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SIMULTANEOUS EFFECTS OF BROWNIAN MOTION AND CLUSTERING OF NANOPARTICLES ON THERMAL CONDUCTIVITY OF NANOFLUIDS[*]

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Abstract– In this paper, Brownian motion of nanoparticles and clusters and resulted micromixing are combined with the aggregation kinetics of clusters to capture the effects of nanoparticles on the thermal conductivity of nanofluids. Starting from kinetic theory, random motion of nanoparticles and induced micro-convection were combined with the kinetics of aggregates and a theoretical model which depends on two semi-empirical parameters was derived. The proposed model attributes the thermal conductivity of nanofluids not only to the intrinsic physical properties, but also to physicochemical parameters which affect the stability state of nanofluids. The more nanofluid is stabilized, the more k_{eff} increases. We have also demonstrated that the thermal conductivity either increases or decreases with respect to the particle size and there is an optimum value for the particle radius at which the thermal conductivity of the nanofluid is maximum. Depending on the chemistry of the solution, the optimized radius of the nanoparticles in a suspension depends on the temperature and pH of the suspension and the volume fraction of the nanoparticles. This behaviour is not feasible without including the effects of aggregation kinetics combined with Brownian motion and induced micro-convection.

Keywords– Nanofluids, Brownian motion, thermal conductivity, heat transfer

1. INTRODUCTION

Manufacturing the micro and nano electromechanical systems and the lack of sufficient heat surfaces in such devices, necessitate employing efficient working fluids with enhanced heat transfer properties [1]. Nanofluids, suspensions of ultrafine nanoparticles in pure fluids [2], have shown enhanced heat properties compared with their base fluids. The enhanced thermal properties of nanofluids contribute to improving the efficiency of heat exchangers and reducing their size. In addition, nano sized particles provide advantages such as less clogging and abrasion, less sedimentation and better stability. More outstanding applications of nanofluids can be envisioned in biomedical engineering and medicine in terms of optimal nano-drug targeting and implantable nano-therapeutics devices.

Many research groups have carried out experiments on transport properties of nanofluids. Experimental studies reveal that thermal conductivity of nanofluids depends on many parameters such as intrinsic thermal properties of particles and base fluid, concentration of nanoparticles [3-7], temperature [3, 4, 8], nanoparticle size [9, 10], and pH of solution [11, 12]. Moreover, it appears that the preparation procedure of nanofluid, employing the means for better dispersion of particles such as addition of surfactants or ultrasonic irradiation of nanoparticles, the methods of measuring the effective thermal conductivity, i.e. intrusive or non-intrusive methods, can all play a role in the reported effective thermal

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conductivity of nanofluids in literature [13]. Ju *et al.* [3] measured the effective thermal conductivity by non-intrusive optimal technique and observed no anomalous behavior for nanofluids and could describe the effective thermal conductivity, k_{eff}, with conventional effective-medium theories. They reported that the thermal conductivity of their nanofluids is not a strong function of temperature. Moreover, by measuring the average diameter of agglomerates, they concluded that the aggregates diameter, present in nanofluid, is much larger than single nanoparticles. In addition, they observed higher conductivity for solutions where surfactant was added. Singh *et al.* [4] observed slight enhancement of thermal conductivity compared to that of the conventional theories and almost no temperature dependence for SiC/Water nanofluids. The pH of the system was 10, so by using optical microscopy of particles, a well-dispersed nanofluid was prepared without adding surfactant. On the other hand, Sinha *et al.* [5] by using ultrasonic irradiation for dispersing nanoparticles showed that the effective thermal conductivity of suspension can be enhanced up to 70% for copper nanofluids with ethylene glycol as the medium. Moreover, they showed that copper nanofluids show superior properties compared to iron ones. Schmidt *et al.* [6] prepared Al2O3/PAO (isoparaffinic polyalphaolefin) and Al2O3/C10H22 (decane) nanofluids and measured thermal conductivity by using two methods: transient optical grating technique and a hotwire. Both methods showed relatively identical results and they reported thermal conductivity 1.6 times greater than mean-flied theories for PAO nanofluid and 3.3 times greater for decane nanofluid. Garg *et al.* [7] measured both conductivity and viscosity of copper/ethylene glycol nanofluids using sonicator for better dispersion. The thermal conductivity increased two times more than the conventional theories and viscosity increased four times that of Einstein's law of viscosity.

Such discrepancies observed in experimental data motivate more and more investigations on the mechanisms responsible for energy transport enhancement in nanofluids. As a result, different researchers have attempted to investigate the origin of these contradictions and developed theoretical models. Some researches argue that the modification and development of classical theories for inhomogeneous mediums can describe the anomalous behavior of nanofluids. For instance, Eapen *et al.* [14] argued that the strong interaction between fluid and clusters of nano-particles for well-dispersed nanofluids results in percolating paths for thermal conduction at clusters interface, leading to an enhanced thermal conductivity of such nanofluids beyond the 3φ Maxwell limit, with φ as concentration of nanoparticles. They supported their results with non-equilibrium molecular dynamics [15]. By analyzing a large group of experimental data sets they concluded that almost all of the reported experimental results for effective thermal conductivity lie between the mean-flied bounds predicted by classical theories; the upper bound occurs when heat conducts through a percolating amorphous-like fluid structure at the cluster interface, while for the lower bound the heat conducts through mixture path. On the other hand, a number of researchers attribute the observed anomalous enhancement of k_{eff} reported in some literature to Brownian motion of nanoparticles and the induced micro-convection. For instance, Jang and Choi [16] assumed that the energy transport in nanofluids consists of four modes; heat conduction in the base fluid, heat conduction in nanoparticles, heat transport resulted by random collision between nanoparticles due to their translational Brownian motion, and micro-convection caused by the random motion of the nanoparticles. The arbitrariness of choosing the Brownian velocity is questionable in their work [17]. In addition, the thickness of the thermal layer and volume fraction of the liquid layer around nanoparticles is being disputed [10]. Similarly, Koo and Kleinstreuer [18] considered the effect of translational Brownian motion and convection induced by Brownian motion and proposed a new model for thermal conductivity of nanofluids. Brownian Dynamics simulation of Bhattacharya *et al.* [19], which is an extension of Molecular Dynamics in order to take into account the micro convection due to Brownian motion of nanoparticles, showed that the k_{eff} enhances with volume fraction. They compared their numerical results with experimental data. However, none of the authors considered the aggregation of nanoparticles. Consequently, their models are not capable of predicting the dependence of k_{eff} on pH and stability of the solution.

