Contribution of Brownian Motion in Thermal Conductivity of Nanofluids

S. M. Sohel Murshed and C. A. Nieto de Castro

***Abstract*—As a hot research topic nanofluids have attracted great interest from researchers worldwide. Although nanofluids are found to exhibit higher thermal conductivity compared to their base fluids, the underlying mechanisms for the enhancement are still debated and not fully understood. In addition, there has been little agreement among different studies and no widely accepted model is also available for the prediction of the effective thermal conductivity of nanofluids. In this study, an improved Brownian motion-based combined thermal conductivity model is reported and a renovated Brownian motion term is used in this model. Besides the Brownian motion of nanoparticles, this model also takes into account several other important factors such as particle size interfacial nanolayer and fluid temperature that are believed to intensify the enhancement of the effective thermal conductivity of nanofluids. The present model shows reasonably good agreement with the experimental results of various aqueous nanofluids and gives better predictions compared to classical and recently developed models used for nanofluids.**

***Index Terms*— Brownian motion, interfacial nanolayer, nanofluids, nanoparticles, thermal conductivity, volume fraction**

I. Introduction

OVER the last several decades, scientists and engineers have attempted to develop fluids, which offer better cooling or heating performance. However, it is only in 1995 that Steve Choi [1] at Argonne National Laboratory of USA coined the novel concept of "*nanofluids*" to meet the cooling challenges facing many high-tech industries.

Nanofluids are a new class of heat transfer fluids which are engineered by dispersing nanometer-sized solid particles in conventional fluids particles, rods or tubes in conventional heat transfer fluids such as water and engine oil. This is a rapidly emerging interdisciplinary field where nanoscience, nanotechnology, and thermal engineering meet. This research topic has attracted tremendous interest from researchers due to their exciting thermal properties and potential applications in numerous important fields such as microelectronics, microfluidics, transportation, manufacturing, medical, and so on [2]-[4]. The impact of nanofluid technology is expected to be great considering that heat transfer performance of heat exchangers or cooling devices is vital in numerous industries. When nanoparticles are properly dispersed, nanofluids can offer numerous benefits besides the anomalously high effective thermal conductivity. Some of these benefits are improved heat transfer and stability, microchannel cooling without clogging, miniaturized systems, and reduction in pumping power. The better stability of nanofluids will prevent rapid settling and reduce clogging in the walls of heat transfer devices. The high thermal conductivity of nanofluids translates into higher energy efficiency, better performance, and lower operating costs. They can reduce energy consumption for pumping heat transfer fluids. Miniaturized systems require smaller inventories of fluids where nanofluids can be used. Thermal systems can be smaller and lighter. In vehicles, smaller components result in better gasoline mileage, fuel savings, lower emissions, and a cleaner environment. With these highly desired thermal properties and potential benefits, nanofluids are thought to have a wide range of applications including transportation sector (because of the higher thermal conductivity nanofluids would allow for smaller, lighter engines, pumps, radiators, and other components) and micro-electromechanical systems [2], [3].

Although significant progress has been made, variability and controversies in the reported data and heat transport mechanisms still exist with nanofluids [2]. Furthermore, there has been little agreement among different studies and no widely accepted model is also available due to inconclusive heat transfer mechanisms of nanofluids. Nevertheless, fundamental understanding of the underlying mechanisms and development of a unanimous theoretical model are crucial for exploiting aforementioned potential benefits and applications of nanofluids. In this paper, a new and improved Brownian motion (BM)-based model is introduced for the prediction of the enhanced thermal conductivity of nanofluids. In addition to the Brownian motion of nanoparticles, this model also takes into account several other key factors such as particle size, fluid temperature and interfacial nanolayer that also contribute to the enhancement of the effective thermal conductivity of nanofluids. The conventional kinetic theory-based Brownian motion term has been renovated using effective diffusion coefficient concept. Besides providing a brief review on theoretical studies and various heat transfer mechanisms of nanofluids, details of the present model development and its validation with the experimental results are also discussed in this paper.

