	$\phi, k_p, k_{bf}$ $\kappa = \frac{k_{bf} R_K}{a_p}$	EMT with interfacial thermal resistance (ITR)
$k_{eff.33} = \left\{ \frac{1 - \phi \left[ \beta_{11} L_{11} \left( 1 - \left\langle \cos^2 \theta \right\rangle \right) + \beta_{33} L_{33} \left\langle \cos^2 \theta \right\rangle \right]}{1 - \phi \left[ \beta_{11} L_{11} \left( 1 - \left\langle \cos^2 \theta \right\rangle \right) + \beta_{33} L_{33} \left\langle \cos^2 \theta \right\rangle \right]} \right\}^{K_{gy}}$		Nan et al. (1997)	$\frac{1+\phi \left[ \int_{-1}^{1}$	$\phi$ , $k_p$ , $k_{0j}$ $L_{ii}$ geometrical factor	Generalized form of EMT with ITR and shape factor

including the effect of nanolayer predicts that the very thin nanolayer has a significant impact on the k of nanofluids, particularly when the particle diameter is less than 10 nm. However, the nanolayer impact is small, and the modified Maxwell formula reduces to the original Maxwell equation in the case of large particles ( $a_p \gg \delta, \beta \to 0$ ). However, the thickness and thermal conductivity of nanolayer were not obtained theoretically.

Yu and Choi [82, 83] extended Equation (17), the nanoscale structural model for spherical nanoparticles, to nonspherical particles and renovated the Hamilton-Crosser model. The nanolayer is expressed as a confocal ellipsoid with a solid particle. They chose ellipsoidal particles since the geometric parameters characterizing them can be changed to represent the various shapes of particles actually used in composites. They also developed a generalized empirical shape factor for anisotropic complex ellipsoids. Their renovated Hamilton-Crosser model is expressed in terms of the equivalent thermal conductivity and equivalent volume fraction of anisotropic complex ellipsoids and includes an empirical shape factor. It can be written as

$$k_{eff} = \left(1 + \frac{m\phi_e A}{1 - \phi_e A}\right) k_{bf} \tag{18}$$

where the parameter A is defined by

$$A = \frac{1}{3} \sum_{j=a,b,c} \frac{\left(k_{pj} - k_{bf}\right)}{k_{pj} + (m-1)k_{bf}}$$
(19)

and

$$\phi_e = \frac{\sqrt{(a^2 + \delta)(b^2 + \delta)(c^2 + \delta)}}{\sqrt{abc}}\phi\tag{20}$$

is the equivalent volume concentration of complex ellipsoids. The equivalent thermal conductivities along the axes of the complex ellipsoid  $k_{pj}$  can be expressed as

$$k_{pj} = \left\{ 1 + \frac{k_p - k_s}{k_p \left[ rd(j,0) - d(j,t) \right] - k_s \left[ rd(j,0) - d(j,t) - r \right]} \right\} k_s$$
 (21)

where j(=a, b, and c) is along the semiaxis directions of the ellipsoid,  $k_p$  and  $k_s$  are the thermal conductivities of the solid ellipsoid and its surrounding layer, r is the volume ratio defined by

$$r = \frac{\sqrt{(a^2 + \delta)(b^2 + \delta)(c^2 + \delta)}}{\sqrt{abc}}$$
 (22)

and d(j, v) is the depolarization factor defined by

$$d(j,v) = \frac{\sqrt{(a^2 + v)(b^2 + v)(c^2 + v)}}{2} \times \int_0^\infty \frac{dw}{(j^2 + v + w)\sqrt{(a^2 + v + w) + (b^2 + v + w) + (c^2 + v + w)}}$$
(23)

The generalized empirical shape factor m ( $m = 3\psi^{-\varepsilon}$ , where  $\varepsilon$  is an empirical parameter and  $\psi$  is the particle sphericity of the complex prolate spheroid particle) is only one adjustable parameter in this model. This model was used to predict the effective thermal conductivity of nanotube-in-oil suspensions. With the empirical factor m, this model showed that the solid and liquid interfacial layers play an important role in correctly predicting the magnitude of the thermal conductivity enhancement of nanotube-in-oil nanofluids.

However, the two static models developed by Yu and Choi are not able to predict the nonlinear behavior of the effective thermal conductivity of nanofluids. Xue [107] is the first to model that aspect of nanofluid thermal conductivity. Although the models based on liquid layering theory predict well the measured thermal conductivity data, both the thickness and conductivity of the liquid layer have to be assumed.

Xue [107] developed a model to include the effect of a nanolayer, based on Maxwell theory and average polarization theory. He assumed that the complex nanoparticle is composed of an elliptical nanopaticle of thermal conductivity  $k_p$  with half-radii of (a, b, c) and an elliptical shell of thermal conductivity  $k_{\text{layer}}$  with a thickness  $\delta$ . The resulting formula for the effective thermal conductivity is

$$9\left(1 - \frac{\phi}{\lambda}\right) \frac{k_{eff} - k_{bf}}{2k_{eff} + k_{bf}} + \frac{\phi}{\kappa} \left[ \frac{k_{eff} - k_{c,x}}{k_{eff} + B_{2,x} \left(k_{c,x} - k_{eff}\right)} + 4 \frac{k_{eff} - k_{c,y}}{2k_{eff} + \left(1 - B_{2,x}\right) \left(k_{c,y} - k_{eff}\right)} \right] = 0$$
 (24)

where  $\lambda = abc/[(a + \delta)(b + \delta)(c + \delta)]$ ,  $k_{c,j}$  is the effective dielectric constant, and  $B_{2,x}$  is the depolarization factor along the x-symmetrical axis, which is derived from the average polarization theory. This model is notable in that it can predict for the first time the nonlinear behavior of the nanotube-in-oil nanofluids. The model predictions agree well with the experimental data using empirical parameters for liquid layer thickness and conductivity value. However, Yu and Choi [83] and Kim et al. [108] have shown that the values of the model parameters such as the depolarization factor are incorrect.

Xue and Xu [109] developed a new equation for the effective thermal conductivity of nanofluids by modifying the Bruggeman model with the effective thermal conductivity of the so-called "complex nanoparticles" consisting of a nanoparticle and its surrounding shell. Their modified Bruggeman model can be expressed as

$$\left(1 - \frac{\phi}{\chi}\right) \frac{k_{eff} - k_{bf}}{2k_{eff} + k_{bf}} + \frac{\phi}{\chi} \frac{\left(k_{eff} - k_{layer}\right) \left(2k_{layer} + k_p\right) - \chi\left(k_p - k_{layer}\right) \left(2k_{layer} + k_{eff}\right)}{\left(2k_{eff} + k_{layer}\right) \left(2k_{layer} + k_p\right) + 2\chi\left(k_p - k_{layer}\right) \left(k_{layer} - k_{eff}\right)} = 0 \tag{25}$$

where  $\chi$  is the volume ratio of spherical nanoparticles to complex nanoparticles, defined as

$$\chi = \left(\frac{a_p}{a_p + \delta}\right)^3 \tag{26}$$

where  $a_p$  is the radius of a particle and  $\delta$  is the thickness of interfacial shell. In Equation (25),  $k_p$  and  $k_{layer}$  are the thermal conductivity of the nanoparticle and interfacial shell, respectively. The modified model is in good agreement with the experimental data on the effective thermal conductivity of CuO/water and CuO/EG nanofluids.

Xie *et al.* [110] derived a new expression for calculating the effective thermal conductivity of nanofluids considering a linear thermal conductivity distribution across the interfacial nanolayer. Their model is given as

$$k_{eff} = \left(1 + 3\Theta\phi_T + \frac{3\Theta^2\phi_T^2}{1 - \Theta\phi_T}\right)k_{bf} \tag{27}$$

with

$$\Theta = \frac{\left(\frac{k_{layer} - k_{bf}}{k_{layer} + 2k_{bf}}\right) \left[ (1 + \gamma)^3 - \left\{ \frac{\left(k_p - k_{layer}\right) \left(k_{bf} + 2k_{layer}\right)}{\left(k_p + 2k_{layer}\right) \left(k_{bf} - k_{layer}\right)} \right\} \right]}{\left(1 + \gamma\right)^3 + 2\left(\frac{k_{layer} - k_{bf}}{k_{layer} + 2k_{bf}}\right) \left(\frac{k_p - k_{layer}}{k_p + 2k_{layer}}\right)}$$
(28)

where  $\phi_T$  is the total volume fraction of the original nanoparticle and nanolayer defined as  $\phi_T = \phi(1 + \gamma)^3$  and  $\gamma$  is the ratio of the nanolayer thickness to the original particle radius defined as  $\gamma = \delta/a_p$ . Their model shows the effects of nanolayer thickness, nanoparticle size, volume fraction, and thermal conductivity ratio of particle to fluid on the thermal conductivity. Moreover, for smaller particles, the effects of particle size and nanolayer thickness become much more conspicuous than for larger ones, which shows that controlling nanolayer structure might be an effective method to yield high thermal conductivity of panofluids

Leong *et al.* [111] proposed a new model for the effective thermal conductivity of nanofluids by considering the effect of the interfacial layer at the solid-liquid interface. Their new model can be written as

$$k_{eff} = \frac{\left(k_{p} - k_{layer}\right)\phi k_{layer} \left[2\beta_{1}^{3} - \beta^{3} + 1\right] + \left(k_{p} + 2k_{layer}\right)\beta_{1}^{3} \left[\phi\beta^{3} \left(k_{layer} - k_{bf}\right) + k_{bf}\right]}{\beta_{1}^{3} \left(k_{p} + 2k_{layer}\right) - \left(k_{p} - k_{layer}\right)\phi \left[\beta_{1}^{3} + \beta^{3} - 1\right]}$$
(29)

where  $\beta$  is defined as  $\beta=1+\gamma$ ,  $\beta_1$  is defined as  $\beta_1=1+\gamma/2$ , and here  $\gamma$  is ratio of the nanolayer thickness to the original particle radius defined as  $\gamma=\delta/a_p$ . This model includes the effects of nanoparticle size, nanolayer thickness, volume fraction, and thermal conductivities of the nanoparticle, nanolayer, and the base fluid. If there is no nanolayer at the solid-liquid interface, i.e.,  $k_{layer}=k_{bf}$  and  $\delta=0$  or  $\beta_1=\beta=1$ , this model reduces to Maxwell-Garnett model. It appears that their model predictions of the thermal conductivity enhancements are more consistent with the experimental results than those of the classical Maxwell theory and the renovated Maxwell model [82]. However, Doroodchi *et al.* [112] have demonstrated that the model of Leong *et al.* [111] is based on an incorrect derivation.

Murshed *et al.* [48] proposed two models for the effective thermal conductivity of nanofluids containing spherical and cylindrical nanoparticles by considering the effect of the interfacial layer at the solid particle/liquid interface. For spherical nanoparticles, the model can be expressed as

$$k_{eff} = \frac{\left(k_{p} - k_{layer}\right)\phi k_{layer}\left[2\beta_{1}^{3} - \beta^{3} + 1\right] + \left(k_{p} + 2k_{layer}\right)\beta_{1}^{3}\left[\phi\beta^{3}\left(k_{layer} - k_{bf}\right) + k_{bf}\right]}{\beta_{1}^{3}\left(k_{p} + 2k_{layer}\right) - \left(k_{p} - k_{layer}\right)\phi\left[\beta_{1}^{3} + \beta^{3} - 1\right]}$$
(30)

and for cylindrical nanoparticles

$$k_{eff} = \frac{\left(k_{p} - k_{layer}\right)\phi k_{layer}\left[\beta_{1}^{2} - \beta^{2} + 1\right] + \left(k_{p} + k_{layer}\right)\beta_{1}^{2}\left[\phi\beta^{2}\left(k_{layer} - k_{bf}\right) + k_{bf}\right]}{\beta_{1}^{2}\left(k_{p} + k_{layer}\right) - \left(k_{p} - k_{layer}\right)\phi\left[\beta_{1}^{2} + \beta^{2} - 1\right]}$$
(31)

where  $\beta$  is defined as  $\beta=1+\gamma$ ,  $\beta_1$  is defined as  $\beta_1=1+\gamma/2$ , and here  $\gamma$  is ratio of the nanolayer thickness to the original particle radius, defined as  $\gamma=\delta/a_p$ . Equation (30) is the same as the model developed by Leong *et al.* [111]. These two models include that the effect of the nanoparticle size, nanolayer thickness, volume fraction, and thermal conductivities of the nanoparticle, nanolayer, and the base fluid. For the calculation of the thickness of the nanolayer at the nanoparticle/liquid interface, they used the following model by Hashimoto *et al.* [113]

$$\delta = \sqrt{2\pi}\sigma\tag{32}$$

where  $\sigma$  is a parameter that characterizes the diffuseness of interfacial boundary whose typical value is within  $0.2 \sim 0.8$  nm. However, this model is not able to predict the nonlinear behavior of the effective thermal conductivity of nanotube-based nanofluids.

