Effect of Clusters on Thermal Conductivity in Nanofluids *

XU Jie(徐洁), YU Bo-Ming(郁伯铭)**, YUN Mei-Juan(员美娟)

Department of Physics, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074

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We propose a new model for the effective thermal conductivities of nanofluids, which is derived from the fact that nanoparticles and clusters coexist in the fluids. The effects of the compactness and the perfectness of the contact between nanoparticles in clusters on the effective thermal conductivity of nanofluids are analysed. The proposed model indicates that the effective thermal conductivity of nanofluids decreases with the increasing concentration of clusters. The model predictions are compared with and are in good agreement with the available experimental data.

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The significant enhancement of the thermal conductivity of nanofluids has attracted more interests recently in experiment and theory. However, none of the existing theories is capable of explaining this significant increase of thermal conductivities of nanofluids. Maxwell[1] built a model for the effective thermal conductivity of a homogeneous suspension with spherical particles, which can be expressed as

$$k_e = \frac{k_p + 2k_f + 2(k_p - k_f)\phi}{k_p + 2k_f - (k_p - k_f)\phi} \cdot k_f \qquad (1)$$

where k_e is the effective thermal conductivity of the suspension, ϕ is the volume fraction of particles in the fluid, k_p and k_f are the thermal conductivities of particles and liquid, respectively. Several researchers[2−4] have developed the theories for the effective thermal conductivity k of multiphase systems. However, the traditional models for composites completely fail to explain the enhancement in the effective thermal conductivity of nanofluids. Many authors gave different renovated models based on the previous works to explain the mechanisms of heat transfer in nanofluids.[5−12] Recently, Keblinski *et al.*[12] qualitatively analysed the effect of clusters in nanofluids at the molecular-level, whereas they did not give an appropriate mathematical expression. Hong *et al.*[13] measured the thermal conductivities of nanofluids versus time. In this work, we derive a model for the effective thermal conductivity of nanofluids by taking into account the effect of clusters in nanofluids. The model predictions are then compared with the available experimental data.

Yu and Choi[5] derived a model for the thermal conductivity of nanofluids by assuming that there is no agglomeration by nanoparticles in nanofluids. In this case the effect of the interfacial interaction between nanoparticles and liquid was taken into account. They assumed that the nanolayer around each particle could combine with the particle to form an equivalent particle, and obtained the equivalent thermal conductivity k_{pe} of equivalent particles as follows:[5]

$$k_{pe} = \frac{[2(1-\beta) + (1+\gamma_t)^3(1+2\beta)]\beta}{(\beta-1) + (1+\gamma_t)^3(1+2\beta)} k_p, \qquad (2)$$

where $\beta = k_i/k_p$ with k_i and k_p being the thermal conductivities of nanolayer and particle, respectively; $\gamma_t = t/r$ with t being the thickness of nanolayer; and r is the original particle radius. The volume concentration ϕ_{pe} of nanoparticles in the fluid will increase due to the nanolayers and is obtained to be[5]

$$\phi_{pe} = (1+\gamma_t)^3\phi \qquad (3)$$

where ϕ is the volume fraction of nanoparticles in the fluid. Yu *et al.*[5] studied the effect of the interfacial layer on the thermal conductivity of nanofluids and modified the Maxwell model by combining Eqs. (2) and (3) to obtain

$$k_{e1} = \frac{k_{pe} + 2k_f + 2(k_{pe} - k_f)(1+\gamma_t)^3\phi}{k_{pe} + 2k_f - (k_{pe} - k_f)(1+\gamma_t)^3\phi} \cdot k_f. \qquad (4)$$

Yu *et al.*[5] concluded that the nanolayer thickness is crucial to the enhancement of the thermal conductivity of nanofluids. Yu *et al.* present the model in which Eq. (4) does not account for the effect of clusters in the fluids on the thermal conductivity. However, many researchers[14,15] have found that nanoparticles and clusters coexist in the fluids and that the effect of clusters is a possible important factor for enhancement of the thermal conductivity of nanofluids.