In this paper, by using the kinetic theory, a unified novel model has been developed which combines effects of Brownian motion and micro hydrodynamics of nanoparticles with kinetics of clusters. The model predicts the effects of stability of suspension on the effective thermal conductivity. In section 2, we derive the theoretical model for k_{eff}. In section 3, the theoretical results are provided and are compared to experimental data sets. A discussion on the comparison between theory and experiment is given and a case study is done in order to demonstrate the feasibility of employing nanofluids rather than pure water as the working fluid. Finally, in section 4, the concluding remarks are presented.

2. DERIVING THE MODEL

As it was mentioned, several mechanisms are proposed as the dominant ones for describing the thermal behavior of nano-colloidal systems (nanofluids). In any colloidal system aggregation occurs and this process is a function of Brownian motion and surface chemistry of nanoparticles. There is a competition between the growth of fractal-like structure of aggregates and the breakup of chains into single particles. The transport properties, such as thermal conductivity, are sensitive to the mentioned process. Consequently, in this paper we assume the suspended nanoparticles enhance energy transport inside the nanofluid, and this is mainly because of two reasons: 1) the presence of the suspended nanoparticles, with higher thermal conductivity compared to the base fluid, increases the effective thermal conductivity of suspension. From this point of view, the enhancement of the effective thermal conductivity based purely on the conduction phenomenon and kinetics of nano clusters does not play a role. This effect is called static part k_{st}. 2) Brownian motion of nanoparticles, which in turn leads to the formation of particle aggregates, enhances the energy transport inside the liquid. This effect is called the dynamic part of the thermal conductivity, k_{dyn}. Consequently, assuming that these effects are independent of each other, the effective thermal conductivity can be written as:

$$k_{\text{eff}} = k_{\text{st}} + k_{\text{dyn}} \tag{1}$$

A number of expressions can be used to calculate the static part. Among them, Maxwell's theory is more traditional and can be expressed as:

$$\frac{k_{\text{st}}}{k_{\text{c}}} = \frac{(\frac{k_{\text{d}}}{k_{\text{c}}}+2)+2\phi(\frac{k_{\text{d}}}{k_{\text{c}}}-1)}{(\frac{k_{\text{d}}}{k_{\text{c}}}+2)-\phi(\frac{k_{\text{d}}}{k_{\text{c}}}-1)} \tag{2}$$

where ϕ is the volume fraction of nanoparticles and k_{c} and k_{d} are the thermal conductivity of the base fluid and particles, respectively.

Now we intend to derive an expression for the k_{dyn}. As it was mentioned in the introduction, two mechanisms appear to be more dominant for the thermal conductivity enhancement: 1) Effect of aggregation of nanoparticles [14, 15, 20, and 21] and 2) effect of Brownian motion and the induced micro-convection [16, 18, and 19]. Brownian motion of nanoparticles has two effects. The first effect is the enhancement of thermal conductivity through micro mixing. From this point of view, the particles at a certain temperature have translational Brownian movements. Because of viscous effects, the Brownian motion of nanoparticles induces a micro convection in the surrounding fluid and therefore more vigorous micromixing takes place. Such a phenomenon is similar to the effects of eddies in turbulent flows, which intensify mixing in the flow. Consequently, parameters affecting Brownian velocity (temperature, T, particle radius, r_p, and particle density, ρ_p) influence the thermal conductivity. The second effect is that the nanoparticles, due to their Brownian motion, approach each other and aggregation can take place, which reduces Brownian velocity and the stability of the suspension. From this point of view, parameters affecting the formation of clusters and stability (attractive and repulsive potentials, V_A and V_R, surface charge, ψ_s, temperature, volume fraction of nanoparticles, ϕ, particle radius, and pH) play a role in evaluating k_{eff}. Consequently, the Brownian motion and formation of clusters are related phenomena. In this paper, a unified novel model is developed considering both effects.

On average, in the analogy with kinetic theory of gases, we assume each degree of freedom of nanoparticles will have an energy of $\frac{1}{2}k_b T$, with k_b as Boltzmann constant and T as temperature. Hence, the total energy of a particle is $\frac{3}{2}k_b T$. By balancing this with the kinetic energy of nanoparticles due to their translational Brownian motion, the Brownian velocity is given by [22]:

$$V_{br} = \sqrt{\frac{3k_b T}{m}} \tag{3}$$

where m is the mass of particles or clusters. For spherical particles $m = m_p = \frac{4}{3}\rho_p \pi r_p^3$ and for clusters it corresponds to the mass of clusters, $m = m_a$, which is to be determined.

To obtain the mass of the clusters, we start with the number of particles in the aggregates. Experimental studies and computer simulations indicate that large Brownian aggregates have a fractal structure [23-24] over a range of measurable length scales. The number of particles in an aggregate, N_{int}, is related to the aggregate radius of gyration R_g and single particle radius r_p through:

$$N_{int} = (\frac{R_g}{r_p})^{d_f} = (1 + \frac{t}{t_{br}}) \tag{4}$$

where d_f is the fractal dimension, t is time, and t_{br} is the characteristic time of Brownian motion. d_f ranges between 1.75 and 2.5 [25]. In the case of a high barrier against clustering, which signifies that aggregation is in the diffusion limited cluster-cluster aggregation regime, DLCCA, $d_f \approx 2.5$. On the other hand, in the case of a weak barrier, which implies that aggregation is in the reaction limited cluster-cluster aggregation regime, RLCCA, we have $d_f \approx 1.8$ [26]. Eq. (4) is a consequence of Smoluchowski approach which assumes a constant (size-independent) stability ratio, W, for all aggregate clusters and that aggregate collisions occur predominately between clusters of approximately equal size. Now from Eq. (4) the mass of clusters can be evaluated as:

$$m_a = m_p\ (1 + \frac{t}{t_{br}}) \tag{5}$$

The Brownian characteristic time can be determined by [24, 27]:

$$t_{br} = \frac{\pi \mu r_p^3 W}{k_b T \phi} \tag{6}$$

where μ is viscosity of fluid and W is the stability ratio and is determined by:

$$W = 2r_p \int_0^\infty \beta(h) \exp(V_{tot} / k_b T)\, (h + 2r_p)^{-2}\, dh \tag{7}$$

where, h is the surface to surface distance of nanoparticles and $\beta(h)$ is a multiplier which takes the hydrodynamic interactions into account and is calculated by [28]:

$$\beta(h) = \frac{6(h/r_\mathrm{p})^2 + 13(h/r_\mathrm{p}) + 2}{6(h/r_\mathrm{p})^2 + 4(h/r_\mathrm{p})} \tag{8}$$