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II. Modeling for the Effective Thermal Conductivity of Nanofluids

A. Existing Models

Previous studies showed that the classical models such as those attributed to Maxwell [5] and Hamilton-Crosser [6] are unable to predict the anomalously high thermal conductivity of nanofluids. This is because these models were developed for continuum medium of well-dispersed mili- or micro-sized solid particles and they do not include the nanoscale effects of particle size such as the interfacial nanolayer at the particle/liquid interface, and motion of particles, which are considered as important factors for the enhancement of the thermal conductivity of nanofluids. For spherical particles, the Hamilton-Crosser model [6] is the same as the Maxwell model [5]. Therefore, the Maxwell model is used as the representative of classical models and it is given as

$$k_{eff} / k_f = \frac{(k_p + 2k_f) + 2\phi_p(k_p - k_f)}{(k_p + 2k_f) - \phi_p(k_p - k_f)} \quad (1)$$

where ϕ_p is the particle volume fraction and k_{eff}, k_f and k_p are the effective thermal conductivity of suspensions, thermal conductivity of base fluid and thermal conductivity of nanoparticle, respectively.

Recently, many theoretical studies have been carried out to predict the anomalously increased thermal conductivity of nanofluids. Several models have also been proposed by considering various mechanisms. However, there has been little agreement among different studies and no widely accepted model is still available. A detailed review of numerous models proposed for the prediction of effective thermal conductivity of nanofluids is provided in recent review article [2] and it will not be elaborated here.

Very few theoretical efforts have been made on the combined static and dynamic effects of nanoparticles. In an attempt to develop such a combined model, Prasher *et al.* [7] considered dynamic contribution of nanoparticles in their thermal conductivity model for nanofluids. However, their model contains three unknown empirical or fitting parameters. In addition, dynamic contribution was coupled with Maxwell's model without taking into account the effect of interfacial layer in their model. Besides particle volume fraction, particles size, temperature, particles dispersions and particle movement should be taken into account in developing model for the effective thermal conductivity of nanofluids. Prasher *et al.*´s [7] model is expressed as

$$k_{eff} / k_f = (1 + A\phi_p \,\mathrm{Re}^m \,\mathrm{Pr}^{0.333}) \frac{(1+2\alpha) + 2\phi_p(1-\alpha)}{(1+2\alpha) - \phi_p(1-\alpha)} \quad (2)$$

where $\alpha = 2R_b k_f / d_p$, d_p is the particle diameter, R_b is the interfacial resistance, and A and m are empirical parameters.

Since nanoparticles in base fluids can easily experience Brownian force, it is plausible that the observed thermal conductivity of nanofluids is from the combined static (thermal properties and interfacial layer) and dynamic (e.g., Brownian motion) mechanisms of dispersed nanoparticles. Thus, this study focuses on development of model by the combination of static and Brownian motion-based dynamic mechanisms of nanoparticles in base fluids.

B. Present Modeling

The effective thermal conductivity of nanofluids is considered to be from both the static and dynamic mechanisms. The effects of these mechanisms are treated to be additive.

A static thermal conductivity model for the nanofluids (non-interacting nanoparticles) was previously developed by considering nanofluids as a mixture of three components-the nanoparticle (radius r_p), the interfacial layer between particle/fluid medium (thickness h), and the fluid medium and it (k_{st}) is expressed as [8]

$$k_{st} = k_f \frac{\phi_p \omega(k_p - \omega k_f)[2\gamma_1^3 - \gamma^3 + 1] + (k_p + 2\omega k_f)\gamma_1^3[\phi_p \gamma^3(\omega - 1) + 1]}{\gamma_1^3(k_p + 2\omega k_f) - (k_p - \omega k_f)\phi_p[\gamma_1^3 + \gamma^3 - 1]} \quad (3)$$

where $\gamma = r_{cp} / r_p = 1 + h / r_p$, r_{cp} is the radius of complex nanoparticle (nanoparticle with interfacial layer), $\omega = k_{lr} / k_f$ (where $\omega > 1$), and k_{lr} is the thermal conductivity of interfacial layer. The detailed discussion and mathematical derivations for this static model containing spherical nanoparticles with interfacial nanolayer can be found elsewhere [8].

