J Therm Anal Calorim (2017) 129:1255–1263
DOI 10.1007/s10973-017-6256-x

An improved model for thermal conductivity of nanofluids with effects of particle size and Brownian motion

Shuangling Dong[1] · **Xiaodong Chen**[2]

Received: 18 May 2016 / Accepted: 6 March 2017 / Published online: 11 March 2017

Abstract Based on the generalized distribution of the temperature field, an improved model for the thermal conductivity of nanofluid has been derived. The impact of particle size and Brownian motion is modeled through the effective volume fraction, based on particle radius. In the special case, the generalized relationship reduces to the classical Maxwell model. On the other hand, the effect of Brownian movement is equivalent to increasing the effective volume fraction of nanoparticles. The effective radius of the nanoparticle is proposed, where the switching time and the equivalent volume fraction depend on the Brownian velocity of the nanoparticles. Considering the above two effects, an effective model is obtained. Comparison of thermal conductivity for Al_2O_3–water nanofluid is made between the present model and several theoretical models. Theoretical predictions on CuO–water nanofluid, ZnO–TiO_2 hybrid nanofluids and MWCNTs nanofluid are also verified against experimental data.

Keywords Nanofluid · Enhanced thermal conductivity · Maxwell model · Particle size · Brownian motion

List of symbols

A	A constant independent of the fluid type (−)
a	Average acceleration of the particle (m s^{-2})
a_1	A constant dependent on the fluid type (–)
Bi	Nanoparticle Biot number (–)
c	An empirical constant (–)
C_p	Specific heat (J kg^{-1} °C^{-1})
c_1	A constant for considering the Kapitza resistance (–)
c_2	A proportional constant (–)
D_f	Fractal dimension (–)
d_f	Diameter of liquid molecule (m)
d_m	Equivalent diameter of a base fluid molecule (m)
d_{max}	Maximum diameter of nanoparticles (m)
d_{min}	Minimum diameter of nanoparticles (m)
d_p	Diameter of nanoparticle (m)
F_D	Drag force (kg m s^{-2})
$\mathbf{G}$	Temperature gradient (°C m^{-1})
k	Thermal conductivity (W m^{-1} °C^{-1})
k_B	Boltzmann constant 1.3805×10^{-23} (J °C^{-1})
n	Mass (kg)
n	Number of particles (–)
Nu	Nusselt number (–)
Pr	Prandtl number (–)
r	Radius (m)
r_B	Radius contributed by Brownian motion (m)
Re	Reynolds number (–)
t_l	Thickness of the interfacial nanolayer (m)
T_0	Temperature (°C)
T_0	Reference temperature 273 (°C)
$\bar{v}_B$	Velocity (m s^{-1})
$\bar{v}_B$	Average Brownian velocity (m s^{-1})

Greek symbols

α	Fraction of the liquid volume (–)
β	Index coefficient (–)
τ	Relaxation time (s)
τ_1	Ratio of particle to effective volume fraction (–)
γ	Dynamic viscosity (kg m^{-1} s^{-1})

✉ Shuangling Dong
doingL@163.com

[1] College of Mechanical and Electrical Engineering, Beijing University of Chemical Technology, Beijing 100029, China

[2] State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China

γ Kinematic viscosity ($m^2\ s^{-1}$)
φ_A Density ($kg\ m^{-3}$)
φ_A Volume fraction of particles in the fluid (–)
φ_A Average volume concentration (–)

Subscripts
0 Reference
B Brownian motion
e Effective
f Base fluid
l Liquid layer
p Nanoparticle
s Solid

Introduction

As a significant challenge in engineering applications, cooling and exchanging heat requires imperative development. With the developments in energy and power devices, heat transfer performance needs to be improvement. Conventionally, the optimized approaches have been taken to increase the heat exchange area with high thermal conductivity fluid, which may need a complicated design with little effect to the expectation [1]. Therefore, new generation of heat transfer working medium is especially needed. Nanofluids have been proposed by dispersing nanoparticles with high thermal conductivity into a base fluid such as mineral oil and water [2]. The heat transport can be improved up to 20% by adding nanoparticles with volume fraction less than 4% [3]. The main four factors contributing to thermal conductivity enhancement include the adsorbed liquid layer at the interface, the nanoparticle aggregation, the nanoparticle Brownian motion and the Brownian motion-induced microconvection [4]. The dynamic enhancement mechanism mainly stems from Brownian motion. As the size of nanoparticle is small, the intensity of Brownian motion is high and it plays a very important role. Brownian motion of particles is considered as a result of the impact of liquid molecules. However, it is very difficult to perform accurate measurements of the Brownian velocity with sufficient resolution due to its complexity. The first successful measurement of the instantaneous movement of particles in air and in water was implemented by Li et al. [5] and Huang et al. [6], respectively. The interaction among the convective flow induced by neighboring particles increases the complexity of the nanoparticle movement in nanofluids [7]. The impact of Brownian motion mainly consists of two parts; one is the energy transport due to microconvection induced by Brownian movement, and the other is the heat conduction through collisions of nanoparticles caused by the Brownian motion [8]. Furthermore, due to the interaction of particle and fluid in the flow regime, it destroys laminar sublayer, reduces the thermal resistance and enhances the heat transfer rate [9].

Numerous experimental results have shown that as nanoparticles are uniformly dispersed, the thermal conductivity of the base fluid can be increased significantly. In addition to experimental studies on the influence of nanoparticle size, volume fraction and temperature, it is very necessary to modeling the experimental data with theoretical investigations to reveal the inherent mechanisms. Classical models for the effective thermal conductivity are the same with general particle suspensions considering the factors of particle concentration and shape. It is not appropriate for the particles with nanoscale. The above models have been improved based on different heat transport mechanisms, such as static mechanism originating from the liquid layering and particle aggregation and dynamic mechanism stemming from Brownian motion and convection.

