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Effect of multipolar interaction on the effective thermal conductivity of nanofluids*

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Nanofluids or liquids with suspended nanoparticles are likely to be the future heat transfer media, as they exhibit higher thermal conductivity than those of liquids. It has been proposed that nanoparticles are apt to congregate and form clusters, and hence the interaction between nanoparticles becomes important. In this paper, by taking into account the interaction between nearest-neighbour inclusions, we adopt the multiple image method to investigate the effective thermal conductivity of nanofluids. Numerical results show that then the thermal conductivity ratio between the nanoparticles and fluids is large, and the two nanoparticles are close up and even touch, and the point-dipole theory such as Maxwell–Garnett theory becomes rough as many-body interactions are neglected. Our theoretical results on the effective thermal conductivity of CuO/water and Al_2O_3/water nanofluids are in good agreement with experimental data.

Keywords: nanofluids, thermal conductivity, multipolar interaction
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1. Introduction

Nanofluids, being a new class of solid/liquid suspensions, are likely to be the future heat transfer media in many branches of industry, including energy supply and production, transportation and electronics, because their thermal conductivities are significantly higher than those of the parent liquids.[1−7] Traditional theory for composites such as Maxwell–Garnett theory (MGT) for effective physical properties gives[8]

$$\frac{K_{\rm e}}{K_{\rm m}} = \frac{K_{\rm p} + 2K_{\rm m} + 2f(K_{\rm p} - K_{\rm m})}{K_{\rm p} + 2K_{\rm m} - f(K_{\rm p} - K_{\rm m})}, \qquad (1)$$

where $K_{\rm p}$, $K_{\rm m}$, $K_{\rm e}$ stand for the thermal conductivity of nanoparticles and the matrix, and the effective thermal conductivity of the nanofluid, respectively, and f is the volume fraction of the dispersed particles. It is well known that MGT is a kind of point-dipole (PD) model, valid for composite systems, in which spherical particles are randomly embedded in a continuous medium. To derive MGT, one always assumes the particles to be sufficiently far from one another, so that many-body and multipolar interaction can be neglected. It was found that the enhancement of thermal conductivity achieved in nanofluids is far in excess of the levels predicted by the conventional theories.[2,8]

Following experimental studies,[1−7] various mechanisms and models have been proposed for studying the anomalous enhancement of effective thermal conductivity. For instance, considering the effect of the solid/liquid interfacial layer, researchers proposed that the enhancement of effective thermal conductivity is due to the ordered layering of liquid molecules near the solid particles.[9−11] Later, the convection caused by the Brownian motion of nanoparticles was proposed as the physical mechanism.[12−14] To our knowledge, all the above models neglected the many-body and multipolar interaction. However, recent experimental studies have shown that nanoparticles are apt to congregate and form clusters.[15,16] It was believed that clustering could affect the enhancement of effective thermal conductivity prominently.[15] On the other hand, the thermal conductivity ratio between nanoparticles and the matrix in nanofluids is usually high. Therefore, the many-body and multipolar interaction must be taken into account. In this paper we adopt the multiple image method with consideration of the interaction between nearest-neighbour nanoparticles to investigate the thermal conductivity of nanofluids.

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2. Theoretical considerations

We consider spherical inclusions with thermal conductivity $K_{\rm i}$ and radius R_0 suspended in a fluids with thermal conductivity $K_{\rm m}$. When the nanofluid is subject to two thermal sources with a definite temperature difference along z-axis, the heat flow in the spherical inclusions and the fluid can be given by

$$\boldsymbol{Q}_{\rm i} = K_i \boldsymbol{F}_{\rm i} \quad \text{in} \quad \Omega_{\rm i}, \tag{2}$$

and

$$\boldsymbol{Q}_{\rm m} = K_{\rm m} \boldsymbol{F}_{\rm m} \quad \text{in} \quad \Omega_{\rm m}, \tag{3}$$

where $\Omega_{\rm i}$ and $\Omega_{\rm m}$ are the domains occupied by the inclusions and fluids respectively, while $\boldsymbol{F}_{\rm i}$ and $\boldsymbol{F}_{\rm m}$ indicate the negative gradient of temperature within the inclusions and fluid, i.e.,

$$\boldsymbol{F}_{\rm i} = -\nabla T_{\rm i} \ \text{ and } \ \boldsymbol{F}_{\rm m} = -\nabla T_{\rm m}. \tag{4}$$