As each nanoparticle is considered to have a nanolayer at the particle/fluid interface and its thickness, h remains in the model, the value of a nanolayer thickness is required to calculate the thermal conductivity of nanofluids. Hashimoto *et al.* [9] established a new definition of the interfacial layer thickness at the surface of spherical micro-domains, which is given as $h = \sqrt{2\pi}\sigma$ where σ is a parameter characterizing the diffuseness of the interfacial boundary and its typical value falls in the range of 0.3 to 0.6 nm. For σ = 0.4 nm, h = 1 nm. In fact, the experimental results of Yu *et al.* [10] and the molecular dynamics simulations performed by Xue *et al.* [11] showed that the typical interfacial layer thickness between the solid (nanoparticles) and liquid phases is of the order of a few atomic distances namely, 1 nm. Hence, an interfacial layer thickness h of 1 nm can reasonably be used to predict the thermal conductivity of nanofluids.

Fig. 1 presents concept of Brownian motion-based dynamic mechanisms of nanoparticles in base fluid. In order

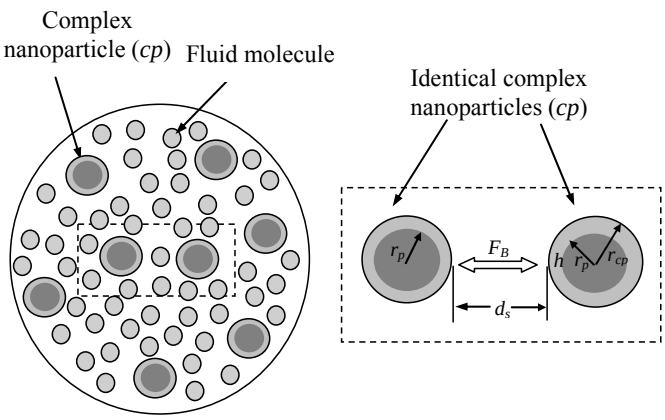

Fig. 1. Concept of BM-based mechanism of nanoparticles in base fluids.

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to determine the Brownian motion of nanoparticles in suspensions containing a specific volumetric loading of nanoparticles, it is important to employ the Brownian motion term which is also a function of the particle volume fraction than the conventional kinetic theory-based formulation for Brownian motion as used by various researchers [7], [12]. Thus, a modified Brownian motion term (U_{MBM}) which was previously deduced by incorporating nanoparticle volume fraction has the form [13]

$$U_{MBM} = \sqrt{\frac{2K_B T(1-1.5\phi_p)}{m}} \tag{4}$$

where m is the mass of the particle, T is the fluid temperature, and K_B is the Boltzmann's constant. It can be seen from (4) that the higher the particle volume fraction, the smaller the diffusion coefficient and thus the weaker the Brownian motion.

For uniform complex nanoparticles (cp) in a base fluid as shown in Fig. 1, the net axial heat flux due to the movement of nanoparticles (U_{MBM}) resulting from the Brownian force (F_B) impacting on them can be written as [13], [14]

$$q''_{dy} \approx -\frac{1}{2} n m_{cp} c_{p-cp} d_s U_{MBM} \nabla T \tag{5}$$

where n is the number density, m_{cp}, c_{p-cp} and d_s are the mass, specific heat, and average separation distance of complex nanoparticles, respectively.