For the theoretical prediction of the effective thermal conductivity, numerous models have been proposed in the literature [10–18]. Table 1 lists the theoretical relationships with parameters of particle size. Including the effect of Brownian movement-induced convection, Prasher et al. [7] developed a semiempirical model with experimentally determined nanoparticle Biot number. They suggested that the convection caused by the Brownian motion of nanoparticles attributed more for the conductivity enhancement. However, there is a large uncertainty in the value of m and it depends on various parameters, such as temperature, volume fraction and particle diameter. Taking into account the fractal distribution of nanoparticle sizes, Xu et al. [12] reported a new model for predicting the thermal conductivity of nanofluids. The proposed fractal model was expressed as a function of the average size of nanoparticles, and the heat convection between nanoparticles and fluids was incorporated. However, their model is complex and there are several empirical parameters, including the fractal dimension and the ratio of the minimum to maximum diameter of nanoparticles. There is also an empirical parameter c due to the uncertainty of the thickness of thermal boundary layer which is primarily relevant to the character of liquids. Considering the interfacial thermal resistance effect, Jang and Choi [13] suggested a model with the diameter of base fluid molecule and an empirical constant, which worked well for nanofluids with metallic or nanotube nanoparticles. However, the impact of the ratio of thermal conductivity of nanoparticles to the base fluid is less than that of the temperature, nanoparticle size and volume fraction. Based on the model of Koo and Kleinstreuer [16], Vajjha and Das [17] developed fraction factor of the liquid volume that travels with a particle and the functional relationships from their experimental data. Their relationship worked well at

Table 1 Predictive models for thermal conductivity proposed by previous researchers

Researchers	Theoretical models
Prasher et al. [7]	$k_{\mathrm{e}}=(1+ARe^{a_1}Pr^{0.333}\varphi)\frac{2k_{\mathrm{f}}+(1+2Bi)k_{\mathrm{p}}+2\varphi[(1-Bi)k_{\mathrm{p}}-k_{\mathrm{f}}]}{2k_{\mathrm{f}}+(1+2Bi)k_{\mathrm{p}}-\varphi[(1-Bi)k_{\mathrm{p}}-k_{\mathrm{f}}]}k_{\mathrm{f}}$
	$Re=\frac{1}{\gamma}\sqrt{\frac{18k_{\mathrm{B}}T}{\pi\rho_{\mathrm{p}}d_{\mathrm{p}}}}$
Xu et al. [12]	$\frac{k_{\mathrm{e}}}{k_{\mathrm{f}}}=\frac{k_{\mathrm{p}}+2k_{\mathrm{f}}-2\varphi(k_{\mathrm{f}}-k_{\mathrm{p}})}{k_{\mathrm{p}}+2k_{\mathrm{f}}+\varphi(k_{\mathrm{f}}-k_{\mathrm{p}})}+c\frac{Nu_{\mathrm{p}}d_{\mathrm{f}}}{Pr}\frac{(2-D_{\mathrm{f}})D_{\mathrm{f}}}{(1-D_{\mathrm{f}})^2}\frac{[(d_{\max}/d_{\min})^{1-D_{\mathrm{f}}}-1]}{[(d_{\max}/d_{\min})^{2-D_{\mathrm{f}}}-1}\frac{1}{d_{\mathrm{p}}}$
Jang and Choi [13]	$k_{\mathrm{e}}=k_{\mathrm{f}}(1-\varphi)+c_1k_{\mathrm{p}}\varphi+c_2\frac{d_{\mathrm{m}}}{d_{\mathrm{p}}}k_{\mathrm{f}}Re^2Pr\varphi$
	$k_{\mathrm{e}}=\frac{2k_{\mathrm{f}}+k_{\mathrm{p}}+2\varphi(k_{\mathrm{p}}-k_{\mathrm{f}})}{2k_{\mathrm{f}}+k_{\mathrm{p}}-\varphi(k_{\mathrm{p}}-k_{\mathrm{f}})}k_{\mathrm{f}}+5\times10^4\alpha\varphi\rho_{\mathrm{f}}C_{\mathrm{pf}}\sqrt{\frac{k_{\mathrm{B}}T}{\rho_{\mathrm{p}}d_{\mathrm{p}}}f(T,\varphi)}$
Vajjha and Das [17]	$f(T,\varphi)=(2.8217\times10^{-2}\varphi+3.917\times10^{-3})\frac{T}{T_0}-3.0669\times10^{-2}\varphi-3.9112\times10^{-3}$
Rizvi et al. [18]	$\frac{k_{\mathrm{e}}-k_{\mathrm{f}}}{2k_{\mathrm{e}}+k_{\mathrm{f}}}=\frac{\varphi}{\varphi-\tau_{\mathrm{l}}}\frac{(k_{\mathrm{e}}-k_{\mathrm{l}})(2k_{\mathrm{l}}+k_{\mathrm{p}})-\tau_{\mathrm{l}}(k_{\mathrm{p}}-k_{\mathrm{l}})(2k_{\mathrm{l}}+k_{\mathrm{e}})}{(2k_{\mathrm{e}}+k_{\mathrm{l}})(2k_{\mathrm{l}}+k_{\mathrm{p}})+2\tau_{\mathrm{l}}(k_{\mathrm{p}}-k_{\mathrm{l}})(k_{\mathrm{l}}-k_{\mathrm{e}})}$

the temperature as nanofluids are commonly used. However, there were empirical functions dependent on the type of nanoparticles and the coefficients in their model were fitted from the experimental data of four nanofluids with CuO, Al_2O_3, ZnO and SiO_2 nanoparticles. Rizvi et al. [18] derived a simple expression to determine the value of thermal conductivity of nanofluid considering the interfacial layer absorbed on the particles. In their model, the thermal conductivity of the interfacial layer was given by