A cluster aggregated by nanoparticles occupies more space than the individual nanoparticle that makes up the cluster. However, the thermal conductivity of clusters is smaller than the thermal conductivity of nanoparticles because there is a thermal contact resistance between nanoparticles when they ag-

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** To whom correspondence should be addressed. Email: yuboming2003@yahoo.com.cn

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gregate. The thermal property of materials was investigated by many researchers.[16−19] Hsu *et al.*[16] proposed a lumped-parameter model for stagnant thermal conductivity of spatially periodic porous media. The clusters formed by nanoparticle agglomeration are analogous to porous media. Therefore, in this work we use the model of Hsu *et al.*[16] to describe the thermal conductivity of the clusters formed by nanoparticles.

Figure 1(a) shows a cluster aggregated by nanoparticles. The effective volume concentration of clusters is larger than that of nanoparticles making up the cluster because there is the interspace between the aggregated nanoparticles. Hsu *et al.*[16] considered the stagnant thermal conductivity of an array of in-line cubes with smaller connecting bars as shown in Fig. 1(b) and selected a unit cell for this three-dimensional periodic porous medium as shown in Fig. 1(c) to build the model for the effective thermal conductivity of porous media. To simplify our analysis, we assume that the nanoparticles within clusters arrange in cubes and that nanoparticle aggregation follows the tactic array structure as shown in Fig. 1(b). Therefore, we can use the model of Hsu *et al.* to analyse the thermal conductivity of clusters.

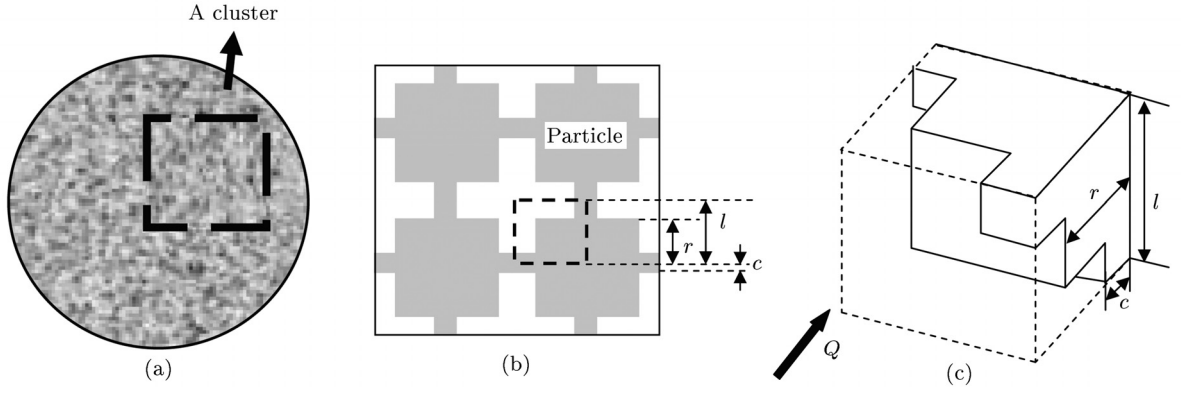

Fig. 1. Aggregation structure of a cluster in our model.

From a geometric consideration as shown in Fig. 1(c), Hsu *et al.*[16] have derived the volume fraction ϕ' of the solid phase in a porous medium,

$$\phi' = (1 - 3\gamma_c^2)\gamma_r^3 + 3\gamma_c^2\gamma_r^2, \tag{5}$$

where $\gamma_r = r/l$ and $\gamma_c = c/r$, r is the radius of nanoparticle, l is the length of a unite cell, c is the width of thermal resistance. The parameter γ_r and γ_c describe the compactness and the quality/perfectness of contact between nanoparticles in the cluster, respectively. A higher value of γ_r means that the nanoparticles aggregate more loosely. A higher value of γ_c implies the smaller contact resistance between nanoparticles in the cluster. Since we assume that the cluster is analogous to a porous medium and the particles arrange in cubes, Eq. (5) is also suitable to describe the volume fraction of nanoparticles in the cluster.

