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A PEDICTION METHOD FOR THERMAL CONDUCTIVITY AND ELECTRIC CONDUCTIVITY OF NANOFLUIDS BASED ON PARTICLES AGGREGATION THEORY

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ABSTRACT

Nanoparticles in nanofluids are in the form of nanoparticle clusters caused by aggregation. In order to calculate the thermal and electric conductivities of the nanofluids, the growth process and three-dimensional space structure of the nanoparticle cluster in the host fluid was simulated, and then the thermal and electric conductivities of the cluster were calculated with the resistance network method. The thermal and electric conductivities of the nanofluid were calculated based on the simulated thermal and electric conductivities of nanoparticle clusters, the volume fraction of nanoparticle clusters to the nanofluid as well as the liquid molecule adsorption layer of the nanoparticle. The simulation method was validated by experimental data.

Keywords: nanofluids, thermal conductivity, electric conductivity, particles aggregation

1. INTRODUCTION

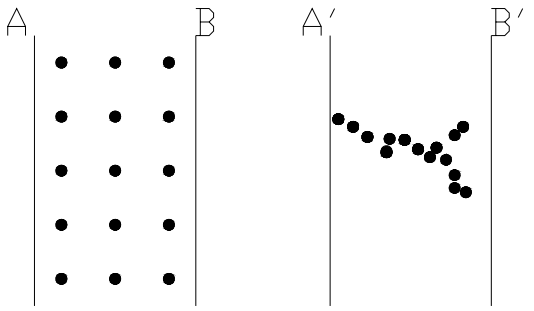
A new type of heat-transfer fluids by suspending nanoparticles in conventional liquids, called as nanofluids, has much higher thermal conductivity than a normally used industrial heat transfer fluids [1] and is able to enhance heat transfer. So they have good prospects in industry [2]. Beside the thermal conductivity, the electric conductivity of nanofluids is a very important property. Any working fluids used in household appliances must ensure strict electric insulation ability. In order to develop nanofluids with good properties, simulation methods for the thermal and electric conductivities are useful.

The traditional thermal conductivity algorithms of solid-liquid phase fluids, such as Maxwell model and Bruggeman model, are imprecise for nanofluids [3-6]. The calculated results by Maxwell model or Bruggeman model are much smaller than the experimental ones, so simulation methods for the thermal conductivity of nanofluids have been studied in order to investigate the mechanism of energy transport enhancement of nanofluids. Jang et al. [3] and Xuan et al. [4] presented that the Brownian motion of nanoparticles at the molecular and nanoscale level was a key mechanism of the thermal conductivity enhancement and devised modified Maxwell models by considering the Brownian motion. Evans et al. [7] used kinetic theory and the molecular dynamics simulations to conclude that it does not show any significant enhancements due to effects associated with Brownian motion induce hydrodynamic effects. The analysis [7] presented that particles aggregation may be responsible for the enhancement instead of Brownian motion.

The experiments [8] corroborated Evans' theory and showed that the thermal conductivities of Tetrahydrofuran hydrates with carbon nanotubes, just like nanofluids, were much greater than the calculated results by Maxwell model or Bruggeman model. Since the Tetrahydrofuran hydrates were solid, it means that influence of the Brownian motion can be ignored in the experiments. The heat path by particles aggregation may be the key mechanism of the thermal conductivity enhancement.

The heat path means that heat can be transferred through the nanoparticles cluster as a path. The influence of the heat path is shown in Fig. 1. The black points refer to nanoparticles while the blank between line A(A') and line B(B') refers to the fluid. If the nanoparticles are

well dispersed, the thermal conductivity between line A and line B can be predicted by Maxwell model. In fact nanoparticles suspended in the host fluid may collide with each other, so particle aggregation may occur and clusters will form. The electron microscopy photo of a cluster is shown in Fig.2. If the particles aggregate to be a cluster and the particles' thermal conductivity is much more than the fluids', the thermal resistance between line A' and line B' will reduce like short circuit. So the thermal conductivity between line A' and line B' is more than the one between line A' and line B'



(a) (b)

Fig. 1 Sketch of the heat path by particles aggregation
(a) Well dispersed nanoparticles
(b) The heat path by a nanoparticle cluster

Wang et al. [5] and Prasher et al. [6] presented each models based on the particles aggregation theory. The thermal conductivities of clusters were calculated by Bruggeman model so the thermal conductivities of nanoparticles clusters with the same particles number are the same and isotropic. In fact the space distributions of clusters are random so the thermal conductivities are anisotropic. The clusters' space structure shall be simulated in order to calculate the clusters' conductivity. The correctness of the Bruggeman model on clusters was not confirmed so the method to calculate the clusters' conductivities accurately shall be researched.