Using $nm_{cp} = \rho_{cp}$ in (5), the dynamic part of thermal conductivity of suspensions due to Brownian motion of nanoparticles (k_{dy}) can be expressed as

$$k_{dy} = \frac{1}{2} \rho_{cp} c_{p-cp} d_s U_{MBM} \tag{6}$$

Applying U_{MBM} for complex nanoparticles from (4) into (6) and making use of $\phi_{cp} = \phi_p \gamma^3$, the following final form of

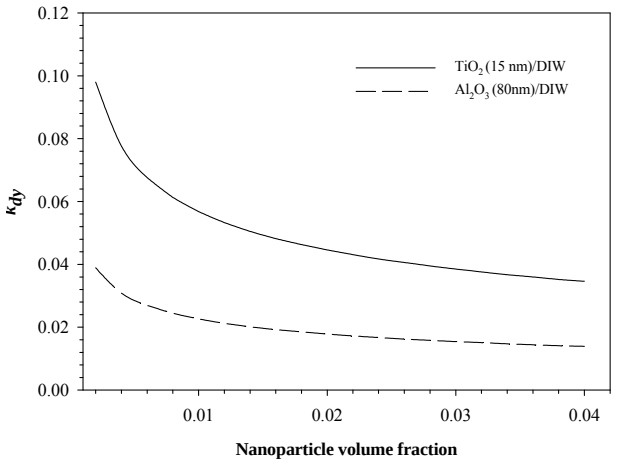

Fig. 2. Dynamic thermal conductivity of nanofluids with nanoparticle volume fraction.

TABLE I
CONTRIBUTIONS OF STATIC AND DYNAMIC MECHANISMS TO THE EFFECTIVE THERMAL CONDUCTIVITY OF TiO_2/DIW-NANOFLUIDS PREDICTED BY (8)

Nanoparticle vol.%	$k_{eff\text{-}nf}$ (W/m-K)	k_{st} (%)	k_{dy} (%)
0.6	0.698	90.3	9.7
1	0.704	91.9	8.1
2	0.733	93.9	6.1
3	0.768	95	5

Brownian motion-contributed thermal conductivity is obtained as

$$k_{dy} = \frac{1}{2} \rho_{cp} c_{p-cp} d_s [\sqrt{\frac{3K_B T(1-1.5\gamma^3\phi_p)}{2\pi\rho_{cp}\gamma^3 r_p^3}} \tag{7}$$

where $d_s = 0.893 r_{cp} \phi_{cp}^{-1/3} = 0.893 r_p \phi_p^{-1/3}$ [15] and density (ρ_{cp}) and specific heat (c_{p-cp}) of complex nanoparticles can be obtained from the formulations given elsewhere [13].

Fig. 2 depicts the effect of nanoparticle volume fraction on the dynamic thermal conductivity component given by (7) for two deionized water (DIW)-based nanofluids. As expected, Fig. 2 shows that the smaller the particle the larger the dynamic (Brownian motion-based) thermal conductivity contribution (k_{dy}). Mainly for smaller size and low volume fraction of nanoparticles, the dynamic contribution of thermal conductivity is significant. The reason is that the smaller the particle size the greater the movement of particles in the fluid. It is also noted that this k_{dy} increases nonlinearly with decreasing particle volume fraction from 0.002 due to large interparticle separation distance (d_s) at such small particle volume fraction. For $\phi_p < 0.002$, the interparticle separation distance (d_s) is too large to cause any interaction through Brownian force of particles. Thus, the dynamic contribution of the thermal conductivity (k_{dy}) is not applicable for $\phi_p < 0.002$.

The effective thermal conductivity of nanofluids is considered to be from both the static and dynamic mechanisms. As mentioned before, the effects of these mechanisms are treated to be additive and the final model for the effective thermal conductivity of nanofluids ($k_{eff\text{-}nf}$) by combining the static part given by (3) and dynamic part given by (7) has the form

$$k_{eff-nf} = \left\{ k_f \frac{\phi_p \omega (k_p - \omega k_f)[2\gamma_1^3 - \gamma^3 + 1] + (k_p + 2\omega k_f)\gamma_1^3[\phi_p \gamma^3(\omega - 1) + 1]}{\gamma_1^3(k_p + 2\omega k_f) - (k_p - \omega k_f)\phi_p[\gamma_1^3 + \gamma^3 - 1]} \right\} + \left\{ \frac{1}{2} \rho_{cp} c_{p-cp} d_s [\sqrt{\frac{3K_B T(1-1.5\gamma^3\phi_p)}{2\pi\rho_{cp}\gamma^3 r_p^3}} \right\} \tag{8}$$