$T_{\rm i}$ and $T_{\rm m}$ can be expressed as

$$T_{\rm i} = \sum_n (c_n R^n + d_n/R^{n+1}) P_n(\cos\theta), \tag{5}$$

$$T_{\rm m} = \sum_n (a_n R^n + b_n/R^{n+1}) P_n(\cos\theta), \tag{6}$$

where $P_n(\cos\theta)$ is the associated Legendre function of order n with argument $\cos\theta$. When a negative temperature gradient F_0 on nanofluid is applied along the z-axis, the boundary conditions will be

$$T_{\rm i}|_{r=\infty} = -F_0 R\cos\theta \ \text{ and } \ T_{\rm m}|_{r=0} = \text{const}. \tag{7}$$

$$T_{\rm m}|_{r=R_0} = T_{\rm i}|_{r=R_0} \ \text{ and } \ K_{\rm m}\frac{\partial T_{\rm m}}{\partial R} = K_{\rm p}\frac{\partial T_{\rm i}}{\partial R}. \tag{8}$$

Substituting Eqs.(7) and (8) into Eqs.(5) and (6), one gets

$$\begin{aligned}
&a_1 = -F_0 \quad , \quad a_n = 0, \quad (n \neq 1),\\
&b_1 = \frac{F_0 R_0^3 (K_{\rm p} - K_{\rm m})}{K_{\rm p} + 2K_{\rm m}}, \quad b_n = 0, \quad (n \neq 1),\\
&c_1 = \frac{-3K_{\rm m}F_0}{K_{\rm p} + 2K_{\rm m}}, \quad c_n = 0, \quad (n \neq 1).
\end{aligned}$$

Then, the temperature distributions take the form

$$T_{\rm m} = -F_0 R\cos\theta + \frac{K_{\rm p} - K_{\rm m}}{K_{\rm p} + 2K_{\rm m}}\frac{F_0 R_0^3 \cos\theta}{R^2}, \tag{9}$$

$$T_{\rm i} = -\frac{3K_{\rm m}}{K_{\rm p} + 2K_{\rm m}} F_0 R\cos\theta. \tag{10}$$

The second term on the right-hand side of Eq.(9) can be taken as the contribution from the point dipole $P_0 (\equiv bK_{\rm m}F_0R_0^3)$, where b is a dipole factor, given by $b = (K_{\rm p} - K_{\rm m})/(K_{\rm p} + 2K_{\rm m})$. In this regard, $T_{\rm m}$ is rewritten as

$$T_{\rm m} = -F_0 R\cos\theta + \frac{\boldsymbol{P}_0 \cdot \boldsymbol{R}}{R^3 K_{\rm m}}. \tag{11}$$

The effective thermal conductivity $K_{\rm e}$ can be defined as follows:

$$K_{\rm e} = \frac{\langle Q\rangle}{\langle F\rangle} = \frac{fK_{\rm p}\langle Q_{\rm i}\rangle + (1-f)K_{\rm m}F_0}{f\langle Q_{\rm i}\rangle + (1-f)F_0}. \tag{12}$$

From Eq.(12), one has $\langle Q_{\rm i}\rangle = 3K_{\rm m}F_0/(K_{\rm p} + 2K_{\rm m})$, and hence[8]

$$\frac{K_{\rm e}}{K_{\rm m}} = 1 + \frac{3fb}{1 - fb}. \tag{13}$$

Equation (13) is the traditional MGT equation which neglects the interaction between nearest-neighbour inclusions. When the spheres are close up, we can take the single sphere as a point dipole, they will be further polarized by mutual polarization. As a result, the point-dipole approximation breaks down and we must consider the multipole moments.