This paper is to present a method which can simulate the thermal conductivities well. In this method, the growth process and three-dimensional space structure of the nanoparticle cluster should be simulated, the influence of particles' aggregation, clusters' fractal dimension, size and volume fraction of nanoparticles, nanoparticle's liquid molecules adsorption layer and fluids temperature should be considered. The electric conductivity of nanofluids shall be researched in order to ensure the nanofluids' insulating ability in industrial application. The simulation method on nanofluids' electric conductivity is proposed from the references to the method on thermal conductivity.

2. SIMULATION OF THE SPACE STRUCTURE OF A NANOPARTICLE CLUSTER

The simulation of nanoparticles aggregation is run in three-dimension mesh in this paper with the method by Witten and Sander [9]. A particle is fixed in the center of mesh as the first particle of the cluster. Then another particle is put in the mesh randomly. The particle moves randomly and each moving distance is one grid. The particle will move all along till it meets the aggregated cluster. The particle will adhere to the cluster and form into a part of the cluster with probability *P* or keep on moving with probability 1-*P*. If the particle is adhered, another particle is put in the mesh randomly. Such process will iterate till the number of particles reaches the predetermined value. The value is proposed to be 14 [4] and the influence of different particles number is discussed in Section **7.** .

The location to insert the particle is on a sphere randomly. The radius of the ball is the maximum diameter of the aggregation plus five grid distance. The research [10] showed the difference between inserting in such location and inserting in infinite distance was imperceptible. The particle is deemed to be impossible of adherence while the distance of the particle and the cluster is more than 2 times of the maximum diameter of the cluster.

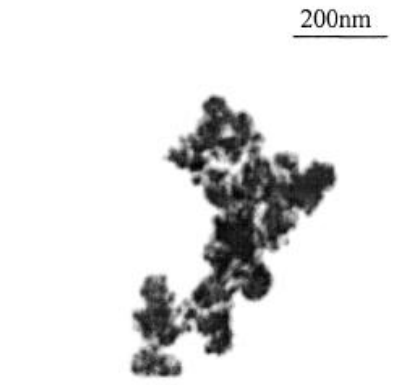


Fig. 2 Electron microscopy photo of a cluster in Cu–water nanofluid [4]

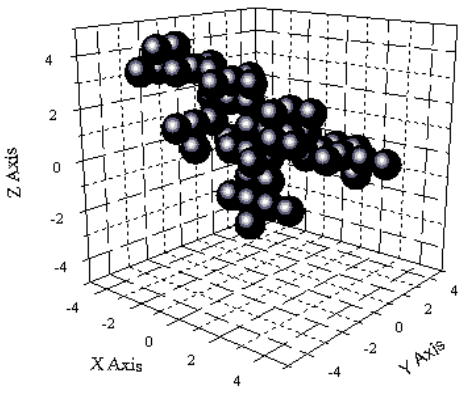


Fig. 3 Simulated space structure of a nanoparticle cluster

The adhesiveness probability *P* must be given in

order to simulate the structure of the nanoparticle cluster. *P* can be yielded by the fractal dimension *D* of the cluster. Assume that there is a sphere and the center of the sphere is the first seed particle of the cluster, the fractal dimension *D* can be decided through the following expression:

$$n = cr^{D} \tag{1}$$

where *c* is the shape factor which is independent of *r*. The fractal dimension *D* can be gotten by calculating different particles number in different radius *r*. The fractal dimension *D* of the cluster' two-dimension projection is about 1.77 [5]. This valve of *D* corresponds to the case when *P* is 0.2. Fig. 2 is the simulated space structure of a nanoparticle cluster of Cu–water nanofluid when *P* is 0.2. Compared with an electron microscopy photo [4], two clusters have the same fractal dimension *D*. The influence of the adhesiveness probability will be discussed in **7.** .