In Eq. (7), V_tot is the overall potential between nanoparticles. According to the Derjaguin-Landau-Verwey-Overbeck (DLVO) theory [27], the overall potential is the sum of attractive potential V_A and repulsive potential V_R. The attractive potential is due to Van der Waals interaction of nanoparticles and is calculated by [29]:

$$V_\mathrm{A} = -A/6\left[\frac{2{r_\mathrm{p}}^2}{h^2 + 4r_\mathrm{p}h} + \frac{2{r_\mathrm{p}}^2}{h^2 + 4r_\mathrm{p}h + 4{r_\mathrm{p}}^2} + \ln\left(\frac{h^2 + 4r_\mathrm{p}h}{h^2 + 4r_\mathrm{p}h + 4{r_\mathrm{p}}^2}\right)\right] \tag{9}$$

where A is Hamaker constant.

The repulsive potential is due to the interaction of electric double layer around nanoparticles and is given by [30]:

$$V_\mathrm{R} = 2\pi r_\mathrm{p}\varepsilon_\mathrm{r}\varepsilon_0\,\psi_\mathrm{s}\exp(-h\kappa) \tag{10}$$

where ε_r is the relative dielectric constant of the liquid, ε_0 is the dielectric constant of free space, ψ_s is the surface charge or potential, and κ is the Debye parameter (inverse of the Debye length). Eq. 10 is valid for small particle dimensions, where $\kappa r_\mathrm{p} < 5$. Thus, it can be employed for nanofluids. However, one can find several other expressions in the literature to evaluate repulsive potential [30]. κ for aqueous solutions without salt is given by [24]:

$$\kappa = 5.023 \times 10^{11}\sqrt{\frac{I}{\varepsilon_\mathrm{r}T}} \tag{11}$$

where I is the ionic strength and is related to the pH of the solution and the concentration of salt ions. For water-based nanofluids, in the absence of salt, it can be determined by:

$$\begin{cases} I = 10^{-\mathrm{pH}} & \textit{if}\quad \mathrm{pH} \le 7 \\ I = 10^{-(14-\mathrm{pH})} & \textit{if}\quad \mathrm{pH} > 7 \end{cases} \tag{12}$$

Surface charge ψ_s is positive and increases with decreasing pH below the isoelectric point (point of zero charge where $\psi_s = 0$) and is negative and decreases with increasing pH above the isoelectric point. ψ_s can be determined experimentally. For Al_2O_3/water and for CuO/water suspensions we have employed the data of Kim *et al.* [31] and Lee *et al.* [11] respectively.

W is a measure of stability of nanofluid; as the stability ratio increases, the suspension becomes more stable and as a result, the barrier of nanofluid against coagulation and aggregation reinforces, which retards the formation of clusters and leads to the increment of Brownian characteristic time. By increasing t_br, the cluster's mass reduces and according to Eq. (3), the Brownian velocity increases. Consequently, each parameter that has an impact on the stability of suspension affects the Brownian characteristic time and velocity. Since *W* strongly depends on particle radius and surface charge, particle dimension and pH of the solution are prominent parameters in evaluating Brownian velocity and cluster's mass.

Now we modify the theory that was proposed by Koo and Kleinstreuer [18] for calculating the effective thermal conductivity of nanofluids, without considering the aggregation effects. According to Fig. 1, we assume that the net heat transfer, q_net, between discrete phase, i.e. nanoparticles and clusters, and continuum phase, i.e. liquid, can be written as:

$$q_{\text{net}} = q_{\text{a}} + q_{\text{p}} \tag{13}$$

where q_{a} and q_{p} are the amount of energy carried by aggregates and particles respectively. We determine each term separately.

We consider two nanoparticles moving with translational Brownian velocity with two different temperatures T_{H} and T_{c} of extent ℓ, where ℓ is the Brownian mean free path or Brownian characteristic length and is a mean distance for a particle to travel along one direction without changing the direction, due to the particle Brownian motion.

q_{p} is given by :

$$q_{\text{p}} = \frac{\Delta Q}{A_{\text{n}}\Delta t} = \frac{pNm_{\text{p}}c_{\text{v}}(T_{\text{H}} - T_{\text{C}})}{A_{\text{n}}\Delta t} = -p(Nmc_{\text{v}}V_{\text{br}}\ell)_{\text{p}}(A_{\text{n}}\Delta t V_{\text{br,p}})^{-1}\frac{\Delta T}{\ell_{\text{p}}} \tag{14}$$

where subscript p denotes primary nanoparticles, p is the probability for a particle to travel along any direction, N is the number of single particles, C_v is the specific heat, ΔT is $(T_{\text{H}} - T_{\text{C}})$ the temperature difference between hot and cold cells, and A_{n} is the cross-sectional area of the system normal to the x-direction (refer to Fig. 1).

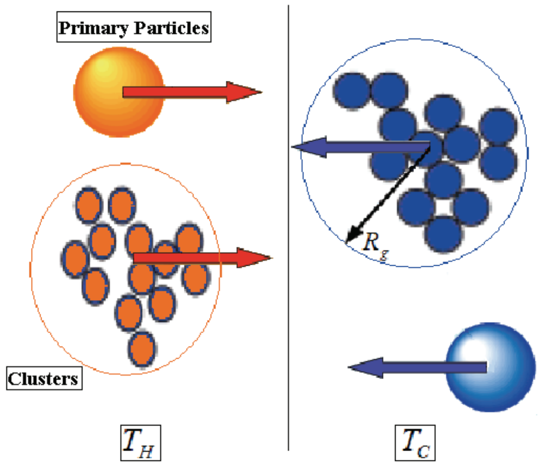


Fig. 1. Sketch of micromixing by Brownian motion of particles and clusters

In a similar procedure we evaluate q_{a} as:

$$q_{\text{a}} = -p(Nmc_{\text{v}}V_{\text{br}}\ell)_{\text{a}}(A_{\text{n}}\Delta t V_{\text{br,a}})^{-1}\frac{\Delta T}{\ell_{\text{a}}} \tag{15}$$

where subscript a is for aggregate. ℓ is the Brownian characteristic length. In order to evaluate ℓ**,** we start with the Langevin equation describing nanoparticles motion [22]:

$$m\frac{\mathrm{d}V}{\mathrm{d}t} = \tilde{G}(t) - 6\pi\mu r_{\text{p}}V \tag{16}$$