Doroodchi et al. [112] derived mathematical models for the effective thermal conductivity of nanofluids using spatial-averaging and point-source methods. The model derived using the point-source method of Maxwell [29] is given as

$$\begin{split} k_{e\!f\!f\!f} = \\ & \begin{bmatrix} \left(38\phi a_p^3 \delta^3 - 6a_p^4 \delta^2 - 2a_p^3 \delta^3 + 6\phi a_p^5 \delta - 6a_p^5 \delta + 24\phi a_p^4 \delta^2 + 12\phi a_p \delta^5 + 30\phi a_p^2 \delta^4 + 2\phi \delta^6 \right) k_{bf} k_p \\ - \left(3a_p^4 \delta^2 + 6\phi a_p^6 + 3a_p^5 \delta + 30\phi a_p^2 \delta^4 + a_p^3 \delta^3 + 44\phi a_p^3 \delta^3 + 2\phi a_p^6 + 12\phi a_p \delta^5 + 24\phi a_p^5 \delta + 42\phi a_p^4 \delta^2 + 3a_p^6 \right) k_{layer} k_p \\ - \left(4a_p^3 \delta^3 - 24\phi a_p \delta^5 + 12a_p^5 \delta - 6\phi a_p^6 + 6a_p^6 + 12a_p^4 \delta^2 - 82\phi a_p^3 \delta^3 - 66\phi a_p^4 \delta^2 - 4\phi \delta^6 - 60\phi a_p^2 \delta^4 - 30\phi a_p^5 \delta \right) k_{layer} k_{bf} \\ - \left(12\phi a_p^5 \delta + 60\phi a_p^2 \delta^4 + 24\phi a_p \delta^5 + 76\phi a_p^3 \delta^3 + 6a_p^4 \delta^2 + 6a_p^5 \delta + 2a_p^3 \delta^3 + 4\phi \delta^6 + 48\phi a_p^4 \delta^2 \right) k_{layer} \end{bmatrix} \\ \hline \begin{bmatrix} \left(-19\phi a_p^3 \delta^3 - 6a_p^4 \delta^2 - 2a_p^3 \delta^3 - 3\phi a_p^5 \delta - 6a_p^5 \delta - 12\phi a_p^4 \delta^2 - 6\phi a_p \delta^5 - 15\phi a_p^2 \delta^4 - \phi \delta^6 \right) k_{bf} k_p \\ + \left(-3a_p^4 \delta^2 + 3\phi a_p^6 - 3a_p^5 \delta + 15\phi a_p^2 \delta^4 - a_p^3 \delta^3 + 22\phi a_p^3 \delta^3 + \phi a_p^6 + 6\phi a_p \delta^5 + 12\phi a_p^5 \delta + 21\phi a_p^4 \delta^2 - 3a_p^6 \right) k_{layer} k_p \\ + \left(-12\phi a_p \delta^5 - 12a_p^5 \delta - 4a_p^3 \delta^3 - 3\phi a_p^6 - 6a_p^6 - 12a_p^4 \delta^2 - 41\phi a_p^3 \delta^3 - 33\phi a_p^4 \delta^2 - 2\phi \delta^6 - 30\phi a_p^2 \delta^4 - 15\phi a_p^5 \delta \right) k_{layer} k_{bf} \end{bmatrix}$$

(33)

Doroodchi *et al.* [112] then used their models to evaluate the nanolayer based models of Yu and Choi [82] and Leong *et al.* [111] and demonstrated that the renovated Maxwell model of Yu and Choi [82] is identical to their models, but the model of Leong *et al.* [111] is based on an incorrect derivation. Therefore, the renovated Maxwell model accounts for the effects of nanolayering accurately, whereas the Leong *et al.* [111] model overstates them. However, their models and the renovated Maxwell model [82] predict effective thermal conductivity enhancements that are not significantly greater than those

predicted by classical Maxwell theory. This implies that nanolayering by itself is unable to account for the effective thermal conductivity enhancements in nanofluids.

# 4.2.2. Combined models

Ren et al. [91] derived a new theoretical model for the effective thermal conductivity of nanofluids, which includes the effects of interfacial nanolayer and microconvection owing to the thermal motion of nanoparticles. They assumed that there are four heat transfer modes in nanofluids: (1) heat transfer by the base fluid; (2) heat transfer by the nanoparticles; (3) heat transfer by the nanolayer; and (4) heat transfer by microconvection. Their new theoretical model can be expressed as

$$k_{eff} = \left(1 + F\left(Pe\right) + 3\Theta\phi_T + \frac{3\Theta^2\phi_T^2}{1 - \Theta\phi_T}\right) k_{bf}$$
(34)

where  $\Theta$  is the function defined by [110] as

$$\Theta = \frac{\left(\frac{k_{layer} - k_{bf}}{k_{layer} + 2k_{bf}}\right) \left[ (1 + \gamma)^{3} - \left\{ \frac{\left(k_{p} - k_{layer}\right) \left(k_{bf} + 2k_{layer}\right)}{\left(k_{p} + 2k_{layer}\right) \left(k_{bf} - k_{layer}\right)} \right\} \right]}{\left(1 + \gamma\right)^{3} + 2\left(\frac{k_{layer} - k_{bf}}{k_{layer} + 2k_{bf}}\right) \left(\frac{k_{p} - k_{layer}}{k_{p} + 2k_{layer}}\right)}$$
(35)

and F(Pe) is given as

$$F(Pe) = 0.0556(Pe) + 0.1649(Pe)^{2} - 0.0391(Pe)^{3} + 0.0034(Pe)^{4}$$
(36)

where Pe is defined as

$$Pe = \frac{\overline{u}L}{\alpha_{bf}} \phi_T^{0.75} \tag{37}$$

In Equation (37),  $\bar{u}$  is the mean velocity of the complex nanoparticle, L is the specific length,  $\alpha_{bf}$  is the thermal diffusivity of the base fluid, and  $\phi_T$  is the total volume fraction of the original nanoparticle and nanolayer defined by Xie *et al.* [110]. The mean velocity of the complex nanoparticle  $\bar{u}$  is defined as

$$\overline{u} = \sqrt{\frac{3k_B T}{m_c}} \quad \text{where} \quad m_c = \frac{4}{3} \rho_p \pi a_p^3 \left\{ \frac{\rho_{layer}}{\rho_p} \left[ \left( 1 + \frac{\delta}{a_p} \right)^3 - 1 \right] + 1 \right\}$$
 (38)

where  $m_c$  is the mass of the complex nanoparticle,  $\rho_p$  is the density of the nanoparticle,  $\rho_{layer}$  is the density of the nanolayer, and  $\delta$  is the thickness of the interfacial nanolayer. Now, the specific length L is defined as

$$L = \left(a_p + \delta\right) \sqrt[3]{\frac{4\pi}{3\phi_T}} \tag{39}$$

This model implies that the parameters of a nanofluid system, such as the nanoparticle size, nanolayer thickness, temperature, volume fraction, and thermal conductivities of the nanoparticle and the base fluid, play important roles in the enhanced thermal conductivity ratios. However, they did not mention a methodology for determining the value of the density of the nanolayer,  $\rho_{layer}$ .

Sabbaghzadeh and Ebrahimi [114] proposed a theoretical model for the effective thermal conductivity of nanotubes (cylinder-shaped particles) for use in nanotubes-in-fluid suspensions. They considered five modes of energy transport in nanofluids: (1) collision among the base fluid molecules; (2) thermal diffusion in nanoparticles, which are covered by the nanolayer in the fluid; (3) thermal diffusion in the nanolayer in the fluid; (4) thermal interaction of dynamic complex nanoparticles (intrinsic nanoparticles and nanolayers) with the base fluid molecules; and (5) collision between nanoparticles due to Brownian motion. They neglected the last term because it is a very slow process. Their theoretical model can be expressed as

$$k_{eff} = k_{bf} \left[ 1 - \phi (1 + M') \right] + \phi \left( k_p + k_{layer} M' \right)$$

$$+ \phi \left( 1 + M' \right) \frac{a_{bf}}{\Pr_{bf} \left( 2a_p + \delta \right)} \left( 0.35 + 0.56 \operatorname{Re}_{bf}^{0.52} \right) \Pr_{bf}^{0.3} k_{bf}$$

$$(40)$$

where

$$M' = \left[ \left( \frac{\delta}{a_p} + 1 \right)^2 - 1 \right] \tag{41}$$

Their theoretical model shows that the effect of nanolayer thickness will be more important for small diameter of nanotubes.

Murshed *et al.* [115] proposed a combined static and dynamic mechanisms-based model for the effective thermal conductivity of nanofluids. Their model included the effects of particle size, nanolayer, Brownian motion of nanoparticle, particle surface chemistry, and interaction potential. The model can be expressed as

$$k_{eff} = \left[ \frac{\phi \omega \left( k_{p} - \omega k_{bf} \right) \left[ 2\beta_{1}^{3} - \beta^{3} + 1 \right] + \left( k_{p} + 2\omega k_{bf} \right) \beta_{1}^{3} \left[ \phi \beta^{3} \left( \omega - 1 \right) + 1 \right]}{\beta_{1}^{3} \left( k_{p} + 2\omega k_{bf} \right) - \left( k_{p} - \omega k_{bf} \right) \phi \left[ \beta_{1}^{3} + \beta^{3} - 1 \right]} \right] k_{bf}$$

$$+ \left[ \phi^{2} \beta^{6} k_{bf} \left( 3\Lambda^{2} + \frac{3\Lambda^{2}}{4} + \frac{9\Lambda^{3}}{16} \frac{k_{cp} + 2k_{bf}}{2k_{cp} + 3k_{bf}} + \frac{3\Lambda^{4}}{2^{6}} + \cdots \right) \right]$$

$$+ \left[ \frac{1}{2} \rho_{cp} c_{p,cp} L_{s} \left\{ \sqrt{\frac{3k_{B} T \left( 1 - 1.5\beta^{3} \phi \right)}{2\pi \rho_{cp} \beta^{3} a_{p}^{3}}} + \frac{G_{T}}{6\pi \mu \beta a_{p} L_{s}} \right\} \right]$$

$$(42)$$

with

$$k_{layer} = \omega k_{bf}, \qquad \Lambda = \frac{k_{cp} - k_{bf}}{k_{cp} + 2k_{bf}}, \qquad k_{cp} = \frac{2\left(k_p - k_{layer}\right) + \beta^3\left(k_p + 2k_{layer}\right)}{\left(k_{layer} - k_p\right) + \beta^3\left(k_p + 2k_{layer}\right)} k_{layer} \tag{43}$$

where  $\omega$  is an empirical parameter that depends on the orderliness of fluid molecules in the interface and the nature and surface chemistry of nanoparticles;  $k_{\rm cp}$  is the thermal conductivity of the complex particle;  $\beta$  is defined as  $\beta=1+\gamma$ ,  $\beta_1$  is defined as  $\beta=1+\gamma/2$ , where  $\gamma$  is the ratio of the nanolayer thickness to the original particle radius defined as  $\gamma=\delta/a_p$ ; and  $G_T$  is the total interparticle potential, or DLVO interaction potential. The significant features of their model are as follows: (1) The model is developed by considering nanoparticles with a thin interfacial layer together with their static and dynamic mechanisms in the base fluid. The particle size effect is also included; (2) The second term on the righthand side of Equation (42) represents the interactions between pairs of spherical nanoparticles in a stationary suspension; (3) The third term on the righthand side of Equation (42), which takes into account the effect of particle Brownian motion, particle surface chemistry, and interparticle interactions, is applicable for  $\phi>0.005$ . As mentioned before, this is because at such a small volume fraction, i.e.  $\phi<0.005$ , the interparticle separation distance is too large to cause any interactions through the Brownian and potential forces of particles; (4) If there are no interaction between pairs of nanoparticles and the interfacial layer, the static part of the model reduces to the Maxwell model and when  $\phi=0$ , the entire model reduces to  $k_{bf}$ . The analysis of their results shows that the major contribution to the enhanced thermal conductivity of nanofluids arises from static mechanisms.

#### 4.2.3. Computational models

Xue *et al.* [97] investigated the effect of the liquid structure at the solid interface on thermal transport by using non-equilibrium molecular dynamics simulations of a simple monoatomic liquid system. They demonstrated that the layering of the liquid atoms at the liquid-solid interface, both in the directions normal and parallel to the solid–liquid interface, shows minor effect on thermal transport properties. However, the results of their MD simulations for a simple monoatomic liquid system may not apply to complex systems like nanofluids.