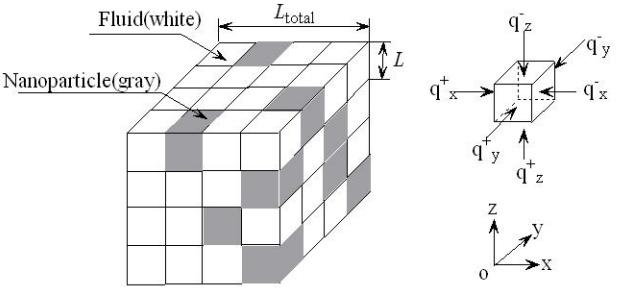
3. SIMULATION OF THE THERMAL CONDUCTIVITY OF A NANOPARTICLE CLUSTER

The resistance network method is used to calculate the thermal conductivity of a nanoparticle cluster while its space structure is simulated. The space of a cluster is discrete in resistance network method as shown in Fig. 4. The gray cells denote nanoparticles and the white cells denote the host fluid. The side length of a sample cube is L_{total} and the side length of each cell is *L*. *L* is equal to the diameter of the nanoparticle which is internal tangent to a cell. The number of cells is $(L_{total}/L)^3$. The heat flux in the positive direction of X axis of one lattice in Fig. 4(b) can be expressed as:

$$q^{x+}_{i,j,k} = k^{x+}_{i,j,k}\left(T_{i-1,j,k} - T_{i,j,k}\right)/L \tag{2}$$

$$k^{x+}_{i,j,k} = \frac{2}{\frac{1}{k_{i-1,j,k}} + \frac{1}{k_{i,j,k}}} \tag{3}$$

where *(i,j,k)* and *(i-1,j,k)* are serial numbers of cells; $T_{i,j,k}$ and $T_{i-1,j,k}$ are temperatures of cell *(i,j,k)* and cell *(i-1,j,k)*, respetively; $k^{x+}_{i,j,k}$ is the thermal conductivity between cell *(i,j,k)* and cell *(i-1,j,k)*; $k_{i,j,k}$ and $k_{i-1,j,k}$ are thermal conductivities of cell *(i,j,k)* and cell *(i-1,j,k)*., respetively



(a) (b)

Fig. 4 The space structure of the nanoparticle cluster and the thermal balance of the lattice
(a) The space structure of the nanoparticle cluster
(b) The thermal balance of the lattice

So the heat flux in the negative direction of *X* axis of one lattice in Fig. 4(b) can be expressed as:

$$q^{x-}_{i,j,k} = k^{x-}_{i,j,k}\left(T_{i+1,j,k} - T_{i,j,k}\right)/L \tag{4}$$

As the net heat flux of a cell is zero in a steady state, the temperature of cell *(i,j,k)*, $T_{i,j,k}$ can be decided:

$$T_{i,j,k} = \frac{k^{x+}_{i,j,k}T_{i-1,j,k} + k^{x-}_{i,j,k}T_{i+1,j,k} + k^{y+}_{i,j,k}T_{i,j-1,k} + k^{y-}_{i,j,k}T_{i,j+1,k} + k^{z+}_{i,j,k}T_{i,j,k-1} + k^{z-}_{i,j,k}T_{i,j,k+1}}{k^{x+}_{i,j,k} + k^{x-}_{i,j,k} + k^{y+}_{i,j,k} + k^{y-}_{i,j,k} + k^{z+}_{i,j,k} + k^{z-}_{i,j,k}} \tag{5}$$

The direct iteration method is used to get the solution of Eq. (5). The iteration will end when the temperature change of every cell is less than the setting value. The boundary surface cells in directions of *Y* axis and *Z* axis are assumed to be adiabatic. The boundary surface cells in direction of *X* axis are assumed to be thermostatic. The thermal conductivity in the in direction of *X* axis, k_x , can be decided:

$$k_x = \frac{L_{tatal}\sum_{i,j} q}{\Delta T} \tag{6}$$

where ΔT is the temperature difference between surface *(1,j,k)* and surface $(L_{total}/L,j,k)$.