$$k_{\mathrm{l}}=\frac{t_l}{r_{\mathrm{p}}\left(r_{\mathrm{p}}+t_{\mathrm{l}}\right)\left[A_1\ln\left(1+\frac{t_{\mathrm{l}}}{r_{\mathrm{p}}}\right)+\frac{B_1t_{\mathrm{l}}}{r_{\mathrm{p}}\left(r_{\mathrm{p}}+t_{\mathrm{l}}\right)}-\frac{C_1}{\lambda}\ln\left(1-\frac{\lambda t_{\mathrm{l}}}{k_{\mathrm{p}}}\right)\right]} \tag{1}$$

where

$$\lambda=\frac{k_{\mathrm{p}}-k_{\mathrm{f}}}{t_{\mathrm{l}}},\quad A_1=\lambda/(k_{\mathrm{p}}+\lambda r_{\mathrm{p}})^2,\quad B_1=1/(k_{\mathrm{p}}+\lambda r_{\mathrm{p}}),\quad C_1=\lambda^2/(k_{\mathrm{p}}+\lambda r_{\mathrm{p}})^2. \tag{2}$$

They analyzed the effect of solvent on the effective thermal conductivity, and comparison was made with the predictions of previous models. However, as Brownian motion effect was not considered in their model, their prediction was always lower than the experimental data.

For the measurement of the effective thermal conductivity, a number of experiments have been undertaken by previous investigators. The influence of temperature, particle size and volume concentration was mainly studied. The measurement by Ho et al. [19] showed that the thermal conductivity of Al_2O_3–water nanofluid increased more than 10% relatively with particle volumetric fraction 3%. Their data agreed well with the experimental result by Wang et al. [20] and theoretical correlation of Rea et al. [21], although their measurement was for low volume fraction and higher than that predicted by Masuda et al. [22]. Vajjha and Das [17] performed experiment on the thermal conductivity of nanofluids dispersing Al_2O_3 or CuO nanoparticles into a base fluid. The temperature measurement ranged from 298 to 363 K with particle volume fraction less than 10%, and theoretical investigation has also been carried out. They developed a model fitted well with their experimental data, although they did not show good agreement with several previous models [13, 23, 24].

In the above investigations, the influence of particle size is represented by the effect of Brownian movement or related to the thickness of the liquid layer. In fact, the effect of particle size and the Brownian movement are two independent effects, although the Brownian velocity is influenced by the particle size. Therefore, this cannot reflect the nature of particle size effect, especially when there is no Brownian motion and the absorbed layer which appears with relatively large particles. On the other hand, numerous dynamic thermal conductivity models related to the Brownian movement have been proposed, which are also shown as the last terms of the first four models in Table 1, all of which are contributed by the microconvection of the fluid near the particles induced by Brownian movement. However, as the complexity of Brownian motion and the interaction between particles and the fluid, it would be very difficult to accurately predict the contribution of particle Brownian motion to the effective thermal conductivity. As shown above, the impact of particle size on the thermal conductivity is generally represented by the additional dynamic model with effects of Brownian motion in previous studies. The basic static thermal conductivity models, such as the classical Maxwell model, contain only the effect of volume fraction and do not include the effect of particle size, which is inconsistent with the real performance of nanofluids. Dynamic models of the thermal conductivity contributed by Brownian motion contain some empirical coefficients such as fractal dimensions and do not seem conducive to practical application and promotion. Based on the above considerations, an improved model for thermal conductivity is proposed in present investigation, including the effects of nanoparticle size and Brownian motion.

Thermal conductivity model

Effect of particle size

In general, the problem of steady-state heat conduction can be described by the Laplace equation

$$\nabla^2 T = 0 \tag{3}$$

where T is the temperature. For the conduction of the particle–fluid suspensions, the boundary conditions are as follows

$$T(r)|_{\mathrm{r}\to\infty} = -\mathbf{G}\cdot\mathbf{r},\quad T(r)\big|_{\mathrm{r}\to\mathrm{r}_\mathrm{a}^-} = T(r)\big|_{\mathrm{r}\to\mathrm{r}_\mathrm{a}^+},\quad k_\mathrm{e}\frac{\partial T(r)}{\partial r}\Big|_{\mathrm{r}\to\mathrm{r}_\mathrm{a}^-} = k_\mathrm{f}\frac{\partial T(r)}{\partial r}\Big|_{\mathrm{r}\to\mathrm{r}_\mathrm{a}^+} \tag{4}$$

where $\overrightarrow{\mathrm{G}}$ represents the temperature gradient, r_a is the radius of a large sphere containing all the dispersed particles in the fluid, k_e denotes the effective thermal conductivity, and k_f is the thermal conductivity of the fluid. The effective thermal conductivity can be obtained by

$$k_\mathrm{e} = \frac{2k_\mathrm{f} + k_\mathrm{p} + 2\varphi(k_\mathrm{p} - k_\mathrm{f})}{2k_\mathrm{f} + k_\mathrm{p} - \varphi(k_\mathrm{p} - k_\mathrm{f})}k_\mathrm{f} \tag{5}$$

It is known as the classical Maxwell's model [10], where φ is the volume fraction in the above equation. Maxwell's model presents the variation of the effective thermal conductivity with the volume concentration. In fact, the thermal conductivity depends directly on the radius of particles. Considering this effect, this work presents a generalized thermal conductivity model, which includes the factor of particle size.