Li *et al.* [116] investigated the effect of the molecular layering at liquid/solid interface on the thermal conductivity of nanofluids using an equilibrium molecular dynamics simulation. They used the Green-Kubo relationships to calculate the thermal conductivity of nanofluids. Focusing on particle movement and surrounding liquid atoms [116], they found that a solidlike, thin liquid layer is formed at the interface between the nanoparticle and liquid, and this nanolayer moves with the nanoparticles due to Brownian motion. They also found that more liquid atoms were attracted to form the liquid layer around the nanoparticle when the size of the nanoparticle is larger. This implies that the number of the atoms in the liquid layer is related to the nanoparticle size. Thus, as shown by these phenomena, the nanolayer can contribute to the anomalous enhancement of the thermal conductivity of nanofluids. Based on their simulation results, they conclude that the thermal conductivity of nanofluids can be significantly enhanced when the thermal conductivity of the nanolayer is larger than that of liquid and the nanoparticle size increases.

The deficiency of nanolayer-based models is that there exists no method to estimate exactly the nanolayer thickness and thermal conductivity. Lee [70] introduced the concept of an electrical double layer (EDL), which is formed on the particle surface in solution and developed equations for the thickness and effective thermal conductivity of the nanolayer. Tillman and Hill [117] reported a method to determine the nanolayer thickness and thermal conductivity profile within the nanolayer. They used a function form to derive the thermal conductivity of the nanolayer, but the function cannot accurately determine the thermal conductivity. Thus, a method of determining the nanolayer thickness accurately should be settled first in the future to build a successful theory for the effective thermal conductivity of nanofluids using the nanolayer.

Table 2 provides a summary of the nanolayer based models for the thermal conductivity of

nanofluids.

#### 4.3. Brownian motion based models

We categorize Brownian motion based models into three sub-models: theoretical models, computational models, and empirical models.

#### 4.3.1. Theoretical models

Xuan *et al.* [69] are the first to develop a dynamic model that takes into account the effects of Brownian motion of nanoparticles. However, their model did not predict the linear increase of conductivity with temperature, as obtained by Das *et al.* [8]. Furthermore, their thermal conductivity equation is dimensionally incorrect.

Jang and Choi [87] developed a theoretical model that takes into account nanoconvection. They considered four modes of energy transport in nanofluids: (1) collision between base fluid molecules; (2) thermal diffusion in nanoparticles in fluids; (3) collision of nanoparticles with each other by translational motion due to the Brownian motion with long wavelength; (4) Brownian motion of nanoparticles with short wavelength, which results from collisions between base fluid molecules and nanoparticles by thermally induced fluctuations. They performed an order-of-magnitude analysis and neglected the third mode because it is much smaller than the other modes. Thus, they derived a general expression for the effective thermal conductivity from modes (1), (2), and (4). The resulting model can be expressed as

$$k_{eff} = k_{bf} \left( 1 - \phi \right) + \beta k_p \phi + C_1 \frac{d_{bf}}{d_p} k_{bf} \operatorname{Re}_{d_p}^2 \operatorname{Pr} \phi$$
(44)

where  $\beta$  is a constant for considering the Kapitza resistance per unit area,  $C_1$  is a proportional constant, and the Reynolds number is defined by

$$\operatorname{Re}_{d_p} = \frac{\overline{C}_{R.M.} d_p}{v} \tag{45}$$

where  $\overline{C}_{R.M.}$  and v are the random motion velocity of a nanoparticle and kinematic viscosity of base fluid, respectively. The random motion velocity can be defined as

$$\overline{C}_{R.M.} = \frac{D_o}{l_{bf}} \tag{46}$$

where  $D_o$  is the diffusion coefficient and  $l_{bf}$  is the liquid mean free path. New model calculations agree with temperature-dependent data of Das  $et\ al.$  [8] while Maxwell-type theories fail to capture the temperature-dependent conductivity. Furthermore, their new model predicts size-dependent conductivity. However, the hypothesis of the existence of convection at the nanoscale has not been established experimentally or theoretically and the random motion velocity of a single nanoparticle has not been measured to confirm that it can be expressed as a function of the diffusion coefficient  $D_o$  and the liquid mean free path  $l_{bf}$ .

Kumar *et al.* [118] developed a unique model for effective thermal conductivity of nanofluids composed of two submodels: (1) a stationary particle model and (2) a moving particle model. The stationary particle model was developed based on Fourier's law of diffusion. In the moving particle model, they adapted the concept of the kinetic theory of gases for effective thermal conductivity of particles and the Stokes-Einstein formula. The proposed combined model can be expressed as

		Table 2. Summary of models considering nanolayer effect (1/2).	2).	
	Investigator	Formulation	Key parameter	Remarks
	Yu & Choi (2003)	$k_{eff} = rac{k_{pe} + 2k_{bf} + 2\left(k_{pe} - k_{bf} ight)(1 - eta)^3 \phi}{k_{pe} + 2k_{bf} - \left(k_{pe} - k_{bf} ight)(1 + eta)^3 \phi} k_{bf}$	$\phi, k_p, k_{tgp}, k_{tayer}, \delta$ $\beta = \delta / a_p$	Modified Maxwell model with nanolayer (NL) effect
	Yu & Choi (2004)	$k_{e\!f\!f} = \left(1 + rac{m\phi_e A}{1 - \phi_e A} ight)k_{bf}$	$\phi$ , $k_p$ , $k_{bf}$ , $k_{layer}$ , $\delta$ $\phi_e$ ; equivalent vol. %	Modified HC model with NL effect and shape factor
	Xue and Xu (2005)	$ \left(1 - \frac{\phi}{\chi}\right) \frac{k_{eff} - k_{bf}}{2k_{eff} + k_{bf}} + \frac{\phi}{\chi} \left(\frac{k_{eff} - k_{toyer}}{2k_{eff} + k_{toyer}}\right) \left(2k_{toyer} + k_{p}\right) - \chi\left(k_{p} - k_{toyer}\right) \left(2k_{toyer} + k_{eff}\right)}{\chi\left(2k_{eff} + k_{toyer}\right) \left(2k_{toyer} + k_{p}\right) - 2\chi\left(k_{p} - k_{toyer}\right) \left(k_{toyer} - k_{eff}\right)} = 0 $	$\phi, k_p, k_{lop} \cdot k_{loper}, \delta$ $\chi = \left(\frac{a_p}{a_p + \delta}\right)^3$	Modified Bruggeman model with NL effect and shape factor
Theoretical models	Xue (2003)	$9\left(1 - \frac{\phi}{\lambda}\right) \frac{k_{eff} - k_{bf}}{2k_{eff} + k_{bf}} + \frac{\phi}{\kappa} \left[ \frac{k_{eff} - k_{c,x}}{k_{eff} + B_{2,x} \left(k_{c,x} - k_{eff}\right)} + 4 \frac{k_{eff} - k_{c,y}}{2k_{eff} + \left(1 - B_{2,x}\right) \left(k_{c,y} - k_{eff}\right)} \right] = 0$	$\phi$ , $k_p$ , $k_{lop}$ , $k_{layen}$ , $\delta$ $B_{2,n}$ ; depolarization factor	Maxwell model with  NL and depolarization factor
	Xie et al. (2005)	$k_{eff} = \left(1 + 3\Theta\phi_T + \frac{3\Theta^2\phi_T^2}{1 - \Theta\phi_T}\right) k_{bf}$	$\phi$ , $k_p$ , $k_{lgp}$ $k_{lgyer}$ , $\delta$ $\phi_T = \phi(1 + \delta la_p)^3$	Linear thermal conductivity distribution assumption with NL
	Leong et al. (2006)	For sphere, $k_{\rm eff} = \frac{\left(k_p - k_{\rm tayer}\right)\phi k_{\rm tayer} \left[2\beta_1^3 - \beta^3 + 1\right] + \left(k_p + 2k_{\rm tayer}\right)\beta_1^3 \left[\phi\beta^3 \left(k_{\rm tayer} - k_{bf}\right) + k_{bf}}{\beta_1^3 \left(k_p + 2k_{\rm tayer}\right) - \left(k_p - k_{\rm tayer}\right)\phi \left[\beta_1^3 + \beta^3 - 1\right]}$	$\phi$ , $k_p$ , $k_{lop}$ $k_{lover}$ , $\delta$ $\beta = 1 + \delta l  a_p$	Multi-medium EMT with NL
	Sabbaghzadeh and Ebrahimi (2007)	$k_{eff} = k_{bf} \left[ 1 - \phi (1 + M') \right] + \phi \left( k_p + k_{layer} M' \right) $ $+ \phi (1 + M') \frac{a_{bf}}{\Pr_{bf} \left( 2a_p + \delta \right)} \left( 0.35 + 0.56 \operatorname{Re}_{bf}^{0.32} \right) \operatorname{Pt}_{bf}^{0.3} k_{bf}$	$\phi, k_p, k_{t_0 p}, k_{t_{t_0 p e p}}, \delta$ $M' = \left[ \left( \frac{\delta}{a_p} + 1 \right)^2 - 1 \right]$	Superposition of each heat transfer mode with NL effect and dynamic consideration for nanotubes
				Table 2. (Continued)

Table 2. Summary of models considering nanolayer effect (1/2). (Continued)

	Investigator	Formulation	Key parameter	Remarks
	Murshed <i>et al.</i> (2008)	For cylinder, $k_{eff} = \frac{\left(k_p - k_{layer}\right)\phi k_{layer}\left[2\beta_1^3 - \beta^3 + 1\right] + \left(k_p + 2k_{layer}\right)\beta_1^3\left[\phi\beta^3\left(k_{layer} - k_{lef}\right) + k_{lef}\right]}{\beta_1^3\left(k_p + 2k_{layer}\right) - \left(k_p - k_{layer}\right)\phi\left[\beta_1^3 + \beta^3 - 1\right]}$	$\phi, k_p, k_{bp} k_{layer}, \delta$ $\beta = 1 + \delta/a_p$	Additional study of Leong et al. with cylindrical shape
Theoretical models	Droodchi $k_{eff} = et  dl. (2009)$	$=\begin{bmatrix} \left[ 38\phi a_{p}^{3}\delta^{2} - 6a_{p}^{4}\delta^{2} - 2a_{p}^{3}\delta^{3} + 6\phi a_{p}^{2}\delta - 6a_{p}^{3}\delta + 24\phi a_{p}^{4}\delta^{2} + 12\phi a_{p}\delta^{3} + 30\phi a_{p}^{2}\delta^{4} + 2\phi\delta^{5} \right) k_{ij}k_{p} \\ - \left( 3a_{p}^{4}\delta^{2} + 6\phi a_{p}^{6} + 3a_{p}^{5}\delta + 30\phi a_{p}^{2}\delta^{4} + a_{p}^{3}\delta^{3} + 44\phi a_{p}^{3}\delta^{3} + 2\phi a_{p}^{6} + 12\phi a_{p}\delta^{5} + 24\phi a_{p}\delta^{5}\delta + 42\phi a_{p}\delta^{4}\delta + 3a_{p}\delta^{5} + 3a_{p}\delta^{6} + 42\phi a_{p}\delta^{5}\delta + 4\phi a_{p}\delta^{5}\delta$	$\int_{\mathcal{A}} \phi,  k_p,  k_{lg,er},  \delta$	Correct B.C of Leong et al. study with multimedium EMT with nanolayer
	Ren et al. (2005)	$k_{eff} = \left(1 + F\left(Pe\right) + 3\Theta\phi_T + \frac{3\Theta^2\phi_T^2}{1 - \Theta\phi_T}\right) k_{bf}$	$\phi$ , $k_p$ , $k_{b\rho}$ $k_{loyer}$ , $\delta$ Peclet number	Thermal conductivity (TC) model with NL and Brownian Motion (BM)
Combined models	Sabbaghzadeh and Ebrahimi (2007)	$k_{eff} = k_{bf} \left[ 1 - \phi (1 + M') \right] + \phi \left( k_p + k_{layer} M' \right) $ $+ \phi (1 + M') \frac{a_{bf}}{P_{rbf} \left( 2a_p + \delta \right)} \left( 0.35 + 0.56 \operatorname{Re}_{bf}^{0.52} \right) P_{tbf}^{0.3} k_{bf}$	$\phi, k_p, k_{bf} k_{layer}, \delta$ $M' = \left[ \left( \frac{\delta}{a_p} + 1 \right)^2 - 1 \right]$	Superposition of each heat transfer mode with NL effect and dynamic consideration for nanotubes

Table 2. Summary of models considering nanolayer effect (1/2). (Continued)