The volume of all nanoparticles in the fluid is v, which can be considered as the volume of the solid phase in a porous medium. Then the effective volume v_c of all clusters can be calculated by $v_c = v/\phi'$. If the total volume of nanofluids is v_t, the volume concentration of nanoparticles in the fluid is $\phi = v/v_t$. The effective volume concentration of clusters in the fluid can be defined by

$$\phi_{ce} = \frac{v_c}{v_t} = \frac{v/\phi'}{v_t} = \frac{\phi}{\phi'} = \frac{\phi}{(1 - 3\gamma_c^2)\gamma_r^3 + 3\gamma_c^2\gamma_r^2}. \tag{6}$$

Hsu *et al.*[16] derived a model for the effective stagnant thermal conductivity of spatially periodic porous media of solid cubes with thermal resistance. Their model is now used to analyse the thermal conductivity of clusters in nanofluids and reads

$$k_{ce} = \Big[(1 - \gamma_r^2 - 2\gamma_c\gamma_r + 2\gamma_c\gamma_r^2) + \frac{\gamma_c^2\gamma_r^2}{\lambda} + \frac{\gamma_r^2 - \gamma_c^2\gamma_r^2}{1 - \gamma_r + \gamma_r\lambda} + \frac{2(\gamma_c\gamma_r - \gamma_c\gamma_r^2)}{1 - \gamma_c\gamma_r + \gamma_c\gamma_r\lambda}\Big] k_f, \tag{7}$$

where $\lambda = k_f/k_p$, k_f and k_p are the thermal conductivities of fluids and particles, respectively. Equation (7) indicates that the thermal conductivity of clusters is related not only to the thermal conductivities of fluids and particles but also to the compactness γ_r and the perfectness γ_c of contact between nanoparticles in a cluster.

If all nanoparticles agglomerate to form clusters, the thermal conductivity of nanofluids can be obtained by modifying Eq. (1) as

$$\begin{aligned} k_{e2} &= \frac{k_{ce} + 2k_f + 2(k_{ce} - k_f)\phi_{ce}}{k_{ce} + 2k_f - (k_{ce} - k_f)\phi_{ce}} \cdot k_f, \\ &= \frac{k_{ce} + 2k_f + 2(k_{ce} - k_f)\phi/[(1 - 3\gamma_c^2)\gamma_r^3 + 3\gamma_c^2\gamma_r^2]}{k_{ce} + 2k_f - (k_{ce} - k_f)\phi/[(1 - 3\gamma_c^2)\gamma_r^3 + 3\gamma_c^3\gamma_r^2]} \cdot k_f, \end{aligned} \tag{8}$$

where ϕ_{ce} and k_{ce} are determined by Eqs. (7) and (6).

In reality, some particles in nanofluids may aggregate to form clusters, and the others do not but remain suspended in the fluids. Therefore, the effective thermal conductivity of nanofluids can be approximated by

$$k_{\text{eff}} = (1-\alpha)k_{e1} + \alpha k_{e2}, \tag{9}$$

where α is the weighted factor and $0 < \alpha < 1$. Equation (9) represents the effective thermal conductivity governed by both the clusters agglomerated and nanoparticles suspended in the fluids.

We take the nanofluid of ethylene glycol with Al_2O_3 nanoparticles, for example, in the average radius 17.5 nm. Figure 2 shows the relationship between the effective thermal conductivity (predicted by Eq. (7)) of a cluster and the values of l and c. It can be seen that the effective thermal conductivity increases with c. This is because the contact between the nanoparticles in a cluster becomes perfect and the thermal resistance is thus reduced and the effective thermal conductivity increases when c increases. This is consistent with the physical situation. Figure 2 also shows that the effective thermal conductivity of a cluster increases with the decrease of the value of l. When l (= 17.5 nm) is equal to the radius r of nanoparticles, we have $\gamma_r = 1$. Based on our model, there is no liquid between particles in a cluster, and the cluster becomes a solid particle, leading to the highest thermal conductivity. The effective thermal conductivity of a cluster is then equal to the thermal conductivity of nanoparticles themselves, i.e. $k_{ce} = k_p$ (= 46.0 W/mK), as shown in Fig. 2. As l increases, the cluster becomes loosely compacted, leading to the decrease of the thermal conductivity.