The typical solution of harmonic function for temperature is

$$T = \left(\frac{k_\mathrm{e} - k_\mathrm{f}}{2k_\mathrm{f} + k_\mathrm{e}}\frac{r_\mathrm{a}^3}{r^3} - 1\right)\overrightarrow{G}\cdot\overrightarrow{r} \tag{6}$$

It can be observed that the equivalent function form of Eq. 6 is taken as

$$T = Ar + Br^{-2} \tag{7}$$

If we consider a generalized temperature distribution, the solution of harmonic function for the temperature becomes

$$T = Ar^\beta + Br^{-(\beta+1)} \tag{8}$$

with a varied coefficient β. Satisfying the same temperature boundary conditions with Eq. 4, the temperature can be deduced as

$$T = \left[\frac{\beta(k_\mathrm{e} - k_\mathrm{f})}{(\beta+1)k_\mathrm{f} + \beta k_\mathrm{e}}\frac{r_\mathrm{a}^{2\beta+1}}{r^{2\beta+1}} - 1\right]\overrightarrow{G}\cdot\overrightarrow{r} \tag{9}$$

The expression for temperature distribution reduces to Eq. 6 when $\beta = 1$. Mathematically, when $\beta = 1$, the temperature takes the form of Eq. 7, corresponding to the linear solution of the temperature distribution. Physically, this limit represents the situation neglecting the effects of particle size on the heat conduction between particle and fluid.

The temperature field can also be obtained by regarding particles immersed in the fluid

$$T = \left[\frac{\beta(k_\mathrm{p} - k_\mathrm{f})}{(\beta+1)k_\mathrm{f} + \beta k_\mathrm{p}}\frac{nr_\mathrm{p}^{2\beta+1}}{r^{2\beta+1}} - 1\right]\overrightarrow{G}\cdot\overrightarrow{r} \tag{10}$$

From the two equations (Eqs. 9 and 10) above, the effective thermal conductivity can be expressed as

$$k_\mathrm{e} = \frac{(\beta+1)k_\mathrm{f} + \beta k_\mathrm{p} + 2\beta\varphi_\mathrm{s}(k_\mathrm{p} - k_\mathrm{f})}{(\beta+1)k_\mathrm{f} + \beta k_\mathrm{p} - \beta\varphi_\mathrm{s}(k_\mathrm{p} - k_\mathrm{f})}k_\mathrm{f} \tag{11}$$

where the effective volume fraction

$$\varphi_\mathrm{s} = \frac{nr_\mathrm{p}^{2\beta+1}}{r_\mathrm{a}^{2\beta+1}} = \frac{nr_\mathrm{p}^3}{r_\mathrm{a}^3}\frac{r_\mathrm{p}^{2(\beta-1)}}{r_\mathrm{a}^{2(\beta-1)}} = \varphi\frac{r_\mathrm{p}^{2(\beta-1)}}{r_\mathrm{a}^{2(\beta-1)}} \tag{12}$$

Thus, the effective thermal conductivity depends directly on the volume fraction and nanoparticle size. It increases with the increase in the volume fraction and the decrease in the particle radius. When $\beta = 1$, the expression degenerates into Eq. 4 which is not related to the particle radius.

In fact, φ_s can also be calculated by

$$\varphi_\mathrm{s} = \varphi\frac{r_\mathrm{p}^{2(\beta-1)}}{r_\mathrm{a}^{2(\beta-1)}} = \left(\frac{\varphi^{2\beta+1}}{n^{2\beta-2}}\right)^{1/3} \tag{13}$$

If the nanoparticles have different radii $r_1, r_2, \ldots, r_n$, the volume fraction φ in the above equations can be replaced by φ_d as

$$\varphi_\mathrm{d} = \varphi_\mathrm{A}\frac{1}{n}\left(\frac{r_1^3}{r_\mathrm{p}^3} + \frac{r_2^3}{r_\mathrm{p}^3} + \cdots + \frac{r_\mathrm{n}^3}{r_\mathrm{p}^3}\right) \tag{14}$$

When the radii of all the particles are the same, the volume fraction $\varphi_\mathrm{d} = \varphi_\mathrm{A}$. This thermal conductivity expression holds true for the condition that the difference in nanoparticle radius is comparatively small, so that the thermal conductivity of a discrete phase medium can be described by an effective property.

It is well known that when the thermal conductivity of the nanoparticle is higher than the fluid, the thermal conductivity increases with the increasing the volume concentration. When the particle radius decreases, the equivalent volume fraction φ_s increases. It is deduced by

Eq. 13 that the effective thermal conductivity becomes higher, which agrees with the experimental results.

Effect of Brownian motion

Brownian motion improves the heat transfer rate between the particles and the fluid; thus, it increases the thermal conductivity of nanofluids. Many researchers attributed the impact of Brownian motion on the heat conduction to the dynamic thermal conductivity [4, 16, 17], which was reflected mainly by the microconvection of the fluids. However, the dynamic thermal conductivity models contain some empirical relations and coefficients, which may not conducive to practical application. This investigation presents a convenient thermal conductivity model related to Brownian motion.

Due to Brownian motion, the effective radius of nanoparticles can be considered to be increased and then the effective volume concentration of the particles becomes higher. For the limiting case, such as when the particle velocity is zero, that is there is no Brownian motion, the effective radius of the nanoparticle is r_p. When the particle velocity is infinitely large, the effective radius of the particle

$$r_e = r_p + r_B \tag{15}$$

The radius contributed by Brownian motion r_B is shown in Fig. 1. This radius can be estimated by multiplying the velocity of Brownian motion and the switching time as

$$r_B = \bar{v}_B \tau \tag{16}$$

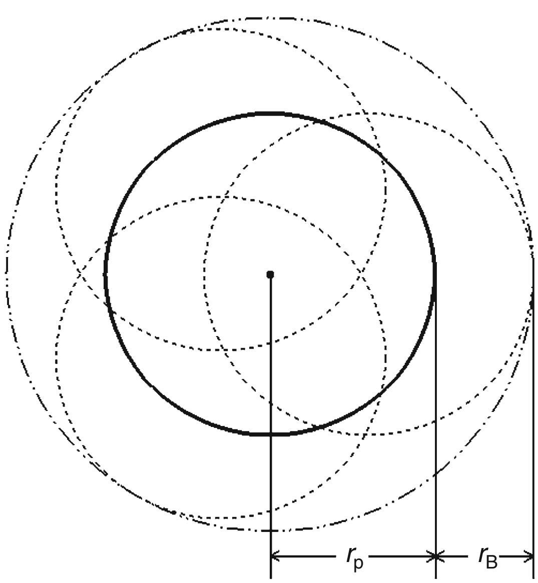

Fig. 1 Effective particle radius with Brownian motion

The switching time relates to the relaxation time of a Brownian particle. The relaxation time [25] can also be expressed by