	Murshed <i>et al.</i> (2009)	$k_{eff} = \begin{bmatrix} \frac{\phi \omega \left(k_{p} - \omega k_{bf}\right) \left[2\beta_{1}^{3} - \beta^{3} + 1\right] + \left(k_{p} + 2\omega k_{bf}\right) \beta_{1}^{3} \left[\phi \beta^{3} \left(\omega - 1\right) + 1\right]}{\beta_{1}^{3}} k_{bf} \\ + \begin{bmatrix} \frac{\phi^{2}}{2}\beta^{6} k_{bf} \left(3\Lambda^{2} + \frac{3\Lambda^{2}}{4} + \frac{9\Lambda^{3}}{16} \frac{k_{ep} + 2k_{bf}}{2k_{ep} + 3k_{bf}} + \frac{3\Lambda^{4}}{2^{6}} + \cdots \right) \right] \\ + \begin{bmatrix} \frac{1}{2} \rho_{ep} c_{p,ep} L_{s} \left\{ \sqrt{\frac{3k_{B} T \left(1 - 1.5\beta^{3}\phi\right)}{2\pi \rho_{ep} \beta^{3} a_{p}^{3}} + \frac{G_{T}}{6\pi \mu \beta a_{p} L_{s}} \right\} \right] \end{bmatrix}$	$\phi$ , $k_{\rm p}$ , $k_{\rm bp}$ $k_{\rm loyer}$ , $\delta$ chemical properties	Effect of BM, surface chemistry, interaction potential
Computational	Xue et al. (2004)		Molecular Dynamics (MD) The NL has no	The NL has no
models				significant effect on TC
	Li et al. (2010)		MD	The NL has a
				significant role in TC

$$k_{eff} = \left[1 + C\left(\frac{2k_BT}{\pi\mu d_p^2}\right) \frac{\phi a_{bf}}{k_{bf} (1 - \phi) a_p}\right] k_{bf}$$

$$\tag{47}$$

where C is a constant,  $k_B$  is the Boltzmann constant,  $\mu$  is the dynamic viscosity,  $d_p$  is the diameter of a particle,  $a_{bf}$  is the radius of the base fluid, and  $a_p$  is the radius of a particle. This model accounts for the dependence of thermal conductivity on particle size, volume fraction, and temperature. Predictions from the combined model agree with experimental data for nanofluids with an extremely small particle concentration. However, an order-of-magnitude estimate for the mean free path of a nanoparticle in a base fluid is  $10^{-2}$  m, which is physically unlikely. Moreover, this model has an inverse cubic dependence on the particle size,  $1/d_p^2 a_p$ . This is inconsistent with the authors' comment that the effective thermal conductivity enhancement is inversely proportional to the radius of the particle,  $1/a_p$ .

Patel *et al.* [119] proposed a cell model for the effective thermal conductivity of nanofluids considering the effects of the high specific surface area of the monodispersed nanoparticles and the microconvective heat transfer due to Brownian motion. This is a modified model of Patel *et al.* [90]. Patel *et al.* [119] developed a new cell model with following assumptions: (1) Nanofluids with low-particle concentration would be used; (2) Interparticle interactions are neglected; (3) Particle/fluid heat transfer is much more significant than particle/particle heat transfer. With these three assumptions, they considered a small control volume, or cell, of the homogenously distributed suspension. The cell consists of a particle surrounded by the liquid interacting with the particle. They categorized a new cell model into two parallel paths, i.e., one related to the heat conduction through the base liquid without considering the suspended particles, and the other a series of heat transfer which includes heat transfer from the liquid to the moving particle, heat propagation by conduction within the particle, and finally heat transfer to the liquid from the particle. In their analysis, they expressed the convective resistance between the liquid and the nanoparticle as the particle interfacial heat transfer coefficient h, which depends on particle velocity. They considered the thermal resistances in parallel and serial configurations appropriately and developed a cell model given by

$$\left(\frac{q_{eff}}{q_{bf}} - 1\right) = \frac{k_p}{k_{bf}} \left(\frac{\pi}{6 + \frac{\alpha_{bf} \cdot \pi \mu a_p}{C \cdot 2k_B T}}\right) \left(\frac{6\phi}{\pi}\right)^{\frac{1}{3}}$$
(48)

where  $q_{\it eff}$  is the effective heat flux of nanofluids,  $q_{\it hf}$  is the heat flux of the base fluid,  $\alpha_{\it hf}$  is the thermal diffusivity of the base fluid, and C is an empirical constant introduced to account for a one-dimensional approximation of the heat flow in the neighborhood of the spherical particle. This model can account for the nonlinear dependence of thermal conductivity of nanofluids on particle concentration at low particle concentrations.

Koo and Kleinstreuer [88] postulated that the enhancement of thermal conductivity of nanofluids is due mainly to Brownian motion. They developed a thermal conductivity model by adding Brownian motion effect to a conventional conductivity model, such as the Maxwell model. Taking into consideration factors such as Brownian motion, temperature, particle size, volume concentration, and the properties of the base fluid and the particle, they developed the model described by

$$k_{eff} = \left[ \frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\phi}{k_p + 2k_{bf} - (k_p - k_{bf})\phi} \right] k_{bf} + \left[ (5 \times 10^4)\beta\phi\rho_p c_{v,p} \sqrt{\frac{k_B T}{\rho_p d_p}} f(T, \phi, \text{etc.}) \right]$$
(49)

where  $\rho_p$  is the density of the particle,  $c_{v,p}$  is the specific heat of the particle,  $k_B$  is the Boltzmann constant,  $d_p$  is the particle diameter,  $\beta$  represents the fraction of the liquid volume that moves with a particle, and f is the factorial function. In Equation (49), the first bracket is the Maxwell model, while the second bracket represents a dynamic model of thermal conductivity due to Brownian motion of a large portion of surrounding liquid traveling with randomly moving nanoparticles. However, it is difficult to obtain the function f theoretically; it can only be determined from experimental data. Furthermore, the average traveling distance without changing its direction,  $l_{at}$ , has to be determined by, for example, molecular dynamics simulations. They assumed that  $l_{at}$  is the same as the diameter of the nanoparticle.

Prasher *et al.* [89] considered three possible mechanisms of thermal energy transfer in nanofluids: (1) translational Brownian motion; (2) the existence of an interparticle potential; and (3) convection in the liquid due to the Brownian movement of the particles. They performed an order-of-magnitude analysis on these three possible mechanisms and deduced that local convection due to the Brownian movement of the nanoparticles is the only mechanism that could explain the anomalous enhancement of thermal conductivity. Prasher *et al.* [89] also reasoned that, if the observed exceptional enhancements of thermal conductivity are due to small particle size, then thermal conductivity for large particle sizes should be explained based on the conventional effective medium theory such as the Maxwell-Garnett model. Therefore, they modified the Maxwell-Garnett model by including the Brownian-motion-induced convection from multiple nanoparticles. Their semi-empirical model can be written as

$$k_{eff} = \left(1 + A \operatorname{Re}^{m} \operatorname{Pr}^{0.333} \phi\right) \left[ \frac{k_{p} + 2k_{bf} + 2(k_{p} - k_{bf})\phi}{k_{p} + 2k_{bf} - (k_{p} - k_{bf})\phi} \right] k_{bf}$$
 (50)

where the Reynolds number Re is defined as

$$Re = \frac{1}{v} \sqrt{\frac{18k_B T}{\pi \rho_p d_p}}$$
 (51)

and A and m are empirical constants. In Equation (51), v is the kinematic viscosity of the fluid,  $k_B$  is the Boltzmann constant,  $\rho_p$  is the density of particle, and  $d_p$  is the particle diameter. In Equation (50), the first bracket represents a general correlation for convective heat transfer coefficient h for the Brownian motion-induced convection from multiple nanoparticles proposed by Prasher  $et\ al.$  [89]. The new model can predict the temperature-dependent thermal conductivity data for nanofluids and shows that the Brownian-motion-induced convection from multiple nanoparticles is the main reason for the observed thermal conductivity enhancement and trend. The model reduces to the Maxwell-Garnett model as Reynolds number becomes zero for larger particles. However, constants A and m can only be determined by experiment. Prasher  $et\ al.$  [89] explained that any model will be semi-empirical in nature because of the complexities involved with the interaction in the convective currents due to multiple nanoparticles.

Shukla and Dhir [120] proposed a microscopic model that takes into account the dependence of nanoparticle characteristics (size, volume fraction, interparticle potential) and liquid properties (viscosity, temperature), based on the theory of Brownian motion of nanoparticles in a fluid. To develop a model for the effective thermal conductivity of nanofluids, they used ensemble averaging techniques assuming the existence of small departures from equilibrium and the presence of pairwise-additive interaction potential between various nanoparticles. The model can be expressed as

$$k_{eff} = \left\{ \frac{k_p + 2k_{bf} + 2\left(k_p - k_{bf}\right)\phi}{k_p + 2k_{bf} - \left(k_p - k_{bf}\right)\phi} \right\} k_{bf} + \frac{n\hat{C}k_BT}{6\pi\mu a_p}$$

$$+ \frac{n^2k_B}{6\mu a_p} \left( \int_0^\infty r^2 g^{eq}(r)\Psi(r|T)dr \right) - \frac{n^2\hat{C}T}{6\mu a_p} \left( \int_0^\infty r^3 g^{eq}(r) \frac{\partial^2 \Psi(r|T)}{\partial T \partial r} dr \right)$$

$$- \frac{n^2\hat{C}}{6\mu a_p k_B T} \left( \int_0^\infty r^3 g^{eq}(r)\Psi(r|T) \frac{\partial \Psi(r|T)}{\partial r} dr \right)$$

$$(52)$$

where n is the number density of nanoparticles,  $\hat{C}$  is the heat capacity of a nanoparticle,  $k_B$  is the Boltzmann constant,  $\mu$  is the dynamic viscosity of the base fluid,  $a_p$  is the radius of the nanoparticles, r is an arbitrary point,  $g^{eq}$  is the equilibrium pair distribution function, and  $\Psi$  is the interparticle potential. In Equation (52), the first term represents macroscopic contribution given by the Hamilton-Crosser model, and the remaining four terms represent contribution from Brownian motion of nanoparticles. In the model, the kinetic contribution to the effective thermal conductivity was neglected. They selected a specific form of the repulsive DLVO potential, which accounts for the electrostatic repulsion between charged spherical nanoparticles in order to design the interparticle interaction between various nanoparticles. The potential function is assumed to be a function of the surface potential, the permittivity of the fluid, and the Debye length. They analyzed the interparticle potential effect on thermal conductivity through calculations involving DLVO interaction between the electric double layers on spherical nanoparticles. These calculations show the importance of long-range repulsive potentials for the enhancement of thermal conductivity of nanofluids. Shukla and Dhir's model can be used to estimate the thermal conductivity of various nanofluids with different nanoparticles, which may interact with each other through a specific interparticle potential such as DLVO, steric, or van der Waals forces. However, their analysis considered only two-body interactions and ignored the effects of higher multibody interactions. Moreover, their model is restricted to relatively large nanoparticles whose size is significantly larger than the molecular dimensions,

Yang [121] developed a thermal conductivity model derived form the kinetic theory of particles in the fluids under relaxation time approximations. This model takes into account convective heat transfer due to the Brownian movement of nanoparticles. Yang's effective thermal conductivity model is expressed as

$$k_{eff} = \left[ \frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\phi}{k_p + 2k_{bf} - (k_p - k_{bf})\phi} \right] k_{bf} + 157.5\phi C_f u_p^2 \tau$$
(53)

where  $C_f$  is the heat capacity per unit volume of the fluid,  $\tau$  is the particle relaxation time, and  $u_p$  is the Brownian velocity of the particle expressed as

$$u_p = \sqrt{\frac{3k_BT}{m_p}} \tag{54}$$

where  $k_B$  is the Boltzmann constant and  $m_p$  is the mass of particle. The first term in Equation (53) is the Maxwell model, which represents diffusive conduction, and the second term corresponds to convection due to the Brownian motion of nanoparticles. In the second term, 157.5 is not a fitting constant, but an analytically obtained value from integration of the fluid velocity over the hydrodynamic boundary layer around the Brownian particle. From this model, Yang found that the relaxation time of particle Brownian motion, which provides a measure of the time required for a particle to forget its initial velocity, could be significantly affected by the long-time tail in Brownian motion, which indicates that particle velocity is astonishingly persistent. However, this particle relaxation time  $\tau$  is difficult to obtain, both experimentally and theoretically.

#### 4.3.2. Computational models

Keblinski *et al.* [81] performed molecular dynamics (MD) simulations to calculate the thermal conductivity of a simple model of the liquid and solid by using the Green-Kubo relationships. Their simulation results demonstrated that collision between nanoparticles due to Brownian motion does not affect the thermal conductivity and the microscopic heat transport mechanism of the simple model while particle/liquid interfaces play an important role in the high overall conductivity of the nanofluids.