We next consider a pair of spheres with equal radius a, separated by a distance r. The sphere 1 is taken as a dipole P_0, which induces an image $P_1^{(1)}$ in sphere 2; at the same time, $P_1^{(1)}$ induces yet another image dipole in sphere 1, and hence an infinite series of image dipoles are formed. The multiple image obeys a set of difference equations, which can be solved exactly. By using the idea of multiple image, we can deduce the total dipole moment of spheres (normalized to P_0) for a transverse field[16]

$$P_{\rm T} = P_0 \sum_{n=0}^{\infty} (-\tau^n)\Big(\frac{\sinh\beta}{\sinh(n+1)\beta}\Big)^3. \tag{14}$$

For a longitudinal field

$$\begin{aligned}
P_{\rm L} = P_0\Big\{&\Big[\sum_{n=0}^{\infty}\tau^n\Big[\frac{\sinh^3\beta}{\sinh^3(n+1)\beta}\Big]\\
&+ \frac{\sinh\beta\sinh^2(n\beta)}{\sinh^3(n+1)\beta}\Big]\Big\}\\
&- \frac{\Big[\sum_{n=0}^{\infty}\tau^2\frac{\sinh\beta\sinh(n\beta)}{\sinh^2(n+1)\beta}\Big]^2}{\Big[\sum_{n=0}^{\infty}\tau^n\frac{\sinh\beta}{\sinh(n+1)\beta}\Big]}.
\end{aligned} \tag{15}$$

Here $\tau = (K_{\rm p} - K_{\rm m})/(K_{\rm p} + K_{\rm m})$, and the parameter β is related to the reduced separation between the particles or clusters with $\cosh\beta = r/2a$.

For touching pairs, the series can be evaluated exactly in terms of polylogarithm functions, which have analytic continuations to the value of τ. The results

for longitudinal fields and transverse field are respectively

$$P_{\rm L} = P_0\Big[\frac{2Li_3(\tau)}{\tau} - \frac{Li_2(\tau)^2}{\tau Li_1(\tau)}\Big],$$
$$P_{\rm T} = -P_0 Li_3(-\tau)/\tau. \tag{16}$$

Here we should mention that, for simplicity, we have assumed that the two spheres have the same size. Since the pairs are generally randomly oriented, the average value $\langle P\rangle$ can be expressed as $\langle P\rangle = (P_{\rm L} + 2P_{\rm T})/3$. Then, the effective thermal conductivity can be written as

$$\frac{K_{\rm e}}{K_{\rm m}} = 1 + \frac{3fb\langle P\rangle/P_0}{1 - fb\langle P\rangle/P_0}. \tag{17}$$

Equation (17) is a new formula which contains the size, the separation of the nanoparticles and includes the interaction between nearest-neighbour inclusions. For point-dipole model, the average value $\langle P\rangle = P_0$, we can obtain the classic MGT formula Eq.(13). Equation (17) is more suitable for studying the effective thermal conductivity of nanofluids, because in real nanofluids, not in the solid/solid system, the nanoparticles are apt to congregate and form clusters.[15,16] In consequence, the interaction between nearest-neighbour inclusions becomes important. In this connection, we should adopt Eq.(17) instead of Eq.(13) to study the effective thermal conductivity in nanofluids.

The analytic multiple image results of Eq.(17) can be used to compare the various models according to the number of terms retained in the multiple image expression: (a) classical Maxwell–Garnett model (point–dipole model) with $n = 0$ term only and (b) multiple-induced-dipole (MID) model with $n = 0$ to ∞ terms.

3. Numerical results

In Fig.1 we plot the effective thermal conductivity enhancement $K_{\rm e}/K_{\rm m}$ as a function of $K_{\rm p}/K_{\rm m}$ at the volume fraction $f = 0.05$. It is evident that the MID theory for touching pairs generally gives higher enhanced $K_{\rm e}/K_{\rm m}$ than do the others. For small $K_{\rm p}/K_{\rm m}$, the difference between MGT and MID theories is small. For large $K_{\rm p}/K_{\rm m}$, which is the common case for nonofluids, the difference between these theories becomes significant. For instance, the maximum enhancement $K_{\rm e}/K_{\rm m}$ is about 120% for MID theory and the minimum $K_{\rm e}/K_{\rm m}$ is about 115% for MGT. We conclude that, the MID theory results in larger enhancement of effective thermal conductivity as we take into account the interaction between nearest-neighbour inclusions.