$$\tau_p = \frac{\bar{v}_B}{a} \tag{17}$$

as the average acceleration

$$a = \frac{F_D}{m_p} = \frac{6\pi\mu r_p \bar{v}_B}{m_p} = \frac{6\pi\mu r_p \bar{v}_B}{\frac{4}{3}\pi r_p^3 \rho_p} = \frac{9\mu\bar{v}_B}{2\rho_p r_p^2} \tag{18}$$

then the Brownian relaxation time

$$\tau_p = \frac{\bar{v}_B}{a} = \frac{2\rho_p r_p^2 \bar{v}_B}{9\mu\bar{v}_B} = \frac{2\rho_p r_p^2}{9\mu} \tag{19}$$

As the velocity autocorrelation function

$$\langle v_B(t) v_B(0)\rangle = \frac{3k_B T}{m_p} e^{-t/\tau_p} \tag{20}$$

The Brownian velocity depends on the temperature of the fluid and the mass of the particle. When

$$t/\tau_p = 12, \quad \sqrt{\langle v_B(t) v_B(0)\rangle} = 2.48 \times 10^{-3} \sqrt{\langle v_B(0) v_B(0)\rangle}. \tag{21}$$

Therefore,

$$\tau = 12\tau_p = \frac{8\rho_p r_p^2}{3\mu} \tag{22}$$

is taken for estimation. The time τ represents the equivalent time when the velocity of the particle is largely reduced subjected mainly by the hydrodynamic force. As the estimation of the relaxation time τ_p, comparison is made with previous investigation [5]. The time calculated by Eq. 19 is 0.53×10^{-4} s, and the time extracted from the experimental data is 0.49×10^{-4} s. It can be seen that they agree well in magnitude order and the difference is primarily due to the unsteady complexity of the random Brownian motion. Generally, the contributed radius r_B is less than the particle radius r_p, that is

$$r_B = O(10^{-1}) r_p \tag{23}$$

When the actual velocity of the particle is v_B, the contributed radius and the Brownian motion velocity satisfy the negative exponential relationship,

$$r_e = r_p + r_B\left[1 - e^{-f(v_B)}\right] \tag{24}$$

which is depicted in Fig. 2. Conveniently, the function is supposed to be

$$f(v_B) = \frac{v_B}{\bar{v}_B} \tag{25}$$

$\bar{v}_B$ is taken as the root-mean-square velocity

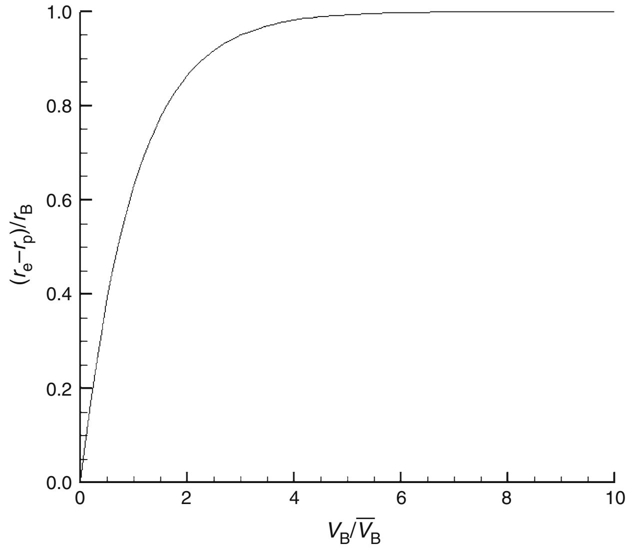

Fig. 2 Increased ratio of effective radius with dimensionless particle Brownian velocity

$$\bar{v}_{\mathrm{B}} = \sqrt{\frac{3k_{\mathrm{B}}T}{m_{\mathrm{p}}}} \tag{26}$$

For instance, if $f(v_{\mathrm{B}}) = 2$, the corresponding radius $r_{\mathrm{e}} = r_{\mathrm{p}} + 0.865r_{\mathrm{B}}$. The effective volume fraction of nanoparticles is calculated by

$$\varphi_{\mathrm{B}} = \varphi \frac{r_{\mathrm{e}}^3}{r_{\mathrm{p}}^3}, \tag{27}$$

and the thermal conductivity becomes $k_{\mathrm{e}}(\varphi_{\mathrm{B}})$.

Verification of the improved model

If we consider both the two effects in the above sections, then an effective model can be obtained by

$$k_{\mathrm{e}} = \frac{(\beta+1)k_{\mathrm{f}} + \beta k_{\mathrm{p}} + 2\beta\varphi_{\mathrm{e}}(k_{\mathrm{p}} - k_{\mathrm{f}})}{(\beta+1)k_{\mathrm{f}} + \beta k_{\mathrm{p}} - \beta\varphi_{\mathrm{e}}(k_{\mathrm{p}} - k_{\mathrm{f}})} k_{\mathrm{f}} \tag{28}$$

where the effective volume fraction

$$\varphi_{\mathrm{e}} = \varphi_{\mathrm{s}} \frac{r_{\mathrm{e}}^3}{r_{\mathrm{p}}^3} \tag{29}$$

The magnitude of β can be determined by Eq. 28 with the experimental data as all the variables are known except β. For Al_2O_3–water nanofluids at room temperature, the index $\beta = 0.92$, which is extracted from the experimental data [26], as shown in Fig. 3. The diameters of Al_2O_3 nanoparticle are 11, 47 and 150 nm with the same volume fraction 1%. The exponent β depends on the type of nanoparticle. The variation in β relates to the actual temperature distribution in the nanofluid, which originates from the different performance of heat conduction in the vicinity of the interface between the particle and the fluid.