Bhattacharya *et al.* [122] developed a technique to predict the effective thermal conductivity of nanofluids using Brownian dynamics simulation coupled with the equilibrium Green-Kubo method. The combined parallel model of the effective thermal conductivity is given as

$$k_{eff} = \phi k_{peff} + (1 - \phi) k_{bf} \tag{55}$$

where  $k_{peff}$  is the effective contribution of the particles towards the overall thermal conductivity of the system. For the calculation of  $k_{peff}$ , they used the Green-Kubo relation as

$$k_{peff} = \frac{1}{k_B T^2 V} \sum_{j=0}^{n} \langle Q(0)Q(j\Delta t) \rangle \Delta t.$$
 (56)

where T is the temperature, V is the volume of the domain, n is the number of time steps used in the simulation,  $\Delta t$  is the time step, and  $\langle Q(0)Q(j \Delta t)\rangle$  is the time-autocorrelation function of Q(t). Based on their simulation results, they conclude that their model can predict the effective thermal conductivity of nanofluids with high accuracy.

Evans *et al.* [92] carried out both an analysis with kinetic theory and the simulation to investigate the effect of the Brownian motion on the effective thermal conductivity of nanofluids. For the simulation, they used the molecular dynamics simulations of heat flow in a model nanofluid with well-dispersed particles. Based on their kinetic theory analysis and results of MD simulation, they concluded that the enhancements of the thermal conductivity of nanofluids are not affected by hydrodynamic effects due to the Brownian motion and that the effective medium theory, such as the Maxwell-Garnett model, can be used for predicting the effective thermal conductivity of nanofluids with well-dispersed nanoparticles.

Vladkov and Barrat [93] simulated the thermal properties of nanofluids by using the molecular dynamics (MD) simulations. Based on their simulation results, they conclude that the Brownian motion of the particle does not affect the cooling process and that the Maxwell-Garnett model can predict the effective thermal conductivity of nanofluids. They also concluded that the essential parameter that influences the effective thermal conductivity is the ratio of the Kapitza length to the particle radius and that the large heat transfer enhancements observed in nanofluids comes from aggregation effects, such as particle clustering and percolation or cooperative heat transfer modes.

Using computer simulation, Li and Peterson [95] analyzed the mixing effect of the base fluid directly adjacent to the nanoparticles due to the Brownian motion of nanoparticles. They used CFX 5.5.1 software (computational fluid dynamics software of British AEA Technology, Inc.) and a finite-volume method for simulating the corresponding temperature, pressure, and velocity fields. They investigated the effects of single, adjacent, and multiple nanoparticles, respectively. Their results imply that Brownian motion induced microconvection and that mixing significantly enhances the macroscopic heat transfer in nanofluids. Their results also indicated that Brownian motion is one of the important factors for anomalous enhancement of the effective thermal conductivity of nanofluids.

Sarkar and Selvam [94] developed the nanofluids systems that consist of a base fluid model of argon and a nanofluid model of copper particles in argon with various nanoparticles concentrations. They used an equilibrium molecular dynamics simulation to model this nanofluid system and used the Green-Kubo relation to calculate the thermal conductivity of the base fluid and nanofluids. They found that the effective thermal conductivity of copper-argon nanofluids was much greater than predicted by the Hamilton-Crosser model at both very low volume concentration (up to 0.4%) and

high volume concentration (up to 8%). From mean square displacement computation by using molecular dynamics simulation, they also found that the movement of liquid atoms in nanofluids increases significantly (1.41 times in 1% nanofluid) compared to the movement of liquid atoms in base fluid, while the nanoparticle movement was 28 times slower than that of the liquid phase in 1% nanofluids. This implies that the Brownian motion of the nanoparticles is far too slow to transport the heat; on the other hand, localized fluid movement around nanoparticles is induced by much faster liquid atoms in nanofluids. They concluded that these phenomena are the main mechanism for enhanced thermal conductivity of nanofluids. However, the simluation cell considered only single nanoparticles and excluded the effects of aggregation.

Jain *et al.* [123] calculated the effective thermal conductivity of nanofluids using Brownian dynamic simulation and the thermal conductivity of nanofluids computed by using the Green-Kubo relation. They considered various parameters, such as particle concentrations ranging from 0.5 to 3 vol.%, particle size raging from 15 to 150 nm, and temperature ranging from 290 to 320 K. Their Brownian dynamic simulations exclude the fluid molecules and include the effect of hydrodynamic interactions related to the base fluid, through a position-dependent interparticle friction tensor. They commented that the simulation based on *N*-coupled Langevin equations, though very fundamental in its formulation, was able to simulate the effects of parameters such as particle concentration, particle size, and temperature of the fluid on the effective thermal conductivity of nanofluids. They assumed that thermal conduction caused by the motion of nanoparticles and the base fluid molecules occurs in parallel, and thus they used the combined parallel model for the calculation of the effective thermal conductivity as

$$k_{eff} = \phi k_{pB} + (1 - \phi) k_{bf} \tag{57}$$

where  $k_{pB}$  is the thermal conductivity owing to the Brownian motion of the nanoparticles. For the calculation of  $k_{nB}$ , they used the Green-Kubo relation as

$$k_{pB} = \frac{1}{k_B T^2 V} \sum_{i=0}^{n} \left( \frac{1}{3(n-j)} \sum_{i=0}^{n-j} \left\langle \mathbf{Q}(i\Delta t) \cdot \mathbf{Q} \left[ (i+j) \Delta t \right] \right\rangle \right) \Delta t.$$
 (58)

where T is the temperature, V is the volume of the domain, n is the number of time steps used in the simulation,  $\Delta t$  is the time step. With this simulation, they showed the effect of particle size, temperature, and volume concentration on the effective thermal conductivity of nanofluids. Based on their simulation results, they conclude that their model can predict the effective thermal conductivity of nanofluids and that the Brownian motion of the particle is the most important phenomenon, the key mechanism for the enhancement in the thermal conductivity of nanofluids.

A summary of Brownian motion based models for the thermal conductivity of nanofluids is listed in Table 3.

## 4.3.3. Empirical models

Chon *et al.* [46] and Vasu *et al.* [124] have developed empirical correlations for the effective thermal conductivity of nanofluids. Although they can predict the effective thermal conductivity of nanofluids very well, they are valid only for the nanofluids whose data were used to formulate the correlation and in the range of the data.

# 4.4. Aggregation based models

We categorize aggregation based models into three submodels: modified models, combined effects models, and computational models.

#### 4.4.1. Modified models

Wang et al. [84] developed a fractal model of the effective thermal conductivity of nanofluids based on the effective medium theory and the fractal theory for the description of nanoparticle cluster and its radial distribution. This model involves the application and improvement of the multicomponent Maxwell-Garnett model by substituting the effective thermal conductivity of the particle clusters,  $k_{cl}$ , which comes from Bruggeman model. Their fractal model can be expressed as

$$k_{eff} = \left[ \frac{(1-\phi) + 3\phi \int_{0}^{\infty} \frac{k_{cl}(a_{cl})n(a_{cl})}{\left[k_{cl}(a_{cl}) + 2k_{bf}\right]} da_{cl}}{(1-\phi) + 3\phi \int_{0}^{\infty} \frac{k_{bf}(a_{cl})n(a_{cl})}{\left[k_{cl}(a_{cl}) + 2k_{bf}\right]} da_{cl}} \right] k_{bf}$$
(59)

where  $a_{cl}$  is the equivalent radius of cluster,  $k_{cl}(a_{cl})$  is the effective thermal conductivity of nanoparticle clusters, and  $n(a_{cl})$  is the radius distribution function. The fractal model predicts well for CuO-water nanofluids when adsorption is included in the analysis, but it underpredicts the enhancement when the adsorption effect is excluded. This model can only predict the effective thermal conductivity of nonmetallic nanofluids.

#### 4.4.2. Combined effects models

Xuan *et al.* [69] developed a theoretical model for the effective thermal conductivity of nanofluids considering Brownian motion and aggregation structures. They assumed that the random motion of the nanoparticles is the main reason for the difference between nanofluids and conventional fluids. Although the suspended nanoparticles are in Brownian motion, some particles may aggregate because of collisions with other particle. Thus, they simulated random motion and the aggregation process of the nanoparticles by using the theory of Brownian motion and the diffusion-limited aggregation model. Their thermal conductivity model can be written as

$$k_{eff} = \left[ \frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\phi}{k_p + 2k_{bf} - (k_p - k_{bf})\phi} \right] k_{bf} + \frac{\rho_p \phi c_{v,p}}{2} \sqrt{\frac{k_B T}{3\pi a_{cl} \mu}}$$
 (60)

where  $a_{cl}$  denotes the apparent radius of the nanoparticle cluster and depends on the fractal dimension of the cluster structure. In Equation (60), the first term is the Maxwell model and the second term corresponds to the component of thermal conductivity enhancement due to the Brownian motion of the suspended nanoparticles and/or clusters. This model indicates that the effective thermal conductivity of nanofluids can be affected by the Brownian motion of the suspended nanoparticles and/or clusters and the structure of the nanoparticles and/or clusters.

Prasher *et al.* [85] combined the aggregation kinetics of nanofluids based on colloidal chemistry with the physics of thermal transport (microconvective effects due to Brownian motion) to study the effects of aggregation on the effective thermal conductivity of nanofluids. The particles well dispersed at initial time (t = 0) agglomerate to form multiple aggregates as time goes on. These aggregates are considered to be new "particles" with an effective radius ( $a_{\rm ag}$ ) that enhance the thermal conductivity of nanofluids. However, this enhancement will decrease as the aggregates continue to agglomerate to form much bigger aggregates. As  $t \to \infty$ , all nanoparticles will agglomerate to form one large aggregate, at which time enhancement of thermal conductivity may not occur because one large aggregate will be settled. The suggested relation is

$$\phi_p = \phi_{\rm int} \phi_{ag} \tag{61}$$

where  $\phi_{\rm p}$  is the volume fraction of the primary particles,  $\phi_{\rm int}$  is the volume fraction of the particles in the aggregates, and  $\phi_{ag}$  is the volume fraction of the aggregates in the entire fluid. The relation

	Investigator	Formulation	Key parameter	Remarks
	Jang and Choi (2004)	$k_{e\!f\!f} = k_{b\!f} \left( (1 - \phi) + eta k_p \phi + C_1 rac{d_{b\!f}}{d_p} k_{b\!g} \operatorname{Re}_{d_p}^2 \operatorname{Pr} \phi$	$\phi, k_p, k_{bf}$ $u_p = \frac{k_B T}{3\pi\mu d_p l_{bf}}$	BM induced nanoconvection
etical lels	Kumar et al. (2004)	$k_{cff} = \left[1 + C\left(rac{2k_BT}{\pi\mu d_p^2} ight)rac{\phi a_{bf}}{k_{bf}\left(1 - \phi ight)a_p} ight]k_{bf}$	$\phi, k_p, k_{bf}$ $u_p = \frac{2k_BT}{(\pi n d_p^2)}$	Consider the effect of BM of particle with kinetic theory
	Patel <i>et al.</i> (2008)	$\left(\frac{q_{\rm eff}}{q_{\rm bf}}-1\right) = \frac{k_p}{k_{\rm bf}} \left(\frac{\pi}{6+\frac{\alpha_{\rm bf}\cdot \pi \mu a_p}{C\cdot 2k_BT}}\right) \left(\frac{6\phi}{\pi}\right)^{\frac{1}{3}}$	$\phi.k_p, k_{b\mathcal{G}}$ $u_p = rac{2k_BT}{(\pi n!d_p^2)}$	Thermal electric approach with BM induced nanoconvection effect
	Koo and Kleinstreuer (2004)		$\phi$ , $k_p$ , $k_{bp}$	BM induced nanoconvection with EMT
		$k_{eff} = \left[\frac{k_p + 2k_{bf} - (k_p - k_{bf})\phi}{k_p + 2k_{bf} - (k_p - k_{bf})\phi}\right] k_{bf} + \left[(5 \times 10^{\circ})\beta\phi\rho_{\nu}c_{\nu,p}\sqrt{\frac{n}{\rho_{\nu}}f}f(T,\phi,\text{etc.})\right]$	$u_p = \sqrt{\frac{\cos b}{\pi \phi_p d_p}}$	
	Prasher <i>et al.</i> (2005)	$k_{eff} = \left(1 + ARe^{m} Pr^{0.333} \phi\right) \left[ \frac{k_p + 2k_{ty} + 2(k_p - k_{ty}) \phi}{k_p + 2k_{ty} - (k_p - k_{ty}) \phi} \right] k_{ty}$	$\psi, k_p, k_{bf}$ $u_p = \sqrt{\frac{18k_BT}{\pi \rho_p d_p^3}}$	BM induced nanoconvection with EMT consider ITR
	Shukla and Dhir (2008)	$k_{eff} = \left\{ \frac{k_p + 2k_{bf} + 2\left(k_p - k_{bf}\right)\phi}{k_p + 2k_{bf} - \left(k_p - k_{bf}\right)\phi} \right\} k_{bf} + \frac{n\hat{C}k_BT}{6\pi\mu a_p}$	$\phi$ , $k_{\rho}$ , $k_{b\rho}$ $\Psi$ : interparticle potential	Consider BM effect based on interparticle potential with EMT
		$+\frac{n^2k_B}{6\mu a_p}\left(\int_0^{\infty}r^2g^{eq}\left(r\right)\Psi\left(r T\right)dr\right)-\frac{n^2\hat{C}T}{6\mu a_p}\left(\int_0^{\infty}r^3g^{eq}\left(r\right)\frac{\partial^2\Psi\left(r T\right)}{\partial T\partial r}dr\right)$		
		$-\frac{n^2\hat{C}}{6\mu a_p k_B T} \left( \int_0^\infty r^3 g^{eq}\left(r\right) \Psi\left(r T\right) \frac{\partial \Psi\left(r T\right)}{\partial r} dr \right)$		