The thermal conductivity of the cell equals that of the fluid if there is no particle in a cell. In order to attain the thermal conductivity of the cell with a particle, the cell should be discretized further and generates many mini cells. The length of each mini cell cube is L_{mini}. If the distance between a mini cell and the center of the big cell is less than or equal to *L/2*, the thermal conductivity of this mini cell is equivalent to that of the nanophase material. Otherwise the thermal conductivity of the mini cell equals that of the fluid. If the number of mini cells is large enough, the mini cells made of nanophase material can be treated as a sphere. The sketch of nanoparticles' meshes with different L_{mini} is shown in Fig. 5. The black and white cells mean the nanophase material and the fluid. Then the thermal conductivity of the big cell with a particle can be calculated by the resistance network method. The inaccuracy of the thermal conductivity of a cell with a particle is great as the number of mini cells is few. If L/L_{mini} >100, then the value of the thermal

conductivity is almost invariable, which means the calculated result is convergent.

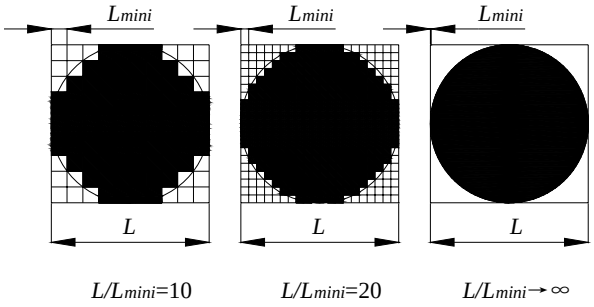


Fig. 5 Nanoparticles' meshes with different L_{mini}

4. SIMULATION OF THE ELECTRIC CONDUCTIVITY OF A NANOPARTICLE CLUSTER

The simulation method of the electric conductivity is similar to the method of thermal conductivity. The current flow in the positive direction of X axis of one lattice can be expressed as:

$$I^{x+}_{\mathrm{i,j,k}} = \left(U_{\mathrm{i\text{-}1,j,k}} - U_{\mathrm{i,j,k}}\right) \Big/ R^{x+}_{\mathrm{i,j,k}} \tag{7}$$

$$R^{+}_{\mathrm{x}} = \left(R_{i-1,\,j,k} + R_{i,\,j,k}\right) \Big/ 2 \tag{8}$$

where (i,j,k) and (i-1,j,k) are serial numbers of cells; $U_{i,j,k}$ and $U_{i\text{-}1,j,k}$ are electric potential of cell (i,j,k) and cell (i-1,j,k); $R^{x+}_{\mathrm{i,j,k}}$ is the resistance between cell (i,j,k) and cell (i-1,j,k); $R_{i,j,k}$ and $R_{i\text{-}1,j,k}$ are resistances of cell (i,j,k) and cell (i-1,j,k).

As the net current flow of a cell is zero in a steady state, the electric potential of cell (i,j,k), $U_{i,j,k}$ can be decided:

$$U_{i,j,k} = \frac{U_{i-1,j,k}\big/R_x^+ + U_{i+1,j,k}\big/R_x^- + U_{i,j-1,k}\big/R_y^+ + U_{i,j+1,k}\big/R_y^- + U_{i,j,k-1}\big/R_z^+ + U_{i,j,k+1}\big/R_z^-}{1\big/R_x^+ + 1\big/R_x^- + 1\big/R_y^+ + 1\big/R_y^- + 1\big/R_z^+ + 1\big/R_z^-} \tag{9}$$

The boundary surface cells in direction of Y axis and Z axis are assumed to be insulated. The electric potential difference of boundary surface cells in direction of X axis is constant. The resistance in the in direction of X axis, R_{x}, can be decided:

$$R_{\mathrm{x}} = \frac{\Delta U}{\sum_{\mathrm{j,k}} I} \tag{10}$$

where ΔU is the electric potential difference between surface (1,j,k) and surface (L_{total}/L,j,k). While the R_{x} is calculated, the electrical conductivity of the nanoparticle cluster in direction of X axis, σ_{x}, can be reached.