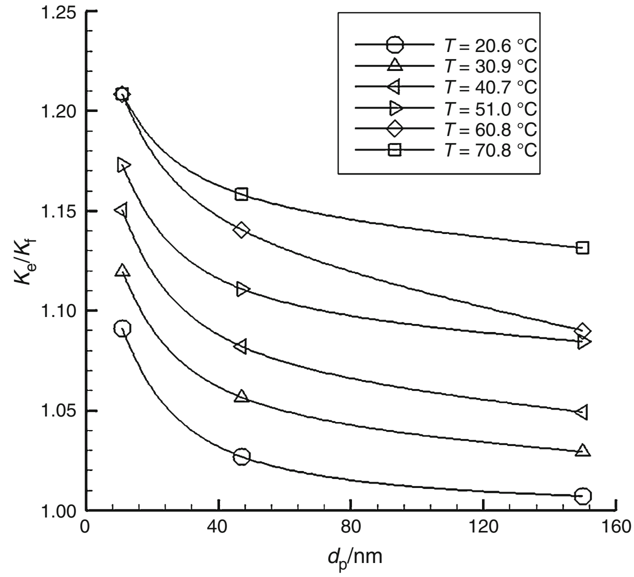

Fig. 3 Particle diameter variation of thermal conductivity enhancement for Al_2O_3–water nanofluids with different temperatures [26]

As the verification of the theoretical prediction, comparison is made between the present model and several theoretical models. Figure 4 shows the variation of thermal conductivity with the volume fraction. The diameter of the Al_2O_3 nanoparticle is 100 nm in nanofluid at temperature 30 °C, and the coefficient $\beta = 0.92$ is appropriate for the estimation by present model. The performances of the six models are also shown in this figure, and all of them have almost linear relationship with the volume fraction. Most models underestimate the thermal conductivity except the one by Xu et al. [12]. That's because they took into account the fractal distribution of nanoparticle sizes when considering the heat convection between nanoparticles and the liquid. Their model also shows good performance when the nanoparticle volume fraction is higher than 0.01. The model of Prasher et al. [7] predicts well when the volume fraction is small as dilute suspensions because the multi-particle interaction can be neglected. Taking into account the impact of Brownian motion, the particle size and the absorbed liquid layer, Murshed and de Castro [15] proposed a model that showed good agreement with some experimental results. However, the model depends on the ratio between thermal conductivity of interfacial layer and the fluid. The contribution of Brownian movement to the thermal conductivity does not apply at volume fraction $\varphi < 0.002$, which is shown in Fig. 4. On the whole, considering the effects of particle size and Brownian motion essentially, it can be observed that the prediction by present model shows satisfactory agreement with the experimental result by Ho et al. [19].

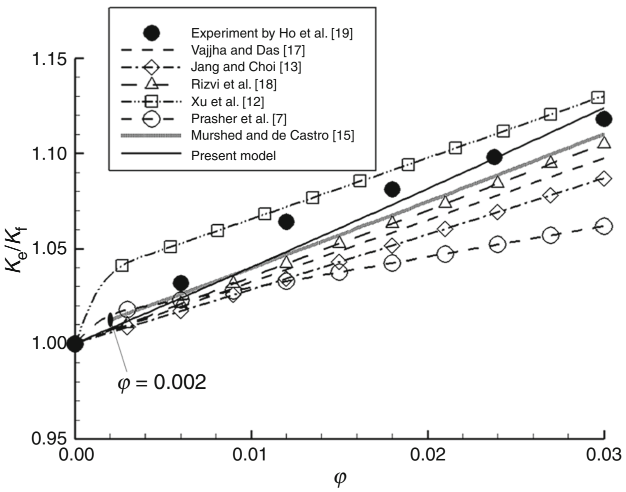

Fig. 4 Comparison of the thermal conductivity variation with volume fraction between experimental data and theoretical predictions for Al_2O_3–water nanofluid

As shown in Fig. 5, the ratio of the effective thermal conductivity to the thermal conductivity of the base fluid increases with temperature. The diameter of the CuO nanoparticle is 29 nm with volume fraction 4%, and the coefficient $\beta = 0.95$ is appropriate for the prediction. The coefficient for CuO is determined from the experimental data in Fig. 1b by Vajjha and Das [27]. It can be seen that the correlation by Koo and Kleinstreuer [16] performs better at low temperatures than at high ones as it has linear relationship with temperature. It is observed that the models of Yu and Choi [11] and Maxwell [10] do not show any obvious variation in thermal conductivity because these models have no explicit relationship with temperature. The model of Chon et al. [24] exhibits the same tendency with Koo and Kleinstreuer [16] but underestimates the conductivity ratio although it shows satisfactory agreement with experimental data at high temperatures. It can be seen that the model of Prasher et al. [23] is clearly sensitive to the temperature and only predicts well at medium value. It is shown that the result

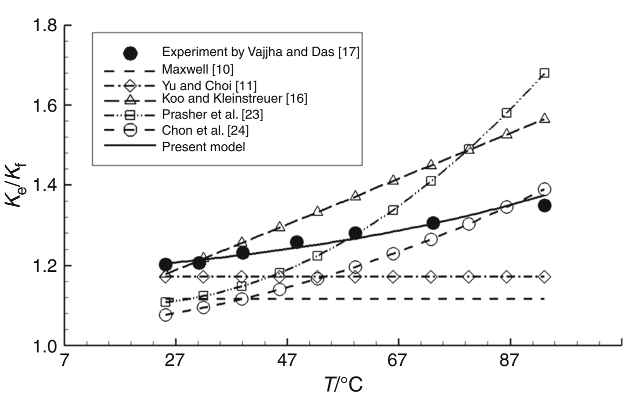

Fig. 5 Comparison of the thermal conductivity variation with temperature between experimental values and theoretical correlations for CuO–water nanofluid with 4% volume fraction