Table 3. Summary of models considering Brownian motion effect (1/2)

	Investigator	Formulation	Key parameter	Remarks
	Yang (2008)		Ø K. K.	BM induced
		$\begin{bmatrix} k + 2k, + 2(k - k, \cdot) \theta \end{bmatrix}$	la d	nanoconvection under
		$k_{eff} = \begin{bmatrix} \frac{-p}{k_p} & \frac{-p-p}{k_{bf}} & \frac{-p-p}{k_{bf}} \end{bmatrix} k_{bf} + 157.5 \phi C_f u_p^2 \tau$	$u_p = \sqrt{\frac{3k_BT}{m_p}}$	relaxation time approximation with Maxwell model
	Keblinski et al. (2002)	k = -4	MD	The BM is negligible
		$k_{peff} = rac{1}{k_B T^2 V} \sum_{j=0}^{n} \left\langle \mathcal{Q}(0) \mathcal{Q}(j \Delta t) \right angle \Delta t.$		effect on nanofluids
	Bhattacharya et al. (2004)		Brownian Dynamics	The BM is significant
			Simulation (BD)	effect on NFs
	Evans et al. (2006)		MD	The BM is negligible
				effect and well matched
				with EMT
Computational	Vladkov and Barrat (2006)		MD	The BM is negligible
models				effect and well
				matched with EMT
				with ITR
	Li and Peterson (2007)		CFX	The BM induced
			(Commercial software)	nanoconvectin is
				significant effect
				on NFs
	Sarkar and Selvam (2007)	•	MD	The BM induced
				nanoconvectin is
				significant effect on NFs
	Jain et al. (2009)	h = h + h + h	BD	The BM induced
		$     \lambda_{eff} = \psi \Lambda_{pB} + (1 - \psi) \Lambda_{bf} $		nanoconvectin is
		1 " ( 1 "-j		significant effect on
		$k_{pB} = \frac{1}{k_B T^2 V} \sum_{j=0}^{1} \left( \frac{1}{3(n-j)} \sum_{j=0}^{L} \left\langle Q(i\Delta t) \cdot Q\left[ (i+j)\Delta t \right] \right\rangle \right) \Delta t.$		NFs

in Equation (61) shows that, in the case of a well-dispersed system,  $\phi_{\rm int}=1$  because there is only one particle in each aggregate and thus  $\phi_{ag}=\phi_{\rm p}$ , while for a medium composed wholly of aggregates,  $\phi_{ag}=1$ , and thus  $\phi_{\rm int}=\phi_{\rm p}$ . They assumed that the maximum thermal conductivity owing to conduction will lie between these two limits. Considering aforementioned phenomena, they modified the Maxwell-Garnett model by substituting the thermal conductivity of the aggregates  $k_{ag}$  and the volume fraction of the aggregates  $\phi_{ag}$  as

$$k_{eff} = \left(1 + A \operatorname{Re}^{m} \operatorname{Pr}^{0.333} \phi\right) \left[ \frac{k_{ag} + 2k_{bf} + 2(k_{ag} - k_{bf})\phi_{ag}}{k_{ag} + 2k_{bf} - (k_{ag} - k_{bf})\phi_{ag}} \right] k_{bf}$$
(62)

They stated that the effective thermal conductivity of nanofluids depends on parameters such as the Hamaker constant, the zeta potential, pH, and ion concentration. They also mentioned that the conductive component of the thermal conductivity ratio can also increase with temperature, depending on the chemistry of the solution. However, they excluded the effects of thermal boundary resistance between the particles and the fluid for simplicity. The modified Maxwell-Garnett model reduces to the original Maxwell-Garnett model for well-dispersed media.

Feng *et al.* [125] developed a new model for effective thermal conductivity of nanofluids that accounts for the effect of the nanolayer and the aggregation effect of nanoparticles. They divided the aggregation model into two parts: the coherent fluid and a quarter of the column of radius  $(a_p + \delta)$ . They further divided the column into two parts: the touching particles and the base fluid. Their model can be expressed as

$$k_{eff} = \left(1 - \phi_{e}\right) \left[ \frac{k_{pe} + 2k_{bf} + 2\left(k_{pe} - k_{bf}\right)\left(1 - \eta\right)^{3} \phi}{k_{pe} + 2k_{bf} - \left(k_{pe} - k_{bf}\right)\left(1 + \eta\right)^{3} \phi} \right] k_{bf}$$

$$+ \phi_{e} \left[ \left(1 - \frac{3}{2}\phi_{e}\right) + \frac{3\phi_{e}}{\eta} \left\{ \frac{1}{\eta} \ln \frac{a_{p} + \delta}{\left(a_{p} + \delta\right)\left(1 - \eta\right)} - 1 \right\} \right] k_{bf}$$
(63)

where  $\phi_e$  is the equivalent volume fraction defined as  $\phi_e = \phi(1+\beta)^3$  and  $\beta = \delta/a_p$  is the ratio of the nanolayer thickness to the original particle radius;  $k_{pe}$  is the equivalent thermal conductivity of the equivalent particles defined by Yu and Choi [82]; and  $\eta = 1 - k_{bf}/k_{pe}$ . It can be shown that if  $\phi_e \rightarrow 2/3$ , the aggregation model dominates the heat transfer and all particles are in the touching state, while if  $\phi_e \rightarrow 0$ , the Maxwell model dominates the heat transfer and all particles are in the nontouching state. They found that the contributions from clusters owing to nanoparticle aggregation increase with decreasing nanoparticle size at a constant volume fraction. This phenomenon is caused by decreasing the average interparticle distance as the particle size decreases, which increases the van der Waals forces, resulting in increased probability of aggregation. Based on this explanation, they concluded that the aggregation of suspended nanoparticles is one of the crucial mechanisms for enhancing the thermal conductivity of nanofluids. However, this model was derived with approximation of two-dimensional lattice model. Thus, the disordering effect and the defect tolerance of nanoparticles in the fluids may be considered for more realistic prediction.

## 4.4.3. Computational models

Prasher et al. [86] demonstrated that the aggregation of nanoparticles can significantly enhance the thermal conductivity of nanofluids. They assumed that a fractal cluster is embedded within a sphere

with a radius equal to the radius of gyration  $R_g$  and is composed of several approximately linear chains, which span the entire cluster and side chains. These linear chains are called the backbone of the cluster, while the other particles are called dead ends [126, 127]. Figure 6 represents the backbone of the cluster and dead ends. The backbone can play an important role in thermal conductivity due to its connectivity. They used the modified Maxwell-Garnett model, Equation (60) for calculating the effective thermal conductivity of the whole system. They showed that predictions of their modified Maxwell-Garnett model are in excellent agreement with detailed numerical calculations on model nanofluids involving fractal clusters. The results also showed the importance of cluster morphology on thermal conductivity enhancements. Based on the results of the numerical simulation, they concluded that conduction-phenomenon-based thermal conductivity of nanofluids can be significantly enhanced as a result of aggregation of the nanoparticles. This aggregation is a function of the chemical dimension of the aggregates and the radius of gyration of the aggregates. However, they excluded the effect of thermal interfacial resistance in their analysis.

Evans *et al.* [128] analyzed and simulated the effect of the aggregation and interfacial thermal resistance on the effective thermal conductivity of nanofluids and nanocomposites. This was an extension of the study of Prasher *et al.* [86], including the effect of interfacial thermal resistance. They also used the modified Maxwell-Garnett model, Equation (60), derived by Prasher *et al.* [85], for calculating the effective thermal conductivity of the whole system, as well as the three-level homogenization theory validated by Monte Carlo simulations. They demonstrated that the aggregation of high conductive nanoparticles in a liquid or solid low-conductivity matrix affects the thermal conductivity enhancement significantly. The key factor is the high aspect ratio backbone of the fractal-like aggregates. Based on the results of their analysis and simulations, they obtained the same results of Prasher *et al.* [86], and they also showed that there was no enhancement in nanofluid thermal conductivity when the particle radius is equal to the Kapitza radius. Thus any enhancement in the thermal conductivity would be degraded.

Table 4 summarizes the aggregation based models for the thermal conductivity of nanofluids.

#### 4.5. Other mechanism based models

Nan et al. [129] developed a simple formula for the effective thermal conductivity of carbon nanotube composites, based on Maxwell-Garnett type effective medium theory. They assumed that the thermal conductivities of the carbon nanotubes along transverse axes  $k_x$  and longitudinal axes  $k_z$  are much higher than the thermal conductivity of the base fluid  $k_{bf}$  Moreover, in the case of the dilute limit case ( $\phi < 0.02$ ), the effective thermal conductivity of carbon nanotube composites can be expressed as

$$k_{eff} = \left(1 + \frac{\phi k_{cnt}}{3k_{bf}}\right) k_{bf} \tag{64}$$

where  $k_{cnt}$  denotes the thermal conductivity of carbon nanotubes. They found that this simple formula predicts much higher thermal conductivity enhancement even in the dilute limit case because of the ultrahigh thermal conductivity and aspect ratio of the carbon nanotubes. Comparing this model to experimental data, Nan *et al.* [129] conclude that the simple model shows good agreement with the nanotube-based composites.

Nan *et al.* [130] also developed a simple equation for predicting the effective thermal conductivity of nanotube-based nanofluids in terms of an effective medium approach accounting for interfacial thermal resistance. The effective thermal conductivity of the nanotube composite with carbon nanotubes randomly dispersed in a matrix can be expressed as

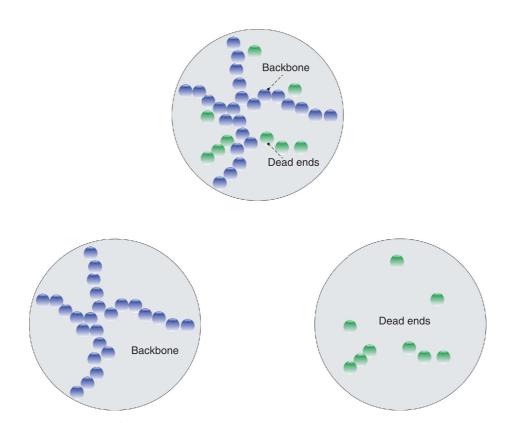


Figure 6. Schematic of 'backbone cluster' and 'dead ends'.