5. INFLUENCE OF THE THERMAL AND ELECTRIC CONDUCTIVITIES OF A NANOPARTICLE CLUSTER BY THE ADSORPTION LAYER

The thermal and electric conductivities of a nanoparticle cluster will be influenced by the liquid molecules adsorption layer on the nanoparticle surface. The layer is constituted by fluid molecules adsorbed by the nanoparticle. The thermal conductivity of a layer is much greater than that of the liquid because the liquid molecules of the layer incline to solid phase. The value of adsorption layer's thermal and electric conductivities is hard to be predicted and is assumed to be the same as that of the nanoparticle in this paper. So the adsorption layer increases the nanoparticles' volume and the influence of the layer is shown in Fig. 6. The y-axis, volume ratio, means the ratio of volume of a nanoparticle with adsorption layer to that without layer. It can be concluded that the smaller the diameter of a nanoparticle is, the larger the increased volume fraction is. If the diameter is much more than layer thickness, the influence of the layer can be ignored.

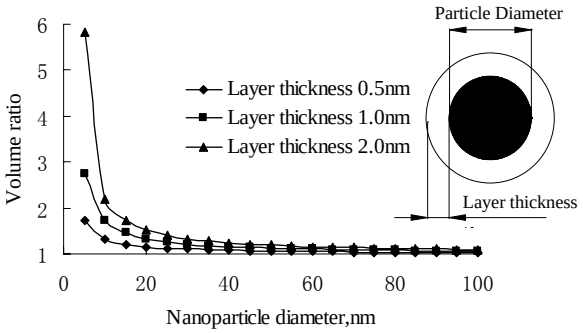


Fig. 6 The influence of liquid molecules adsorption layer

The thickness of adsorption layer, δ_{T}, will change with fluids' temperature. Jang proposed that δ_{T} is in inverse proportion to the Prandtl number [3], which states that the higher the temperature is, the larger the increased adsorption layer volume fraction and the nanofluids' conductivity are. The thickness of hydrodynamic boundary adsorption layer is proposed to be 3 times of the fluid molecule's diameter [3]. So δ_{T} is assumed to be 1.2 nm, 3 times of water molecule's diameter, in 30ºC in the paper.

The thermal and electric conductivities between two contacted nanoparticles will change due to molecules layers changing the contact surface area of nanoparticles. In Fig. 7, the black points and white blank refer to the circle mean nanoparticles and the adsorption layer, respectively. The value of adsorption layer's thermal and electric conductivities and the area of adsorption layers' contact surface are hard to be predicted. The bigger the contact surface area is, the larger the thermal and electric conductivities between the two particles are. The influence of the thermal and electric conductivities between two particles will be discussed in Section **7.** . The contact between two particles with layers is regard as point contact in this paper.

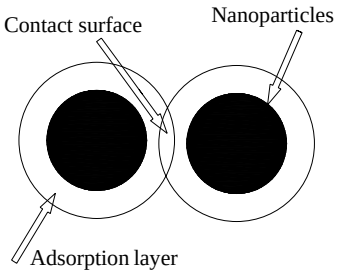


Fig. 7 Sketch of the adsorption layer's contact surface

6. SIMULATION METHOD OF THE THERMAL AND ELECTRIC CONDUCTIVITIES OF NANOFLUIDS

After the thermal and electric conductivities of nanoparticle clusters are calculated, the volume fraction of nanoparticle clusters to the host fluid should be calculated in order to get the thermal and electric conductivities of the nanofluid. The volume fraction of nanoparticle clusters to the fluid, Φ_1 can be expressed as:

$$\Phi_1 = \Phi_2 / \Phi_3 \qquad (11)$$

where Φ_2 is the volume fraction of nanoparticles to the nanofluid and Φ_3 is the volume fraction of nanoparticles to the nanoparticle cluster. The value of Φ_3 can be achieved by simulated cluster's space structure.