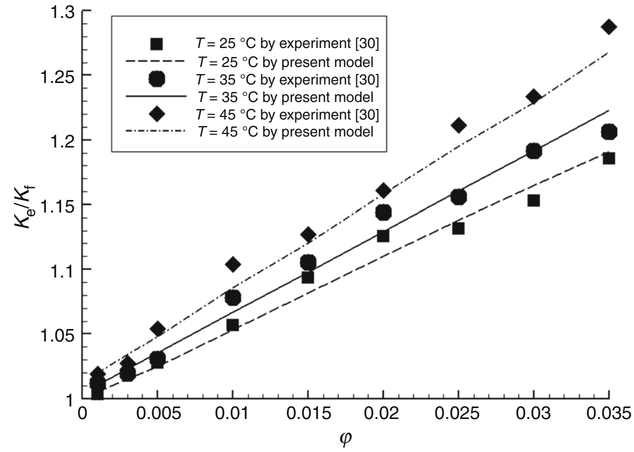

Fig. 6 Comparison of the thermal conductivity variation with volume fraction between experimental data and present theoretical predictions for $ZnO–TiO_2$/EG hybrid nanofluids

by present model agrees well with the experimental data by Vajjha and Das [17].

Recently, a lot of experimental studies have been conducted on thermal conductivity of carbon nanotube nanofluids as well as hybrid nanofluids [28–34]. As shown in Fig. 6, the ratio of the effective thermal conductivity to the thermal conductivity of the increases with the volume fraction. The base fluid is ethylene glycol (EG) with an equal volume of zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles dispersed [30]. The average diameter of ZnO nanoparticle is 40 and 30 nm for TiO_2. The hybrid thermal conductivity is obtained by averaging for the prediction as the two particles have equal volume. The results at three temperatures 25, 35 and 45 °C are extracted for comparison. The present model shows relatively satisfactory agreement with experimental data at these temperatures. Figure 7

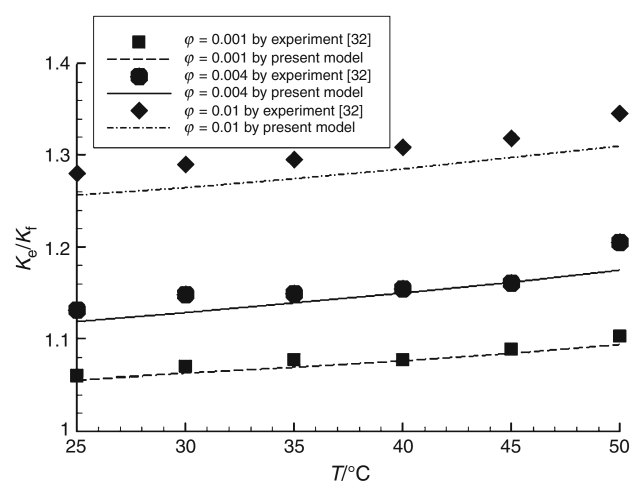

Fig. 7 Comparison of the thermal conductivity variation with temperature between experimental values and theoretical correlation for MWCNTs nanofluid with different volume fractions

shows the variation of thermal conductivity with the temperature ranging from 25 to 50 °C. COOH-functionalized multiwalled carbon nanotubes (MWCNTs) were dispersed in a mixture of 60 vol% water and 40 vol% ethylene glycol [32]. The equivalent radius is calculated from the volume of MWCNTs for coarse estimation. With the increase in the volume fraction, the present model underestimates the thermal conductivity which may originate from two aspects. First, the shape of MWCNTs is not sphere, and the present prediction is suitable for spherical particles. Second, as the volume fraction is higher, MWCNTs tend to aggregate which may increase the thermal conductivity.

Conclusions

Based on the generalized nonlinear solution of the temperature distribution, the expression for the variation of the thermal conductivity and the effective volume fraction with the particle radius are obtained. In the linear limit, the modified equation reduces to the original Maxwell equation. On the other hand, the effect of Brownian motion is equivalent to increasing the radius of the particle and then the volume fraction. A convenient expression of effective volume fraction has been proposed, which contains the velocity of Brownian movement. Considering the two main contributions, the modified model for thermal conductivity has been proposed. The specific exponent coefficient is obtained referenced with the experimental data of nanofluids. By comparison with the experimental data on the dependences of temperature and volume fraction, the effectiveness of this model has been verified. Furthermore, rational analysis of the impact of temperature distribution exponent needs intensive investigation. If the exact effective radius of the Brownian motion could also be obtained, a more accurate thermal conductivity model will be given.

Acknowledgements This research was supported by the National Natural Science Foundation of China (No. 51406098) and the Fundamental Research Funds for the Central Universities of China (ZY1614). We also thank the China Postdoctoral Science Foundation (No. 2015T80082) and the Opening fund of State Key Laboratory of Nonlinear Mechanics.