Here, it is supposed that the force acting on a single isolated spherical particle, say in translational motion, is a combination of a force $\tilde{G}(t)$ characterizing the very rapid motions associated with the molecular motion time scale ($\sim 10^{-13}s$ for water) plus a frictional drag force $-6\pi\mu r_{\text{p}}V$ associated with the much slower fluid response to the particle motion. A simple analysis of Eq. 16 leads to a characteristic relaxation time, $\tau = \frac{m}{6\pi\mu r_{\text{p}}}$, over which the particle moves in a deterministic manner. Thus, the mean free path can be approximated by:

$$\ell = \tau V_{\mathrm{br}} = \frac{m V_{\mathrm{br}}}{6\pi\mu r} \tag{17}$$

By assuming $\frac{\Delta T}{\ell} \to \nabla T$ and considering $\frac{Nm}{A_{\mathrm{n}} \Delta t V_{\mathrm{br}}} = \rho\phi$ and $q = -k_{\mathrm{br}} \nabla T$, we obtain:

$$k_{\mathrm{br,a}} = p(\phi\, \rho c_{\mathrm{v}}\, V_{\mathrm{br}}\, \ell)_{\mathrm{a}} \tag{18}$$

and

$$k_{\mathrm{br,p}} = p(\phi \rho c_{\mathrm{v}}\, V_{\mathrm{br}}\, \ell)_{\mathrm{p}} \tag{19}$$

By combining Eq. (13) and the Fourier laws of heat transfer, $q_{\mathrm{net}} = -k_{\mathrm{br}} \nabla T$, the following result will be obtained:

$$k_{\mathrm{br}} = k_{\mathrm{br,a}} + k_{\mathrm{br,p}} \tag{20}$$

The volume fraction of particles and aggregates which appeared in the Eq. (18) and Eq. (19), can be given by [26]:

$$\phi_{\mathrm{a}} = \phi^{\frac{d_\ell - d_{\mathrm{f}}}{d_{\mathrm{f}} - 3}} \tag{21}$$

$$\phi_{\mathrm{p}} = \phi - \phi_{\mathrm{a}} \tag{22}$$

where d_ℓ is the fractal dimension of backbones and is $1.4 < d_\ell < d_{\mathrm{f}}$.

Clearly, as the nanoparticles move randomly, hydrodynamic interaction takes place. That is, a portion of the surrounding fluid is affected, i.e. fluid at the immediate vicinity of the particle is carried by the particle motion due to viscous effects, leading to micro-scale mixing and heat transfer. The affected volume may be determined by solving the Stokes equation. For a single sphere it is not a difficult task, however, when the number of nanoparticles increases and they are put together in clusters, it is necessary to solve the complete Navier-Stokes equations to obtain the actual volume which is carried by nanoparticles and clusters. In order to avoid this, a simplification has been made. In conjunction with Koo and Kleinstruer [18], we define semi-empirical parameters, β_{p} and β_{a} , which represent the fraction of the liquid volume traveling with a particle and cluster respectively. β_{p} and β_{a} decrease with volume fraction due to the viscous effect of moving particles and clusters.

By substituting ℓ and V_{br} from Eq. (17) and Eq. (3), respectively into Eq. (18) and Eq. (19), and substituting the resulting equations into Eq. (20), the Brownian thermal conductivity is obtained as follows:

$$k_{\mathrm{br}} = 9064\ (\rho C_{\mathrm{v}}) \times \frac{k_{\mathrm{b}} T}{\mu\, r_{\mathrm{p}}} [\beta_{\mathrm{p}} (\phi - \phi^{\frac{d_\ell - d_{\mathrm{f}}}{d_{\mathrm{f}} - 3}}) + \beta_{\mathrm{a}} \phi^{\frac{d_\ell - d_{\mathrm{f}}}{d_{\mathrm{f}} - 3}} (1 + t / t_{\mathrm{br}})^{-1/3}] \tag{23}$$

Equation (23) is considered as k_{dyn}. Then by substituting Eq. (2) and Eq. (23) into Eq. (11), the effective thermal conductivity of nano-colloidal suspensions is evaluated. For the first time, Eq. (23) determines k_{eff} by taking Brownian motion of nanoparticles and clusters, as well as aggregation kinetics, into account.

-Determination of β_{p} and β_{a} : Before evaluating β_{p} and β_{a} , it is important to recall that the number of non-clustered particles decreases over time, which gives rise to an increment of particles within the clusters and, as a result, β_{p} decreases [24]. Similarly, as mentioned by Koo and Kleinstreuer [18], because of hydrodynamic interactions, the increasing of the volume fraction causes the reduction of β_p. Therefore, taking those two effects into account, we speculate β_p as follow:

$$\beta_p = f_1(\phi) \times f_2(t/t_{br}) \tag{24}$$

where $f_1(\phi)$ is a descending function. It simulates hydrodynamic effects of increasing the volume fraction, and $f_2(t/t_{br})$ is a descending function which is responsible for decreasing non-cluster particles with time.

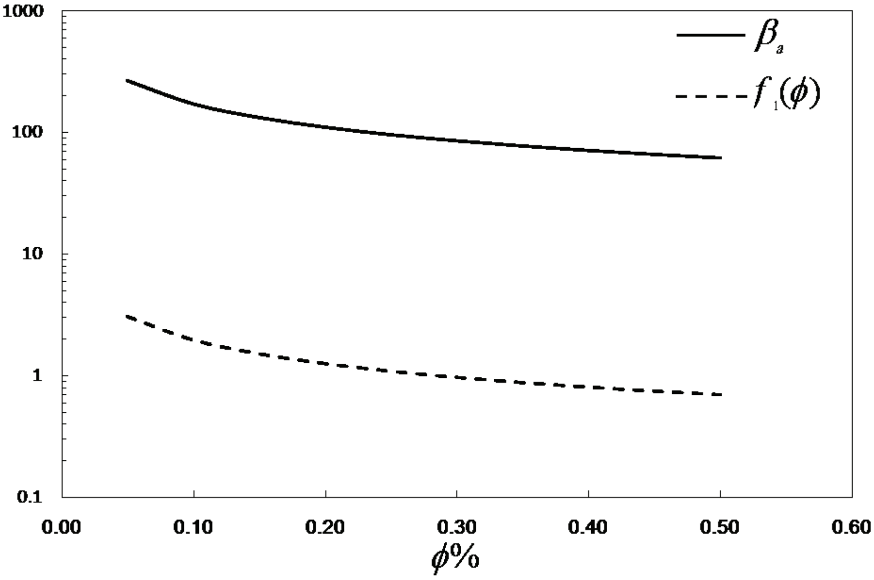


Fig. 2. β_a and $f_1(\phi)$ empirical functions obtained from experimental data.