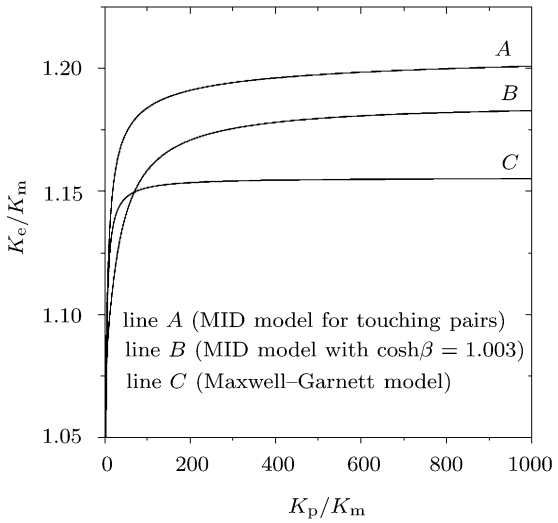


Fig.1. $K_{\rm e}/K_{\rm m}$ as a function of $K_{\rm p}/K_{\rm m}$ at the volume fraction $f = 0.05$.

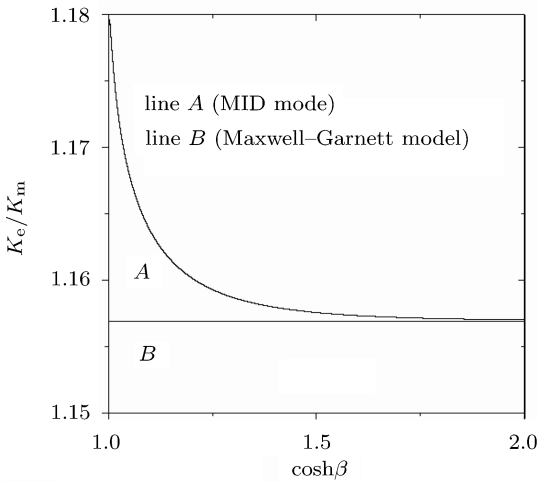


Fig.2. $K_{\rm e}/K_{\rm m}$ as a function of separation $\cosh\beta(= r/2a)$ at the volume fraction $f = 0.05$ and $K_{\rm p}/K_{\rm m} = 500$.

Next, we study the enhancement $K_{\rm e}/K_{\rm m}$ against the reduced separation ($\cosh\beta$) at $K_{\rm p}/K_{\rm m} = 500$ and $f = 0.05$, as shown in Fig.2. The enhancement predicted by the MID theory agrees with that by MGT theory for large reduced separation. Actually, when the separation between nanoparticles is large, the interaction between nanoparticles is too weak to be taken into account. However, when the separation between nanoparticles reduces, the difference between the two theories shows. This is due to the fact that, for small separation between nanoparticles, the influence of mutual interaction becomes important, and we

must take it into account to calculate effective thermal conductivity enhancement.

To further verify the validity of our formula, we compare theoretical results with the experimental data of CuO/water[6] and Al_2O_3/water[7] nanofluids. In the calculations, the thermal conductivity of CuO, water, and Al_2O_3 are taken as 69, 0.604, and 46W/mK, respectively.[6,7] In Fig.3, we find that the theoretical results given by MID theory for touching pairs are in good agreement with the experimental data. The theoretical results of classic MGT theory and MID theory for the reduced separation $\cosh\beta = r/2a = 1.003$ are all lower than the experimental data.

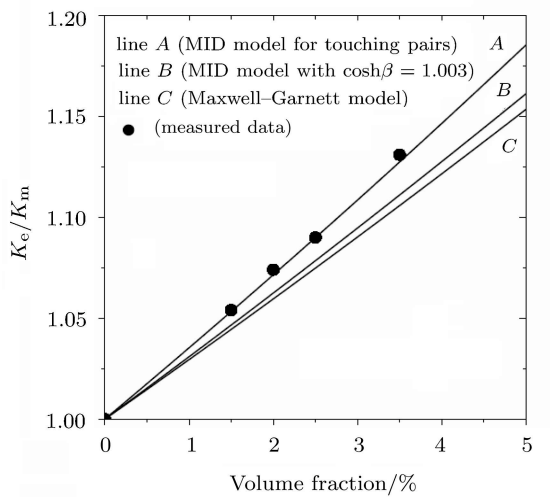


Fig.3. Comparison of our model with experimental data for CuO/water nanofluids in Ref.[6].

