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Technical Note

Thermal conductivity enhancement of nanofluids in conjunction with electrical double layer (EDL)

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ABSTRACT

A novel expression for the thermal conductivity of nanofluids is proposed, which incorporates the kinetic theory to describe the contribution of the Brownian motion of the nanoparticles with a more realistic definition of the mean free path, and additionally to consider the contribution of the interparticle interaction due to the existence of the electrical double layer (EDL). It is shown that this model is applied to Au/water nanofluids satisfactorily with respect to temperature, volume fraction and particle size. In the case of dense Al_2O_3/water nanofluids, the effect of the interparticle interaction due to EDL on enhancing the thermal conductivity is more prominent than in the case of dilute Al_2O_3/water nanofluids. The model proposed in this paper shows that interparticle interaction due to EDL is the most responsible for the enhancement of thermal conductivity of nanofluids.

1. Introduction

Thermal conductivity of nanofluids (liquids with suspended nanoparticles) is significantly higher than that of the base liquid even for negligible nanoparticle concentrations. Therefore, nanofluids are attracting extensive attention as the next-generation heat transfer media. As is well known, Maxwell first proposed that liquids with suspended solid particles exhibit enhanced thermal conductivity [1]. However, it was Choi who practically led the way to utilize the enhanced thermal conductivity with stable suspensions of nanofluids [2].

Since then, various models have been proposed to explain the mechanism of thermal conductivity enhancement of nanofluids with increasing temperature and decreasing nanoparticle size [3–6]. By using molecular dynamics simulations, Vladkov and Barrat [7] showed that in the absence of collective effects, the heat conductivity of the nanofluid is well described by the classical Maxwell–Garnet equation model. Through an order-of-magnitude analysis, Prasher et al. showed [8,9] that the localized convection caused by the Brownian motion of the nanoparticles is the key mechanism for enhancing the effective thermal conductivity of nanofluids. Furthermore, the relationship between the Brownian motion and enhanced thermal conductivity was observed with the optical visualization of the particle motions and experimental measurement of thermal conductivity [10]. Recently, Lee et al. showed that surface charge states are mainly responsible for enhancing the thermal conductivity of nanofluids [11].

From the microscopic point of view, thermal conductivity of nanofluids is a very complex thermodynamic property which involves non-equilibrium behavior, so that the classical Maxwell model cannot explain its dependence on temperature. In fact, the kinetic theory reveals that the effective thermal conductivity of the particle is directly proportional to its mean velocity. Thus, the objective of the present study is to propose a theoretical model to which the kinetic theory is applied with a more realistic definition of the mean free path of the nanoparticle demonstrating the Brownian motion than in a previous study, and (more importantly) to which the kinetic theory is applied, for the first time, to take into account of the interparticle interaction due to the existence of EDL.

2. Theoretical approach

The model proposed in this study consists of the stationary mode (based on classical theory), the single particle motion mode (based on thermal conductivity of nanofluids deduced from the kinetic theory regarding the Brownian motion), and the interparticle interaction mode (based on thermal conductivity of nanofluids deduced from the kinetic theory regarding the particle motions induced by EDL).

2.1. Stationary mode

We start our argument by assuming that stationary thermal conductivity of nanofluids obeys the Maxwell model [1]. Therefore,

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Nomenclature

A	Coulomb constant (9.0×10^9 N m^2 C^{-2})
b	outer radius of virtual shell (m)
c	derivative constant (J m^{-2} K^{-1})
$\hat{c}_v$	specific heat (J K^{-1})
d	diameter of nanoparticle (m)
D	particle diffusion constant (m^2 s^{-1})
F	force (N)
k	thermal conductivity (kJ s^{-1} m^{-1} K^{-1})
k_B	Boltzmann constant (1.3807×10^{-23} J K^{-1})
l	mean free path of molecules or nanoparticles (m)
m	mass (kg)
N	number of atoms
n	particle concentration (m^{-3})
q	electric charge (C)
r	particle radius (m)
t	time (s)
T	absolute temperature (K)
T_D	Debye temperature (K)
$\bar{u}$	mean velocity (m s^{-1})

Greek letters

ε_0	permittivity of vacuum (8.8542×10^{-12} F m^{-1})
ε_{bf}	dielectric constant of medium
ζ	zeta potential (mV)
κ	Debye–Hückel parameter (m^{-1})
ϕ	volume fraction of nanoparticle
μ	viscosity of medium (N s m^{-2})
τ	relaxation time (s)

Subscripts

Br	Brownian motion
EDL	electrical double layer
eff	effective
bf	base fluid
Mw	Maxwell
np	nanoparticle

enhanced thermal conductivity by the Maxwell model is expressed as

$$k_{Mw} = k_{bf}\left(\frac{k_{np} + 2k_{bf} + 2(k_{np} - k_{bf})\phi}{k_{np} + 2k_{bf} - (k_{np} - k_{bf})\phi}\right). \quad (1)$$

This model is valid only when the thermal energy transport in nanofluids takes place as a diffusive process and cannot apparently consider other effects such as particle size, concentration, and temperature of nanofluids considered.