$$k_{eff} = \frac{3 + \phi \left(\beta_x + \beta_z\right)}{3 - \phi \beta_x} \tag{65}$$

with

$$\beta_{x} = \frac{2(k_{xx} - k_{bf})}{k_{xx} + k_{bf}}, \qquad \beta_{z} = \frac{k_{zz}}{k_{bf}} - 1$$
 (66)

where  $k_{xx}$  and  $k_{zz}$  are the equivalent thermal conductivities along transverse axes and longitudinal axes of composite unit cells, respectively, i.e., a nanotube surrounded by a very thin interfacial thermal barrier layer and can be expressed as

$$k_{xx} = \frac{k_{cnt}}{1 + \frac{2a_K}{d_{cnt}}} \frac{k_{cnt}}{k_{bf}}, \qquad k_{zz} = \frac{k_{cnt}}{1 + \frac{2a_K}{L_{cnt}}} \frac{k_{cnt}}{k_{bf}}$$
(67)

where  $d_{\it cnt}$  and  $L_{\it cnt}$  are the diameter and length of the nanotubes, respectively; and  $a_{\it K}$  is the Kapitza radius defined as

$$a_K = R_K k_{bf} (68)$$

Table 4. Summary of models considering aggregation effect

	Investigator	Formulation	Key parameter	Remarks
Modified models	Wang et al. (2003)	$k_{eff} = \begin{bmatrix} (1 - \phi) + 3\phi \int_0^{\infty} \frac{k_{cl}(a_{cl}) n(a_{cl})}{k_{cl}(a_{cl}) + 2k_{bf}} da_{cl} \\ (1 - \phi) + 3\phi \int_0^{\infty} \frac{k_{bf}(a_{cl}) n(a_{cl})}{k_{cl}(a_{cl}) + 2k_{bf}} da_{cl} \end{bmatrix} k_{bf}$	$\phi, k_p, k_{bf}$ $D_f$ :fractal dimension	Modified Bruggeman model with aggregation (Agg) effect
	Xuan et al. (2003)	$k_{eff} = \left[ \frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\phi}{k_p + 2k_{bf} - (k_p - k_{bf})\phi} \right] k_{bf} + \frac{\rho_p \phi_{c_{V,D}}}{2} \sqrt{\frac{k_B T}{3\pi a_{el} \mu}}$	$\phi$ , $k_p$ , $k_{bf}$ $D_f$ :fractal dimension	EMT approach with Agg and BM effect
Combined effects models	Prasher <i>et al.</i> (2006)	$k_{eff} = \left(1 + A \operatorname{Re}^{m} \operatorname{Pr}^{0.333} \phi\right) \left[ \frac{k_{ag} + 2k_{bf} + 2\left(k_{ag} - k_{bf}\right)\phi_{ag}}{k_{ag} + 2k_{bf} - \left(k_{ag} - k_{bf}\right)\phi_{ag}} \right] k_{bf}$	$\frac{\phi, k_p, k_{bf}}{a_p} = \left(1 + \frac{t}{t_p}\right)^{\overline{D}_f}$	EMT approach based on the Agg kinetics and BM effect
	Feng <i>et al.</i> (2007)	$k_{eff} = (1 - \phi_e) \left[ \frac{k_{pe} + 2k_{bf} + 2(k_{pe} - k_{bf})(1 - \eta)^3 \phi}{k_{pe} + 2k_{bf} - (k_{pe} - k_{bf})(1 + \eta)^3 \phi} \right] k_{bf}$ $+ \phi_e \left[ \left( 1 - \frac{3}{2} \phi_e \right) + \frac{3\phi_e}{\eta} \left\{ \frac{1}{\eta} \ln \frac{a_p + \delta}{(a_p + \delta)(1 - \eta)} - 1 \right\} \right] k_{bf}$	$\phi$ , $k_p$ , $k_{bf}$ $\phi_T = \phi(1 + \delta / a_p)^3$	EMT approach with NL and Agg effect
Computational	Prasher <i>et al.</i> (2006, APL)		Monte Carlo simulation (MC)	Agg with 3 level EMT theory, this model can be well matched with MC simulation results
models	Evans et al. (2008)		MC	Additional study of Prasher et al. 06 APL with ITR

where  $R_K$  is the Kapitza resistance. For the case of the dilute limit case ( $\phi$  < 0.01), the effective thermal conductivity of carbon nanotube composites can be simplified as

$$k_{eff} = 1 + \frac{\phi p}{3} \frac{\left(k_{cnt} / k_{bf}\right)}{p + \frac{2a_K}{d_{cnt}} \frac{k_{cnt}}{k_{bf}}}$$
(69)

where p is the aspect ratio of nanotubes ( $p = L_{cnt}/d_{cnt}$ ). This simple expression demonstrates that interface thermal resistance diminishes the thermal conductivity enhancement. Thermal conductivity of carbon nanotubes without interface thermal resistance would be much higher than that with the interface thermal resistance. If a carbon nanotube has no interface thermal resistance and  $p \gg 1$ , the effective thermal conductivity of carbon nanotube composites can further be simplified as

$$k_{eff} = \left(1 + \frac{\phi k_{cnt}}{3k_{bf}}\right) k_{bf} \tag{70}$$

which is independent of geometric parameters of nanotubes and is same as the expression by Nan *et al.* [129]. With the results of their analysis, they conclude that the effective thermal conductivity of carbon nanotube-based nanofluids is limited by interface thermal resistance. If a carbon nanotube has high interface thermal resistance across the nanotube-matrix interface, this causes a significant degradation in thermal conductivity enhancement.

Xue [131] developed a new model for the effective thermal conductivity of carbon nanotube-based nanofluids accounting for orientation distribution. They derived two formulae for the effective thermal conductivity of CNTs-based nanofluids, based on Maxwell theory. The first formula is

$$k_{eff} = \left[ \frac{(1 - \phi) + (4\phi / \pi) \sqrt{k_{cnt} / k_{bf}} \arctan(\pi / 4\sqrt{k_{cnt} / k_{bf}})}{(1 - \phi) + (4\phi / \pi) \sqrt{k_{bf} / k_{cnt}} \arctan(\pi / 4\sqrt{k_{cnt} / k_{bf}})} \right] k_{bf}$$
(71)

and the second formula is

$$k_{eff} = \left[ \frac{(1 - \phi) + 2\phi \left\{ k_{cnt} / \left( k_{cnt} - k_{bf} \right) \right\} \ln \left\{ \left( k_{cnt} + k_{bf} \right) / 2k_{bf} \right\}}{(1 - \phi) + 2\phi \left\{ k_{bf} / \left( k_{cnt} - k_{bf} \right) \right\} \ln \left\{ \left( k_{cnt} + k_{bf} \right) / 2k_{bf} \right\}} \right] k_{bf}$$
(72)

The formation of these two models depends on determination of distribution function. These models imply that dispersion of very small amount of CNTs can cause a remarkable enhancement in the effective thermal conductivity of CNTs-based nanofluids.

Murshed *et al.* [39] developed a new model for predicting the effective thermal conductivity of nanofluids accounting for the geometric structure of uniformly dispersed nanoparticles in base fluids along with the particle size. They mentioned that in order to achieve better stability of nanofluids, it is important to ensure homogeneous distribution of nanoparticles in the base fluid. They considered body-centered cubic arrays to be ideal for their study: these arrays have the maximum number of points for heat flow analysis (eight), and they show slightly higher heat flow rate compared to other periodic arrays, such as simple cubic and face-centered cubic. They considered two thermal circuits, each of which was in one-dimensional conduction with a two-phase system. One circuit included thermal resistances offered by the solid and fluids phases in parallel (upper bound), and thus the

effective thermal conductivity of two-phase medium can be expressed as

$$k_{eff} = \phi k_p + (1 - \phi) k_{bf} \tag{73}$$

The other circuit included thermal resistances in series (lower bound) to the direction of heat flow, and the effective thermal conductivity of the two-phase medium can be written as

$$k_{eff} = \frac{\phi}{k_p} + \frac{\left(1 - \phi\right)}{k_{bf}} \tag{74}$$

Their new model for the effective thermal conductivity of nanofluids is given as

$$k_{eff} = \frac{k_{bf} \left[ 1 + 0.27\phi^{4/3} \left( \frac{k_p}{k_{bf}} - 1 \right) \right] \left[ 1 + \frac{0.52\phi}{1 - \phi^{1/3}} \left( \frac{k_p}{k_{bf}} - 1 \right) \right]}{1 + \phi^{4/3} \left( \frac{k_p}{k_{bf}} - 1 \right) \left( \frac{0.52\phi}{1 - \phi^{1/3}} + 0.27\phi^{1/3} + 0.27 \right)}$$
(75)

This model can predict the effective thermal conductivity of nanofluids more accurately than the classical models of Maxwell, Hamilton-Crosser, and Bruggeman. The model shows that in homogeneously dispersed nanofluids, the particle size affects the thermal conductivity implicitly through the volume fraction and the particle distance.

Gao and Zhou [132] presented differential effective medium theory for the effective thermal conductivity of nanofluids by simultaneously taking into account the geometric anisotropy and the physical anisotropy. The geometric anisotropy arises from the large aspect ratio of carbon nanotubes, and the physical anisotropy comes from the interfacial thermal resistance [130]. Their model is given as

$$1 - \phi = \left(\frac{k_{bf}}{k_{eff}}\right)^{3A} \left(\frac{k_{bf} + B_1}{k_{bf} + B_1}\right)^{3C_1} \left(\frac{k_{bf} + B_2}{k_{eff} + B_2}\right)^{3C_2}$$
(76)

where

$$A = \frac{2L_z \left(-5 - 8L_z - 3L_z^2\right)}{\left(2 + 6L_z\right)\left(3L_z - 5\right)}$$
(77)

and

$$B_{1,2} = \frac{k_z - 3k_x \left(-1 + L_z\right) - 3k_z L_z \pm N}{-10 + 6L_z}$$
(78)

and

$$C_{1,2} = \frac{N\left(1 + 8L_z - 9L_z^2\right) \pm \left[k_x\left(-1 + L_z\right)^2\left(13 + 21L_z\right) + k_z\left(1 + 5L_z + 47L_z^2 - 21L_z^3\right)\right]}{N\left(-10 + 6L_z\right)\left(1 + 3L_z\right)}$$
(79)

with

$$N = \sqrt{k_z^2 (1 - 3L_x)^2 + 9k_x^2 (-1 + L_z)^2 + 2k_x k_z (13 + 12L_z - 9L_z^2)}$$
(80)

where  $L_z$  [ $L_x = (1 - L_z)/2$ ] is the depolarization factor of spheroidal particles and z denotes the rotational axis; and  $k_z$  and  $k_z$  are the thermal conductivities along transverse axes and longitudinal axes, respectively. They found that the adjustment of the particle shape is helpful to achieve appreciable enhancement of the effective thermal conductivity of nanofluids. For randomly isotropic spherical inclusions, their formula reduces to the Bruggeman model. Their model can predict the nonlinear relationship between the effective thermal conductivity and the volume fraction, even for very low volume concentrations. However, their model cannot explain the strong dependence of enhancement on temperature, and to achieve such a dependence, Brownian motion must be considered for nanoparticles with small sizes.

Xue [133] developed a new formula for predicting the effective thermal conductivity of carbon nanotube-based nanofluids accounting for the interface thermal resistance with an average polarization theory. In developing the procedure, their approach is very similar to Nan *et al.* [130]. Their model can be written as

$$9(1-\phi)\frac{k_{eff}-k_{bf}}{2k_{eff}+k_{bf}} + \phi \left[\frac{k_{eff}-k_{zz}}{k_{eff}+0.14(2a_{cnt}/L_{cnt})(k_{zz}-k_{eff})} + \frac{4(k_{eff}-k_{xx})}{2k_{eff}+0.5(k_{xx}-k_{eff})}\right] = 0$$
(81)

where

$$k_{xx} = \frac{k_{cnt}}{1 + \frac{2a_K}{d_{cnt}}} \frac{k_{cnt}}{k_{bf}}, \qquad k_{zz} = \frac{k_{cnt}}{1 + \frac{2a_K}{L_{cnt}}} \frac{k_{cnt}}{k_{bf}}$$
(67)

Their model predicts that the thermal conductivity enhancement of nanofluids increases quickly as the thermal conductivity of the base fluid decreases and increases as the thermal conductivity of the carbon nanotube increases [133].

Minnich and Chen [134] introduced a modified effective medium approach formulation for nanocomposites and assumed that the characteristic length of the inclusion is equal to or less than the phonon mean free path. Their modified effective medium approach formulation can be expressed as

$$k_{eff} = \left[ \frac{1}{3} c_{v,bf} v_{pho,bf} \frac{1}{(1/l_{bf}) + (\Phi/4)} \right] \left[ \frac{k_p (1 + 2\kappa) + 2k_{bf} + 2\phi \left\{ k_p (1 - \kappa) - k_{bf} \right\}}{k_p (1 + 2\kappa) + 2k_{bf} - \phi \left\{ k_p (1 - \kappa) - k_{bf} \right\}} \right]$$
(82)

where  $c_{v,bf}$  is the volume specific heat of the base fluid,  $v_{pho,bf}$  is the phonon group velocity of the base fluid,  $l_{bf}$  is the phonon mean free path of the base fluid, and  $\Phi$  is the interface density for spherical particles defined as

$$\Phi = \frac{4\pi \left(d_p / 2\right)^2}{L_{av}} = \frac{6\phi}{d_p}$$
 (83)

where  $L_{av}$  is the average length of a side of a cube that encloses one nanoparticle. In Equation (82),  $\kappa$  is a dimensionless parameter defined as

$$\kappa = \frac{a_K}{\left(d_p / 2\right)} \tag{84}$$

where  $a_K$  is the Kapitza radius defined as

$$a_K = R_K k_{bf} (68)$$

where  $R_K$  is the Kapitza resistance (thermal boundary resistance). Their results show good agreement with Monte Carlo (MC) simulations and solutions to the Boltzmann equation [134]. They also found that the thermal conductivity in nanocomposites is governed by the interface density and that thermal boundary resistance (TBR) plays an important role in determining the effective thermal conductivity.