References

1. Ghadimi A, Saidur R, Metselaar HSC. A review of nanofluid stability properties and characterization in stationary conditions. Int J Heat Mass Transf. 2011;54:4051–68.
2. Mahian O, Kianifar A, Kalogirou SA, et al. A review of the applications of nanofluids in solar energy. Int J Heat Mass Transf. 2013;57:582–94.
3. Ramesh G, Prabhu NK. Review of thermo-physical properties, wetting and heat transfer characteristics of nanofluids and their applicability in industrial quench heat treatment. Nanoscale Res Lett. 2011;6:1–15.
4. Fan J, Wang L. Review of heat conduction in nanofluids. J Heat Transf. 2011;133:040801.
5. Li T, Kheifets S, Medellin D, Raizen MG. Measurement of the instantaneous velocity of a Brownian particle. Science. 2010;328:1673–5.
6. Huang R, Chavez I, Taute KM, Lukic B, Jeney S, Raizen MG, Florin EL. Direct observation of the full transition from ballistic to diffusive Brownian motion in a liquid. Nat Phys. 2011;7:576–80.
7. Prasher R, Bhattacharya P, Phelan PE. Thermal conductivity of nanoscale colloidal solutions (nanofluids). Phys Rev Lett. 2005;94:025901.
8. Koo J, Kleinstreuer C. Laminar nanofluid flow in microheat-sinks. Int J Heat Mass Transf. 2005;48:2652–61.
9. Das SK, Choi SUS, Yu W, Pradeep T. Nanofluids: science and technology. Hoboken, NJ: Wiley-Interscience; 2007.
10. Maxwell JC. A treatise on electricity and magnetism. 2nd ed. Cambridge: Oxford University Press; 1904.
11. Yu W, Choi SUS. The role of interfacial layers in the enhanced thermal conductivity of nanofluids: a renovated Maxwell model. J Nanopart Res. 2003;5:167–71.
12. Xu J, Yu B, Zou M, Xu P. A new model for heat conduction of nanofluids based on fractal distributions of nanoparticles. J Phys D Appl Phys. 2006;39:4486–90.
13. Jang SP, Choi SUS. Effects of various parameters on nanofluid thermal conductivity. J Heat Transf. 2007;129:617–23.
14. Xia G, Jiang H, Liu R, Zhai YH. Effects of surfactant on the stability and thermal conductivity of Al_2O_3/de-ionized water nanofluids. Int J Therm Sci. 2014;84:118–24.
15. Murshed SM, de Castro CA. Predicting the thermal conductivity of nanofluids—effect of Brownian motion of nanoparticles. J Nanofluids. 2012;1:180–5.
16. Koo J, Kleinstreuer C. A new thermal conductivity model for nanofluids. J Nanopart Res. 2004;6:577–88.
17. Vajjha RS, Das DK. Experimental determination of thermal conductivity of three nanofluids and development of new correlations. Int J Heat Mass Transf. 2009;52:4675–82.
18. Rizvi IH, Jain A, Ghosh SK, Mukherjee PS. Mathematical modelling of thermal conductivity for nanofluid considering interfacial nano-layer. Heat Mass Transf. 2013;49:595–600.
19. Ho CJ, Huang JB, Tsai PS, Yang YM. Water-based suspensions of Al_2O_3 nanoparticles and MEPCM particles on convection effectiveness in a circular tube. Int J Therm Sci. 2011;50:736–48.
20. Wang X, Xu X, S. Choi SU. Thermal conductivity of nanoparticle-fluid mixture. J Thermophys Heat Transf. 1999;13:474–80.
21. Rea U, McKrell T, Hu L, Boungiorno J. Laminar convective heat transfer and viscous pressure loss of alumina-water and zirconia-water nanofluids. Int J Heat Mass Transf. 2009;52:2042–8.
22. Masuda H, Ebata A, Teramae K. Alteration of thermal conductivity and viscosity of liquid by dispersing ultra-fine particles(dispersion of Al_2O_3, SiO_2 and TiO_2 ultra-fine particles). NetsuBussei (Japan). 1993;4:227–33.
23. Prasher R, Bhattacharya P, Phelan PE. Brownian-motion-based convective-conductive model for the effective thermal conductivity of nanofluids. J Heat Transf. 2006;128:588–95.
24. Chon CH, Kihm KD, Lee SP, Choi SUS. Empirical correlation finding the role of temperature and particle size for nanofluid (Al_2O_3) thermal conductivity enhancement. Appl Phys Lett. 2005;87:153107.
25. Uma B, Swaminathan TN, Radhakrishnan R, Eckmann DM, Ayyaswamy PS. Nanoparticle Brownian motion and hydrodynamic interactions in the presence of flow fields. Phys Fluids. 2011;23:073602.
26. Chon CH, Kihm KD. Thermal conductivity enhancement of nanofluids by Brownian motion. J Heat Transf. 2005;127:810.

27. Vajjha RS, Das DK. A review and analysis on influence of temperature and concentration of nanofluids on thermophysical properties, heat transfer and pumping power. Int J Heat Mass Transf. 2012;55:4063–78.
28. Esfe MH, Saedodin S, Yan WM, Afrand M, Sina N. Study on thermal conductivity of water-based nanofluids with hybrid suspensions of CNTs/Al_2O_3 nanoparticles. J Therm Anal Calorim. 2016;124:455–60.
29. Afrand M, Toghraie D, Sina N. Experimental study on thermal conductivity of water-based Fe_3O_4 nanofluid: development of a new correlation and modeled by artificial neural network. Int Commun Heat Mass Transf. 2016;75:262–9.
30. Toghraie D, Chaharsoghi VA, Afrand M. Measurement of thermal conductivity of ZnO–TiO_2/EG hybrid nanofluid. J Therm Anal Calorim. 2016;125:527–35.
31. Afrand M. Experimental study on thermal conductivity of ethylene glycol containing hybrid nano-additives and development of a new correlation. Appl Therm Eng. 2017;110:1111–9.
32. Soltanimehr M, Afrand M. Thermal conductivity enhancement of COOH-functionalized MWCNTs/ethylene glycol-water nanofluid for application in heating and cooling systems. Appl Therm Eng. 2016;105:716–23.
33. Esfe MH, Afrand M, Karimipour A, Yan WM, Sina N. An experimental study on thermal conductivity of MgO nanoparticles suspended in a binary mixture of water and ethylene glycol. Int Commun Heat Mass Transf. 2015;67:173–5.
34. Harandi SS, Karimipour A, Afrand M, Akbari M, D'Orazio A. An experimental study on thermal conductivity of F-MWCNTs-Fe_3O_4/EG hybrid nanofluid: effects of temperature and concentration. Int Commun Heat Mass Transf. 2016;76:171–7.