2.2. Single particle motion mode

The Brownian motion which represents the behavior of nanoparticles in colloids is characterized by the Stokes–Einstein relation in the form of $D = k_B T/3\pi\mu d$, so that the mean velocity of nanoparticles due to the Brownian motion can be calculated as

$$\bar{u}_{Br} = \frac{k_B T}{3\pi\mu d_{np} l_{bf}}. \quad (2)$$

We assume that a nanoparticle freely moves over the length of the mean free path of the base fluid molecules [4].

The effective thermal conductivity of the particle is directly proportional to its mean velocity according to the kinetic theory [12]. Thus the thermal conductivity due to the particle motion can be expressed as

$$k_{Br} = c\bar{u}_{Br}. \quad (3)$$

An estimate using the kinetic theory shows that $c = nl_{np}\hat{c}_v/3$, where $\hat{c}_v$ is the specific heat per particle which is estimated by the Debye model for the particle. In the present study, $\hat{c}_v = 3Nk_B$ for Au particle or $\hat{c}_v = 3Nk_B\frac{4\pi^4}{5}\left(\frac{T}{T_D}\right)^3$ for Al_2O_3 particle [12]. Therefore, the thermal conductivity due to the Brownian motion can be written as

$$k_{Br} = \frac{nl_{np}\hat{c}_v}{3}\frac{k_B T}{3\pi\mu d_{np} l_{bf}}. \quad (4)$$

However, without giving any detailed account, Kumar et al. simply assumed that l_{np} of nanoparticles was on the order of 1 cm to obtain high values of thermal conductivity [13]. The gold particles used were 17-nm in mean diameter and 0.00026 vol%, so that the distance between the particles was approximately 1.24 μm (which was approximately 73 times longer than the particle diameter). This assumption is not only unphysical but also inconsistent with their own experimental conditions, as will be shown later. On the other hand, in the present study, we used $l_{np} = 1/\left(\sqrt{2}n\pi d_{np}^2\right)$ as the mean free path of the nanoparticle based on the assumption that *all particles move about with a Maxwellian velocity distribution* [12], which is physically more viable.

2.3. Interparticle interaction mode

In the light of the fact that most colloidal particles are surrounded by electrical double layers (EDLs), it can be readily assumed that nanoparticles suspended in the base fluid in the form of colloidal particles are also surrounded by EDLs. General characteristics of the colloid are introduced in Ref. [14]. Dual forces, i.e. repulsion due to Coulomb force and attraction due to van der Waals force, respectively, are exerted on nanoparticles in the colloid. Coulomb force prevents coalescence of the particles, but van der Waals force induces coalescence if the distance between the particles exceeds the energy barrier. Due to the existence of the EDL, sufficient Coulomb force acts on nanoparticles in stable nanofluids [14]. Therefore, we can derive an expression for thermal conductivity enhancement of nanofluids by using the concepts of the interparticle interaction and the kinetic theory [12]. In this study, the interparticle interactions are considered by using the Kuwabara's cell model [15], as shown in Fig. 1, where each sphere is enclosed by a virtual shell of outer

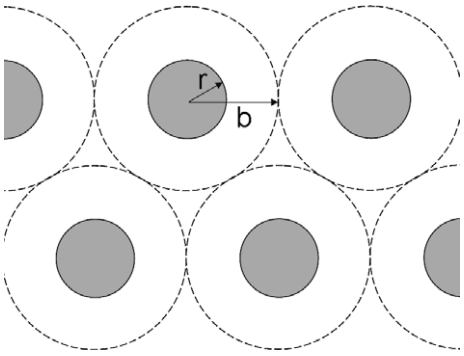

Fig. 1. Spherical particles of radius r in concentrated suspensions in the cell model [15].

radius b. Then the particle volume fraction ϕ is given by $\phi = (r/b)^3$. The nearest half-distance between the centers of two neighboring particles is given by $b = r\phi^{-1/3}$.