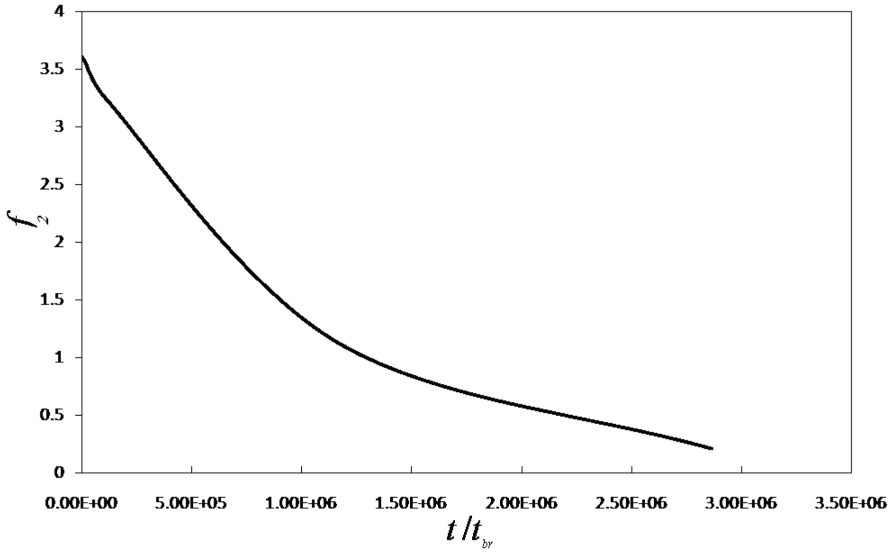


Fig. 3. Curve fitting of f_2 as a function of t/t_{br}

The functions β_p and β_a are empirical parameters and may be obtained by using experimental data. Here we used the experimental data from Lee *et al.* [11] to evaluate them. Figure 2 shows the curve fitting graphs for $f_1(\phi)$ and β_a with respect to volume fraction. Both $f_1(\phi)$ and β_a decrease with ϕ, as expected.

Figure 3 shows the curve fitting graph for $f_2(t/t_{\mathrm{br}})$ with respect to t/t_{br}. As it was mentioned before, it is a descending function. Then, the shape of function $f_2(t/t_{\mathrm{br}})$ can be obtained by the curve fitting procedure.

$$f_2(t/t_{\mathrm{br}}) = 3.6\exp(-0.000001\, t/t_{\mathrm{br}}) \tag{25}$$

3. RESULTS AND DISCUSSION

In the following, the effects of essential parameters which affect the thermal conductivity of nanofluids are examined. Our results are compared with the existing experimental data sets to validate the present model. The properties of the base fluid (water) and nanoparticles (Al_2O_3 and CuO) and the values of the needed constants are given in Tables 1-3, respectively.

Table 1. Properties of water

$\rho\ (kg/m^3)$	$c_v\ (J/kg\ K)$	$\mu\ (pa.\mathrm{sec})$	ε_r	$k\ (W/m^3.K)$
980	4191	$\ln\frac{\mu}{0.001792} = -1.94 - 4.8\left(\frac{T}{273.16}\right) + 6.74\left(\frac{273.16}{T}\right)^2$	8	0.611

Table 2. Properties of nanoparticles

	$k\ (W/m^3.K)$	$A\times10^{-21}\ (J)$
Al_2O_3	*36.9*	*2.84*
CuO	*32.9*	*1.24*

Table 3. Constants

k_b (*J/kg*)	d_{f}	d_ℓ	$\varepsilon_0(\mathrm{A^2s^4\ kg^{-1}m^{-3}})$
1.38×10^{-23}	*1.8*	*1.4*	8.85×10^{-12}

a) Volume fraction of nanoparticles

Conventional theories contradict the observed experimental results. They are not able to predict the observed enhancement; the experimental results are far beyond conventional theories. Also, by increasing the concentration of nanoparticles, nonlinear behaviour of thermal conductivity, which cannot be predicted by traditional theories is observed. We intend to investigate such contradiction and elucidate them by our model. We use the experimental data given by Lee *et al.* [11] and Prasher *et al.* [10] to evaluate the validity of the model.

Lee *et al.* [11] investigated the effect of the surface charge state of the 25nm CuO nanoparticles in aqueous suspension on the thermal conductivity experimentally. They showed that the value of pH of the nanofluid strongly affected the thermal performance of the fluid. With a further diverged pH value from the isoelectric point, the nanoparticles in the suspension tend to be more stable and the thermal conductivity is enhanced. To assess the validity of the present model, a comparison with their results has been made and results are depicted in Fig. 4. As shown, the results are in good agreement with the experimental data. In addition, results of Maxwell equation are also depicted in Fig. 4 and it is obvious that traditional theories are not capable of predicting the observed enhancement. By increasing volume fraction, on one hand, due to increasing k_{st} and increasing the volume of fluid carried by nanoparticles and clusters, the effective thermal conductivity increases. On the other hand, by increasing volume fraction, the formation of clusters intensifies, which in turn reduces the stability of suspension and barrier against aggregation. These two reasons together make a nonlinear trend of thermal conductivity. Figure 4 shows nonlinear behaviour of thermal conductivity with volume fraction of nanoparticles, specifically at higher concentrations.