The important features of this model are summarized as follows:

i. The model takes into account the effect of nanolayer together with the static and dynamic mechanisms of nanoparticles in the base fluid. The particle size effect is also included in the model.

ii. The second term on the right hand side of (8) is the dynamic contribution of thermal conductivity (k_{dy}), which

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takes into account the effect of particle Brownian motion as well as temperature. This term (k_{dy}) is only applicable for particle loading of $\phi_p > 0.002$. In this part (k_{dy}), the conventional kinetic theory-based Brownian motion term has been renovated using effective diffusion coefficient concept to incorporate the effect of volume fraction on Brownian motion of nanoparticles.

iii. The model can also predict the temperature-dependent thermal conductivity of nanofluids.

iv. If there is no interfacial layer, the static part of the model reduces to the Maxwell model [5].

C. Determination of contribution to $k_{eff\text{-}nf}$

Table 1 demonstrates the contributions of static and dynamic mechanisms to the effective thermal conductivity of TiO_2 (15 nm)/DIW-based nanofluids predicted by the present model i.e., (8). As can be seen from Table 1, while the major contributions arise from static mechanisms such as volume fraction, particle size and interfacial nanolayer, Brownian motion-based dynamic mechanism can also play significant role in enhancing the thermal conductivity of nanofluids particularly at low volume fraction of nanoparticles. This dynamic mechanisms can also be significant for smaller-sized nanoparticles, typically < 20nm (Fig. 2).

III. Results and Discussion

The present model is validated by comparing its results with experimental data. The thermal conductivity of nanofluids was obtained from using transient hot-wire technique which has been described elsewhere [16]. The predictions by the present model are also compared with the results from Maxwell model i.e., (1) as well as results obtained from a representative recent model developed for nanofluids i.e., (2).

Figs. 3 to 5 demonstrate that the present model shows fairly good agreement with the experimental results and gives far better predictions compared to Maxwell's model as well as model developed by Prasher *et al.* [7]. As shown in Fig. 3, the predictions by the present model for TiO_2 (15 nm)/DIW-based nanofluids are in good agreement with the experimental results which are completely under-predicted by Maxwell's [5] and Prasher *et al.*'s [7] models.

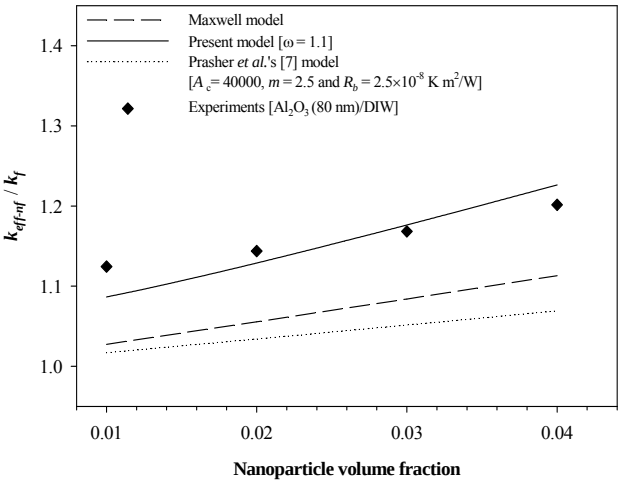

Fig. 4. Comparison of present model's predictions with experimental results and results from other models for Al_2O_3/DIW-based nanofluids.

The present model shows better agreement with the experimental results for Al_2O_3/water-based nanofluids as shown in Fig. 4. It can also be seen that the thermal conductivity of this nanofluids predicted by Prasher *et al.*'s [7] model are much lower than the experimental data.