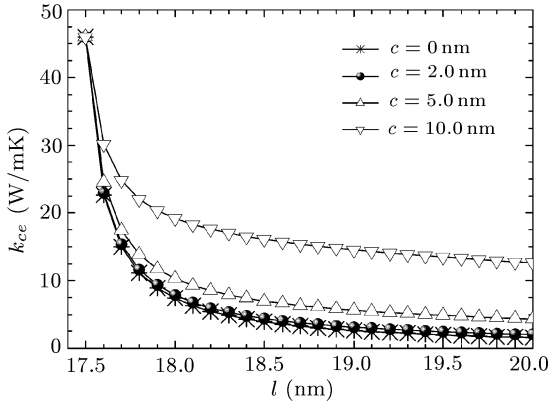

Fig. 2. Effective thermal conductivity of a cluster versus the length l of a unite cell.

Figure 3 shows the relationship between the effective thermal conductivities of the nanofluid and the volume concentration of ethylene glycol with Al_2O_3 nanoparticles of the average radius 17.5 nm in the fluid. The solid line in Fig. 3 shows the effective thermal conductivity k_{e1} of the nanofluid without nanoparticle agglomeration. We take t = 2.0 nm and $k_i = k_p$ in Eq. (4) in the calculation. The dashed line in Fig. 3 represents the effective thermal conductivity k_{e2} of the nanofluid with all nanoparticles agglomerated, and here we take c = 5.0 nm and l = 19.0 nm in Eq. (8). It can be found from Fig. 3 that the effective thermal conductivity k_{e2} of the nanofluid when all nanoparticles aggregate in the fluid is less than the effective thermal conductivity k_{e1} of the nanofluid when no agglomeration of nanoparticles takes place in the fluid. This is consistent with the physical situation. Hong *et al.*[13] found that the effective thermal conductivity of nanofluids would decrease with time. The reason is that nanoparticles agglomerate to form clusters rapidly after the oscillating/shaking is stopped.

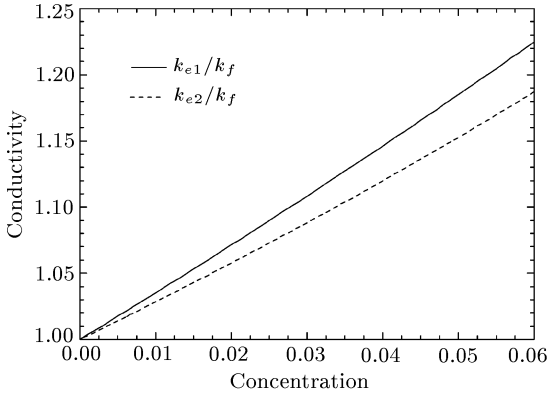

Fig. 3. Dimensionless effective thermal conductivity versus the volume concentration of nanoparticles in the fluid.

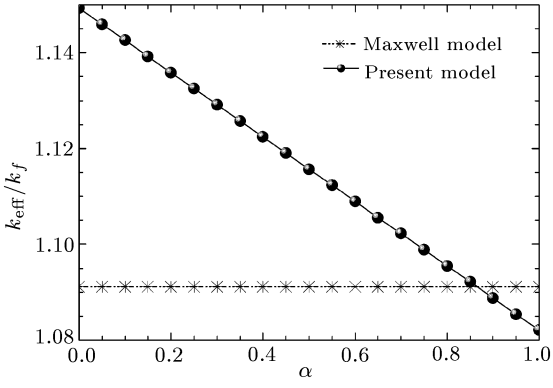

Fig. 4. Effective thermal conductivity of nanofluids versus the volume concentration of the aggregated nanoparticle clusters.