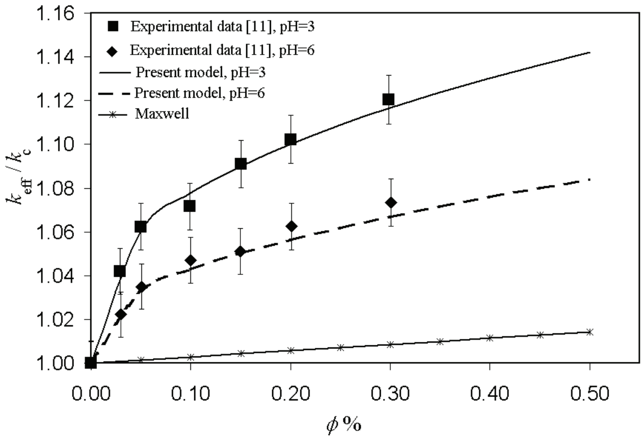


Fig. 4. Effective thermal conductivity as a function of volume fraction at different pH. Note that Maxwell results are not capable of predicting the observed enhancement. In addition, nonlinear behaviour is observed as the volume fraction increases. Further deviation of pH from pH_{iso} results in higher thermal conductivities because of the increasing stability

b) pH of solution

Altering pH from the iso-electric point increases the surface charge of nanoparticles. Hence the repulsive potential increases, resulting in more stability of suspension. The more stabilized nanofluid signifies the less formation of clusters and therefore the faster Brownian velocity of aggregates. As Brownian velocity of nanoparticles and clusters increase, the more the volume of the surrounding fluid carried by them. Thus, the induced micro-convection increases and thorough micromixing enhances the effective thermal conductivity.

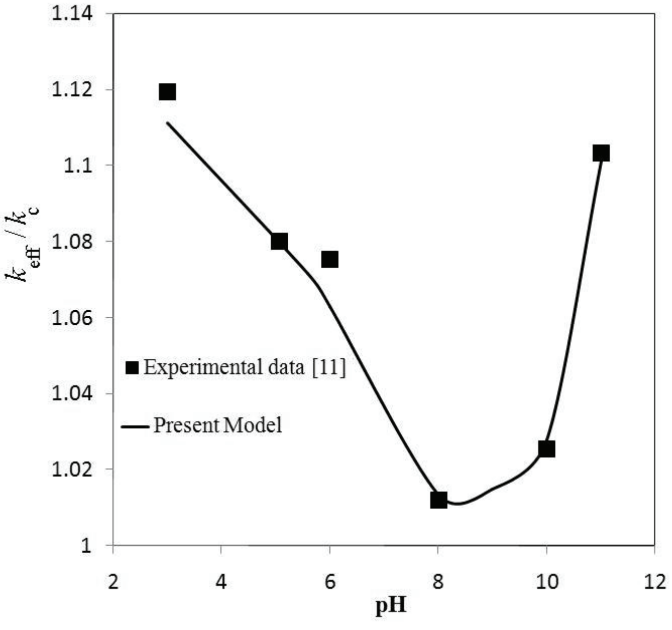


Fig. 5. Effect of pH on the effective thermal conductivity of the CuO-water nanofluid. Deviation of pH from iso-electric point, pH=8 in this case, strengthens the stability and enhances k_{eff}

Lee *et al.* [11] measured k_{eff} and ψ_s for CuO/water nanofluids for different pH at a very low concentration of nanoparticles. Due to the small volume fraction, k_{st} is small and the Brownian conductivity is dominant in assessing the effective thermal conductivity. Figure 5 represents the comparison between the measured normalized thermal conductivity and the results obtained by the present model. Comparison with experimental data indicates that the results obtained by the present model and the experimental data have the same trend. For about pH = 8, which is approximately pH for iso-electric point, the surface charge vanishes and the repulsive barrier against the clustering subsides, leading to significant aggregation. As the deviation of pH from its iso-electric value becomes larger, surface charge of nanoparticles increases and the interparticle repulsive potential reinforces the stability, thus formation of clusters is retarded, which results in higher Brownian velocity and hence more thorough micromixing. As a result, the dynamic enhances, and the effective thermal conductivity of nanofluid increases as pH differs from $\mathrm{pH}_{\mathrm{iso}}$.

c) Particle size

From the particle dimension point of view, suspensions with nanoparticles have different characteristics compared to milli and micrometer size particles. First, the size dependence is not significant in suspensions with milli and micrometer size particles. Second, an inconsistent relation between the nanofluids behaviour and the particle size exists. For instance, in some experiments the effective thermal conductivity ratio increases with respect to the particle size, while in other experiments with the same nanofluid [10, 32], both increment and decrement of k_{eff} are observed. We try to explore the reasons for these contradictions and justify them by means of the present model.

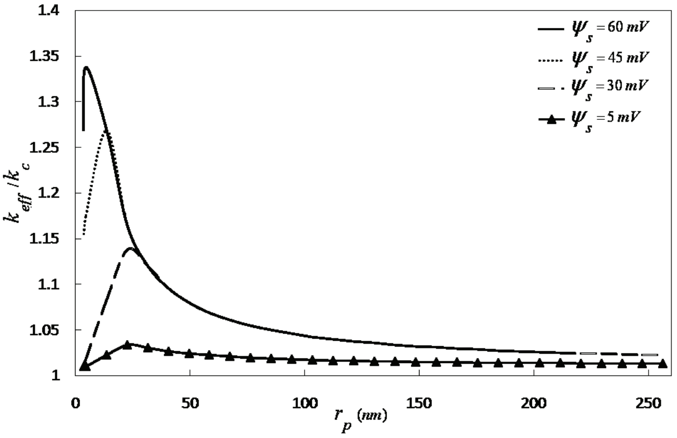


Fig. 6. Thermal conductivity as a function of nanoparticle radius. A maximum of k_{eff} for a specific nanofluid at different surface charges, which corresponds to different repulsive potential, with respect to the nanoparticle's radius is achieved

Figure 6 illustrates k_{eff} as a function of particle size at room temperature and $\phi = 0.3\%$ for CuO/water nanofluid and various surface charge values. Results show that an optimized radius exists at any surface charge. The reason for this behaviour is that when particle size diminishes, the Brownian velocity increases and more vigorous micromixing takes place, causing higher thermal conductivities. However, for smaller particles, the formation of clusters accelerates which has a negative effect on thermal conductivity and leads to the decreasing of k_{eff}. The heavier clusters possess lesser Brownian velocities and hence lower induced micro-convection. Consequently, depending on the parameters affecting the stability of suspension, at a particular particle size, the effective thermal conductivity reduces.