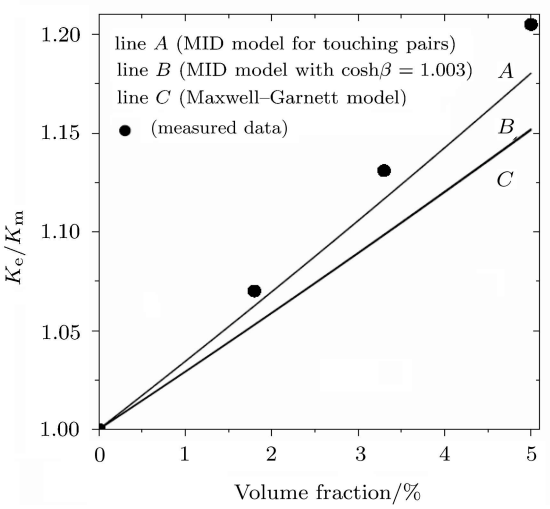


Fig.4. Comparison of our model with experimental data for Al_2O_3/water nanofluid in Ref.[7].

Next, we take one step forward to compare our theoretical results with experimental data of Al_2O_3/water nanofluids. Numerical results are shown in Fig.4. Our theoretical results given by MID theory for touching pairs also agree with the Al_2O_3/water experimental data. However, there exist certain discrepancies. Actually, although the interaction of nearest-neighbour nanoparticles is a key factor for enhancing the effective thermal conductivity, it appears that other factors such as inclusion shape, the Brownian motion and surface chemistry should be considered simultaneously.

Recently, Grechko and Pustovit[17] proposed a new dipole–dipole model to take into account the pair interaction between particles. The expression for effective physical properties is given by

$$K_{\mathrm{e}} = K_{\mathrm{m}}\left(1 + \frac{3fb}{1 - fb - \dfrac{2}{3}fb\ln\dfrac{8+b}{8-2b}}\right). \qquad (18)$$

Here, we compare our MID model with Eq.(18) based on dipole–dipole (DID) model. Numerical results are shown in Fig.5. It is evident that MID model yields higher enhancement $K_{\mathrm{e}}/K_{\mathrm{m}}$ than DID model does. This demonstrates that strong interaction is usually accompanied with large enhancement of effective thermal conductivity.

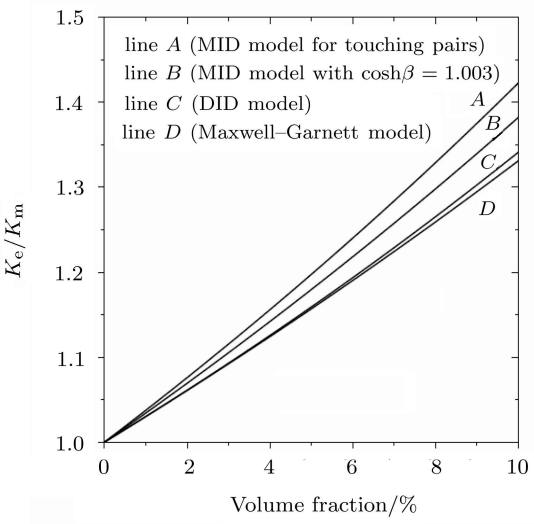


Fig.5. $K_{\mathrm{e}}/K_{\mathrm{m}}$ as a function of the volume fraction f at $K_{\mathrm{p}}/K_{\mathrm{m}} = 500$.

4. Conclusions

In summary, considering the many-body and multipolar interaction between nanoparticles or clusters, we adopt the multiple image method to investigate the effective thermal conductivity of nanofluids. Compared with other conventional models, the multiple image method contains the size, the separation

of the particles or clusters and the interaction between nearest-neighbour inclusions. It is found that strong many-body and multipolar interaction and large $K_{\rm p}/K_{\rm m}$ ratio are usually accompanied with large enhancement of effective thermal conductivity. Our theoretical results on the effective thermal conductivity of CuO/water and Al_2O_3/water nanofluids are in good agreement with the experimental data. Since the mechanism of the thermal behaviour in nanofluids is complex, although our theoretical results reveal that the multiple interaction between nearest-neighbour nanoparticles is a key factor, it appears that other factors such as the effect of solid/liquid interfacial layer, the Brownian motion and the surface chemistry should be considered simultaneously.

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