While Φ_1 is calculated, the resistance network method is used to get nanofluids' conductivity. If the total number of cells in mesh is N, the number of cluster cells and pure fluid cells are $\Phi_1 N$ and $(1-\Phi_1)N$. The types of these cells are determined randomly. Because of the randomness of nanoparticle clusters' growth, the thermal and electrical conductivity of different clusters and the conductivity of the same cluster in direction of different axes are different. The thermal and electrical conductivities of different clusters in direction of different axes are calculated. These different clusters are inserted into the resistance network randomly as cells to calculate the nanofluids' conductivity. The conductivities of different calculation examples still differ owing to the examples' randomness. Enough examples should be calculated, and then the resistance network can be used again. The different calculation examples are inserted into the new network randomly as cells and the new examples' conductivity can be calculated. Such process will be iterated till the variance of different examples fits the demand. If the number of network's cells is 20*20*20 and the number of calculation examples is 100, the variance of examples is less than 0.01% after 5 iterations.

7. SIMULATION AND EXPERIMENTS

The number of nanoparticles in clusters should be gotten in order to simulate the space structure of clusters. The mean number of particles is 14, according to Xuan's calculation [4]. The thermal conductivities of Al_2O_3-water nanofluids with different numbers of particles are calculated. The nanoparticles volume fraction is 3% and the result is shown in Fig. 8. Expression k_{eff}/k_f denotes the ratio of nanofluid's thermal conductivity to pure fluid's one.

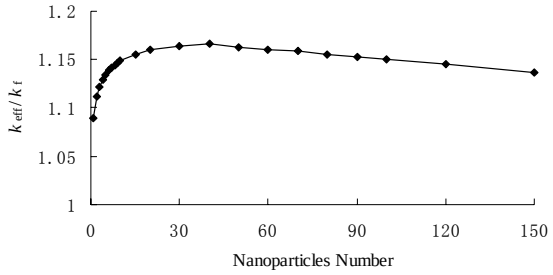


Fig. 8 Nanofluid's thermal conductivity with different particles number

The conductivity increases rapidly with particles number's increment. The conductivity's increment slows up while the number is more than 10. The conductivity's get its maximum value when the number is about 40, and afterwards the conductivity decreases slowly. The variance of conductivity is less than 2% if the number is between 10 and 120. Xuan's proposition is confirmed by the calculation and is accepted in this paper.

The clusters' particles stacking density is determined by the adhesiveness probability P. While the adhesiveness probability P decreases, the fractal dimension and the particles stacking density decrease and clusters' volume increases. So the relationship between adhesiveness probability and the thermal conductivity ratio, k_{eff}/k_f, is shown in Fig. 9. The fluid is Al_2O_3-water nanofluid and the nanoparticles volume fraction is 3%. The nanoparticles numbers are 10 and 100. While the number is little, the clusters' space structures with different adhesiveness probability are similar. So the thermal conductivity ratio is almost constant while the number is 10. The tendency that the thermal conductivity ratio will increase with the adhesiveness probability's increase is obvious while the number is 100. But the ratio difference between the adhesiveness probability 0.1 and 1.0 is less than 1.0% so it can be ignored. The influence of the probability needs to be further studied if there are big clusters which are

made up of several small clusters and have thousands of particles in the nanofluid.

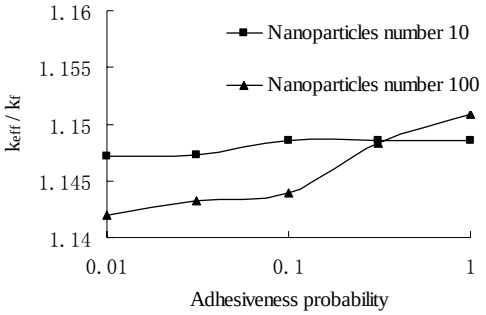


Fig.9 Nanofluid's thermal conductivity with different adhesiveness probability

The thermal and electric conductivities between two particles are determined not only by the nanoparticles and the fluid's conductivities, but also by the contact surface between two particles. The thermal and electric conductivities increase with the surface area's increase. The relationship between k_p/k_f and k_{eff}/k_f, is shown in Fig. 10. k_p means the thermal conductivity between two particles. It can be concluded that the higher k_p/k_f is, the higher k_{eff}/k_f is. While k_p/k_f is more than 200, the k_{eff}/k_f tends to the fixed value.