Figure 7 represents the experimental results of Prasher *et al.* [10] and a comparison with the present model. It is shown that thermal conductivity of nanofluid, k_{eff}, initially increases with increasing r_{p}, then it reaches a climax and finally decreases. Reduction in k after the peak takes place is due to aggregation effects. Figure 7 shows that the proposed model is in reasonable agreement with the experimental data and both the experimental data and the model show a peak. It can be seen that the k_{eff} increases with temperature and agreement is better for $T = 70^\circ C$, while for $T = 80^\circ C$ the quantitative agreement is not completely satisfactory. Prasher et al [10] tried to change the empirical parameters of their model to fit it with their study. However, we are looking for universal functions. It should be noted that β_p and β_a obtained from the previous section are used for making Fig. 7 results. Therefore, one suggestion for the present model is to update hydrodynamic interaction coefficients. As a result, one limitation for the present model is that it works better for moderate temperatures which are involved with less vigorous hydrodynamic interactions.

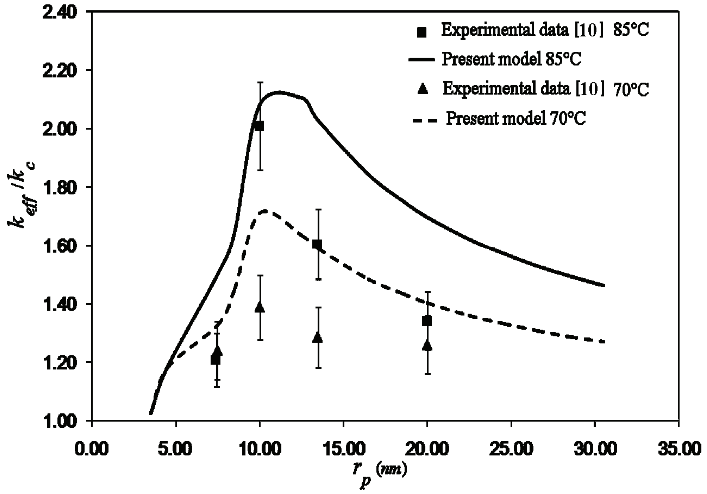


Fig. 7. Comparison of thermal conductivity ratio versus particle size with experimental data [10]

It is delineated in Figs. 6 and 7 that when temperature decreases or in the case of higher surface charges, which corresponds to a further difference between the fluid pH and pH_{iso}, the maximum of thermal conductivity shifts to smaller values. The reason is that by the reduction of temperature or enhancement of surface charge, the barrier of suspension against aggregation reinforces and the formation of clusters retards. Therefore, when nanofluid is more stabilized, i.e. when repulsive potential exceeds attractive potential, the maxima of k_{eff} shifts to smaller particle size.

A promising conclusion can be drawn here: by increasing the stability of nanofluid, e.g. differing pH from pH_{iso}, adding surfactants, etc. the effective thermal conductivity of nanofluid solution is enhanced. Consequently, the stability of nanocolloidal suspensions has a key role in determining the effective thermal conductivity.

d) Temperature

Thermal conductivity of nanofluids is a stronger function of temperature compared with that of base fluids. For instance, in an experimental study of Patel *et al.*[9], even for vanishing volume fractions of 0.00011%, with 30°C enhancement in temperature, a 13% increase of k_{eff} was observed. Figure 8 depicts the variation of thermal conductivity with temperature for Al/water nanofluid with 25*nm* particle radius and 0.5% volume fraction, with the same surface charge and different ionic strength. It can be seen that the results of the present model are able to clarify the contradiction observed in different experimental studies. Depending on the physicochemical properties of suspension, weak or strong dependence of the thermal conductivity on temperature is attained. It is obvious that k_{eff} increases with respect to temperature. Based on the present model, this behaviour can be explained; the higher temperature signifies more Brownian motion and therefore more micromixing occurs. It can also be concluded that with higher ionic strength, k_{eff} decreases. The reason is that by the enlargement of κ with higher *I*, the repulsive potential is reduced and accordingly the thermal conductivity is decreased. This behaviour explains why some experiments observe the immense dependence of k_{eff} on temperature while other results do not match with such large enhancement; this is mainly because of the different physicochemical properties.