The surface charge of nanoparticles can be obtained by measuring the zeta potential ζ. The surface charge on a particle is expressed from the model of a concentric sphere [14] as

$$q = 4\pi\varepsilon_{bf}\varepsilon_0\zeta r(\kappa r + 1). \tag{5}$$

If the thickness of electrical double layer extends wide into the nonpolar media, then $\kappa r \ll 1$. Thus, Eq. (5) reduces to

$$q = 4\pi\varepsilon_{bf}\varepsilon_0\zeta r. \tag{6}$$

In nonpolar media, several tens of mV can be obtained as the magnitude of ζ from electrophoresis measurements. In the present study, we use pure water as the base fluid so that Eq. (6) is applicable because $\kappa r < 0.05$.

Repulsion due to Coulomb force existing between the nanoparticles in the nanofluid can be represented as

$$F = \frac{Aq^2}{\varepsilon_{bf}(r\phi^{-1/3})^2}. \tag{7}$$

Therefore, Coulomb force due to the EDL acts on the particles, so that we can express the force by Newton's law as follows:

$$F = m\,d\bar{u}_{EDL}/dt. \tag{8}$$

In the kinetic description of particles such as free electrons, it is convenient to introduce a parameter called the relaxation time, τ, which is the period between consecutive collisions or encounters with another particle [12]. Thus, we can express the characteristic time τ_{np} of the nanoparticle by the relaxation time as follows:

$$\tau_{np} = l_{np}/\bar{u}_{EDL}. \tag{9}$$

Consequently, during the characteristic time or the relaxation time, Eq. (8) which represents the force acting on the particle can be written as

$$F = m\bar{u}_{EDL}^2/l_{np}. \tag{10}$$

Equating Eq. (10) with Eq. (7), the mean velocity ($\bar{u}_{EDL}$) of the nanoparticles due to the EDL can be expressed as

$$\bar{u}_{EDL} = \sqrt{\frac{Aq^2 l_{np}}{\varepsilon_{bf} m_{np}(r\phi^{-1/3})^2}}, \tag{11}$$

where m_{np} is the mass of the nanoparticle. Finally, the thermal conductivity due to the EDL (k_{EDL}) can be obtained along the same line as Eq. (3)

$$k_{EDL} = \frac{n l_{np}\hat{c}_v}{3}\sqrt{\frac{Aq^2 l_{np}}{\varepsilon_{bf} m_{np}(r\phi^{-1/3})^2}}. \tag{12}$$

Since the enhanced thermal conductivity by the Maxwell model, that due to the Brownian motion, and that due to the electrical double layer are all independent of each other, we adopt the principle of superposition to express the overall thermal conductivity enhancement of nanofluids by adding Eqs. (1), (4) and (12), as follows:

$$k_{eff} = k_{Mw} + k_{Br}\left(1 + \frac{k_{EDL}}{k_{Br}}\right). \tag{13}$$

Eq. (13) can explain the mechanism of enhanced thermal conductivity of nanofluids by taking account of various effects including particle size, liquid temperature, particle volume fraction, the Brownian motion and interparticle interaction.

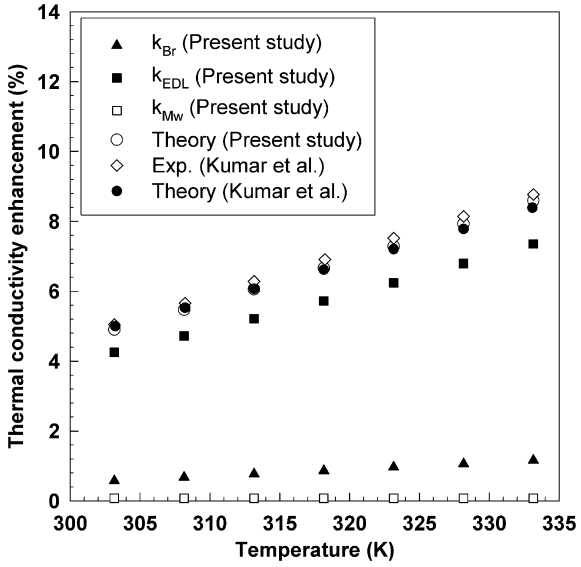

Fig. 2. Comparison of thermal conductivity enhancement of Au/water nanofluids (containing 0.00026% Au particles with 17-nm mean diameter) with respect to temperature obtained by the present model with the theoretical and experimental data given by Kumar et al. [13].