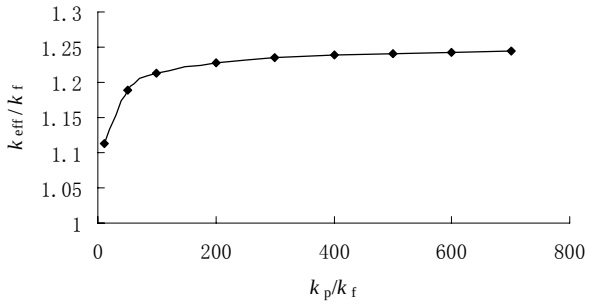


Fig.10 Nanofluid's thermal conductivity with different k_p/k_f

In order to validate the simulation method, thermal conductivities of three kinds of Cu-water and Al_2O_3-water nanofluids with different particle diameters and different volume fractions are simulated and compared with experimental data [4,11], as shown in Fig. 11. The nanofluids' temperature is 30ºC. The maximal deviation of simulation is 3.9%. The thermal conductivities of Al_2O_3-water nanofluids in different temperature are simulated and compared with experimental data [12], as shown in Fig. 12. The maximal deviation is 4.1%. These deviations are acceptable and also justify the simulation method is practical.

The electric conductivities of Cu-water, Al-water, Ni-water and Al_2O_3-water nanofluids with different volume fractions are measured and simulated as shown in Fig. 13. The nanofluids' temperature is 30ºC. The mean particles diameters of Cu, Al, Ni and Al_2O_3 are 25, 18, 20 and 20 nm respectively. Expression σ_{eff}/σ_f denotes the ratio of nanofluid's electric conductivity to pure fluid's one. The maximal deviation of simulation is 10.1%. Except the maximum point, the deviations of others are less than 5%, which means the simulation method is practical.

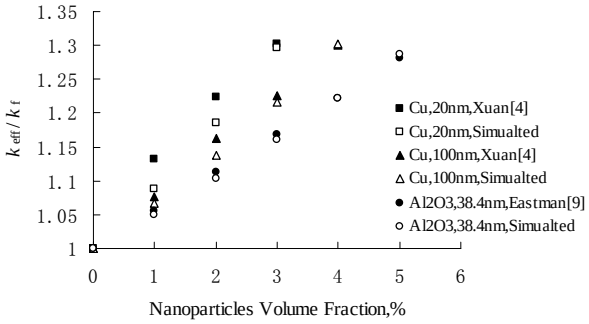


Fig. 11 Simulated results and experimental data of nanofluids' thermal conductivity in different volume factions

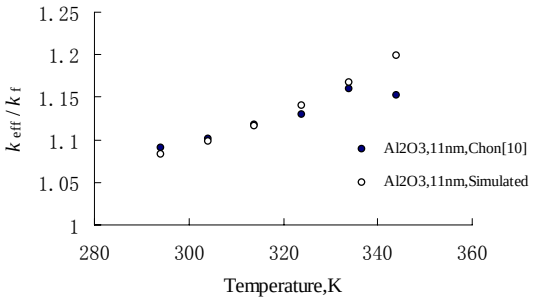


Fig. 12 Simulated results and experimental data of nanofluids' thermal conductivity in different temperatures

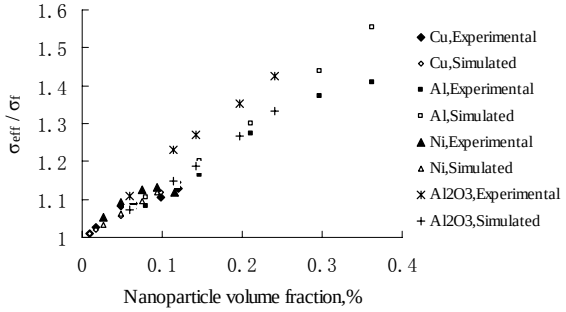


Fig. 13 Simulated results and experimental data of nanofluids' electric conductivity in different temperatures

8. CONCLUSIONS

Nanoparticles in nanofluids are in the form of nanoparticle clusters. The growth process and space structure of clusters can be simulated. The clusters'

thermal and electric conductivities can be calculated by resistance network method and then the nanofluids' thermal and electric conductivities can be gained. Experiments and simulation validate that the key factors of conductivity enhancement are particles aggregation, nanoparticles' size and fluids temperature.

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