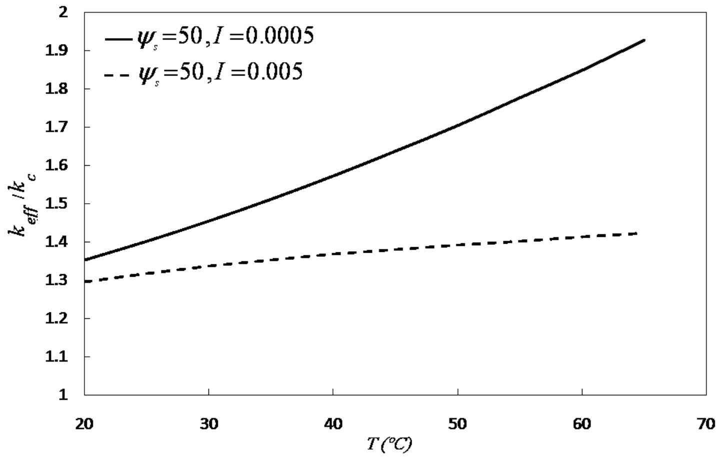


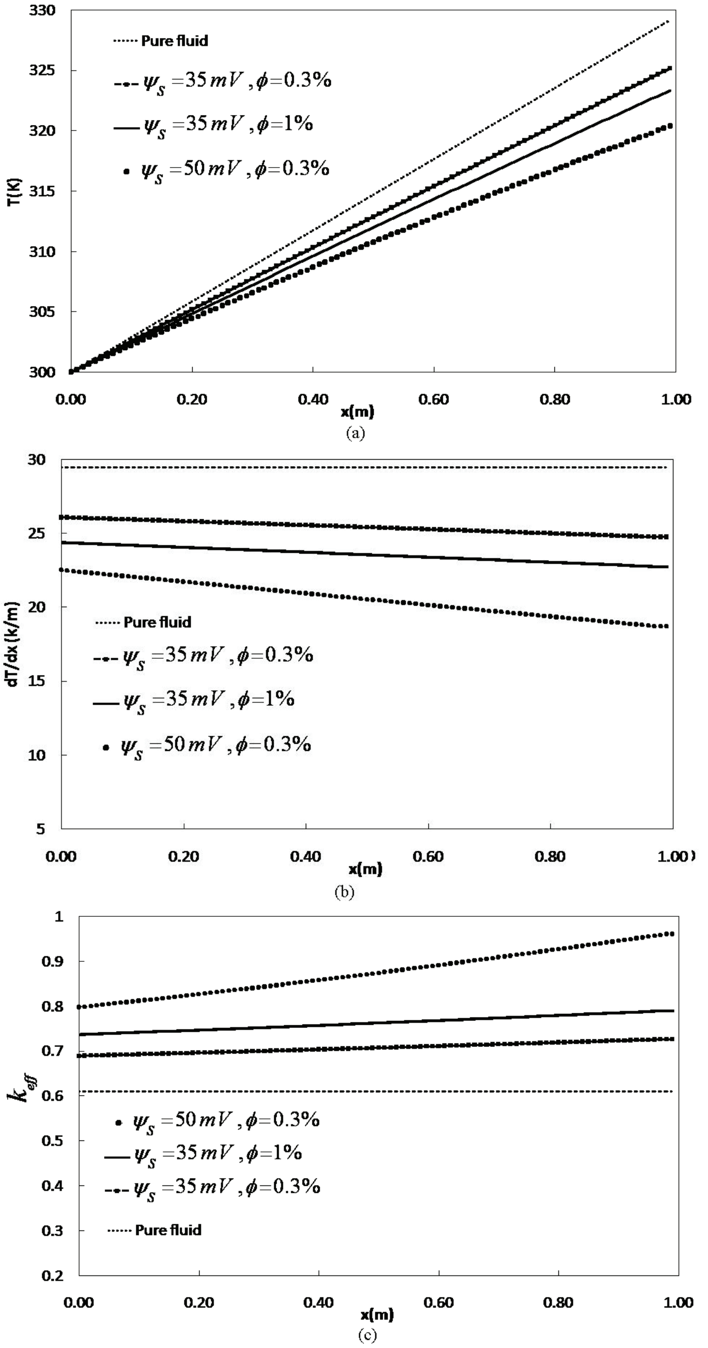
Fig. 8. Normalized nanofluid thermal conductivity as a function of temperature. Different behaviour is exhibited when physicochemical properties change.

e) Case study

A sample problem is solved considering a steady state with no internal heat generation, and constant heat flux for a quiescent nanofluid. The problem is one-dimensional and the only component of heat flux is in x-direction. The axial conduction heat flux component can be expressed as:

$$q = -k_{\mathrm{eff}} \frac{dT}{dx} \tag{26}$$

The implicated boundary condition is T = 300 *K* @ x = 0 *m*. Figure 9 shows the profiles of temperature, temperature gradient, and effective thermal conductivity in pure water and uniform nanofluids for a heat flux of 18 (W/m^2). The nanofluid is CuO/water with 25*nm* particle size and a constant ionic strength of $I = 5\times10^{-4}\ mol/m^3$. The temperature at *x= 1m* for the nanofluid with $\phi = 0.3\%$, $\psi_s = 50mV$ is lower than that of water with constant thermal conductivity by 9 *K*, which obviously signifies the more vigorous conductive heat transfer resulted by the presence of nanoparticles. Comparing the effective thermal conductivity of nanofluids with the same surface charge of $\psi_s = 35\ mV$ and different volume fractions of $\phi = 0.3\%$ and $\phi = 1\%$ reveals that, as we expected, by increasing volume fraction the k_{eff} increases. Comparing nanofluids with the same volume fraction of $\phi = 0.3\%$ and different surface charge of $\psi_s = 35\ mV$ and $\psi_s = 50\ mV$ demonstrates that by increasing the repulsive potential, which leads to a more stabilized suspension, the effective thermal conductivity of nanofluids increases. For the case we studied here, the k_{eff} of nanofluid with $\phi = 0.3\%$ and $\psi_s = 50\ mV$ is the maximum one, because of more micro-mixing effects. In addition, referring to Fig. 9b shows that the effect of Brownian motion is the enhancing heat transfer between hot and cold regions in a suspension, resulting in a sharper variation in temperature gradient.



(a)

(b)

(c)

Fig. 9. Comparison between pure fluid and nanofluid with different volume fraction and surface charge, a-Temperature, b- Temperature gradient, c-thermal conductivity profiles

4. CONCLUSION

Prediction of effective thermal conductivity for nanofluids is still a hot debate. In this paper, a new model for nanofluid thermal conductivity has been introduced. This model takes into account several important factors in determining the thermal conductivity of nanofluids. These factors are temperature, particle size, Hamaker constant, intrinsic properties of particle and fluid, surface charge and time. Brownian motion and resulted micro mixing of nanoparticles and clusters, as well as aggregation kinetics of nanoparticles and clusters are the key elements in the evaluation of nanofluid thermal conductivity in the present study. We argue that any effort to understand the behaviour of nanofluids is not comprehensive without considering such effects simultaneously. In fact, the present approach is similar to that of kinetic theory for evaluating the thermal conductivity of gases. The only difference is the existence of inter-particle potentials which are omitted for ideal gases. In order to capture inter-particle interactions, the Smoluchowski approach and the DLVO theory were employed to calculate the mass of clusters.

The present model includes two empirical parameters which should be obtained by experimental data. For a precise determination of β_a and β_p, more experimental data sets, especially for small volume fraction of nanoparticles, are required. Regarding theoretical background, a future work can be devoted to analyzing the hydrodynamic interactions of nanoparticles.

Results indicate that for higher volume fractions the increment of k_{eff} reduces. This stems from the nonlinear behaviour of the thermal conductivity with nanoparticle concentration. It was also demonstrated that the reduction of particle radius is not beneficial in all cases, but depends on the stability of suspension instead. As a result, by enhancing the stability of nanofluids, it is possible to achieve higher thermal conductivities with the same nanofluid. Time is a key factor in formation and enlargement of clusters. Thus, it is worth hindering aggregation by means of methods such as utilizing ultrasonic equipment or adding surfactants. Also, since stability ratio greatly depends on the repulsive potential, any parameter which affects the repulsive potential has a significant influence on the thermal conductivity. Therefore, pH, salt concentration and dielectric constant are among the important factors determining k_{eff}. In addition, surfactants and similar third agents which enhance repulsive barrier of suspension play a role in the increment of thermal conductivity ratio. Consequently, any error in ψ_s can lead to a significant error in evaluating k_{eff}. It is strongly recommended that future experimental works always report chemical parameters such as surface charge, pH, and the age of nanofluid.

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