3. Results and discussion

This study was motivated by Kumar et al. [13] in the sense that we apply the kinetic theory to thermal conductivity enhancement of nanofluids. However, we adopt a more physically viable model for l_{np} and, more importantly, consider interparticle interaction due to EDLs, which causes significant changes in the estimation of l_{np} and $\bar{u}_{np}$. Fig. 2 shows a comparison of the thermal conductivity enhancement with respect to temperature obtained by the present theoretical model with the experimental and theoretical data given by Kumar et al. [13] who claimed that nanoparticles do not affect each other in dilute nanofluids. However, the surface charge on a gold nanoparticle in the gold nanofluid is on the order of magnitude of 10^{-18} C, where the absolute values of ζ of 20-nm diameter

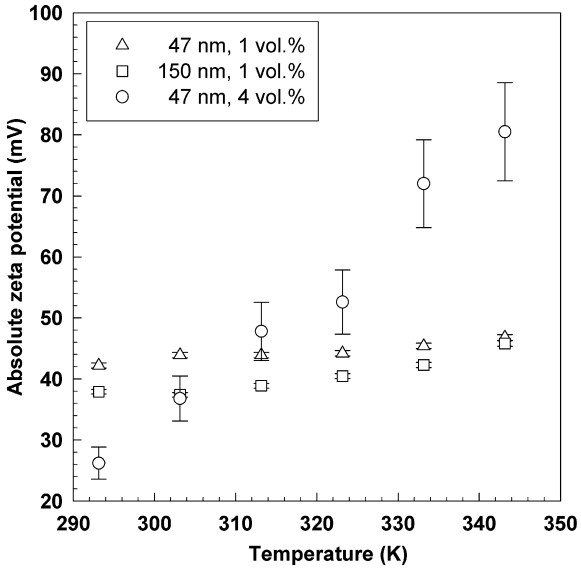

Fig. 3. Measured zeta potential of Al_2O_3/water nanofluids.

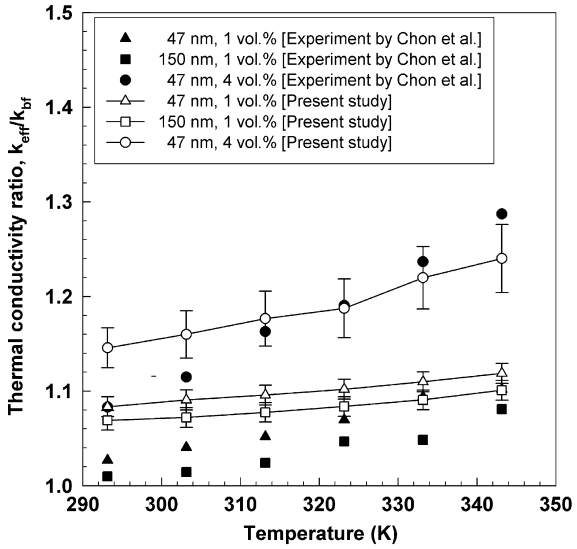

Fig. 4. Comparison of thermal conductivity enhancement of Al_2O_3/water nanofluids with respect to temperature obtained by the present model with the theoretical and experimental data given by Chon et al. [17].

particles are in the range of 40–90 mV [16]. As shown in Fig. 2, thermal conductivities induced by interparticle interaction due to the EDL are about 6.3–7.4 times greater than those induced by the Brownian motion. Predicted values by the present model are in good agreement with the experimental data obtained by Kumar et al. [13].

To further verify the validity of the present theoretical model, it was applied to the experimental data obtained by Chon et al. for Al_2O_3/water nanofluids [17]. Fig. 3 shows the measured ζ of Al_2O_3/water nanofluids which were prepared by using the same nanoparticles (Nanophase Inc. and Nanostructured and Amorphous Materials Inc.) and the same method as Chon et al. [17]. As shown in Fig. 3, the ζ's of nanofluids increased slightly with increasing temperature for low volume fraction of 1 vol%. However, at high volume fraction of 4 vol%, some nanoparticles settled down during the measurement of ζ, so that the measured values showed about 10% deviation. Effective thermal conductivity of nanofluids can be obtained by using the measured ζ. Fig. 4 shows a comparison of the thermal conductivity ratios obtained by the present model with the experimental data by Chon et al. [17]. For the cases of 1 vol% of both 47 and 150-nm diameter nanoparticles, the estimated thermal conductivity ratios (k_{eff}/k_{bf}) of the nanofluids hardly increase with increasing temperature. Nevertheless, the estimated thermal conductivities are in good agreement with the measured ones within ±5.9% deviation. In the case of 4 vol% of 47-nm diameter, the enhancement of thermal conductivities matched the experimental data with increasing temperature.

4. Conclusion

A theoretical model has been proposed to delineate the mechanism of thermal conductivity enhancement of nanofluids for various particle sizes and species, particle volume fractions and temperatures. The kinetic theory is applied to represent the contribution of the Brownian motion to the thermal conductivity with more realistic model for mean free path, and to incorporate the contribution of interparticle interaction due to EDL. The present model shows that the latter contributes more significantly to the thermal conductivity enhancement of nanofluids.

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