Jung and Yoo [135] proposed a novel model for the effective thermal conductivity of nanofluids. They adopted the kinetic theory to show the effect of Brownian motion with a mean free path and the interparticle interaction due to the electrical double layer (EDL). The effect of interparticle interaction due to the existence of electrical double layer was considered by Jung and Yoo for the first time. Their model consists of the stationary mode (based on conventional theory), the single particle motion mode (based on thermal conductivity of nanofluids considering the kinetic theory with Brownian motion), and the interparticle interaction mode (based on thermal conductivity of nanofluids and originating from the kinetic theory regarding the particle motions induced by electrical double layer). Their model can be expressed as

$$k_{eff} = \left[ \frac{k_p + 2k_{bf} + 2(k_p - k_{bf})\phi}{k_p + 2k_{bf} - (k_p - k_{bf})\phi} \right] k_{bf} + \frac{\phi l_p \hat{c}_v}{3} \frac{k_B T}{3\pi\mu d_p l_{bf}} + \frac{\phi l_p \hat{c}_v}{3} \sqrt{\frac{Ae_c^2 l_p}{\varepsilon_{bf} m_p (a_p \phi^{-1/3})^2}}$$
(85)

where  $l_p$  is the mean free path of the nanoparticle,  $l_{bf}$  is the liquid mean free path,  $\hat{c}_v$  is the specific heat per particle as estimated by the Debye model per particle, A is the Coulomb constant,  $e_c$  is the electrical charge,  $\varepsilon_{bf}$  is the dielectric constant of the base fluid, and  $m_p$  is the mass of the nanoparticle. The mean free path of the nanoparticle based on the assumption that all particles move about with a Maxwellian velocity distribution is given as

$$l_p = \frac{1}{\sqrt{2}\phi\pi d_p^2} \tag{86}$$

Their model shows that the interparticle interaction due to the electrical double layer contributes significantly to the enhancement of the thermal conductivity of nanofluids.

Table 5 summarizes other mechanism based models for the thermal conductivity of nanofluids and shows the formulation, key parameters for determining thermal conductivity, and remarks.

In summary, classical EMT-based static models cannot predict the magnitude and trend of the thermal conductivity of nanofluids, although predictions of EMT-based models agree with some data that do not show anomalously enhanced or temperature- or particle-size-dependent conductivities. New static models developed to improve classical models are much better than effective medium based classical models in narrowing the gap between thermal conductivity enhancement data and model predictions. However, new static models are unable to capture other features such as the dependence of the thermal conductivity of nanofluids on nanoparticle size and fluid temperature. However, new models based on a combination of static and dynamic mechanisms appear to predict not only the magnitude of the enhanced thermal conductivity but also other features of the thermal conduction behavior of nanofluids. In the future, comprehensive models that can predict all the novel features of nanofluids, including size- and temperature-dependent thermal conductivity should be developed based on new mechanisms as well as the classical diffusion mechanism.

### 5. CONCLUDING REMARKS

Pioneering scientists and engineers have discovered novel properties in nanofluids that are utterly unexpected in conventional suspensions of micro- or millimeter-sized solid particles. They have proposed mechanisms of energy transport in nanofluids based on the links between nanoparticle structure and/or dynamics and thermal properties and developed various models for k of nanofluids. Although there have been numerous experimental, theoretical, analytical, and numerical studies, most of the issues related to the data, mechanisms, and models are still unresolved and pose many formidable challenges. Therefore, much research is still required in the future in order to resolve critical issues such as data inconsistencies, the sufficiency and suitability of classical and new mechanisms, and the discrepancies between experimental data and model predictions.

### 5.1. Data inconsistencies

Despite the problem of conflicting experimental data, it is generally agreed that thermal conductivity behavior of nanofluids has features that cannot be explained by the classical effective medium theories alone. The classical effective medium theories significantly underpredict the magnitude of most thermal conductivity enhancement data. Moreover, they are inherently unable to predict the size- and temperature-dependent thermal conductivity of nanofluids. As shown in Figure 2, nanofluids produced by one-step processes set themselves apart from those produced by two-step methods. Furthermore, nearly all nanofluids used so far for the studies of their k are polydisperse systems of nanoparticles and aggregated nanoparticles. However, it is highly desirable to make monodisperse nanofluids for discovery of mechanisms and development of new models for the thermal conductivity of nanofluids. Therefore, it is recommended to produce high-quality nanofluids with well-dispersed monosize nanoparticles using a one-step process [5, 27, 136] with little or no dispersants. It is crucial to generate a thermal conductivity database using such high-quality nanofluids for the discovery and validation of mechanisms behind all the features of the thermal conductivity of nanofluids.

### 5.2. Mechanisms

Effective medium theories based on the underlying assumption of diffusive conduction and motionless nanoparticles are not sufficient to predict the new features of the thermal conductivity of nanofluid. A number of microscale and macroscale mechanisms have been proposed to explain the magnitude and trend of the thermal conductivity of nanofluids. New models based on the proposed heat conduction mechanisms in nanofluids can predict both the magnitude and trend of the thermal conductivity of nanofluids. However, they cannot accurately predict experimental data. Therefore, the proposed concepts and mechanisms behind the thermal conductivity behavior of nanofluids remain to be validated. Therefore, more systematic experiments with well-dispersed, well-characterized nanofluids and a better understanding of the physics of fluid flow and heat transfer at the nanoscale are needed to establish the fundamental mechanisms of heat conduction in nanofluids. Understanding the underlying mechanisms of heat conduction in nanofluids is the essential requirement for the development of models that can accurately predict the k behavior of nanofluids.

Table 5. Summary of models considering other effects

	Investigator	Formulation	Key parameter	Remarks
	Nan et al. (2003)	$k_{eff} = \left(1 + rac{\phi k_{cm}}{3k_{bf}} ight)k_{bf}$	$\phi$ , $k_{bf}$ $k_{cm}$	The CNT NFs results can be well predicted by conventional EMT
	Nan et al. (2004)	$k_{eff} = 1 + rac{\phi p}{3} \frac{\left(k_{cnt} / k_{bf} ight)}{p + rac{2a_K}{d_{cnt}} \frac{k_{cnt}}{k_{bf}}}$	$\phi$ , $k_{bf}$ , $k_{cnt}$ $k_{xv}$ , $k_{zz}$ : equivalent TC along with each axis	EMT approached model with ITC
	Xue (2005)	$k_{eff} = \left[ \frac{(1 - \phi) + (4\phi / \pi) \sqrt{k_{cm} / k_{bf}}}{(1 - \phi) + (4\phi / \pi) \sqrt{k_{bf} / k_{cm}}} \arctan\left(\pi / 4 \sqrt{k_{cm} / k_{bf}}\right) \right] k_{bf}$ $k_{eff} = \left[ \frac{(1 - \phi) + 2\phi \left\{k_{cm} / \left(k_{cm} - k_{bf}\right)\right\} \ln\left\{\left(k_{cm} + k_{bf}\right) / 2k_{bf}\right\}}{(1 - \phi) + 2\phi \left\{k_{bf} / \left(k_{cm} - k_{bf}\right)\right\} \ln\left\{\left(k_{cm} + k_{bf}\right) / 2k_{bf}\right\}} \right] k_{bf}$	$\phi$ , $k_{bp}$ $k_{cut}$ Distribution function	EMT approach with orientation distribution
Other mechanism based models	Murshed <i>et al.</i> (2006)	$k_{eff} = \frac{k_{bf} \left[ 1 + 0.27\phi^{4/3} \left( \frac{k_p}{k_{bf}} - 1 \right) \right] \left[ 1 + \frac{0.52\phi}{1 - \phi^{1/3}} \left( \frac{k_p}{k_{bf}} - 1 \right) \right]}{1 + \phi^{4/3} \left( \frac{k_p}{k_{bf}} - 1 \right) \left( \frac{0.52\phi}{1 - \phi^{1/3}} + 0.27\phi^{1/3} + 0.27 \right)}$	φ, k <sub>p</sub> , k <sub>pp</sub>	Thermal resistance approach with geometrical structure of nanoparticle
	Gao and Zhou (2006)	$1 - \phi = \left(\frac{k_{bf}}{k_{eff}}\right)^{3A} \left(\frac{k_{bf} + B_1}{k_{bf} + B_1}\right)^{3C_1} \left(\frac{k_{bf} + B_2}{k_{eff} + B_2}\right)^{3C_2}$	$\phi$ , $k_p$ , $k_{bf}$ $L_z$ : depolarization factor	Differential EMT with geometrical structure
	Xue (2006)	$9(1-\phi)\frac{k_{eff}-k_{bf}}{2k_{eff}+k_{bf}}+\phi\left[\frac{k_{eff}-k_{zz}}{k_{eff}+0.14(2a_{ent}/L_{ent})\left(k_{zz}-k_{eff}\right)}+\frac{4\left(k_{eff}-k_{xx}\right)}{2k_{eff}+0.5\left(k_{xx}-k_{eff}\right)}\right]=0$	$\phi$ , $k_p$ , $k_{tg}$ $k_{xx}$ , $k_{xz}$ ; equivalent TC along with each axis	Similar with Nan et al. 04
	Minnich and Chen (2007)	$k_{eff} = \left[ \frac{1}{3} c_{v,bf} v_{pho,bf} \frac{1}{\left(1/I_{bf}\right) + (\Phi/4)} \right] \left[ \frac{k_p (1+2\kappa) + 2k_{bf} + 2\phi \left\{ k_p (1-\kappa) - k_{bf} \right\}}{k_p (1+2\kappa) + 2k_{bf} - \phi \left\{ k_p (1-\kappa) - k_{bf} \right\}} \right]$	$\phi$ , $k_p$ , $k_{bf}$ $\Phi$ : Interface density	EMT approach with surface phonon scattering
	Jung and Yoo (2009)	$k_{eff} = \left[ \frac{k_p + 2k_{bf} + 2\left(k_p - k_{bf}\right)\phi}{k_p + 2k_{bf} - \left(k_p - k_{bf}\right)\phi} \right] k_{bf} + \frac{\phi l_p \hat{c}_v}{3} \frac{k_B T}{3\pi \mu d_p l_{bf}} + \frac{\phi l_p \hat{c}_v}{3} \sqrt{\frac{Ac_c^2 l_p}{\varepsilon_{bf} m_p \left(a_p \phi^{-1/3}\right)^2}}$	$\phi$ , $k_p$ , $k_{bf}$ Zeta potential	EMT with BM and EDL effects

#### 5.3. Models

Classical EMT-based static models fail to predict the magnitude and trend of the thermal conductivity of nanofluids, although there are some data supporting EMT. New static models are much better than classical models based on the effective medium theories in narrowing the gap between thermal conductivity enhancement data and model predictions. However, they are unable to capture other features such as the dependence of the thermal conductivity of nanofluids on nanoparticle size and fluid temperature. However, new models based on a combination of static and dynamic mechanisms appear to predict not only the magnitude of the enhanced thermal conductivity, but also other features of the thermal conduction behavior of nanofluids.

#### 5.4. Future research directions

The inconsistencies in the reported thermal conductivity data from different groups can be due to differences in sample quality, dependence of thermal conductivity on many factors, and differences in measurement uncertainties. The first step to resolve data inconsistencies is to produce high-quality nanofluids having both suspension stability and high conductivity, preferably without any dispersants or stabilizers especially for reference nanofluids, using one-step processes known for making such nanofluids. Nanofluids produced in this way for thermal conductivity measurements should then be characterized, including their detailed microstructures such as particle size, shape, distribution, the levels of agglomeration/clustering, and surface properties and detailed dynamics of nanoparticles such as particle motion and interactions with base fluids. The next step to reduce data inconsistencies due to differences in sample quality and differences in measurement uncertainties is to conduct round-robin tests using identical high-quality reference samples and proven accurate methods and apparatuses for measuring the thermal conductivity of nanofluids.

The controversy regarding the proposed mechanisms of the thermal conductivity of nanofluids comes primarily from a lack of understanding of the scientific basis for these mechanisms. Therefore, the proposed concepts and mechanisms behind the thermal conductivity behavior of nanofluids remain to be validated. More systematic experiments with well-dispersed, well-characterized nanofluids and a better understanding of the physics of fluid flow and heat transfer at the nanoscale are needed to establish the underlying mechanisms of heat conduction in nanofluids.

The classical EMT-based models with the assumptions of motionless particles and the diffusive heat transfer in both continuous matrix phase and dispersed phase can predict thermal conductivity of suspensions of micrometer- or larger-sized particles but fail to predict the thermal conductivity data for most nanofluids. New models based on a combination of static and dynamic mechanisms appear to predict not only the magnitude of the enhanced thermal conductivity, but also other features of the thermal conduction behavior of nanofluids. However, the mechanisms used in the new models remain to be validated. In the future, comprehensive science-based models should be developed based on new mechanisms as well as the classical diffusion mechanisms. Development of comprehensive science-based models that are capable of accurately predicting the new novel features including the size and temperature dependent thermal conductivity of nanofluids will further advance the new field of nanofluids.

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