Figure 4 presents the effective thermal conductivity of nanofluids of ethylene glycol with Al_2O_3 nanoparticles of the average radius 17.5 nm. It is found that the results predicted by the Maxwell model are independent of the concentration of clusters. This is inconsistent with the physical situation and therefore the Maxwell model fails to explain the ther-

mal conductivity versus the concentration of clusters. When all nanoparticles do not aggregate in the fluid, i.e. $\alpha = 0$, the thermal conductivity of nanofluids is the highest, $k_{\rm eff}/k_f = 1.15$. In this case, the thermal conductivity is totally determined by the fluid with all nanoparticles suspended in the fluid. Then, the effective thermal conductivity of nanofluids decreases with the increase of the concentration α of clusters. When all nanoparticles aggregate in the fluid, i.e. $\alpha = 1.0$, the thermal conductivity of nanofluids is the lowest, $k_{\rm eff}/k_f = 1.083$. When α is in the range of 0.86–1.0, the results (see the solid line with circles) by the present model are less than those by the Maxwell model. This is because the thermal conductivity of clusters is smaller than the nanoparticles.

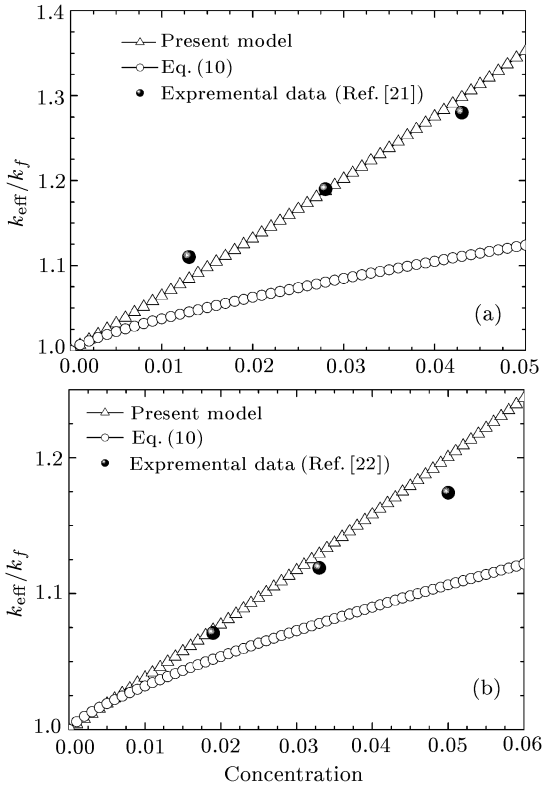

Fig. 5. Effective thermal conductivity of nanofluids versus the volume concentration of nanoparticles in comparison of the present model predictions with the experimental data for Al_2O_3–water with (a) $r = 6.5\,$nm, $t = 2.0\,$nm, $k_i = k_p$, $l = 8.5\,$nm, $c = 1.0\,$nm, $\alpha = 0.05$, and (b) $r = 30.2\,$nm, $t = 2.0\,$nm, $k_i = k_p$, $l = 31.0\,$nm, $c = 5.0\,nm$, $\alpha = 0.05$.

Figures 5(a) and 5(b) compare the present model predictions with the available experimental data for Al_2O_3 nanoparticles of the average radius 6.5 nm and 30.2 nm added in water, respectively. Chon *et al.*[20] obtained an empirical correlation for the nanofluid effective thermal conductivity $k_{\rm eff}$,

$$\frac{k_{\rm eff}}{k_f} = 1 + 64.7 \times \phi^{0.7460} \left(\frac{d_f}{d_p}\right)^{0.3690} \cdot \left(\frac{k_p}{k_f}\right)^{0.7476} Pr^{0.9955} Re^{1.2321}. \quad (10)$$

where Pr and Re are the Prandtl number and Reynolds number for fluids, respectively. The figure clearly indicates that the effective thermal conductivity of the nanofluids increases with the nanoparticle volume concentration ϕ. Figure 5 also indicates that good agreement is found between the model predictions and the experimental data. However, Eq. (10) predicts the values lower than the experimental data.

In summary, we have proposed a new model for the effective thermal conductivities of nanofluids, which is derived by taking into account the fact that nanoparticles and clusters coexist in the nanofluids. The reasonable predictions have been shown by the proposed model, and good agreement between the model predictions and experimental data is found.

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