Fig. 5 demonstrates that for CuO/water-based nanofluids, the present model fits very well with the results obtained from Eastman *et al.* [17] and gives better predictions compared to other models. Like other types of nanofluids, Prasher *et al.*'s model [7] also under-predicts the thermal conductivity of this nanofluid. Although their model considers the effect of particle size and microconvection, it could not predict the anomalously high thermal conductivity of nanofluids. This may be because their model includes effect of interfacial resistance and does not consider the effect of interfacial layer, particle movement and surface chemistry, which play significant roles in suspensions containing nanoparticles. It is also noted that suggested values of three unknown parameters i.e. R_b, A_c, and m were needed in the calculation of thermal conductivity when using Prasher *et al.*'s [7] model. Currently, these empirical parameters cannot be obtained by experimental or theoretical mean.

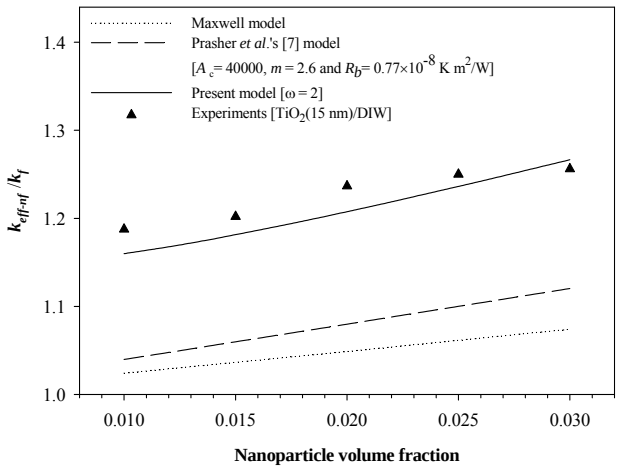

Fig. 3. Comparison of present model's predictions with experimental results and predictions of other models for TiO_2 /DIW-based nanofluids.

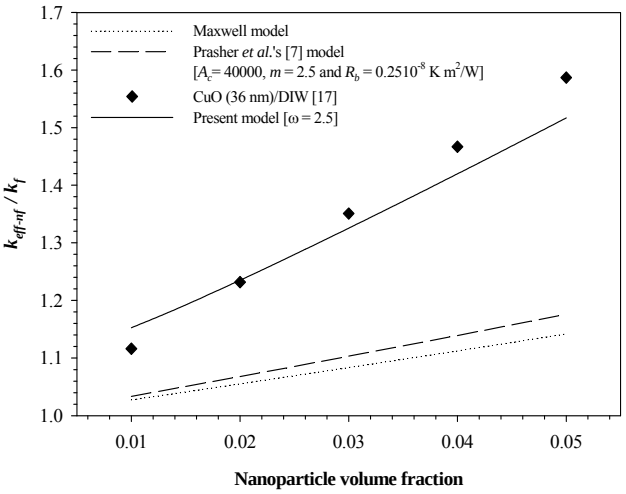

Fig. 5. Comparison of present model's predictions with experimental data [17] and other models' predictions for CuO/DIW-based nanofluids.

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IV. Concluding Remarks

An improved model for the prediction of the observed thermal conductivity of nanofluids is reported in this paper. The model is developed by incorporating both static and dynamic mechanisms that are behind the anomalous thermal conductivity of nanofluids. In addition to the effect of Brownian motion of nanoparticles, the model also takes into account other important factors such as particle size, fluid temperature, and interfacial nanolayer. Compared to existing classical and other recently developed models, present model shows much better agreement with experimental results. This is attributed to the incorporation of those key static and dynamic mechanisms in the present model. In the dynamic part, the conventional kinetic theory-based Brownian motion term has been renovated using effective diffusion coefficient concept in order to formulate the Brownian motion of a suspension containing a certain volumetric loading of nanoparticles. It is found that the major contribution to the enhanced thermal conductivity of nanofluids arise from the static mechanisms. However, the Brownian motion-based dynamic mechanism is also significant for nanofluids with smaller-size and low concentration of nanoparticles. It can be inferred that the thermal conductivity of nanofluids is due to both the static and dynamic mechanisms.

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